QUARTERLY PROGRESS REPORT

October 1 to December 31, 2016

Florida International University's Continued Research Support for the Department of Energy's Office of Environmental Management

Principal Investigator:

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Prepared for:

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Office of Environmental Management
Under Cooperative Agreement No. DE-EM0000598

Applied Research Center
Florida International University

Introduction

The Applied Research Center (ARC) at Florida International University (FIU) executed work on four major projects that represent FIU-ARC's continued support to the Department of Energy's Office of Environmental Management (DOE-EM). The projects are important to EM's mission of accelerated risk reduction and cleanup of the environmental legacy of the nation's nuclear weapons program.

The period of performance for FIU Performance Year 7 under the DOE Cooperative Agreement (Contract # DE-EM0000598) is August 29, 2016 to August 28, 2017. The information in this document provides a summary of the FIU-ARC's activities under the Cooperative Agreement for the period of October 1 to December 31, 2016. Executive highlights during this reporting period include:

***Project 1*: High level waste (HLW)/waste processing**

FIU is assisting DOE EM to meet the challenges of an aging HLW infrastructure through the development of robotic inspection tools and the evaluation of sensors that can assist in assessing the integrity of the DSTs and the waste transfer components. To aid in the evaluation of these systems, FIU is evaluating a number of sensors that can provide structural information on components that are in locations that are difficult to access as well as developing a number of robotic systems that can provide environmental and structural information in locations that are difficult or dangerous to access.

1. FIU received a suite of sensors from Permasense that are based on guided waves and can be used to provide thickness measurements as well as locate anomalies in pipes and fittings used in the waste transfer system. This information will be valuable in understanding erosion and corrosion characteristics. A few advantages of the system are that no couplants are needed between the sensor and the surface being evaluated. Typical systems require gel couplants which makes it difficult to obtain long-term real-time data. The system is also wireless, which provides a significant advantage in terms of cable management and potential loss of signals. The system was received, training was provided and the sensors were installed on 2- and 3-inch pipeline components for validation.
2. The design of the miniature rover has been updated and a prototype was manufactured. The system was displayed at the DOE Fellows Induction Ceremony along with a mockup sectional of the tank and refractory channels. To simulate the outer wall of the tank, the testbed included a mold of the tank constructed from wood with painted sheet metal contoured to match the shape. Transparent plastic was attached to 3D printed magnetic posts in order to simulate the walls of the refractory channels. The magnetic posts are movable, which allows for the creation of multiple test channel configurations using the same parts. The modified design of the miniature rover was also tested to determine its ability to pull a tether around 30 degree bends and to determine its maximum pulling load. The tests were conducted on concrete surfaces with bricks to emulate the corners. Results indicate that the rover can pull up to 5 lbs and the refractory mock up with two 30 degree bends created a force on the tether of 4.5 lbs. A design modification will be implemented to lower the connection point of the tether and reduce the moment on the rover, which should significantly increase the load margin.

Project 2: **Environmental remediation (ER)**

FIU is assisting DOE EM to meet the challenges of managing the environmental restoration of subsurface contamination in soil and groundwater. In support of this effort, FIU is working in collaboration with PNNL to investigate the effect of ammonia gas on the uranium subsurface sequestration process at Hanford as well as collaborating with SRNL to develop a surface water model of the Tims Branch watershed at the Savannah River Site (SRS).

1. A manuscript by DOE Fellow Robert Lapierre for Waste Management 2016 based on his research and titled "Characterization of U(VI)-Bearing Precipitates Produced by Ammonia Gas Injection Technology into Unsaturated Sediments," has been rated as a "Paper of Note." As Gary Benda, WM Symposia Deputy Managing Director, wrote in his notification of the rating, "*Paper achieved the superior level rating based on the paper review judging criteria. It demonstrated superb knowledge and understanding, and lays the foundation for future waste management endeavors."*
2. A manuscript entitled, Effects of Ammonium on Uranium Partitioning and Kaolinite Mineral Dissolution, written by Hilary Emerson, Yelena Katsenovich, and Jim Szecsody and DOE Fellow Silvina Di Pietro, was accepted for the publication in the *Journal of Environmental Radioactivity*.
3. An abstract entitled, "Effects of Ammonia and Variable Redox Conditions on Mineral Dissolution," authored by DOE Fellow Silvina Di Pietro, Hilary Emerson, Yelena Katsenovich, and Jim Szecsody was submitted to the American Chemical Society (ACS) Spring 2017 Conference. Vasileios Anagnostopoulos will be one of the 254th ACS Fall National Meeting & Exposition organizers for the session on "Fate, Transport and Remediation of Radionuclides in the Environment." The purpose of this session is to highlight recent developments in radionuclide fate and transport in the environment and emerging remediation strategies.
4. FIU has developed a MIKE 11 model of the Tims Branch A-014 outfall tributary, representative of the stream flow, and has begun running test simulations. Currently, the model produces results that visually represent the natural hydrology within the channel. This stream model will be coupled with the MIKE SHE overland flow model to complete the surface hydrology model development for this part of the Tims Branch stream. A report for the development of the MIKE 11 model of the A-014 outfall tributary has been drafted and is undergoing internal review.

Project 3: **Deactivation and decommissioning (D&D)**

FIU is assisting DOE EM to meet high priority D&D needs and technical challenges across the DOE complex through technology development, demonstration and evaluation. FIU is investigating the use of intumescent coatings to mitigate the release of radioisotopes during fire and/or extreme heat conditions that can potentially occur at a DOE contaminated facility/ building.

1. FIU is performing a series of tests to subject test coupons of intumescent coatings to increasing temperatures using a muffle furnace along with adhesion and impact testing of these test coupons on various types of substrates in support of SRS 235-F D&D requirements. Utilizing the testing protocols outlined in ASTM D3359, Standard Test

Methods for Measuring Adhesion by Tape Test, FIU conducted a series of adhesion tests on 4"x4" stainless steel coupons prepared under environmentally controlled conditions at 72ºF and 43% humidity. Adhesion tests were conducted before and after subjecting the prepared test coupons to extreme heat conditions in a muffle furnace at temperatures between 600-800ºF for 15 minute periods.

2. FIU is preparing to conduct a cold demonstration / test and evaluation of applying intumescent coatings in a full-scale SRS 235-F hot cell mock-up testbed. The design phase for the full-scale hot cell was completed, reviewed, and approved by the project task stakeholders (SRS 235-F site personnel, SRNL, and ARC). The decision was made to pursue a combination middle and corner cell design using the actual hot cell dimensions from the site's schematics. A raised floor will also be incorporated to best mirror the operational conditions experienced at the site. Construction of the testbed has begun.

***Project 4:* STEM workforce development**

FIU created the DOE Fellows Program in 2007 to assist DOE EM to address the problem of an aging federal workforce. The program provides training, mentorship, and professional development opportunities to FIU STEM students. The DOE Fellows provide critical support to the DOE EM research being conducted on high impact/high priority research being conducted at FIU.

1. FIU completed the DOE Fellows Fall 2016 selection process by reviewing a total of twenty-five (25) applications received from interested FIU students, interviewing a selection of ten (10) candidates, and selecting and hiring four (4) new DOE Fellows for the program.
2. On November 3, 2016, FIU conducted the tenth (10^{th}) annual DOE Fellows Induction Ceremony. This year, eleven (11) FIU STEM students were inducted as DOE Fellows. Ms. Stacy Charboneau (Associate Principal Deputy Secretary for Field Operations, DOE EM) was one of the keynote speakers for the ceremony. Other distinguished guests from DOE EM included Mr. Barton Barnhart (Director, Office of Infrastructure Management & Disposition Policy), Mr. Kurt Gerdes (Director, Office of Subsurface Closure), and Mr. Andrew Szilagyi (Director, Office of Infrastructure and D&D). The guests had an opportunity to participate in morning tours of the ARC research laboratories and listen to DOE Fellows presenting their research work.
3. The DOE Fellows completed development of abstracts on their research to be presented at Waste Management 2017 during the student poster session. A total of 17 student abstracts have been submitted to the conference.

Project deliverables and milestones during this reporting period include:

Program-Wide:

- FIU completed the FIU Performance Year 6 Year End Report, summarizing the work completed for all project tasks during the last year. FIU also received comments from DOE on the FIU Performance Year 7 Project Technical Plan. FIU researchers completed revisions to the FIU Performance Year 7 Project Technical Plan based on comments received from DOE and submitted the final documents to DOE on November 17, 2017.

***Project 1*: High level waste (HLW)/waste processing**

- Milestone 2016-P1-M18.2.1 has been delayed due funding delays. The milestone will be reforecast when the funding issues are resolved.

***Project 2:* Environmental remediation (ER)**

- To complete milestone 2016-P2-M1, three draft papers were submitted to Waste Management Symposia by 11/4/16 to be published in the WM Symposia proceedings: 1) Removal of U(VI) in the Alkaline Conditions Created by NH3 Gas (abstract #17288); 2) Iron Behavior in Microcosms Simulating Bioreduction in Savannah River Site Sediments (abstract #17389); and 3) Ammonia Gas Treatment for Uranium Immobilization at DOE Hanford Site (abstract #17067).
- Milestone 2016-P2-M2 was completed with the submission of an abstract entitled, "Effects of Ammonia and Variable Redox Conditions on Mineral Dissolution," to the ACS Spring Conference on November 30, 2016.
- A summary of the work completed to date on subtask 2.1 for the acidification of SRS F/H Area soil and, more specifically, to the creation of different profile acid-impacted soil samples through monitoring of the concentrations of Fe, Al and Si in the leachates, was sent to DOE and the SRS points-of-contact on December 15, 2016 (FIU milestone 2016-P2-M4).
- Preliminary development of the MIKE 11 stream flow model for the A-014 outfall tributary (subtask 3.1, milestone 2016-P2-M3) was completed and a summary of the work was sent to DOE and SRS on December 8, 2016.

***Project 3:* Deactivation and decommissioning (D&D)**

- Milestones 2016-P3-M1.2 and 2016-P3-M3.1, completion of draft papers on WIMS and D&D KM-IT for submission to the Waste Management Symposium, was completed in November.

***Project 4:* STEM workforce development**

- Milestone 2016-P4-M1 was completed with the development of the draft summer internship reports. These deliverables are available on the DOE Fellows website (https://fellows.fiu.edu/internships-reports/).
- FIU also completed milestone 2016-P4-M2 and associated deliverable with the final selection and recruitment of the DOE Fellow Class of 2016.
- Milestone 2016-P4-M3 was completed with the conduction of the induction ceremony for the DOE Fellows Class of 2016, held on November 3, 2016.

The program-wide milestones and deliverables that apply to all projects (Projects 1 through 4) for FIU Performance Year 7 are shown on the following table.

Task	Milestone/ Deliverable	Description	Due Date	Status	OSTI
Program-wide (All Projects)	Deliverable	Draft Project Technical Plan	9/30/16	Complete	
	Deliverable	Monthly Progress Reports	Monthly	On Target	
	Deliverable	Quarterly Progress Reports	Quarterly	On Target	
	Deliverable	Draft Year End Report	10/13/17	On Target	OSTI
	Deliverable	Presentation overview to DOE HQ/Site POCs of the project progress and accomplishments (Mid-Year Review)	4/7/17*	On Target	
	Deliverable	Presentation overview to DOE HQ/Site POCs of the project progress and accomplishments (Year End Review)	9/29/17*	On Target	

**Completion of this deliverable depends on availability of DOE-HQ official(s).*

Project 1
Chemical Process Alternatives for Radioactive Waste

Project Manager: Dr. Dwayne McDaniel

Project Description

Florida International University has been conducting research on several promising alternative processes and technologies that can be applied to address several technology gaps in the current high-level waste processing retrieval and conditioning strategy. The implementation of advanced technologies to address challenges faced with baseline methods is of great interest to the Hanford Site and can be applied to other sites with similar challenges, such as the Savannah River Site. Specifically, FIU has been involved in: modeling and analysis of multiphase flows pertaining to waste feed mixing processes, evaluation of alternative HLW instrumentation for in-tank applications and the development of technologies to assist in the inspection of tank bottoms at Hanford. The use of field or *in situ* technologies, as well as advanced computational methods, can improve several facets of the retrieval and transport processes of HLW. FIU has worked with site personnel to identify technology and process improvement needs that can benefit from FIU's core expertise in HLW. The following tasks are included in FIU Performance Year 7:

Task No	Task
Task 17: Advanced Topics for Mixing Processes	
Subtask 17.1	Computational Fluid Dynamics Modeling of HLW Processes in Waste Tanks
Task 18: Technology Development and Instrumentation Evaluation	
Subtask 18.2	Development of Inspection Tools for DST Primary Tanks
Subtask 18.3	Investigation Using an Infrared Temperature Sensor to Determine the Inside Wall Temperature of DSTs
Task 19: Pipeline Integrity and Analysis	
Subtask 19.1	Pipeline Corrosion and Erosion Evaluation
Subtask 19.2	Evaluation of Nonmetallic Components in the Waste Transfer System

Task 17: Advanced Topics for HLW Mixing and Processing

<u>Task 17 Overview</u>

This task will use the knowledge acquired at FIU on multiphase flow modeling to build a CFD computer program in order to obtain simulations at the engineering-scale with appropriate physics captured for the analysis and optimization of various mixing processes. Focus will be given to turbulent fluid flow in nuclear waste tanks that exhibit both Newtonian and non-Newtonian fluid characteristics.

The objective of this task is to provide the sites with mathematical modeling, validation, and testing of computer programs to support critical issues related to HLW retrieval and processing. FIU engineers will work directly with site engineers to plan, execute, and analyze the results of the research and development.

Task 17 Quarterly Progress

Subtask 17.1: CFD Modeling of HLW Processes in Waste Tanks

CFD for Pipeline Transport of Bingham Plastic Fluids

An approach was developed to obtain higher order gradients in Star-CCM+. The reason for the development of this approach was because raw data extracted from this application required transformation into arrays of field variables with rows and columns associated with increasing location in the x and y directions. Figure 1-1 shows plots of position in the x and y directions versus cell index for raw data obtained on a two-dimensional plane created inside a three dimensional domain of a QDNS simulation with approximately 450,000 computational cells. It was observed that an increase of index did not represent an organized periodic pattern for positions in the x or y directions, as shown in Figure 1-1. Based on this fact, any filed variables obtained on this plane did not follow an organized pattern. In addition, raw data obtained from Star-CCM+ was in the form of column vectors and needed to be converted into matrices for further processing. Therefore, reshaping and sorting operations on data into columns and rows of constant x and y were necessary. Additional processing on the data was performed to obtain components of velocity in three directions, as shown in Figure 1-2. Currently, research is ongoing to program data into Star-CCM+ and obtain the dissipation rate and Kolmogorov length scale for each individual time step based on higher order gradients. A comparison between turbulent dissipation rate (TDR) data obtained using higher gradients (ongoing) and first-order gradients (the raw data) can be performed later.

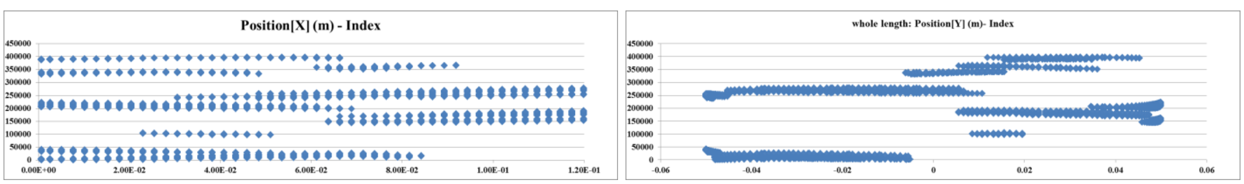

Figure 1-1. Plot of location versus index obtained on a 2d plane along computational domain.

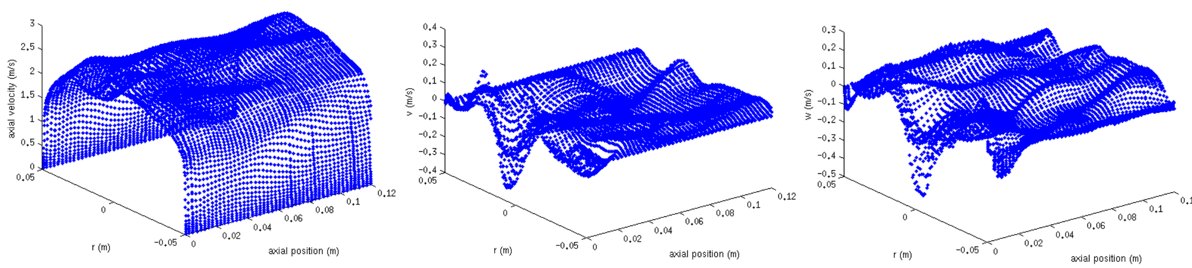

Figure 1-2. Axial, radial, and tangential components of velocity after data re-arrangements.

In the effort to improve accuracy of RANS-HB's Predictions, a QDNS-HB simulation study of pipe flow of Bingham fluid was conducted. Figure 1-3 shows the results of the QDNS simulation inside a pipe with almost 1 million computational cells at T = 7.5 seconds. Here, contour of axial velocity and averaged velocity (along a probe at the outlet with experimental data) are displayed. Results indicated that good agreement exists between the simulation and experimental data. In addition, velocity magnitude and TDR data are shown for various structures of turbulence obtained from iso-surfaces of Q-criterion in Figure 1-3(c-d). To better separate regions of low and high dissipation, the maximum value on the scale was set to 0.1, which shows strong dissipation occurring at the walls of the domain.

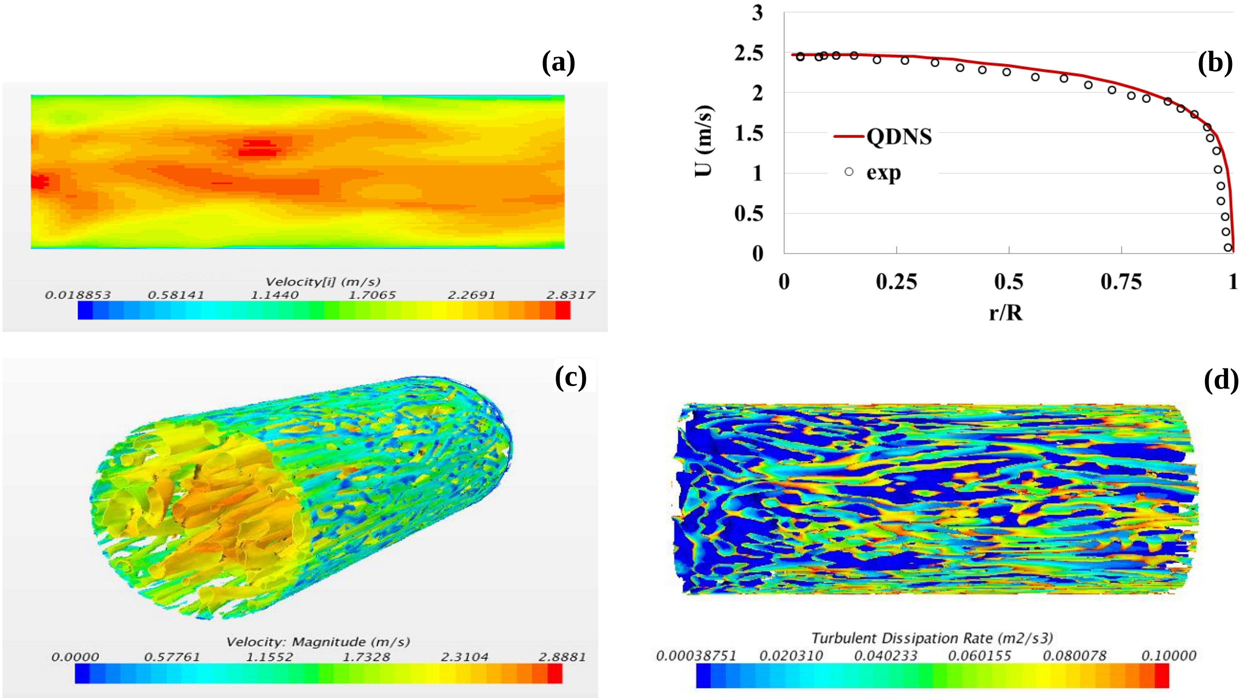

Figure 1-3. Q-DNS simulation results-contour of axial velocity, agreement with experimental data, turbulent scales colored by velocity and dissipation.

Shear dependency analysis in Dissipative Scales

An analysis was performed on results obtained from both the RANS-alpha and Q-DNS-HB simulations. In this analysis, variation of the shear rate against a quantity defined by Eq.(1) was obtained for dissipative scales. u_{rms} and η represent velocity and length scale of turbulent scales. In this equation, K, v, and ε, represent turbulent kinetic energy (TKE), kinematic viscosity, and TDR, respectively. The quantity u_{rms}/η has the same units as shear rate which is sec^{-1} and is zero for non-dissipative scales. Generally, η represents the Kolmogorov length scale which is the smallest scale in turbulent flow and is based on the average value of ε obtained from spatial analysis. Here, this length scale is similarly obtained but from local values of TDR. In RANS, TKE and TDR are obtained from the solution to the closure equations of k and ε and are directly accessible from STAR-CCM+. In Q-DNS, TKE and TDR must be obtained from fluctuations of velocity components. For this purpose, values of u_{rms}, TKE, and TDR are obtained from Eq.(2), Eq.(3), and Eq.(4).

$$\frac{u_{rms}}{\eta} = \frac{\sqrt{\frac{2K}{3}}}{\frac{\upsilon^{3/4}}{\varepsilon^{1/4}}} \qquad \text{(Eq.1)}$$

$$u_{rms} = \sqrt{\frac{1}{3}\left(u_{x,rms}^{2} + u_{y,rms}^{2} + u_{z,rms}^{2}\right)}\ , \quad u_{x,rms} = \sqrt{\overline{\acute{u}_x^{2}}}\ , \quad u_{y,rms} = \sqrt{\overline{\acute{u}_y^{2}}}\ , \quad u_{z,rms} = \sqrt{\overline{\acute{u}_z^{2}}} \qquad \text{(Eq.2)}$$

$$TKE = \frac{\acute{u}_x^{2} + \acute{u}_y^{2} + \acute{u}_z^{2}}{2} \qquad \text{(Eq.3)}$$

$$TDR = \mu\ (2\overline{\frac{\delta \acute{u}_x}{\delta x}^{2}} + 2\overline{\frac{\delta \acute{u}_y}{\delta y}^{2}} + 2\overline{\frac{\delta \acute{u}_z}{\delta k}^{2}} + \overline{\left(\frac{\delta \acute{u}_x}{\delta y} + \frac{\delta \acute{u}_y}{\delta x}\right)^{2}} + \overline{\left(\frac{\delta \acute{u}_x}{\delta z} + \frac{\delta \acute{u}_z}{\delta x}\right)^{2}} + \overline{\left(\frac{\delta \acute{u}_y}{\delta z} + \frac{\delta \acute{u}_z}{\delta y}\right)^{2}}\ ) \qquad \text{(Eq.4)}$$

In RANS, extensive analysis was performed for four turbulent flows with Re = 10000, 15000, 20000, and 25300. The purpose of these investigations was to observe similarities between profiles. For the quantity u_{rms}/η, FIU observed similar profiles that are all non-linear and grow with an increase of Reynolds number, as shown in Figure 1-4(a). This is a result of higher shear and velocity rms in higher Reynolds numbers. In addition, each profile has comparable maximums on the x and y axes. Perhaps normalization of the results could make all profiles coincide; this requires additional investigation. Additional and similar analysis was performed using the ratio of turbulent dissipations to turbulent kinetic energy or TDR/TKE which has the same units as shear rate (1/sec). For each Reynolds number shown in Figure 1-4(b), a profile with a small slope is preceded with a profile having a significantly larger slope. The former is indicative of variations in the vicinity of solid boundaries and the slope of this profile grows with increasing Reynolds number. In contrast, variations with almost equal slopes are observed in small values of TDR/TKE for different Reynolds numbers. Similarity between these profiles suggest that a correlation can be obtained and implemented into the RANS-HB modeling to directly modify the shear rate based on TDR/TKE values.

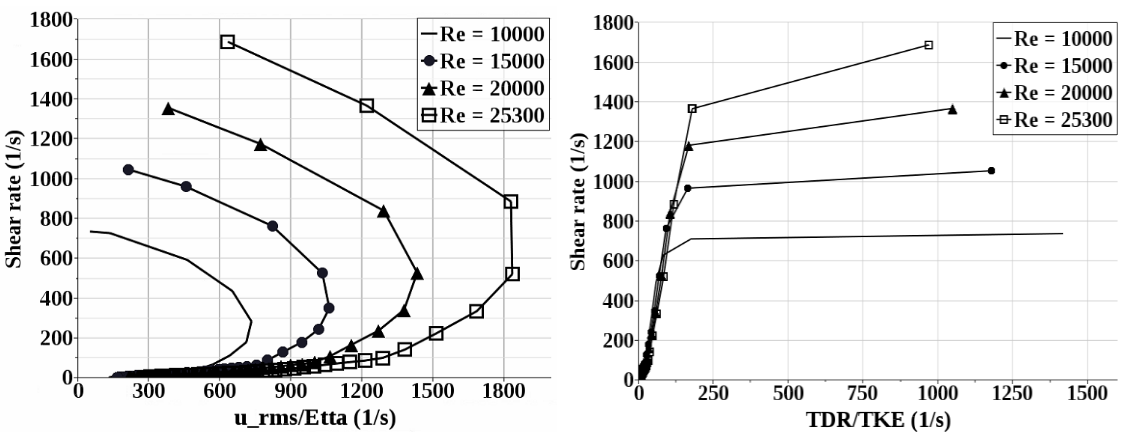

Figure 1-4. Variation of Shear Rate versus Different Ratios.

The same analysis of shear rate was performed for QDNS_HB simulation results for Re=25300. Variation of shear rate versus u_{rms}/η, as shown in Figure 1-5(a), indicated that a qualitative similarity existed between Q-DNS and RANS-alpha simulations. However, significantly smaller values were observed for the RANS approach.

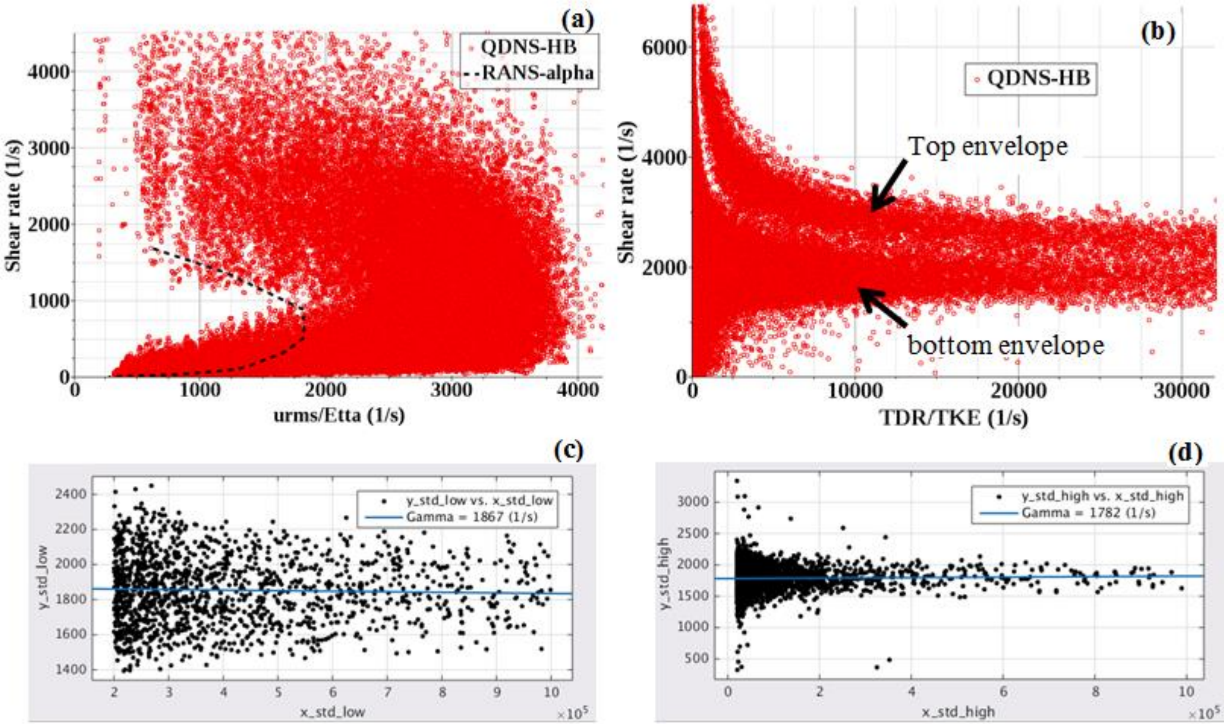

Figure 1-5. Variation of Shear Rate versus Different Ratios.

Variation of shear rate versus TDR/TKE, as shown in Figure 1-5(b), revealed two envelopes which were partly similar. The top envelope was found to contain computational cells on solid boundaries and in structures that existed in core flow regions, as shown in Figure 1-6. It was found that the top envelope was related to regions of small u_{rms}/η, which could be separated from the bottom envelope by u_{rms}/η <400 s^{-1}.

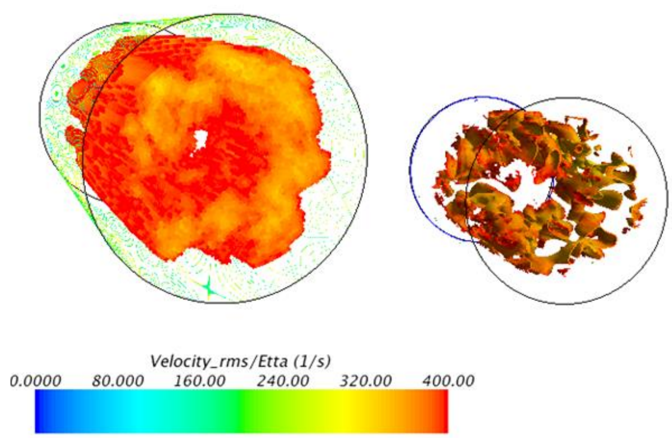

Figure 1-6. Structures Found in Core Flow Which Belong to Top Envelope in Figure 1-5.

Another observation from Figure 1-5(b) was that both top and bottom envelopes showed a reduction of shear rate with an increase of TDR/TKE. However, a region of almost constant shear rate was found in small values of TDR/TKE for the bottom envelope. Since more attention was given to higher values of the dissipation rate, trends of the variation was of major importance in higher values of TDR/TKE. A regression analysis was performed in Matlab, as shown in Figure 1-5(c-d), and values of 1867(1/s) and 1782 (1/s) were obtained for top and bottom envelopes, respectively.

An algorithm was developed that used the converged shear rate values obtained previously in the RANS-HB simulation. In this algorithm, the distinction between converged values is based on values of u_{rms}/η for each cell in RANS-HB simulations. Eq.(5) shows the model that was used for alteration of shear rate in the RANS-HB simulation:

$$\Upsilon = \begin{cases} 1867\,(1/s) & \frac{u_{rms}}{\eta} \leq \frac{u_{rms}}{\eta}\_TSH \;\&\; \varepsilon_{HB} > \varepsilon\_THS \\ 1782\,(1/s) & \frac{u_{rms}}{\eta} > \frac{u_{rms}}{\eta}\_TSH \;\&\; \varepsilon_{HB} > \varepsilon\_THS \\ \Upsilon_{HB} & \varepsilon_{HB} \leq \varepsilon - THS \end{cases} \qquad \text{(Eq.5)}$$

In this model, index HB refers to simulation with HB viscosity model. Υ_{HB} is unaltered shear rate which is obtained directly from velocity field, and parameters ε-THS and u_{rms}/η _TSH are defined as thresholds for the dissipation rate and u_{rms}/η, respectively. FIU set the ε-THS to an extremely small number to engage the entire dissipation range into modifications. Sensitivity of the model can be further reduced by increasing the ε-THS values. The value of u_{rms}/η _TSH was obtained from Q-DNS, as discussed earlier, and was set to 400 s^{-1}. The shear rate obtained from the above model was then supplied to the HB viscosity model, which is defined by Eq.(6).

$$\mu = \frac{\tau_\gamma}{\gamma} + k\,\gamma^{(n-1)} \qquad \text{(Eq.6)}$$

Application of the proposed shear modification model was tested in a RANS-HB simulation of flow with Re = 25300. Results of this implementation are shown in Figure 1-7 and labeled as “RANS_HB(modified)”. FIU compared this result with those obtained from the RANS-alpha method and observed an excellent match. Also, this result was less than 2 percent different from the results obtained from the Q-DNS-HB results, as shown in Figure 1-3(b).

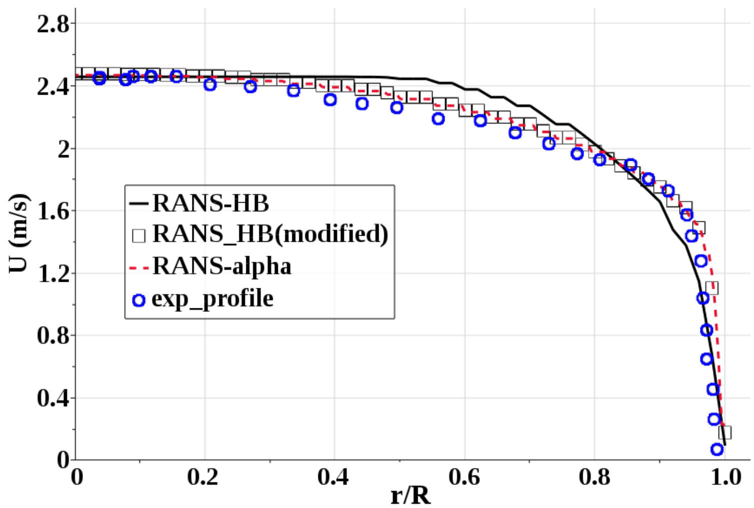

Figure 1-7. Improvement of RANS-BH's predictions.

Literature review on experimental and numerical studies related to HLW mixing and transfer

Selection of baseline experimental and simulation data is a critical step in conducting numerical simulations of waste mixing and transfer. An extensive literature review is being conducted in order to obtain correct properties and dimensions that can be used in construction of the computational domains, meshes, and simulations.

According to Rector et al. (2010), solids in the tanks at Hanford are generally composed of submicron particles of Boehmite and Gibbsite (in the form of AL_2O_3). The presence of these components can introduce particle gels with non-Newtonian behaviors; more specifically, a Bingham plastic type of fluid may exist (Lee 2012). By referring to observations of Powell et al. (1995), Wells et al. (2013) explains that slurry rheology may change from Newtonian to non-Newtonian and can cause significant reduction of mobilization of the clay layer. The effect can be a 40% increase of required flow rate to achieve the same waste mobilization metric, as usually identified by the effective cleaning radius (ECR). According to Adamson and Gauglitz (2011), suspending particles of a non-Newtonian slurry with higher yield stress is more difficult, but once erosion happens, particles stay suspended to a greater degree, as compared to situations with slurries with a lower yield stress. The combined effect will be higher concentrations in the transfer lines.

It is critical to know how the yield stress varies with the concentration of solids in the slurry. According to Lee (2012), a simulant composed of 22 wt% and 28 wt% Kaolin clay in water will have a yield stress of 3 Pa and 10 Pa, respectively. These stress values are recommended by RPP-PLAN-51625 for the simulant representing the slurry in Hanford tanks. In particular, this yield stress of the sediment layer at the bottom of the tank may be significantly different from the liquid above the solid sediment, the supernatant, which has suspended particles in it. This information is critical for the simulation since, if the mixture multiphase model is used, then different rheograms are needed for the solid layer and the supernatant. Therefore, a portion of the literature review will be dedicated to finding this variation.

In this research effort, attention will be given to the properties of different simulants used in full-scale or scaled experiments and simulations related to processes at or between Hanford tanks. Focus will be on reported data of tests conducted in 2011 and 2013, as well as related simulations. Details and reports regarding simulant development and refinement processes are provided by Wells et al. (2011) and Lee (2012a, 2012b).

Test 2011-Complex Five-Part Simulant

According to Wells et al. (2013), a complex 5-part solid simulant and water were used in SSMD testing in 2011. The 5-part solid simulant was composed of gibbsite, zirconium oxide, silicon carbide, stainless steel, and bismuth oxide, with composition and properties listed in Table 1-1. The simulant mixture was a solid weight percent of 19% in water, with 10% being contributed by zirconium oxide (d50 12 micron), 6% gibbsite (d50 10 micron), and three spike particles at a concentration of 1% each of bismuth oxide (d50 38 micron), silicon carbide (d50 150 micron), and stainless steel (d50 128 micron) (Jenson et al. 2012).

Table 1-1. Properties of Complex 5-part Simulant (Wells et al., 2013 & Jenson et al., 2012)

Component	Density (g/mL)	Median Particle Size (micron)	UDS Mass Fraction	UDS Volume Fraction
Gibbsite	2.42	10	0.32	0.523
Zirconium Oxide	5.7	12	0.53	0.368
Silicon Carbide	3.2	150	0.05	0.062
Stainless Steel	8	128	0.05	0.025
Bismuth Oxide	8.9	38	0.05	0.022

Other properties, such as critical shear stress and settling velocities, have been reported individually (for each solid constituent) by Wells et al. (2013) and in bulk (mixture) by Wells et al. (2011), respectively. The reported values are based on tests with water (1.0 g/mL, 1.0 cP) as the working fluid and are shown in Figure 1-8. It is important that for the 5 part simulant, only small differences exist between results reported for the three modes: 1) no-flow unsonicated, 2) flowing, and 3) sonicated flow. Also, these results could be used for simulations that use water as the supernatant, which is the case for the simulations reported in Wells et al. (2011, 2013) and Rector et al. (2011). An investigation can be performed on using these properties with other supernatants such as 68 wt% water and 32 wt% sodium thiosulfate to observe differences in various metrics, such as solid concentration.

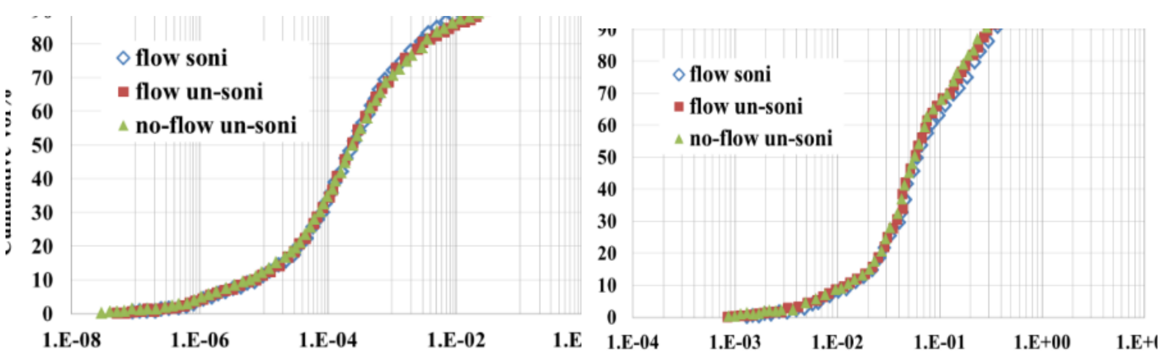

Figure 1-8. Properties and composition of undissolved solids in five-part simulant (Wells et al., 2011).

To obtain nozzle velocities for the 2011 tests with a 5-part simulant in water, FIU reviewed reports from Jensen et al. (2012) and Greer and Thien (2012). Rotational speeds of the mixer jet were obtained from the report by Wells et al. (2013).

Table 1-2. Test Conditions in 2011 (according to Wells et al., 2013)

Test Case	Scale	Nozzle Velocity (ft/s)	Jet Rotation Rate (rpm)	Solid Simulant	Supernatant
1	1:21	16.9	1.53	5-part	water
2	1:21	22.1	1.53	5-part	water
3	1:21	24.8	1.53	5-part	water
4	1:21	27.6	1.53	5-part	water
5	1:8	22.3	0.77	5-part	water
6	1:8	28.7	0.77	5-part	water
7	1:8	31.9	0.77	5-part	water
8	1:8	35.4	0.77	5-part	water

Results of the 2011 test using a 5-part simulant was provided by Wells et al. (2013) and are shown in Table 1-3. In this table, the first and second rows refer to pre-transfer effective cleaning radius (ECR) in normalized (divided by tank diameter) and non-normalized modes, respectively. The third column shows the concentration of UDS in the transfer line. In addition, information about concentration of each solid component for pre- and batch-transfer are available for a nozzle velocity of 16.9 ft/s in the report of Greer and Thien (2012). Data in Tables 1-3 and 1-4 represent average values if more than one measurement was taken for pre-transfer or batch transfer tests.

Table 1-3. Metrics Measured for 5-part Simulant (Wells et al., 2013)

metric ⬇	**43” tank Nozzle vel. (ft/s)**				**120” tank Nozzle vel. (ft/s)**			
	16.9	**22.1**	**24.8**	**27.6**	**22.3**	**28.7**	**31.9**	**35.4**
ECR/D	0.407	0.452	0.456	0.488	0.382	0.446	0.443	0.489
ECR (inch)	17.469	19.378	19.337	20.787	22.545	52.992	53.221	56.249
UDS	0.522	0.611	-	-	0.591	0.713	-	-

Table 1-4. UDS Concentration Measured for Each Solid Component of 5-part Simulant, (Greer and Thien, 2012)

mode	SiC	Bi2O3	ZrO2	Al(OH)3	SS
Pre-transfer	0.0115	0.011	0.5905	0.3725	0.0135
Batch 1	0.01325	0.01225	0.71	0.25325	0.01175
Batch 2	0.0105	0.00825	0.64925	0.3235	0.00775
Batch 3	0.0095	0.013	0.65125	0.318	0.00775
Batch 4	0.01575	0.009	0.67675	0.29075	0.0075
Batch 5	0.01025	0.00925	0.647	0.32425	0.009
Avg. of Batch	0.01185	0.01035	0.66685	0.30195	0.00875

Test 2013

The 2013 test used supernatants composed of water, glycerin, sodium thiosulfate, and sodium bromide with different concentrations, as reported by Lee et al. (2012 and 2013). Physical properties of these liquid simulants are listed in Table 1-5. To date, no reports were found in the literature about the variation in composition of liquid simulants, such as sodium bromide and sodium thiosulfate, in SSMD and full-scale testing. One possible assumption is that the concentration of ingredients does not change during mixing and transfer processes.

For the solid simulant, Lee (2012) introduced simulants with up to four undissolved solids (UDS), which were gibbsite ($Al(OH)_3$), sand, stainless steel, and zirconium oxide (ZrO_2). Properties of these particles are listed in Table 1-6. This table shows a broad variation in particle sizes between and within categories.

Table 1-5. Properties and Composition of Liquid Simulant (Lee et al., 2012-2013)

Simulant Properties @ 20ºC			Weight Fraction			
			Water	Sodium Thiosulfate	Glycerin	Sodium Bromide
Density	1.29 ± 5%	g/mL	0.68	0.32	0.0	0.0
Viscosity	3.6 ± 1%	g/m.s (cP)				
Density	1.098	g/mL	0.88	0.12	0.0	0.0
Viscosity	1.62	g/m.s (cP)				
Density	1.37 ± 5%	g/mL	0.471	0.334	0.195	0.0
Viscosity	15 ± 20%	g/m.s (cP)				
Density	1.32 ± 5%	g/mL	0.58	0.38	0.04	0.0
Viscosity	8.0 ± 20%	g/m.s (cP)				
Density	1.135	Density	0.47	0.0	0.53	0.0
Viscosity	8.03	Viscosity				
Density	1.37	Density	0.63	0.0	0.0	0.37
Viscosity	2.00	Viscosity				

Table 1-6. Properties and Composition of Undissolved Solids (Lee and Thien, 2013 & Wells et al., 2013)

Compound	Density (g/mL)	Median Particle Size, (micron)	UDS Mass Fraction		
			Low	Typical	High
Small gibbsite	2.42	1.3	1	0.27	0
Large gibbsite	2.42	10	0	0.44	0.03
Small sand	2.65	57	0	0	0.35
Medium sand	2.65	148	0	0.13	0
Large sand	2.65	382	0	0	0.21
Zirconium Oxide	5.7	6	0	0.10	0.08
Stainless Steel	8.0	112	0	0.06	0.33

Information about various test cases in 2013 is available in Table 1-7. The letter "H" refers to the highlighted rows and columns in Tables 1-5 and 1-6. A calculation for the highlighted column in Table 1-6 shows that the density of total solids is about 3584.2 kg/m^3. This table shows four cases in a small tank (scale 1:21 and 40-inch diameter) and four cases in a large tank (scale 1:8

and 120-inch diameter). According to Lee and Thien (2013), only 13 wt% of the slurry was solid. Wells et al. (2013) provided measured concentrations of the solid compounds in these experiments, as shown in Table 1-9. This table shows pre-transfer concentration values and batch transfer values inside the parenthesis. The term pre-transfer refers to samples taken from a recirculation loop by diverting the entire loop into a container according to Greer and Thien et al. (2012). The last row of Table 1-9 shows the mass fraction of the total solids that was transferred after the 5^{th} batch. This means that after 5 batch transfers, 34.1 wt% of initial total solids has been removed from the 43”-tank and 66.9 wt% remained. The initial solid weight can be found by multiplying the volume of the solid layer by its density, which was found to be 3584.2 kg/m^3. The solid volume itself depends on the configuration of the sediment inside the tank and more investigation is in progress to find the initial configuration of the solid layer. Moreover, geometrical dimensions for tanks and mixer jet pump installations were extracted from Lee and Thien (2013) and Jensen et al. (2012), as shown in Table 1-8.

Table 1-7. Test Conditions in 2013 (Lee and Thien, 2013 & Wells et al., 2013)

Test Case	Scale	Nozzle Velocity (ft/s)	Jet Rotation Rate (rpm)	Solid Simulant	Supernatant Properties	Capture Velocity (ft/s)
1	1:21	18.2	1.29	H*	H	11.3
2	1:21	22.1	1.56	H	H	11.3
3	1:21	26.1	1.84	H	H	11.3
4	1:21	33.9	2.39	H	H	11.3
5	1:8	28.7	0.73	H	H	11.3
6	1:8	31.1	0.79	H	H	11.3
7	1:8	33.5	0.85	H	H	11.3
8	1:8	38.3	0.97	H	H	11.3

* Refers to highlighted rows and columns in Tables 1-5 and 1-6.

Table 1-8. Geometrical Dimensions for Tank and Accessories (Lee and Thien, 2013)

Property	43" Tank	120" Tank
Tank internal diameter (m)	1.1	3.05
Mixer Jet Pump Nozzle Diameter (m)	0.0071	0.0203
Mixer Jet Pump Nozzle Elevation (m)	0.0218	0.0610
Mixer Jet Pump Suction Diameter (m)	0.0135	0.0373
Mixer Jet Pump Suction Elevation (m)	0.0061	0.0170
Mixer Jet Pump Axial Offset in 0° & 180° angles(m)	0.3230	0.8840
Transfer Pump Suction Diameter (m)	0.28	0.32
Transfer Pump Suction Velocity (m/s)	1.16 – 3.44	1.16 – 3.44
Transfer Pump Suction Elevation (m)	0.0071	0.0203
Transfer Pump Axial Offset in 90° angles (m)	0.0884	0.244
Transfer Pump Suction Inlet Diameter (m)	0.0064-0.0122* 0.0071**	0.0081-0.0139* 0.0081**
Transfer Line Diameter (m)	0.0095* 0.0079**	0.0095* 0.0095**

* lee (2012) for SSMD of AY-102 tank. ** Jensen et al. (2012) for SSMD of AY-102 tank.

Table 1-9. Pre-transfer Concentration Values in lbs/gal Measured for Solids in 2013 test (Wells et al., 2013)

Element	43" Tank Nozzle Vel. (ft/s)				120" Tank Nozzle Vel. (ft/s)			
	18.2	**22.1**	**26.1**	**33.9**	**28.7**	**31.1**	**33.5**	**38.3**
$Al(OH)_3$	0.033 (0.046)	0.047 (0.044)	0.049 (0.044)	0.045 (0.041)	0.052 (0.043)	0.042 (0.046)	0.045 (0.453)	0.042 (0.049)
Sand	0.359 (0.556)	0.767 (0.744)	0.805 (0.804)	0.902 (0.877)	0.888 (0.747)	0.8723 (0.893)	0.967 (0.928)	1.048 (0.955)
ZrO_2	0.093 (0.116)	0.118 (0.106)	0.127 (0.108)	0.122 (0.111)	0.138 (0.104)	0.112 (0.105)	0.110 (0.113)	0.914 (0.119)
SS	0.026 (0.016)	0.0473 (0.021)	0.1438 (0.124)	0.326 (0.219)	0.240 (0.128)	0.247 (0.147)	0.254 (0.209)	0.534 (0.286)
Total btch trns*	0.341	0.429	0.497	0.578	0.478	0.566	0.616	0.678

* Total batch transferred

For simulations in Star-CCM+, data and geometrical dimensions pertaining to the 2013 tests with four-component simulation will be considered, including information in Tables 1-5 through 1-9. Other considerations are included in the following paragraphs.

Air lift circulators

According to Greer and Thien (2012), the AY-102 tank contains 22 air lift circulators (ALC) with 0.8 meter diameters which extend down to within 0.8 meters of the tank floor. The report by Lee (2012) indicated that these ALCs are simulated in the scaled tanks and are marked as removable. For consistency between tests and simulations, a discussion on ignoring these ALCs in future simulations will be initiated and reports on communications will be provided in a later report.

Transfer lines and bottom of the tank

According to Lee and Thien (2013), the transfer line was off the center but equidistant from each mixer jet pump, as is the case in the schematic of the full-scale tank shown in Lee (2012). In simulations, the data in Table 1-8 will be used for creation of the computational domain. Also, the bottom of the tank is flat for all scaled and full-size tanks and the radius at the corner of the tanks are 1.6 inch and 0.6 inch in 120" and 43" tanks, respectively, according to Lee (2012).

Thickness of sediment layer and liquid layer

According to Jensen et al. (2012), AY-102 contains up to 1.78 m of settled solids. This number is 1.4 meters in reports of Thien et al. (2011) and Greer and Thien (2012). However, no records of solid layer thickness inside the scaled tanks were found to date. One possible estimate can be a scaled-down solid layer via scale factors (1:8 and 1:21). For calculations, FIU used the values reported by Greer and Thien (2012) and obtained H_{solid} =1.4/8= 0.175 m and H_{solid} =1.4/21= 0.067 m, for the large and small tanks, respectively. Using the same estimate for the liquid layer, FIU obtained H_{iquid}=9.2/8= 1.15 m and H_{liquid} =9.2/21= 0.43 m, for the large and small tanks, respectively. Here, 9.2 m is the liquid height in the AY-102 tank, as reported by Greer and Thien (2012). If this scaling estimate is accurate, a 13 wt% solid containment, as reported by Lee and Thien (2013), must be attained. Using the total solid density of 3584.2 kg/m^3 and liquid density of 1370 kg/m^3, FIU obtained the solid to liquid mass fraction of ρ_{solid} * H_{solid}*A_{tank} / ρ_{solid} * H_{solid}*A_{tank} = 3584.2 *0.175/(1370*1.15) = 0.398, which provides a 40 wt% of solid in the scaled 120" tanks. This discrepancy suggests that a reconfirmation of the solid and liquid heights in the scaled tanks is needed.

Data collection times

According to Jensen et al. (2012), for the 120" vessel, batch transfer times corresponding to suction velocities of 6 to 11.3 ft/s are approximately 127 to 237 minutes. For the 43.2" tank, these times are approximately 8 to 14 minutes for the same velocities. These times are 1071 – 1667 minutes for the full-scale AY-102 tank, corresponding to 7.26 to 11.3 ft/s velocities at the suction inlet, respectively. Measurement data by Jenson et al. (2013) show periods of 12500 to 60000-seconds for data collection. Data collection times are as large as 80000 seconds in the report of Well et al. (2013). In the case of simulation work, a 50000-second data collection period was reported by Wells et al. (2013). These researchers reported on monitoring the solid concentration during batch transfer for single particle simulation (ZrO_2) and at flow rates of 80 and 90-gpm inside the 120" tank.

Need for scaled and full-system CFD modeling

According to Peurrung et al. (2013), modeling and scaled testing of waste handling processes is a necessity since full-scale vessel testing may be too costly and time consuming. For this reason, design and optimization of several processes in waste mixing and transport are based on results from pilot-scale experiments, which are difficult to extrapolate to full-scale behavior, according to Rector et al. (2010). Thus, both scaled and full-scale CFD simulations are needed. These researchers used high-performance multiphase flow simulations to resolve design, operational safety, and optimization issues for high-level waste transport processes.

The current approach in simulating these systems is to use one of the commercial CFD programs with a multi-fluid option to model the different phases. The primary drawback with this approach is that some programs are limited in their parallel scaling. As an example, use of Fluent code design verification was rejected due to substantial difficulty in result validation, according to Peurrung et al. (2013). However, FIU's up-to-date research shows that Star-CCM+ has appropriate parallel computing performance and ease of implementation of user defined functions which suggests a level of suitability for this CFD application.

Challenges

Numerical simulation of mixing of solid-liquid slurries using high-speed fluid jets is a technical challenge because of the large separation of spatial and time scales (Rector et al., 2010). Peak jet velocity at the nozzle is on the order of 10 meters per second, which results in a Courant limit time step on the order of thousandths of a second. Therefore, a complete cycle of rotation of the high-speed jets in a tank takes approximately 1 minute and the simulation needs a large number of time steps. For example, a typical pulse-jet simulation takes weeks or even months to complete on a mid-size computer cluster for a single proposed operational configuration, according to Rector et al. (2010). In addition, CFD simulation must consider the strong interactions between fluid flow, solid transport, and erosion/suspension from/to the sediment layer, as shown in Figure 1-9. Peurrung et al. (2013) concluded that jet mixing simulations of a scaled tank experiment can take only 5 hours using 5000 processor cores while it may take 336 hours (two weeks) if run on a cluster with 64 processor cores. Therefore, an essential step in conducting simulation of the mixing system is obtaining an estimate of the minimum number of processors needed to simulate mixing and transport processes as quickly and accurately as possible.

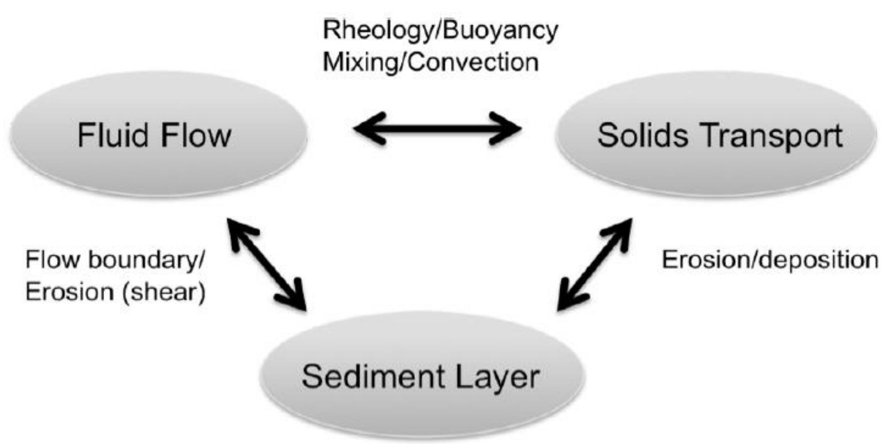

Figure 1-9. Interactions of liquid, suspended solids and settled solid fields during tank mixing operations, image and description from Rector et al., (2010).

Capability of Star-CCM+ in handling suspension/emulsion

The presence of solid particles that are suspended in a Newtonian fluid can lead to a significant change in viscosity. The effect is more pronounced with an increase in the volume fraction of solid particles, which directly affects the viscosity of mixture, and the mixture may behave like a non-Newtonian fluid. In Star-CCM+, this behavior is handled by the *Suspension Rheology* model. This model is used for discrete phase particles suspended in a liquid, as a continuous phase. Currently, use of the *Suspension Rheology* model is not feasible due to its use of continuum phase representation for the solid phase instead of discrete particles.

Models Utilized in Star-CCM+

The sediment layer at the bottom of double-shell tanks needs to be modeled during simulation of flow inside the tanks. This requires that the simulation starts with a known shape of the sediment layer, which can change by mobilization of the particles (effect of turbulent jet) and settling of the particles. In order to examine the ability of Star-CCM+ in creating a sediment layer, a region with an initial solid volume fraction equal to the maximum packing ratio was needed. Creation of a multi-region domain, with the initialized condition of ε_solid = max_packing ratio (= 0.624) was used. FIU evaluated the creation of a multi-region domain with an interface between regions by creating two regions with completely different phase volume fractions as initial conditions. FIU continues the erosion analysis based on the flow of water over the patched area.

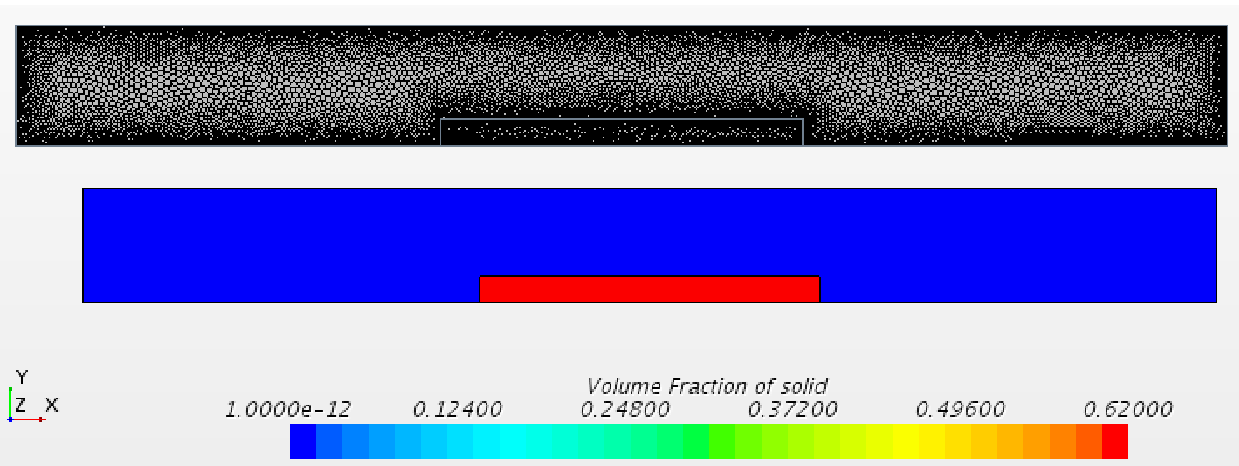

Figure 1-10. Mesh and initialization of a multiple region domain created in Star-CCM+.

In this period of performance, a domain with a jet and sediment layer was created in STAR-CCM+ and flow was simulated using a Eulerain-Eulerian multiphase flow approach with a laminar solver. Additionally, analysis of data obtained from QDNS simulations continued and a paper on the topic was submitted to the 2017 Waste Management Symposia.

Numerical Simulation

General approaches in the literature regarding the simulation of the mobilization of sediment first requires the erosion of the sediment surface and then focuses on the suspension of the sediment. FIU focused on literature and simulations for the initial erosion of the solid phase. These simulations were conducted to better understand the fundamental problems and limitations that exist with current simulation methods.

The literature contains a number of numerical studies on sediment erosion using an Eulerian-Eulerian approach, which is also referred to as the two-fluid model (TFM) approach. In this approach, both solid and fluid phases are treated as a continuum and equation sets are solved separately for each individual phase that is present in the flow. Some of the research using this method has been conducted by Parsi et al. (2015), Rector et al. (2010), He et al. (2009), and Gustavasson and Almstedt (2000). An alternative approach is the Euler-Lagrange method where the solid is treated as a discrete phase (particles) and has been used by Mercier et al. (2014) and Kim et al. (2015). In this work, the first approach is considered and the following paragraphs explain the details of the procedure.

Initially, a multiphase simulation of a jet flow inside a single-region domain was considered (no sediment). The purpose of the simulation is to quickly evaluate the performance of the TFM solver in STAR-CCM+ using a simple flow. The liquid was modeled as water and the solid phase as aluminum with a particle size of 1 mm. The solid phase was initially evenly distributed in the domain. Figure 1-11 shows the distribution and velocity contour of the solid phase inside this domain with the water jet flow.

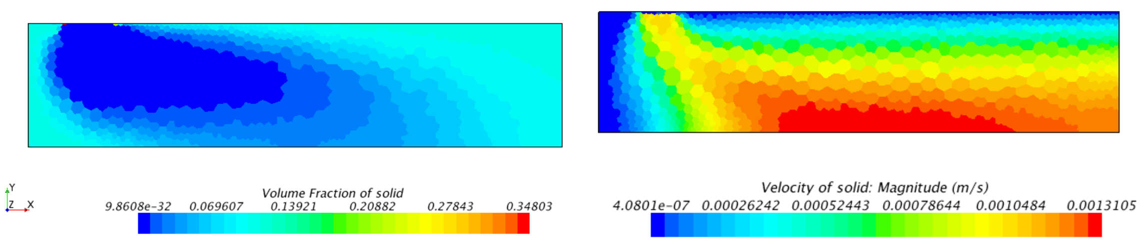

Figure 1-11. Multiphase simulation of jet flow in a single-region domain.

After successful convergence of the simulations, the jet flow inside a multi-region domain was considered. This domain is shown in Figure 1-12 and consists of a jet at the inlet with the pressure at the outlet set to zero. A single-phase simulation was considered initially to ensure that the flow across the interfaces between the two regions was continuous. Results are shown in Figure 1-13.

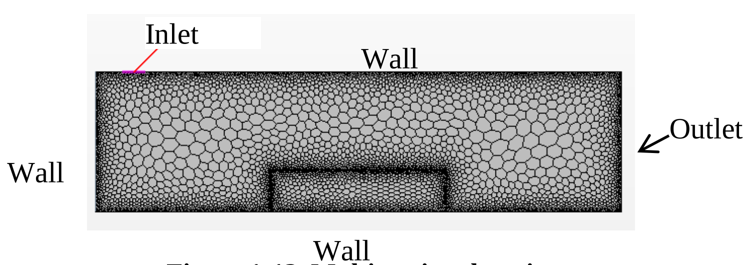

Figure 1-12. Multi-region domain.

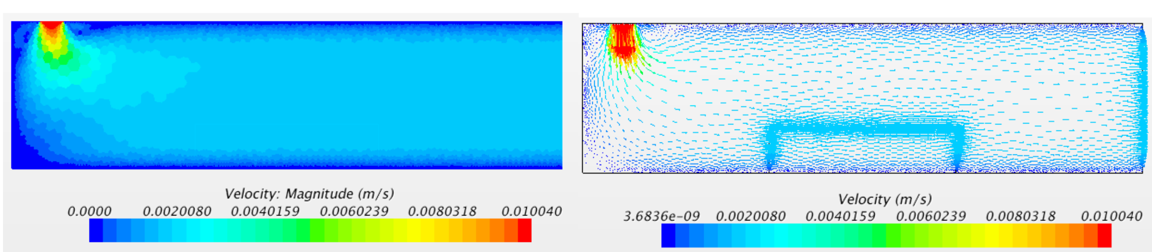

Figure 1-13. Single-phase simulation of jet flow in a multi-region domain.

In the next step, a multiphase simulation inside the multi-region was considered. The smaller region initially contained the solid as shown in Figure 1-14, and for initial evaluations, granular pressure, temperature and viscosity were not solved. An initial constant viscosity was used for the solid phase. Simulation results, shown in Figure 1-14, indicate diffusion of the solid which smeared the interface between solid and fluid. The results here do not show erosion and suspension of the solid which is directly associated with the viscosity inside and on top of the sediment. The results suggest that additional investigations using erosion conditions and modified viscosity is necessary.

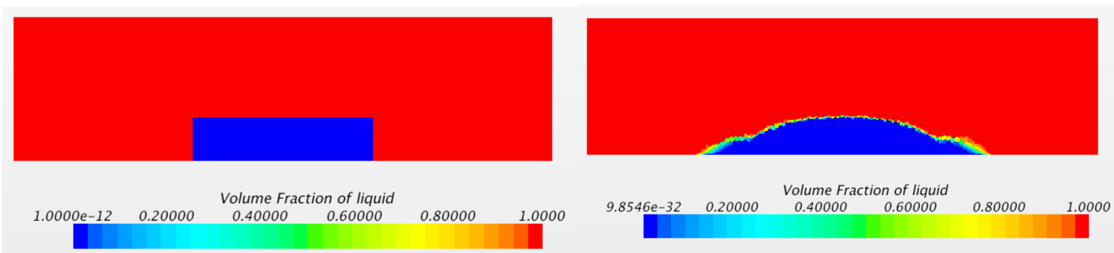

Figure 1-14. Multiphase simulation of jet flow in a multi-region domain.

According to Marcier et al. (2012-2014), Bonelli et al. (2012), and Rector et al. (2010), erosion occurs if shear stress on the sediment is greater than its yield stress. Initially, values of the shear stress were obtained and it was observed that maximum shear stress was approximately 0.064 Pa in the areas close to the jet inlet and lower values were observed on the top of the sediment layer. These shear stress values were lower than the yield stress values found in Bonelli et al. (2006), Marcier et al. (2012-2014), and Bamberger et al. (2010). Therefore, implementation of the erosion law was pointless, since even at small yield stress values, no erosion would occur at this stress level. As an alternative, an artificial viscosity for the liquid was assigned to regions where the solid volume fraction was equal or larger than 0.624. This artificial viscosity was set to a large value (ten times larger than the viscosity of the liquid) to reflect higher resistance to flow inside the smaller domain. Initial conditions are shown in Figure 1-15.

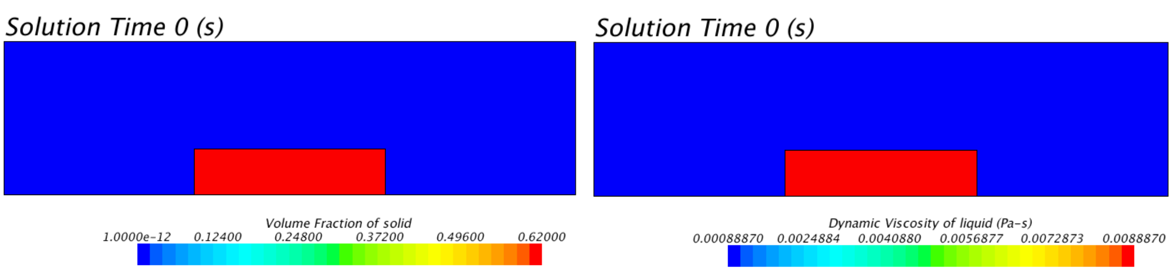

Figure 1-15. Initial conditions for simulation of jet flow in a multi-region domain.

An example simulation with the above parameters was conducted for 60 seconds and results are shown in Figure 1-16. The sediment layer was deformed and suspended in the liquid. Results show that there was still residue left in the domain after 60 seconds, which was an unrealistic situation caused by the artificial viscosity assigned to the solid region. Continuity of flow across the interfaces and flow inside the smaller regions are shown after the solid is pushed from the domain.

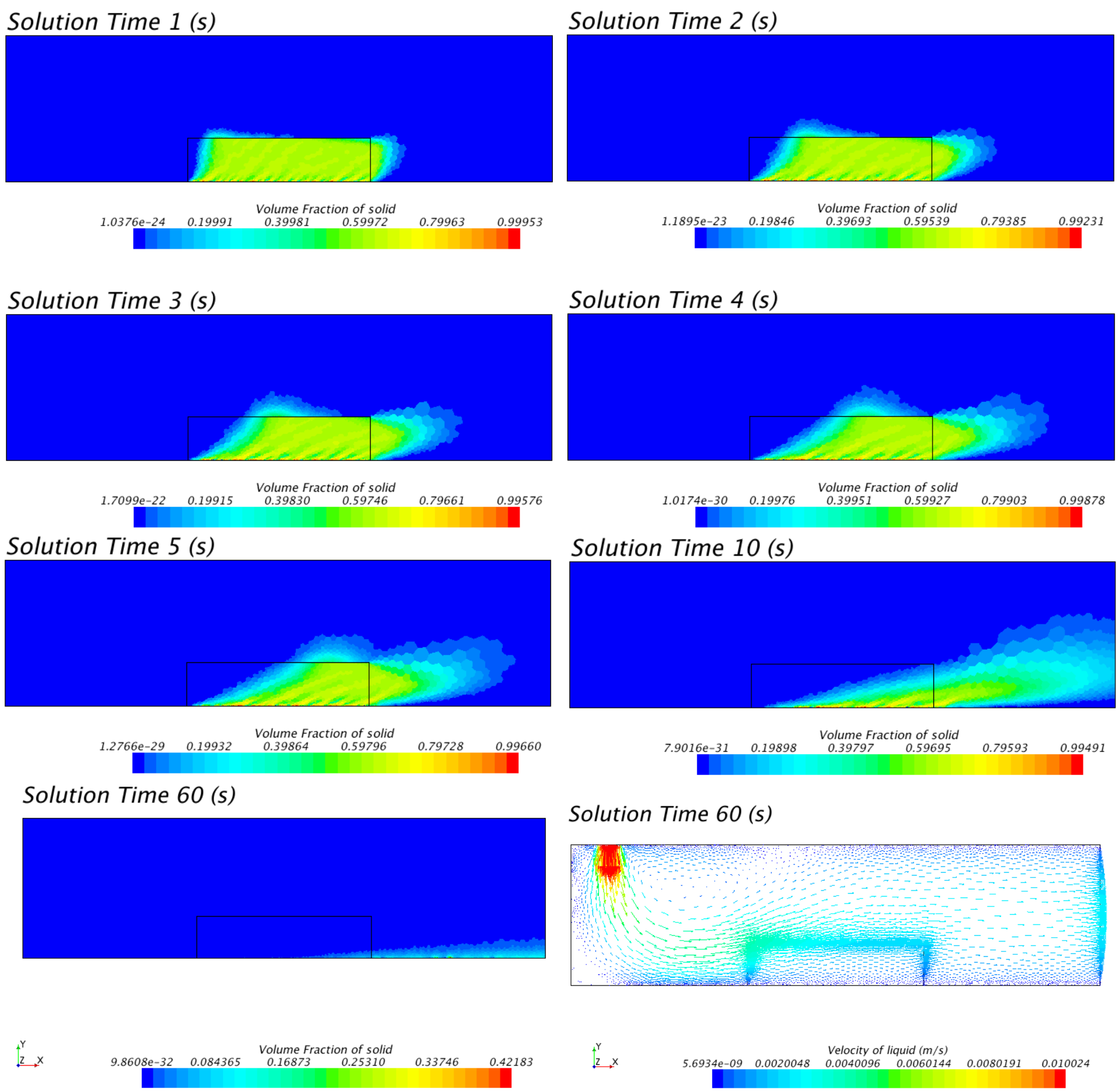

Figure 1-16. Evolution of flow from 0 sec to 60 sec, contour of solid volume fraction.

The work presented here shows that simulating erosion without changing the volume fraction directly in STAR-CCM+ is possible. It was shown that without solution of the granular temperature and pressure, a symmetric diffusion occurs to the solid layer, which does not comply with asymmetric boundary conditions of the simulation. However, setting a large value of viscosity in the solid layer resulted in deformation of the sediment layer and diffusion of the solid in the liquid phase (suspension). This solid diffusion increased over time at an extremely slow rate, which was related to the fact that the artificial viscosity was set to a significantly large value. Future efforts will focus on incorporation of the calculation for solid pressure and granular temperature, which sets additional bounds to the solid volume fraction.

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Subtask 17.2: Computational Fluid Dynamics Modeling of a Non-Newtonian Fluid Undergoing Sparging for Estimating PJM Mixing Times

During the first month of this quarter, a literature review of bubbles and bubble columns was conducted for this task. Experimental studies of a bubble travelling through a Bingham plastic type fluid were found (Dubash et al., 2004 and Tripathi et al., 2015), which will give insight into the results that should be obtained from FIU's study. Similarly, experimental studies involving the mixing of bubble columns have been obtained (Mcclure et al., 2015) which will also aid in the interpretation of the results that will be obtained. Some CFD modeling of bubble columns with Newtonian fluid were found. For example, Hekmat et al (2010) investigated mixing flow structures in air lift reactors through CFD simulations. Mcclure et al. have numerous recent numerical investigations of bubble columns through both CFD and experiments (2016, 2014) which look into aspects of mixing. These investigations provided the relevant physics models applicable to this research.

Following the literature review, the CAD model transported to Star-CCM+ was meshed and set up with the appropriate physics models. The mesh refinement regions in the simulation are shown below.

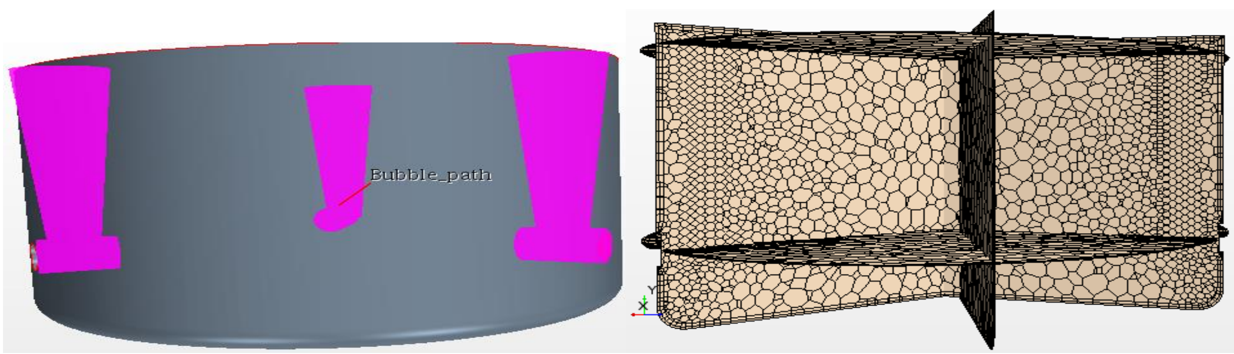

Figure 1-17. Mesh refinement region (left) and polyhedral Mesh of domain (right).

As can be seen in Figure 1-17, the mesh refinement zones are placed where the trajectories of the bubbles are expected to be.

The simulation conducted was numerically unstable. Different approaches were attempted in order to attain numerical stability. The Star-CCM+ version was switched from mixed precision to double precision. According to Star-CCM support documents, double precision helps with convergence issues in multiphase flows. Under-Relaxation parameters were set to low values recommended by Star-CCM+ support documents for multiphase flows. Additionally, smaller time steps and larger inner iterations were attempted. None of the above measures affected the convergence of the simulation; the typical residual plot obtained is shown below.

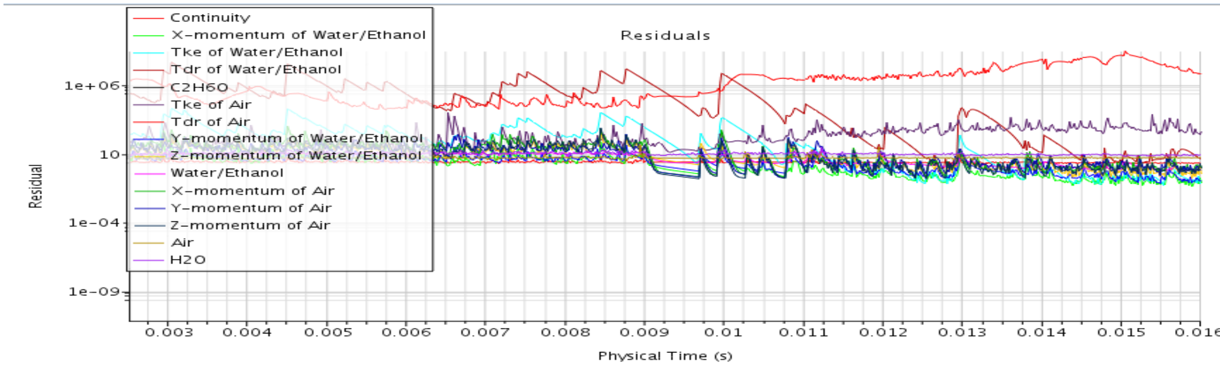

Figure 1-18. Typical residual plot.

As shown in Figure 1-18, all simulations were diverging at approximately .015 seconds.

In the second month of the reporting period, numerous attempts were made in order to gain insight on the root of divergence of this current model. Through the use of a simpler geometry but same physical models, it was discovered that the mesh at the inlet was too coarse. Refinement of this region led to a more stable model, but still showed residuals which were unsatisfactory. In response to this observation, the convergence of a 2D, steady state, laminar simulation with the same exact physics models was studied. This geometry is shown below:

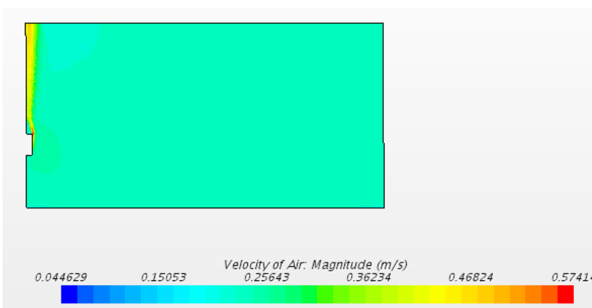

Figure 1-19. Velocity profile of 2D geometric domain.

Effects of density and drag models were shown to have little effect on the residuals. The optimum mesh density was found to be 0.1 inch, having residuals of 10^{-4} which are satisfactory. Turbulence modeling and transient analysis in 2D simulations were initiated and showed to experience lower residuals, but still unsatisfactory.

During the third month, further approaches were attempted to reduce the high residuals observed in current simulations. The same 2D simulation ran in Star-CCM+ has been run in ANSYS Fluent. Exactly the same physics was applied to the Fluent simulation with the exception of the outlet boundary condition. Unlike Star-CCM+, Fluent has a premade degassing boundary condition available which is more suitable for the outlet. Below are the residuals and velocity contour of the Fluent simulation:

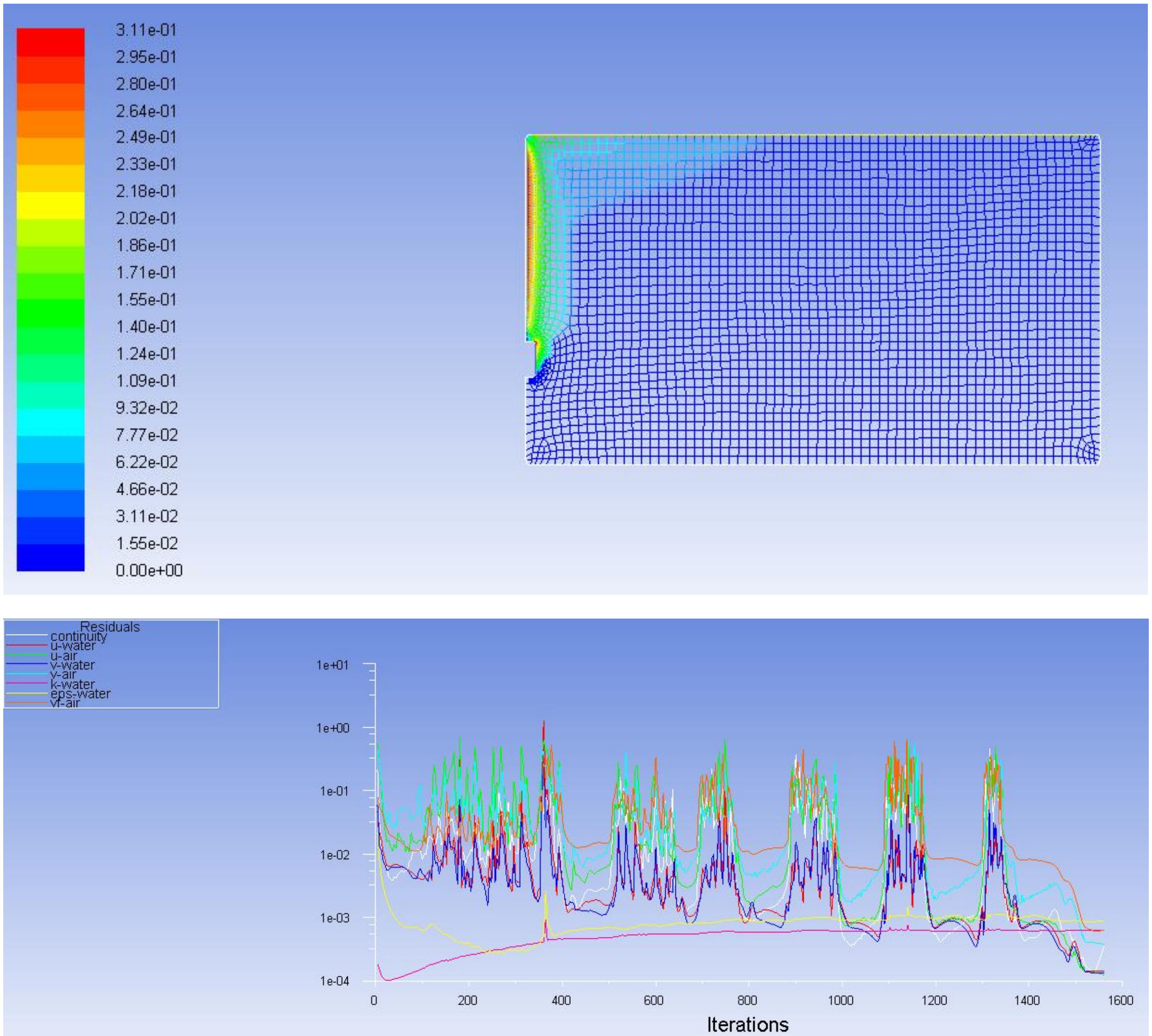

Figure 1-20. Air Velocity profile (top) and residuals of steady state simulation (bottom).

A steady state 2D simulation of the same physical phenomena on ANSYS Fluent showed results with much lower residuals (residuals in the order of 10e-4). This was not the case with the current Star-CCM+ simulation having some residuals as high as 10e0. Taking a step forward, the same simulation using transient analysis results with the following residuals:

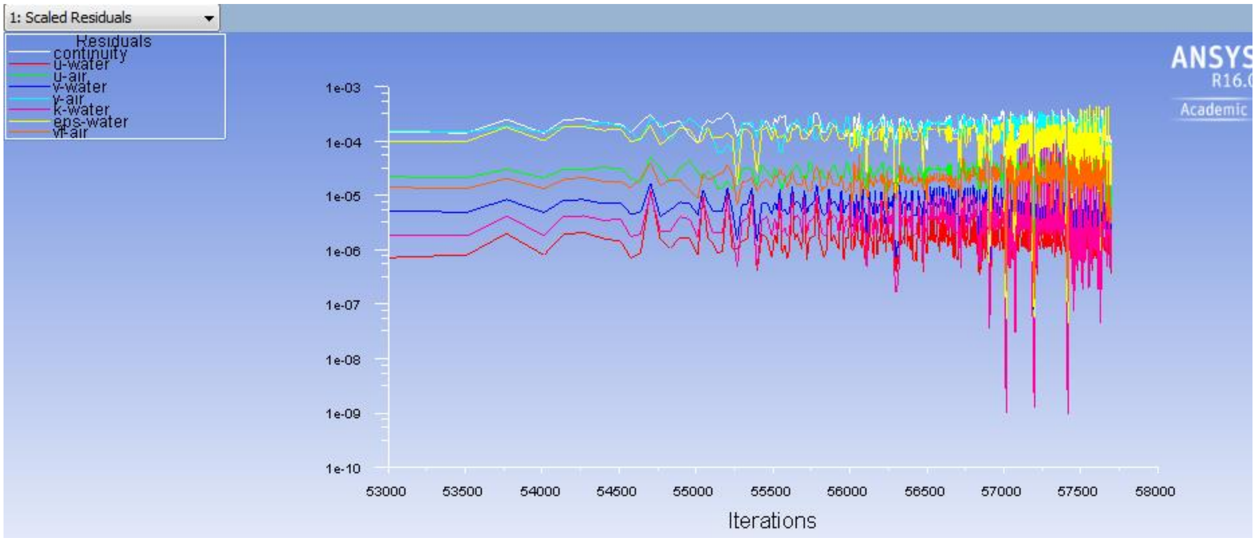

Figure 1-21. Residuals of transient simulation on ANSYS Fluent.

Transient simulation also showed relatively lower residuals. Although the residuals are lower in ANSYS Fluent, the continuity residual is one of the highest residuals, which is unacceptable. Mesh refinement analysis showed that the residuals shown are maintained with refined meshes.

In addition to using ANSYS, technical support from CD-Adaptco was obtained to help troubleshoot the high residuals and a flow-split outlet boundary condition was recommended instead of a permeable wall. Physically, these two outlet conditions can accomplish the same task. With these boundary conditions, the following unscaled residuals were obtained.

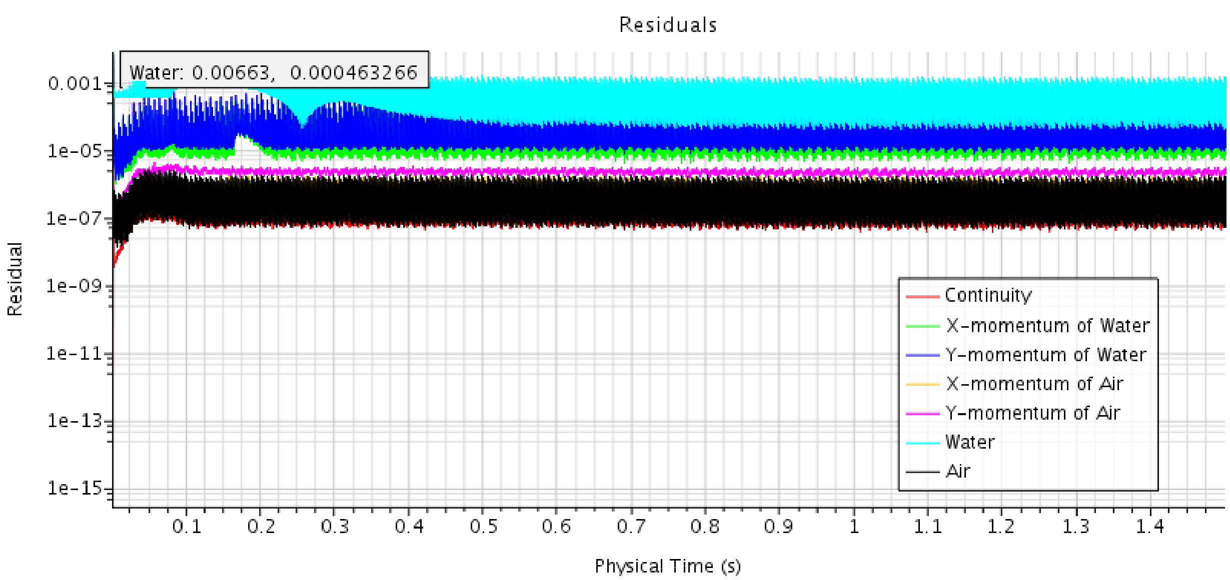

Figure 1-22. Unscaled residuals (transient, 2D, Laminar).

Similar residuals are observed in magnitude to the simulations in ANSYS with the exception that the continuity residuals are three orders of magnitude less. The residuals which pertain to the water have the highest residual. This is expected as there are transient flow structures in this simulation.

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Task 18: Technology Development and Instrumentation Evaluation

Task 18 Overview

The objective of this task is to assist site engineers in developing tools and evaluating existing technologies that can solve challenges associated with the high level waste tanks and transfer systems. Specifically, the Hanford Site has identified a need for developing inspection tools that provide feedback on the integrity of the primary tank bottom in DSTs. Under this task, FIU is developing inspection tools that can provide visual feedback of DST bottoms from within the insulation refractory pads and other pipelines leading to the tank floor.

As part of the Hanford DST integrity program, engineers at Hanford are also interested in understanding the temperatures inside the primary tanks and to safeguard against exceeding specified limits. These limits are set to ensure that the tanks are not exposed to conditions that could lead to corrosion of the tank walls. Previously, analysis was conducted to determine the viability of using an infrared (IR) temperature sensor within the annulus space to estimate the temperature of the inside wall of the tank. The analysis suggested that variations due to heat loss would be minimal and reasonable estimates using the sensor within the annulus is viable. Under this task, FIU is also evaluating the ability of IR sensors to detect inner tank wall temperatures via bench scale testing.

Task 18 Quarterly Progress

Subtask 18.2: Development of Inspection Tools for DST Primary Tanks

The main activities for the pneumatic crawler were focused on assembling the full-scale sectional mockup of a double shell tank (DST), and continuing the improvement of the design. In addition, minor improvements were made to the software framework that controls the inspection tool. FIU has also started reviewing inspection technologies that have the potential to be integrated into the crawler.

The assembly of the mockup dominated most of the efforts during this period. As shown below, the full-scale mockup has been redesigned to be more versatile. The supporting struts in the original design were removed. In the redesign, the refractory pad will lay on the floor covered by the metal plates. The initial configuration will use 1/8" thick metal plates with dimensions of 3' by 4'. In this simpler configuration, different thicknesses and defects (such as cracks, rust, dust, welds, misalignment, bends, punctuations, surface residue and roughness) can be easily simulated manually by swapping plates. For moving heavier plates, FIU is planning to use a portable crane.

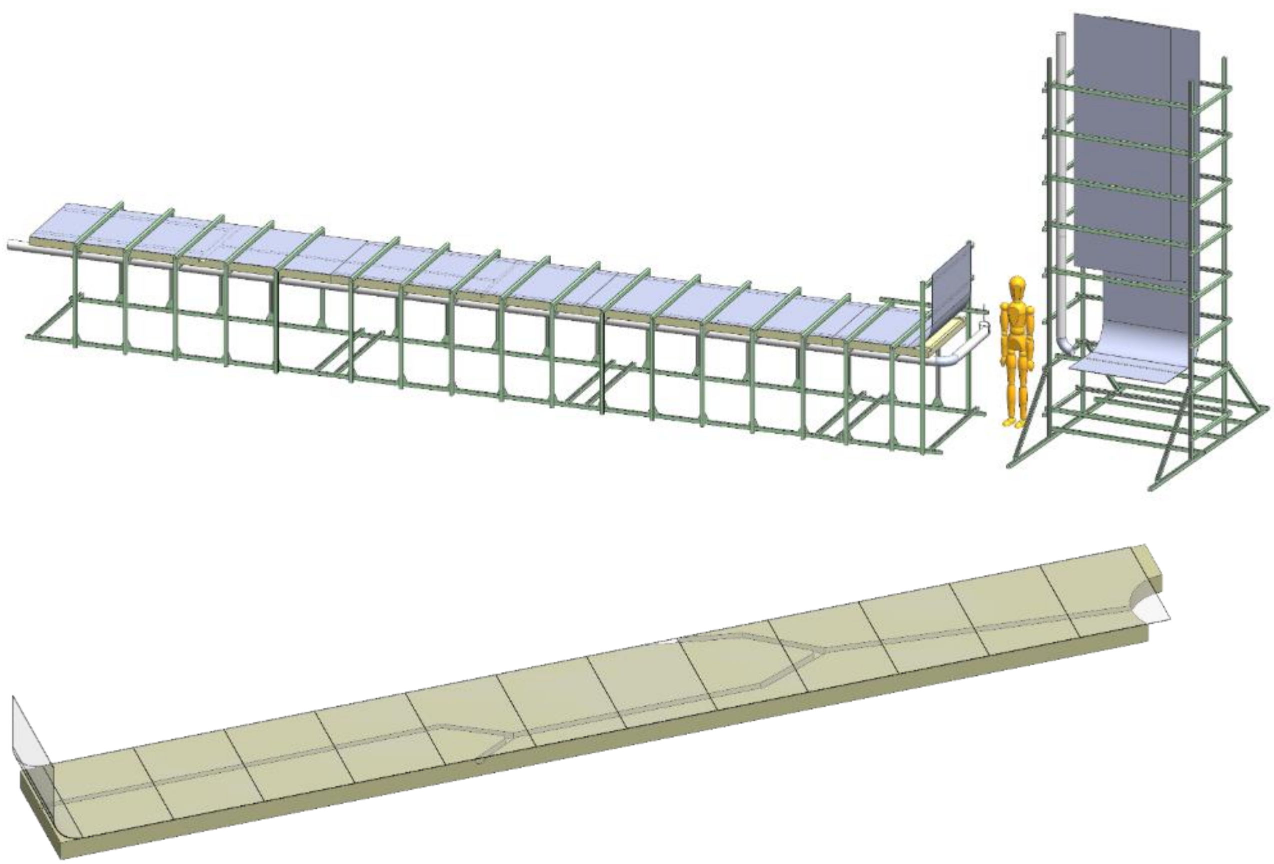

Figure 1-23. Original full-scale mockup (top) and redesign (bottom).

The design of an automatic cable management system was started, and several reel mechanisms were investigated for tether handling. The following figure shows a small scale version of the cable management system currently being designed. A small scale version is more suitable for development and testing. The unit will also be used in the deployment platform of the mini rover. However, later on, the system will be scaled up for the pneumatic crawler.

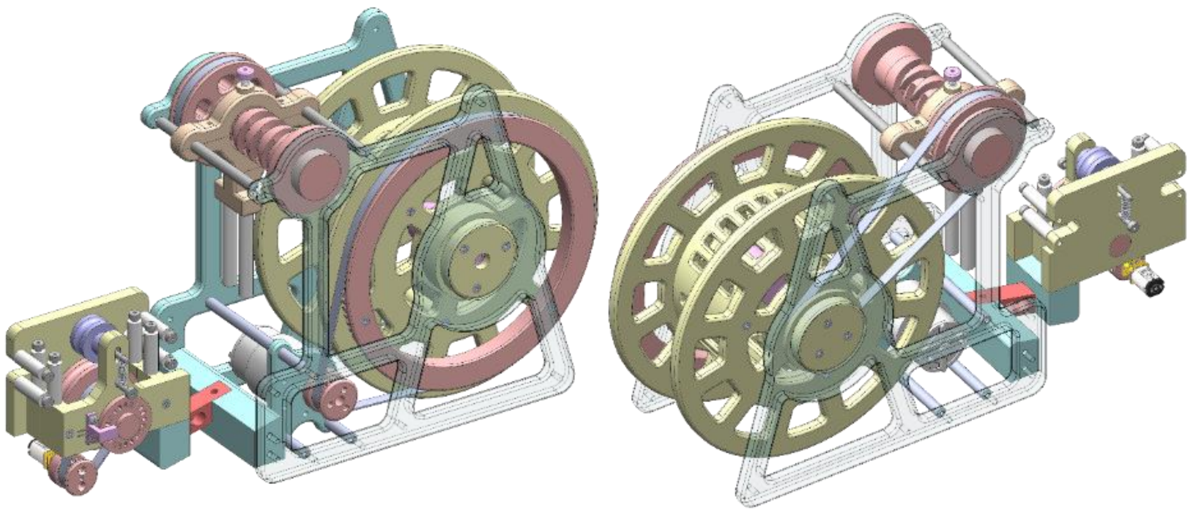

Figure 1-24. Cable management systems.

The cable management system consists of a self-layering spool guide to keep the cable reel neat, tidy, and protected from damage. A load cell senses the movement of the inspection tool and a mechanism slides back and forth in sync with the spool wind so that the reel is always properly wound. The system is completely automated and designed to retrieve the tool in case of failure. An automated cable management system is important to contain eventual cross-contamination and prevent radiation spread.

FIU has also reviewed advances in serial communication protocols, drop-in camera chips, and microcontrollers, which respectively would improve tether communication, image quality and miniaturization of the modules. In addition, LIDAR and SONAR sensors were investigated for augmented navigation and pipe mapping during inspection.

Another improvement to the current design has been the redesigning of the suspension guides. Shown in Figure 1-25, the current guides center the modules using tail arms tensioned by extension springs.

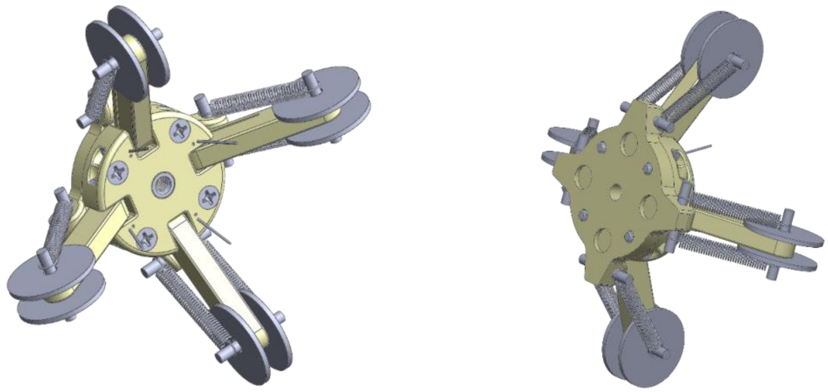

Figure 1-25. Suspension guides.

The guides significantly reduce module bouncing and dragging; however, the current design is inherently unbalanced. An alternative four link configuration is currently being investigated which improves the stability of the crawler and minimizes the module redesign. However, the available clearance around the modules poses a challenge to the redesign.

For the miniature magnetic rover, efforts were focused on designing and manufacturing a bench-scale sectional mockup of a double shell tanks (DST), and continuing with maneuverability tests. In addition, minor improvements were made to the wiring of the unit's tether. FIU has also continued reviewing tether management technologies that have the potential to be leveraged with FIU's design.

Figure 1-26 shows a rendering of the bench-scale sectional mockup built at FIU. The mockup consists of a thin carbon steel plate bent over a wooden frame. The dimension shown are fully representative of a section of the tank knuckle. The mockup has been used in maneuverability tests, where replicas of ventilation channels are attached magnetically to the bent plate. Figure 1-27 shows a Y pattern channel configuration currently being used in tests and are representative of the cooling channels found in a majority of the AY Tanks.

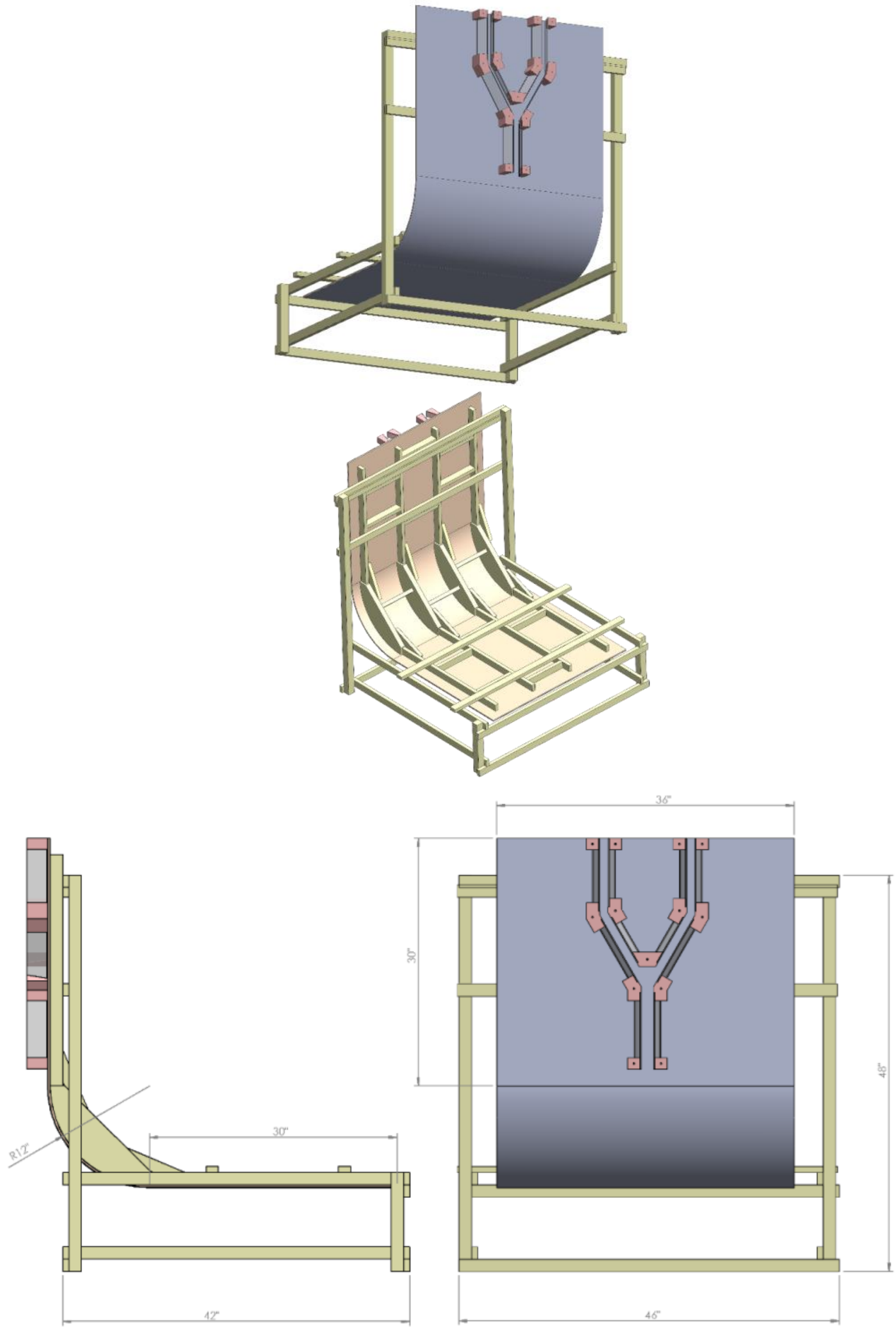

Figure 1-26. Bench scale sectional mockup design.

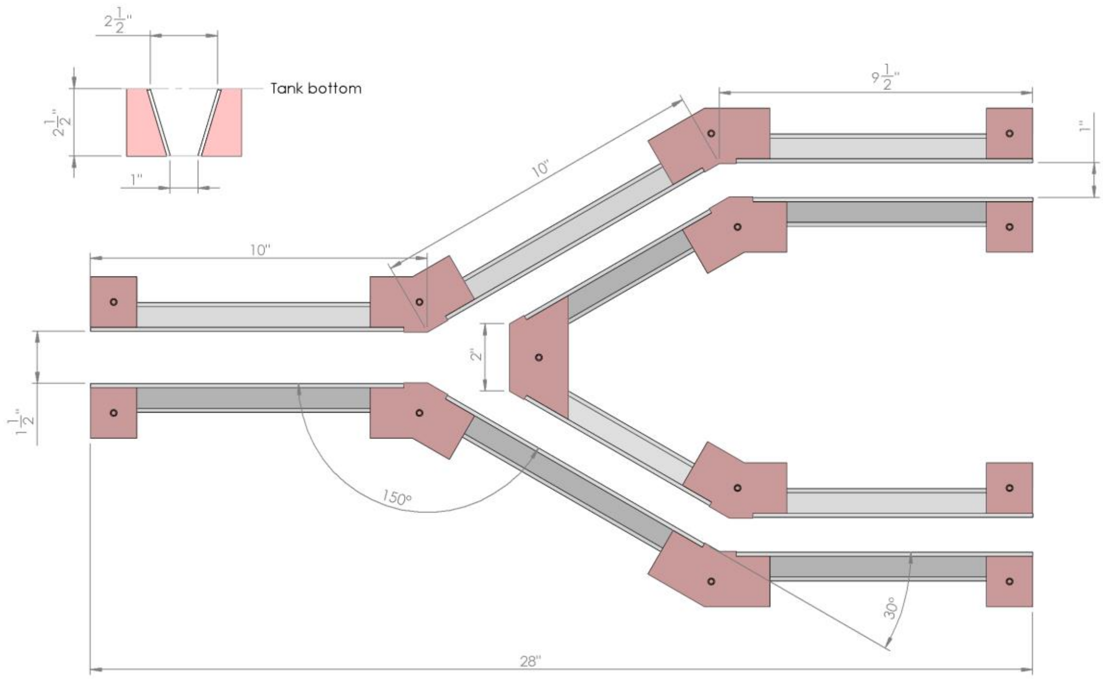

Figure 1-27. Mockup channel layout.

Figure 1-28 shows the mockup with the channels on the tank side. As noted previously, the channels are attached to the plate via magnets and can be easily moved to any location or reconfigured as needed. Figure 1-29 demonstrates how the inspection tool will navigate through the ventilation channels and provides a means to access clearances and control issues.

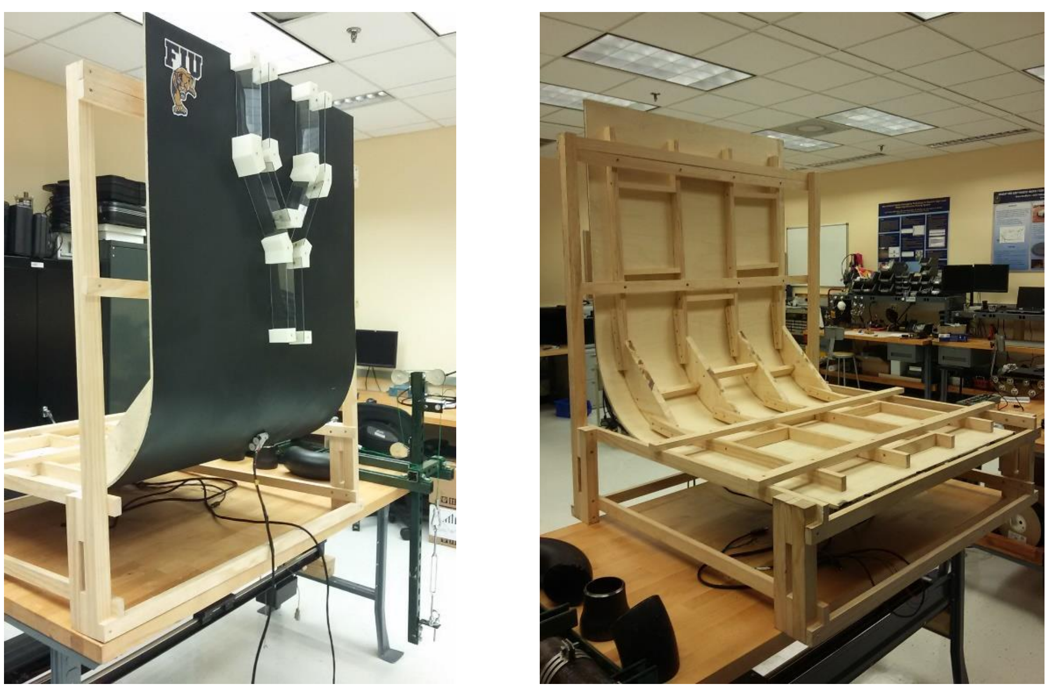

Figure 1-28. Bench scale sectional mockup.

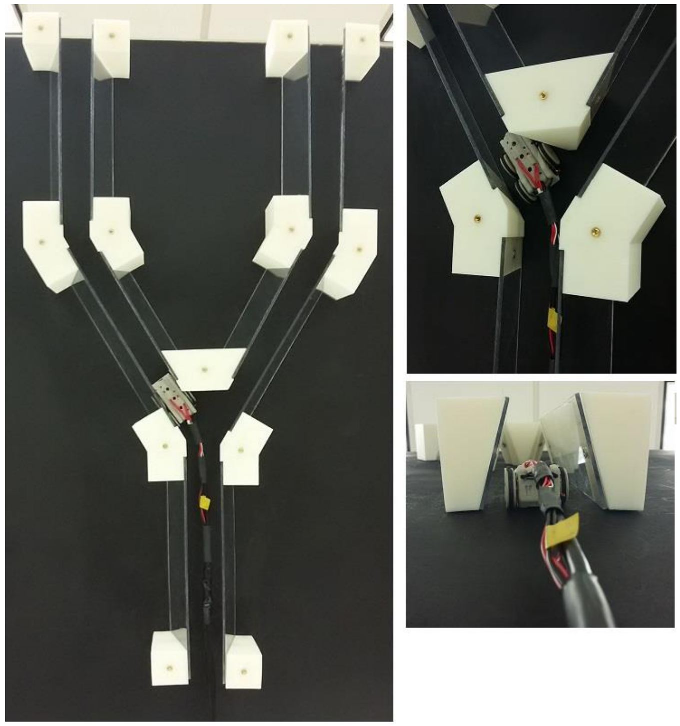

Figure 1-29. Maneuverability test.

FIU finalized the design of the miniaturized rover and manufactured a final prototype. It was displayed at the DOE Fellows Induction Ceremony on November 3 along with the test bed.

The new design (Figure 1-30) added 2 LEDs in order to provide light for the unit as it travels through the annulus and channels. A smooth Ethernet cable was integrated into the unit in order to make it easily detachable and replaceable. FIU also began testing of the camera with an extended cable; some design modifications will be needed, which will be addressed in the near future.

Figure 1-30. Rover which utilizes 2 LEDs along with a smoother Ethernet cable.

Instead of controlling individual motors on the rover, a joystick was used to control the Rover's throttle and direction of motion. The joystick was connected to a microcontroller and motor driver as shown in Figure 1-31. The setup is simple and compact, and allowed the operator to easily control the rover. The same microcontroller will also be used to control the cable reel of the cable management system. An electrical enclosure is currently being designed to house all the controller components to make the setup more portable.

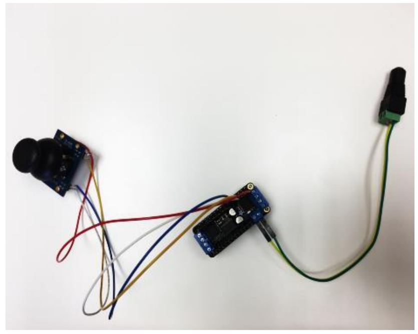

Figure 1-31. Joystick (left) connected to the micro-controller and motor driver (center) with separate power source.

During the month of December, FIU integrated the mini rover with the cable management system. The cable management system was controlled with a DC motor with its control signal coming from a different channel joystick. A bench test was conducted with the setup and the mini rover managed to navigate to the end of a mock-up channel without any cable entanglement. Work is currently being performed to integrate a load cell onto the cable management system so that the cable length can be adjusted automatically depending on the pull force of the mini-rover.

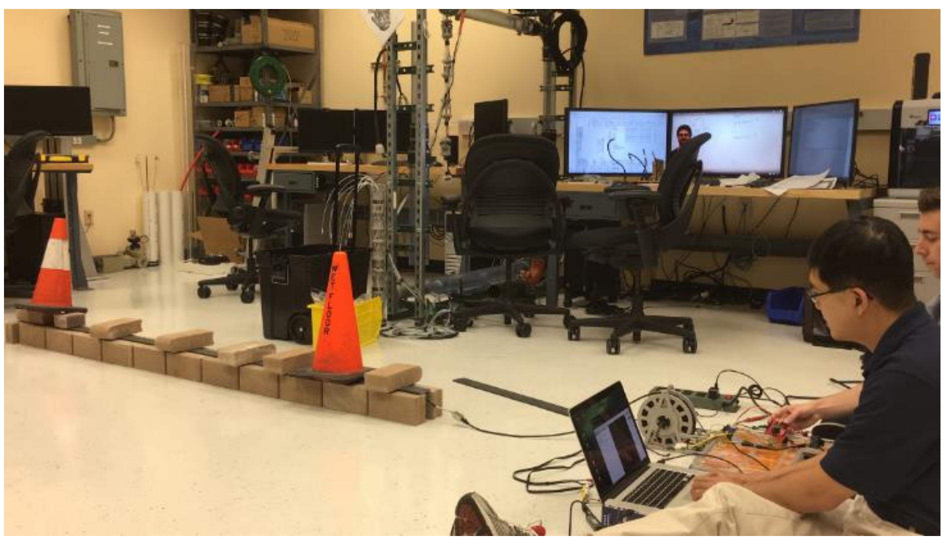

Figure 1-32. Initial bench test of the mini rover, integrated with the cable management system and control systems.

Figure 1-33. Outdoor-test with the mini rover pulling a cable of 50 feet. Two sets of concrete blocks were placed along the cable to simulate the corners along the ventilation channels underneath the tank.

After the bench test, an outdoor test was also conducted to determine the maximum pull force that can be generated by the mini rover. This is important to ensure that the current version of the mini rover has the capability of pulling a cable of at least 37 feet, which is the radius of the waste tank to be inspected. The experiment was conducted on an asphalt surface, with two sets of concrete blocks placed along the cable to simulate the number of corners (~30 degrees) that the mini rover has to pass through. Even though the mini rover managed to pull a cable of 50 feet, the drag force generated was approximately 4.5 pounds. This is about 0.5 pounds less than the pull force of the rover (when the wheels lose traction). This is due to the cable attaching point on the mini rover being too high with respect to its center of gravity (CG). The shortcoming will be improved in the next version where the cable attaching point will be moved to be aligned or lower than the CG. In addition, one magnet from underneath the mini rover will be moved forward so that the downward force can be concentrated at the front of the mini rover to counter the moment produced due to the cable's tension.

Further enhancements were also made to the overall design of the mini rover. Mostly focused on the internal arrangement of components for the tool, these modifications completely enclose the components within the tool. This was done by first rewiring, but future designs will implement a custom made PCB (represented in the pictures below as the green piece). Another major design modification was the connecting point of the tool. Previous designs had a cable extending out of the rear, which needed to be plugged into an adapter to connect it to another cable. This new design allows for the second adapter to be bypassed; the cable can now be plugged directly into the unit.

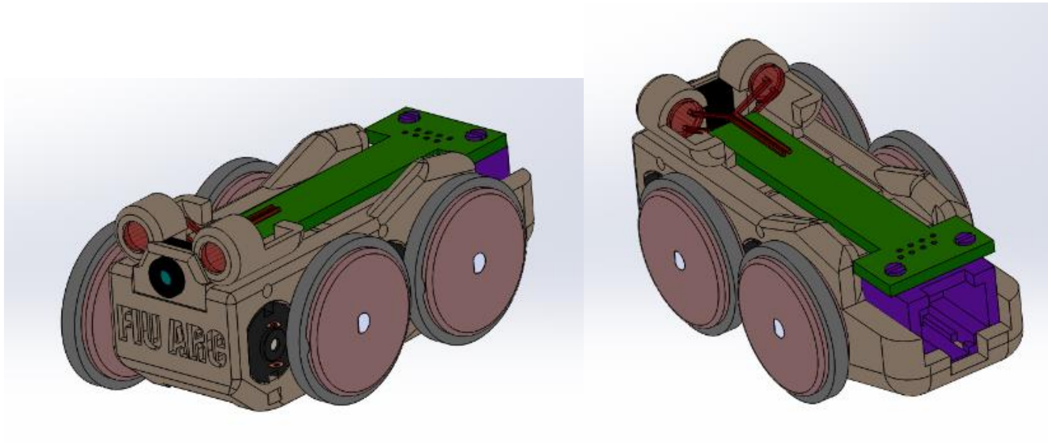

Figure 1-34. The improved version of the mini rover, with custom designed PCB board (green color board) for cleaning wiring of the rover components. The connection point of the cable is embedded inside the mini rover, bypassing the need for a second adapter.

Subtask 18.3: Investigation Using an Infrared Temperature Sensor to Determine the Inside Wall Temperature of DSTs

During this quarter, FIU completed the second phase of experiments using the IR sensor and hermitically sealed thermocouples which provided automated real-time temperature measurements.

Initially, background work required for improving the testing and data analysis of the IR sensor was conducted. This included the epoxy based fixing of the hermitically sealed thermocouples (HST's) onto the surface of the plate for continuous temperature measurement and ensuring that the data acquisition system and the Raytek sensor are calibrated properly. Some of the HST's were fixed to the plate surface and verified to be functional. FIU also developed a conference paper for the Waste Management Conference in March.

During the month of November, the second phase of testing using the ½-inch thick carbon steel plate and the hermitically sealed thermocouples (HSTs) was conducted and the results obtained were presented.

The experimental procedure included fixing 3 HSTs on the bottom surface of the plate touching the water using a two part epoxy. HSTs were placed at lengths of 1, 2, and 3 ft. from one end of the plate as shown in Figure 1-35 (left). To fix the HSTs, the surface was prepared by brushing it with metallic brushes to remove the surface rust and provide a smoother finish. The plate was raised from the tank using a forklift to provide access to the bottom surface. The epoxy has a curing time of 1 day; so after 24 hrs., some of the HSTs were tested by connecting them to the Omega DAQ system and conducting initial verification tests. Additionally, the tank was covered with a rubber insulation sheet around the outer tank walls and on the top to reduce heat transfer and ensure proper heating (Figure 1-35 right).

The next step included filling the tank with water so that it touched the inner surface. A 4000W coil heater was used to raise the temperature to 120°F. Data was continuously collected until the temperature reached 170°F. In addition to the bottom surface thermocouples, three other thermocouple reading were taken at the same locations on the top surface. This was done to check the actual variation in temperature at both surfaces and to compare the results with theoretical calculations.

Figure 1-35. HSTs fixed under the plate (left) and tank covered with insulation (right).

Figure 1-36 shows the omega DAQ system with thermocouples connected and a typical dashboard reading (collecting temperature data for the HST's). The results obtained at certain data points with approximately 8-10°F intervals are provided in Table 1-10. It is observed that out of the three bottom surface HST's, only one HST could provide accurate readings up to 170°F while the others failed. The one at the center was unable to collect any data. Possible reasons could be improper application of the epoxy. The third sensor collected data up to 150°F (column B3) and then failed as indicated in Table 1-10. This is likely due to the failure of the epoxy bond at higher temperatures.

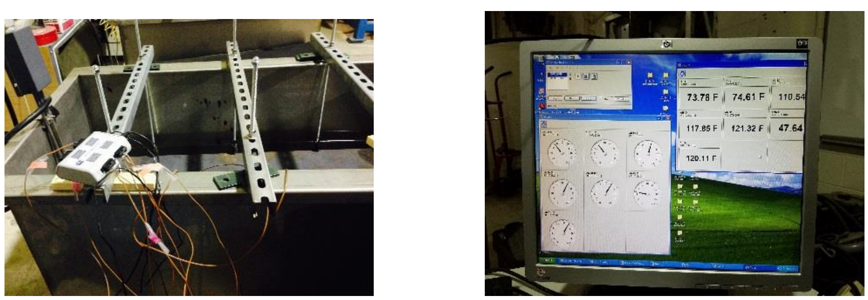

Figure 1-36. DAQ system with attached thermocouples (left) and DAQ dashboard (right).

In addition to the HST readings, the Raytek sensor was also used to manually collect data at regular intervals. Table 1-10 (columns R1, R2 and R3) provides the temperatures collected using the Raytek sensor at the top locations. Emissivity of the sensor was adjusted to 0.75. It was observed that the Raytek readings are consistently higher than the thermocouple readings at corresponding locations.

Table 1-10. Experimental Results with ½" Carbon Steel Plate (°F)

Data point	T1	T2	T3	B1	B3	R1	R2	R3
1	106.5	96.2	101.2	110.1	108.99	111.2	109.7	108.5
2	119.5	111.4	110.8	122.05	121.29	123.5	125.1	119.2
3	126.2	120.4	120.5	131.1	130.4	134.1	133.8	125.6
4	134.5	121.5	122.4	140.1	139.2	141.2	138.7	138.9
5	143.63	133.3	131.6	150.9	148.51	156.2	149.8	147.5
6	152.7	142.7	154.5	159.5	93.3	168.2	164.1	159.7
7	156.8	156.6	150.5	165.2	85.7	172.1	171.1	165.2

@ T – Top, B – Bottom, R – Raytek

During the month of December, the experiments reported in the previous month were repeated due to anomalies in the results obtained. The new results obtained were analyzed and the inferences are presented. The experiment was conducted using a ½-inch carbon steel plate floating on the water surface inside the tank. Temperature measurements were made at 6 different locations on the plate (3 on the top and 3 underneath) using hermitically sealed thermocouples (HST's) and at 3 top locations using the Raytek IR sensor. The emissivity of the plate was chosen to be 0.75, as a standard, for the Raytek sensor.

Water temperature in the tank was raised to 120ºF and then temperature readings were recorded at intervals of 10ºF from 120ºF to 170ºF (based on the actual DST temperature approximations). The results obtained are shown in Table 1-11.

Table 1-11. Experimental Results with ½-inch Carbon Steel Plate (Temperature readings in ºF)

Data point	T1	T2	T3	B1	B2	B3	R1	R2	R3
1	111.14	104.23	106.07	114.67	109.28	108.78	109.2	106.4	104.7
2	115.35	111.12	111.19	120.1	115.34	115.12	116.7	112.7	109.9
3	123.27	111.83	117.29	130.2	126.05	125.4	132.9	128.9	124.6
4	132.12	116.57	125.98	140.32	135.96	135.27	143.9	141.7	133
5	142.09	132.99	137.44	150.06	145.25	144.53	152	145.7	141.7
6	152.91	142.71	138.7	160.17	154.42	153.67	157	155	153.1
7	162.73	151.41	148.01	170.05	164.45	163.6	165.2	167.2	166.2

@ T – Top, B – Bottom, R – Raytek

In Table 1-11, the columns T1, T2 and T3 represent the thermocouple readings while R1, R2 and R3 represent the Raytek sensor readings at the same locations. Hence, these are compared. It is evident that the average difference between the corresponding readings for location 1 is 5.3ºF, while for locations 2 and 3 the difference is 12.3ºF and 6.9ºF, respectively. It is observed that the temperature difference increased with an increase in temperature. In most cases, the Raytek sensor showed a higher value. In addition, the temperatures at the top 3 locations (T1, T2 and T3) were compared to the bottom 3 locations (B1, B2 and B3) to investigate the heat transfer effects. From the results, it is inferred that the average temperature difference was 6.5ºF, 11.4ºF, and 8.8ºF, respectively, for the three locations. According to theoretical calculations, the average readings can be approximated to about 4-5ºF, taking into account the temperature gradient with location and time.

To conclude, the Raytek sensor was calibrated and tested for temperature measurements and is found to be capable of temperature measurements in DSTs within specified limits.

Task 19: Pipeline Integrity and Analysis

Task 19 Overview

The objective of this task is to support the DOE and site contractors at Hanford in their effort to evaluate the integrity of waste transfer system components. The objective of this task is to evaluate potential sensors for obtaining thickness measurements of HLW pipeline components. Specific applications include straight sections, elbows and other fittings used in jumper pits, evaporators, and valve boxes. FIU will assess the accuracy and use of down selected UT systems for pipe wall thickness measurements. FIU will also demonstrate the use of the sensors on the full-scale sectional mock-up test bed of the DSTs. An additional objective of this task is to provide the Hanford Site with data obtained from experimental testing of the hose-in-hose transfer lines, Teflon® gaskets, EPDM O-rings, and other nonmetallic components used in their tank farm waste transfer system under simultaneous stressor exposures.

Task 19 Quarterly Progress

Subtask 19.1: Pipeline Corrosion and Erosion Evaluation

During this performance period, FIU installed the Permasense guided wave sensor system on a custom designed pipe layout. In addition, the basic training required for operating the equipment for real-time data measurement was received. Currently, the system is set up for collecting thickness data for a period of 3 months to verify and validate the sensors.

During the month of October, a basic pipe layout was modeled in solid works to accommodate 2-inch and 3-inch sections in the waste transfer pipes. The pipe layout included straight and elbow sections joined by a reducer. Figure 1-37 shows the CAD drawing along with the weld specifications at four sections. The material used was black/carbon steel and the butt welding of the sections was outsourced.

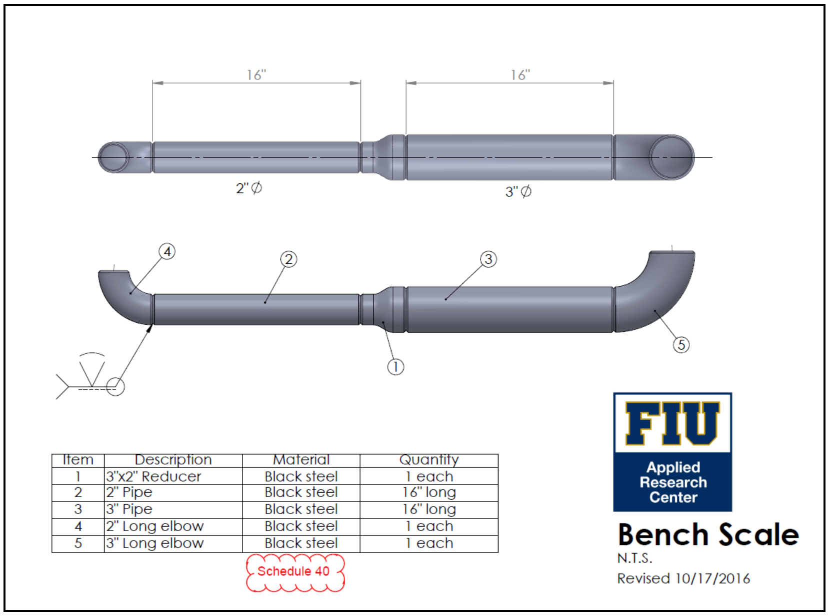

Figure 1-37. CAD drawing of the pipe layout.

The initial installation of the sensors was conducted by the Permasense trained personnel as per the requirements of the purchase. Figure 1-38 shows the installed sensors, one on the 2-inch elbow and the other on the 3-inch straight section. It should be noted that the installation required a specified torque (30 Nm or 22 lbsf.ft) applied on the clamps to completely eliminate the air gap between the sensor tip and the test surface. The clamps are custom designed for each section.

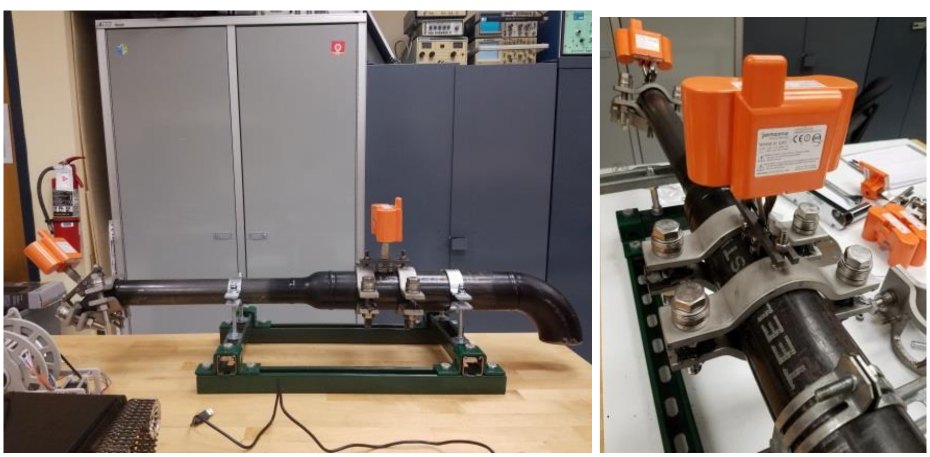

Figure 1-38. Permasense sensor system: a) on pipe section and b) detailed view

During the month of November, FIU completed the installation of the Permasense guided wave sensor system on the custom designed pipe layout. In addition, all the training required for operating the equipment for real-time data measurement has been completed.

Two of the WT210 series sensors were installed on a 2-inch straight section and a 3-inch elbow of the custom designed pipe. The complete sensor system (including the 2 previously installed sensors) is as shown in Figure 1-39 (left). The detailed view is shown in Figure 1-39 (right). The 3-inch elbow used a custom made clamp to accommodate the curvature as seen in the figure.

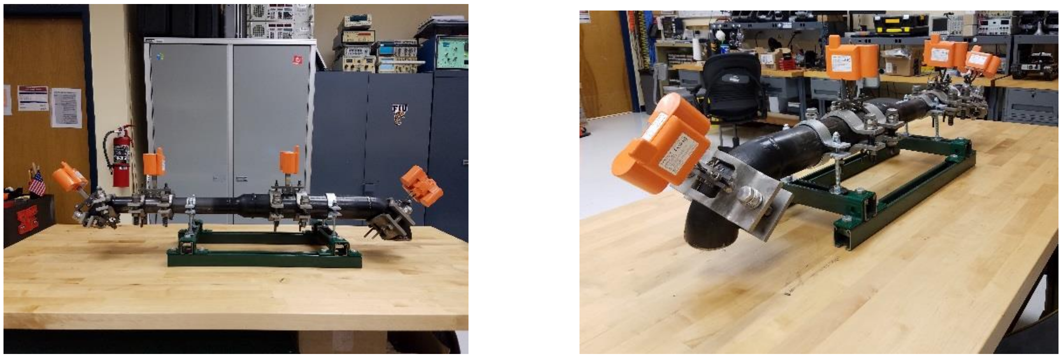

Figure 1-39. Permasense sensor system: on pipe section (left) and detailed view (right).

Upon installation of the sensors, the system was integrated with a wireless Gateway and a software (consisting of SQL server database) for data collection and analysis. The wireless gateway (from Emerson) has a range of 10-150 ft. from the sensors. The software has the capability to record real time data approximately every 15 minutes. Currently, it is configured to collect data every six hours. The waveform/signal response is as shown in Figure 1-40 left. The peak to peak distance between the first and the second peaks of the waveform (A-scan) is used to calculate the thickness/distance travelled assuming known acoustic velocity in the material. The calculated real-time data (pipe thickness) is as shown in Figure 1-40 right.

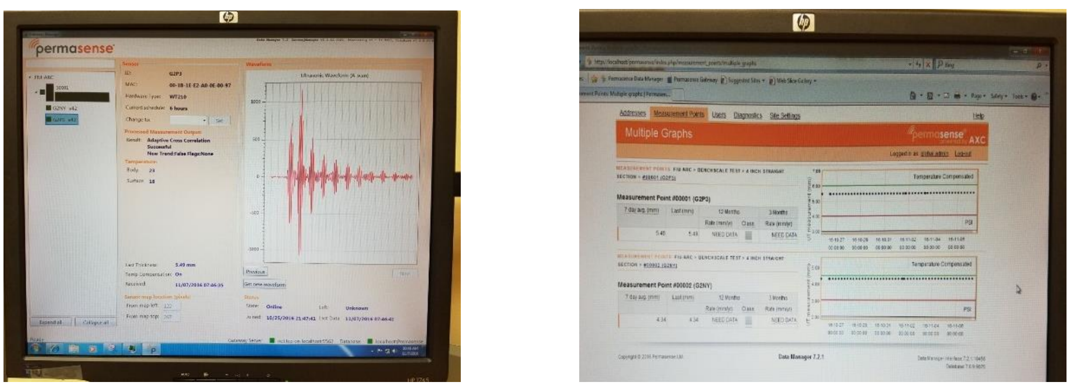

Figure 1-40. Sensor software: ultrasonic waveform (right) and thickness graphs (right).

During the month of December, FIU worked on verifying and validating the data collected using the Permasense sensors. These sensors were installed during the last performance period and are set to record the thickness readings from the carbon steel pipe layout detailed in the previous performance period. During this performance period, the sensors have been successfully collecting the data and there has been no change in the readings since the thickness remained the same.

In addition, during the month of December, FIU investigated the option of circulating abrasive fluids through the pipe section to obtain real-time thickness data while erosion takes place. A basic literature review has been conducted and it was found that certain acids tend to corrode carbon steel rapidly. A generic list of corrosive fluids has been studied and a condensed list includes: acetic acid, aluminum sulfate, ammonium chloride, ammonium phosphate, ammonium sulfate, ammonium sulfite, aniline, benzoic acid, boric acid, calcium hypochlorite, carbon dioxide, carbonic acid, chlorine gas, chromic acid, citric acid, copper sulfate, ethyl chloride, ferric chloride, formic acid, hydrochloric acid, hydrogen sulfide, liquid, nitric acid, oleic acid, oxalic acid, phosphoric acid, picric acid, silver nitrate, sodium chloride, sodium hypo-chloride, sodium thiosulfate, sulfuric acid, sulfurous acid, vinegar, whiskey, wine, zinc chloride, zinc sulfate. These options are being investigated to determine the most feasible and harmless fluids. Some of the parameters being considered include the rate/time of corrosion, safety and amount of corrosion (expected thickness change).

Currently, FIU is in the process of acquiring real-time thickness data for a period of 3 months to verify the sensor system as well as narrowing down the abrasive fluid options for generating rapid corrosion in the pipe.

Subtask 19.2: Evaluation of Nonmetallic Components in the Waste Transfer System

The aging of the nonmetallic components as well as data collection continued for this reporting period. A couple of small leaks appeared and were easily repaired by using a sealing tape instead of epoxy as FIU has done in the past. The Stretch & Seal® self-fusing silicone tape was wrapped around the area on the pipe near the leak and essentially sealed it instantly. With the epoxy, the loop would have needed to be shut down and the area where the leak was completely dried. The epoxy would then be applied and allowed to dry for at least 6 hours before the loop could be restarted. In addition, one of the ball valves on loop 3 was replaced after it developed a leak from the valve stem. Loop 3 contains the caustic solution at the mid-level temperature (130°F). These valves were from a different manufacturer and likely had issues handling the elevated temperature and caustic material. A few minor leaks from other locations along the loops were also noted and repaired.

Also during this time, the motor adapter barrier and impeller on loop pump #1 began leaking and was replaced. During the replacement process, it was observed that the pump's impeller was beginning to fall apart. It was replaced with another spare impeller that was in stock. However, when FIU contacted the parts vendor to order a replacement impeller, FIU was informed that the impeller and drive magnet for the pump had been redesigned by the manufacturer. Figure 1-41 shows the old impeller (top left) and the new impeller (lower right). The new impeller design has a smaller base diameter. Figure 1-42 shows the new drive magnet (top left) and the old drive magnet (lower right). The new drive magnet design has eight magnets while the old design only has six. FIU believes that the reason the motor adapter barrier keeps failing on loop #1 is due to the old design impeller not leaving enough space between the impeller and the motor adapter barrier. Since loop #1 is operating at the highest temperature (175°F), when the impeller expands due to the high temperature, it rubs against the motor adapter barrier, resulting in the failure of the barrier.

Figure 1-41. Old (top) and new (bottom) pump impellers.

Figure 1-42. Old (top) and new (bottom) drive magnets.

For the benefit of time, FIU will keep pump #1 operating with the old impeller and drive magnet combination unit until the motor barrier fails. At which time FIU will replace the impeller and drive magnet with the new design set.

Due to minor delays that required some level of down time for the loops, a spreadsheet was created to estimate the aging completion dates for the six-month and one-year aging. The spreadsheet keeps track of the total number of days the loops have been run as well as the number of days the loops have been down.

Table 1-12. 6-Month Aging Timeline

6 Months Test	
Total days on	138
Total days test	183
Days left	45
End testing date	1/15/2017

Table 1-13. 1-Year Aging Timeline

1 Year Test	
Total days on	138
Total days test	365
Days left	227
End testing date	7/16/2017

Assuming no unforeseen shutdowns, the anticipated completion dates for the six-month and one-year aging are January 15, 2017 and July 16, 2017, respectively.

Milestones and Deliverables

The milestones and deliverables for Project 1 for FIU Performance Year 7 are shown on the following table. Milestone 2016-P1-M18.2.1 has been delayed due funding delays. The delay in completing the assembly of the full-scale sectional mockup of a double-shell tank has been communicated to the site points-of-contact as well as the DOE HQ Project Lead, Gary Peterson, during regular project teleconferences. A re-forecasted date of completion will be set once future funding amounts and dates are known.

FIU Performance Year 7 Milestones and Deliverables for Project 1

Task	Milestone/ Deliverable	Description	Due Date	Status	OSTI
Task 17: Advanced Topics for Mixing Processes	2016-P1-M17.1.1	Complete literature review and selection of baseline experimental cases	2/3/17	On Target	
	Deliverable	Draft Summary Report for Subtask 17.1.1	2/17/17	On Target	OSTI
	2016-P1-M17.1.2	Complete CFD simulations of air sparging experiments	4/21/17	On Target	
	Deliverable	Draft Summary Report for Subtask 17.1.2	5/5/16	On Target	OSTI
Task 18: Technology Development and Instrumentation Evaluation	2016-P1-M18.2.1	Complete assembly of full-scale sectional mock-up test bed	12/16/16	Reforecast Date TBD	
	Deliverable	Draft Summary Report for Subtask 18.3.1	4/14/17	On Target	OSTI
	2016-P1-M18.2.2	Complete evaluation of sensor integration into inspection tools	5/26/17	On Target	
	Deliverable	Draft Summary Report for Subtask 18.2.3	6/30/17	On Target	OSTI
	2016-P1-M18.2.4	Complete conceptual design of miniature rover platform	8/25/17	On Target	
	2016-P1-M18.2.5	Complete conceptual design of 6 inch peristaltic crawler	8/25/17	On Target	
	2016-P1-M18.3.1	Complete bench-scale testing for temperature measurements using IR sensors	3/31/17	On Target	

Task 19: Pipeline Integrity and Analysis	2016-P1-M19.1.1	Assess the accuracy of the down selected UT system via bench-scale testing	5/12/17	On Target	
	2016-P1-M19.1.2	Develop test loop for evaluating UT sensors	8/25/17	On Target	
	2016-P1-M19.2.1	Complete experimental testing of 6 month aged materials	3/17/17	On Target	
	Deliverable	Draft Summary Report for Subtask 19.2.2	3/31/17	On Target	OSTI
	Deliverable	Draft Summary document on UT assessment for Subtask 19.1.1	5/26/17	On Target	OSTI

Work Plan for Next Quarter

Task 17: Advanced Topics for Mixing Processes

- FIU will complete the literature review on baseline experimental and simulation data. Additional investigations on the sediment layer thickness will be conducted and selection of the experimental case data will be finalized. In addition, the computational domain based on the selected experimental data will be created and meshed in Star-CCM+. More investigations using the mixture multiphase model in STAR-CCM+ with a solid content-based viscosity model will be pursued.

- Given that there are a number of obstacles in creating a workable simulation, the path forward includes: a simulation of a bubble column carried out by Dale D. McClure et al. (2013) on ANSYS CFX will be replicated using the same software. A successful replication of this simulation, already validated by experimental data, will create a good foundation on which to continue the proposed research.

Task 18: Technology Development and Instrumentation Evaluation

- For the inspection tools, the manufacturing of the full-scale sectional mockup of the DST will be completed. The construction of the mockup has been delayed due to budgetary constraints.
- For the peristaltic crawler, FIU will continue to validate the device in full-scale tests. The device's instrumentation module will be finalized and incorporated with basic environmental sensors such as temperature, pressure and humidity. FIU will also continue the design of an automated cable management system. Modifications will continue to be incorporated in the design as needed.
- For the miniature rover, the final design of the cable management system will be completed and a prototype will be manufactured. Efforts will also be made to demonstrate the rover in the full-scale mockup. Minor design changes will be made after the testing is completed.
- For the IR sensor task, FIU will continue with the third set of experiments using a 1/4 – inch thick plate if needed. The results obtained from all the experiments will be compared with theoretical heat transfer calculations. In addition, advanced heat transfer based simulation models will be generated to verify and validate the experimental results and to predict the waste temperatures inside the tanks away from the walls.

Task 19: Pipeline Integrity and Analysis

- For the ultrasonic sensor task, FIU will verify and validate the Permasense UT sensors for thickness measurement on the carbon steel pipe section. Upon completion of a period of 3 months, an abrasive fluid will be selected which will be circulated through a pipe loop to evaluate the ability of the sensors to measure real-time changes in thickness. Several parameters such as the type of fluid, time of circulation, safety of the fluids and the wear rate on carbon steel material will be investigated. Various types of pumping systems will also be considered. In addition, other options of simulating thickness changes such as sand blasting will be investigated. Finally, the option of using magnetic sensors as suggested by Permasense, will be explored.

- For the non-metallic materials task, efforts during the next quarter will include completion of the aging of the specimens for the 6-month set. The HIHTL components, gaskets and O-rings will be removed from the loop and pressure tested. The material coupons will also be removed and their material properties will be evaluated. Aging of the remaining sets will continue for another six months.

Project 2
Environmental Remediation Science and Technology

Project Description

This project will be conducted in close collaboration between FIU, Hanford Site, Savannah River Site, and the Waste Isolation Pilot Plant (WIPP) scientists and engineers in order to plan and execute research that supports the resolution of critical science and engineering needs, leading to a better understanding of the long-term behavior of contaminants in the subsurface. Research involves novel analytical methods and microscopy techniques for characterization of various mineral and microbial samples. Tasks include studies which predict the behavior and fate of radionuclides that can potentially contaminate the groundwater system in the Hanford Site 200 Area; laboratory batch and column experiments, which provide relevant data for modeling of the migration and distribution of natural organic matter injected into subsurface systems in the SRS F/H Area; laboratory experiments investigating the behavior of the actinide elements in high ionic strength systems relevant to the Waste Isolation Pilot Plant; surface water modeling of Tims Branch at SRS supported by the application of GIS technology for storage and geoprocessing of spatial and temporal data.

The following tasks are included in FIU Performance Year 7:

Task No	Task
Task 1: Remediation Research and Technical Support for the Hanford Site	
Subtask 1.1	Sequestering uranium at the Hanford 200 Area vadose zone by in situ subsurface pH manipulation using NH_3 gas
Subtask 1.2	Investigation of microbial-meta-autunite interactions - effect of bicarbonate and calcium ions
Subtask 1.3	Evaluation of ammonia fate and biological contributions during and after ammonia injection for uranium treatment
Task 2: Remediation Research and Technical Support for Savannah River Site	
Subtask 2.1	FIU's support for groundwater remediation at SRS F/H Area
Subtask 2.2	Monitoring of U(VI) bioreduction after ARCADIS demonstration at the SRS F-Area
Subtask 2.3	Humic acid batch sorption experiments into the SRS soil
Subtask 2.4	The synergetic effect of HA and Si on the removal of U(VI)
Subtask 2.5	Investigation of the migration and distribution of natural organic matter injected into subsurface systems
Task 3: Surface Water Modeling of Tims Branch	
Subtask.3.1	Modeling of surface water and sediment transport in the Tims Branch ecosystem
Subtask 3.2	Application of GIS technologies for hydrological modeling support
Subtask 3.3	Biota, biofilm, water and sediment sampling in Tims Branch

Task 4: Sustainability Plan for the A/M Area Groundwater Remediation System	
Subtask 4.1	Sustainable Remediation Analysis of the M1 Air Stripper
Subtask 4.2	Sustainable Remediation Support to DOE EM Student Challenge
Task 5: Remediation Research and Technical Support for WIPP	

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

Task 1 Overview

The radioactive contamination at the Hanford Site created plumes that threaten groundwater quality due to potential downward migration through the unsaturated vadose zone. FIU is supporting basic research into the sequestration of radionuclides such as uranium in the vadose zone, which is more cost effective than groundwater remediation. One technology under consideration to control U(VI) mobility in the Hanford vadose zone is a manipulation of sediment pH via ammonia gas injection to create alkaline conditions in the uranium-contaminated sediment. Another technology need for the ammonia remediation method is to investigate the potential biological and physical mechanisms associated with the fate of ammonia after injection into the unsaturated subsurface.

Task 1 Quarterly Progress

Subtask 1.1. Remediation Research with Ammonia Gas for Uranium

During the month of November, a paper entitled, "Effect of Ammonium on Uranium Partitioning and Kaolinite Mineral Dissolution," and authored by Hilary Emerson, DOE Fellow Silvina DiPietro and Yelena Katsenovich was accepted by the Journal of Environmental Radioactivity. In addition, DOE Fellow Di Pietro submitted an abstract for the student poster session at the Waste Management Symposia in Phoenix, AZ in March 2017 and received confirmation that she will be giving an oral presentation at the Waste Management and American Chemical Society Conferences in March and April of 2017. Further, ICP-OES analysis and kinetic modeling continued for samples from Di Pietro's summer internship and final data assessment is also still in progress. Control (without solids) samples were prepared for batch samples with ammonia gas treatment.

Ammonia Gas Treated Controls for Batch Experiments with Pure Minerals

Samples were prepared in triplicate with one liter stock 3.2 mM NaCl or synthetic porewater solutions treated with ammonia gas (5%NH_3/95%N_2) to a pH of ~11.6 (Figure 2-1) with monitoring of E_h and pH during injection. The initial E_h was 695 and 599 for NaCl and synthetic porewater, respectively. It is important to note that the Eh decreases with gas injection, likely due to removal of dissolved oxygen. Therefore, a theoretical oxygen concentration (Figure 2-2) was calculated based on equation 1 below and a Henry's constant of 1.26×10^{-3} M/bar for O_2 (Langmuir 1997).

$$Eh = 1.23 + 0.0148 \log(P_{O2}) - 0.0592pH \qquad \text{Eq. 1}$$

Furthermore, the pH increases with increasing injection of ammonia gas due to partitioning of ammonia gas to the aqueous phase and further changes in speciation based on equation 2.

$$H_2O + NH_3 \leftrightarrow NH_4^+ + OH^- \qquad pK_b=4.74 \qquad \text{Eq. 2}$$

It is important to understand the effects of gaseous injection versus liquid addition on the final redox conditions, because it could lead to a reduction of uranium and subsequent changes in speciation in both the aqueous and solid phases. For example, the reaction below in equation 3 represents the theoretical reduction of UO_2^{2+} to U^{4+} in the aqueous phase. Furthermore, reduction of uranium is expected to occur around 250 mV (E_h with respect to a SHE) (Zachara, Brown et al. 2007). Therefore, it is possible that U may reduce in these systems based on Figure 2-1.

$$UO_2^{2+} + 4H^+ + 2e^- \rightleftharpoons U^{4+} + 2H_2O \qquad E^o = 0.334\ V \qquad \text{Eq. 3}$$

Following injection of ammonia gas to pH~11.6, an aliquot of uranium was added to reach a total concentration of either 50 or 500 ppb. After three days of equilibration, the aqueous phase was centrifuged at 5000 rpm for 30 minutes and analyzed by KPA to check for losses of U due to precipitation and sorption to the vial walls. Recovery in the NaCl system was 101±7% for triplicate samples at 50 and 500 ppb. However, recovery was significantly decreased in the synthetic porewater and visible precipitation occurred following the centrifugation step. The percent recovered in the aqueous phase was 22±6 and 67±1% for 50 and 500 ppb initial U concentrations, respectively. These results show that the removal of uranium in control samples in the presence of synthetic porewater is concentration dependent. However, it is difficult to determine which processes are dominating as co-precipitation and sorption processes may be occurring simultaneously as calcite is expected to precipitate from solution.

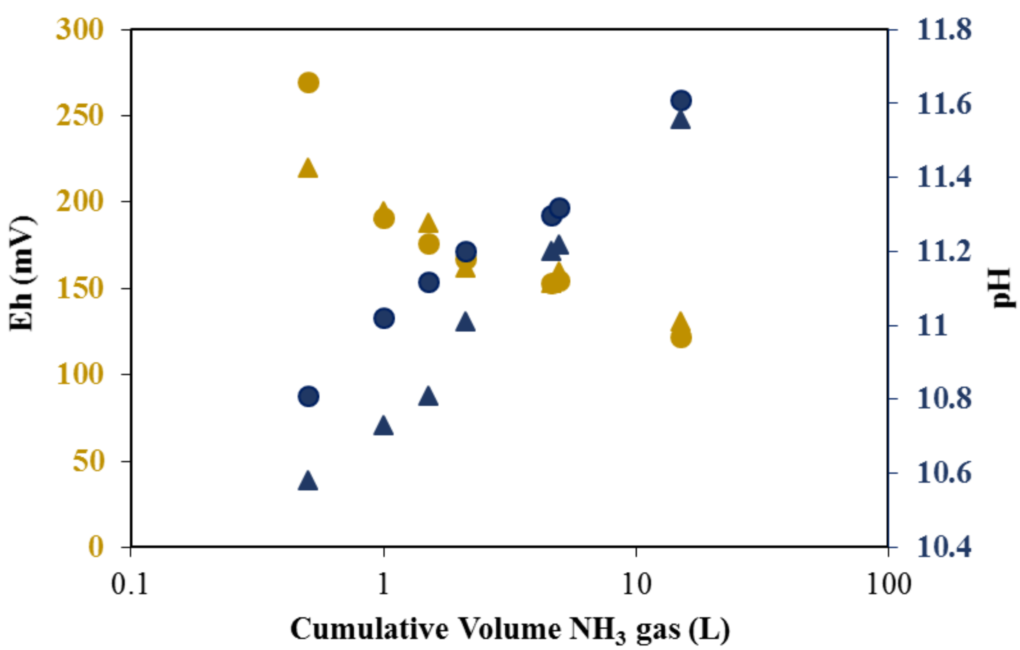

Figure 2-1. Ammonia gas treatment of 3.2 mM NaCl (circles) or synthetic porewater (triangles) with change in Eh with respect to a SHE in mV (yellow) and pH (blue) with respect to the volume of ammonia gas injected, Note: the initial E_h of the NaCl and synthetic porewater prior to gas injection was 695 and 599, respectively.

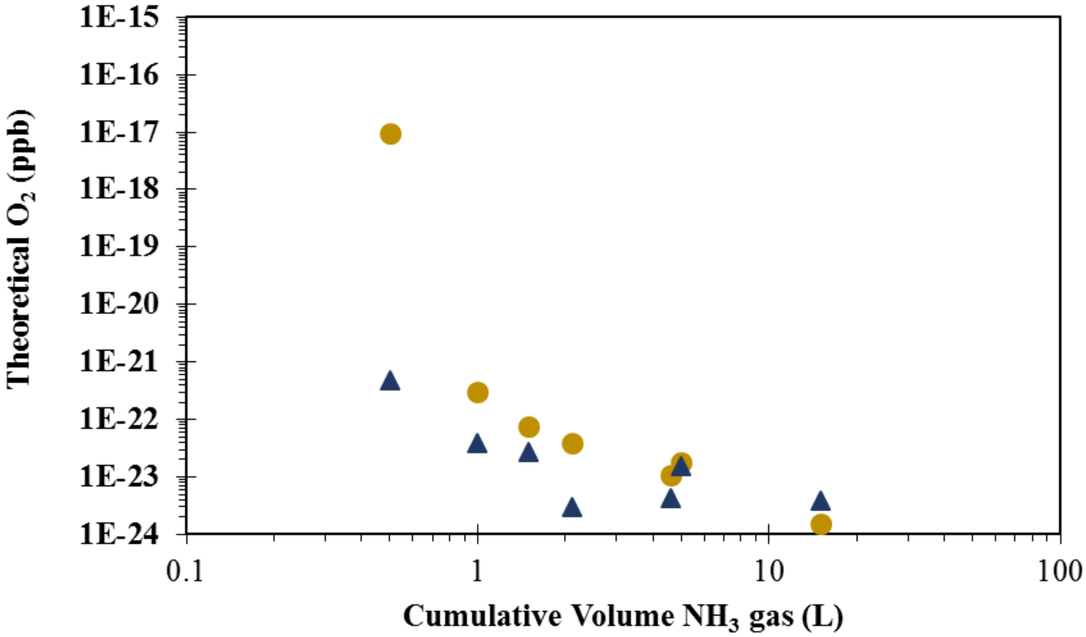

Figure 2-2. Theoretical oxygen concentration with respect to the volume of ammonia gas injected into one liter of 3.2 mM NaCl (yellow) or synthetic porewater (blue).

Results for U-ammonia controls presented above show: (1) a decrease in redox potential which likely correlates to oxygen removal, (2) significant removal of U following ammonia gas treatment in synthetic groundwater controls but not in the NaCl system after three days of equilibration, and (3) increased removal of U with increased concentration. It must be noted that the control samples were prepared with ammonia gas injection into the control solutions (synthetic groundwater or NaCl) followed by immediate injection of U. Based on these results, complementary sample protocols were added: (1) sampling at additional time points was conducted, (2) 5 ppb U controls were prepared with synthetic groundwater (in addition to 500 and 50 ppb U), (3) synthetic groundwater controls were prepared with U after allowing the suspension to equilibrate (i.e., calcite precipitates to form and be removed from the aqueous phase), and (4) synthetic groundwater controls were prepared with U added before ammonia gas addition. Although the sample analysis is still in progress, it is expected that these controls will provide evidence on the impact of U concentration and calcite precipitation on U removal from the aqueous phase in the synthetic groundwater.

Uranium analysis results for the remaining batch experiment controls are still in progress due to mechanical issues encountered with the KPA. However, some interesting conclusions can be drawn from the pH and redox potential measurements of the controls prepared following different protocols:

1. 15 mL batch controls (with U and without minerals) prepared immediately following injection of gas into one liter stock solutions (U added to 15 mL batch samples after pH adjustment)

2. 15 mL batch controls prepared greater than one week after pH adjustment of one liter stock solutions (U added to 15 mL batch samples after pH adjustment)

- No mixing of stock prior to addition
- Sonication of stock for 15 minutes prior to addition

3. Ammonia gas added directly to 15 mL batch controls (with U added prior to injection of gas)

Based on the results shown in Figure 2-3, the ORP appears to be consistent within the batch samples over the time of sampling (up to 21 days) with injection of gas directly into the 15 mL tubes. However, the pH is clearly decreasing with time. Furthermore, a comparison of the pH for gas injection into either the bulk one liter stock solution versus the individual tubes based on Figure 2-3 below shows that there is a significantly greater error between samples for injection into the individual tubes.

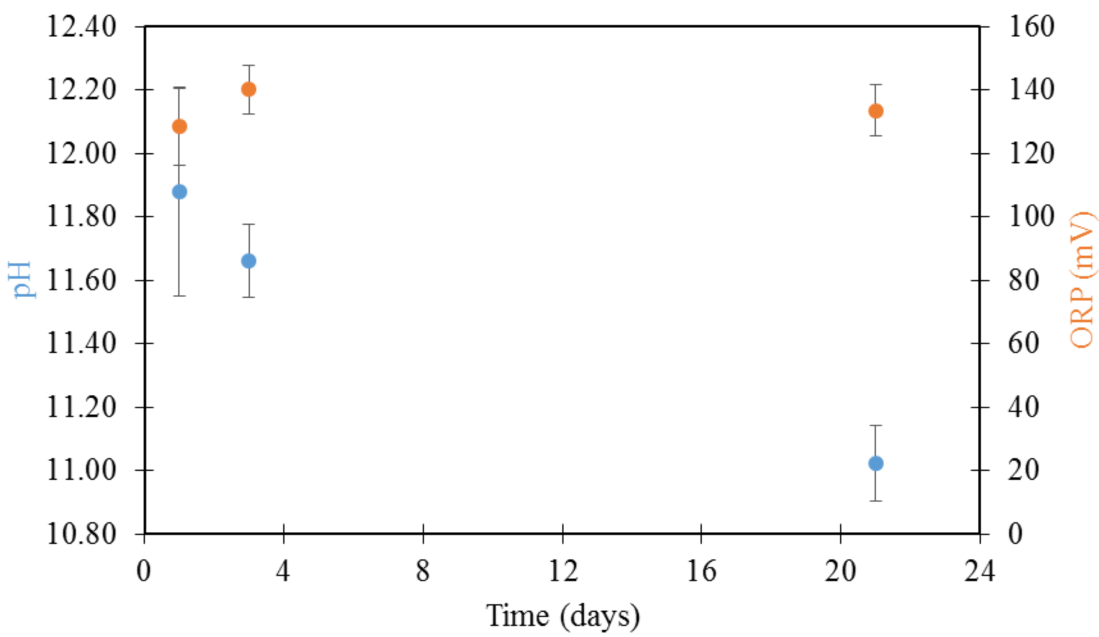

Figure 2-3. Results of injection of gas into individual 15-mL samples of SGW, step 3, with pH measurements in blue and ORP measurements in millivolts shown in orange based on the second y-axis.

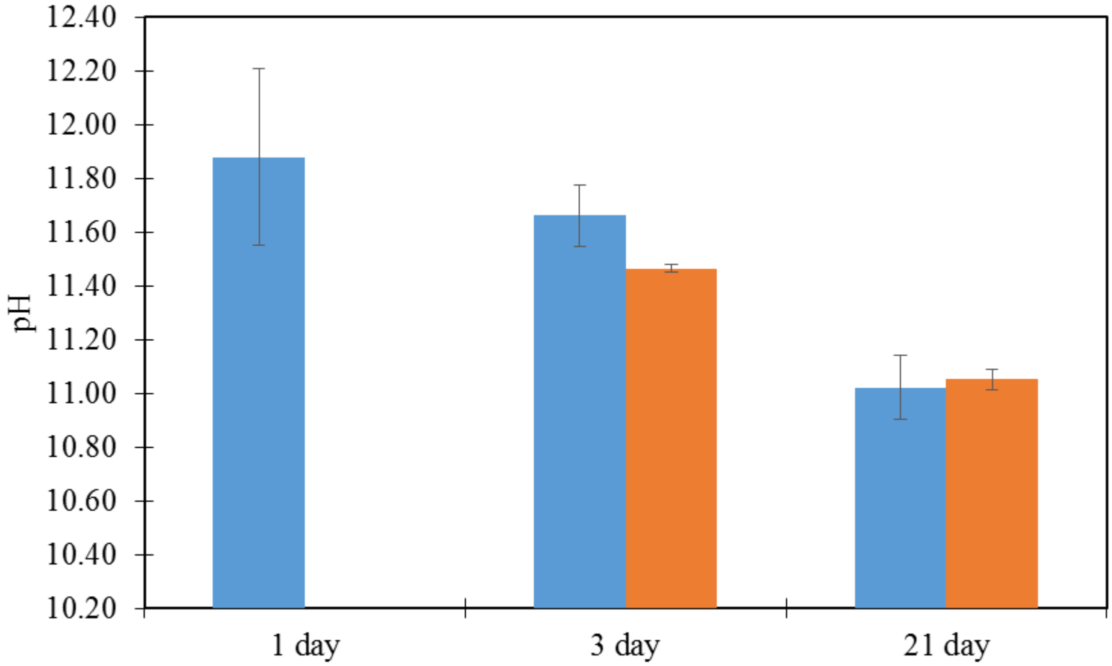

Figure 2-4. pH measurements with respect to time for batch control experiments for SGW following method #1 (orange) and #3 (blue).

During the month of January, samples will be prepared inside a 95%N_2/5%NH_3 gas atmosphere within a glovebag. It is expected that this will reduce the changes with pH with respect to time and reduce the error between samples that was recorded for individual injection. Furthermore, this will allow for a more representative system of the conditions created during injection and allow for calcite precipitation to occur in the presence of U (for SGW groundwater composition only, not NaCl) as would be expected in the field.

Sequential Extractions on Uranium Precipitates Prepared in the Absence of Minerals

FIU also continued with the preparation of 12 U-bearing precipitate samples. An additional filtration step was included in the sample preparation procedures compared to the previous set of samples. This step consisted of vacuum filtering all 12 samples using Millipore 0.2 micron filters and then collecting the solid particles from the filters. This physical filtration allows the complete separation of solid particles from the liquid.

Additionally, FIU completed the sequential extraction experiment for the first set of 12 unfiltered samples, in which preparation hasn't included ammonia gas injections. In addition, FIU started sequential extractions with the set of 12 unfiltered samples, in which preparations included ammonia gas injections. For the purpose of drawing conclusions on the stability of the U-bearing precipitates after executing sequential extraction, a range from weak extractants such as synthetic groundwater that will access highly labile U, to very strong extractants such as 8 M HNO_3 that will remove hard-to-extract U, will be employed. Adapted from Szecsody (2015), the type of extractant solutions, time of exposure and targeted compounds for the sequential extraction experiments are presented in Table 2-1.

Table 2-1. Solutions for Sequential Extraction Procedure

Step	Solution	Time (h)	Target Compounds
1	**Synthetic groundwater**	1	Aqueous U phases
2	**Carbonate solution:** 0.0144M $NaHCO_3$ + 0.0028M Na_2CO_3 (pH 9.3); 2 liters: 2.42 g $NaHCO_3$ + 0.592 g Na_2CO_3 + balance DI H_2O to 2.0 liters	1	Adsorbed U phases
3	**Acetate solution:** 2 liters: 136.1 g sodium acetate•$3H_2O$ + 30 mL glacial acetic acid (17.4 mol/L), pH 5.0, balance DI H_2O to 2.0 liters	1	Dissolved some U-Carbonates
4	**Acetic acid solution:** concentrated glacial acetic acid, pH 2.3; 2 liters: 50.66 mL glacial acetic acid (17.4 mol/L) + 47.2 g $Ca(NO_3)_2$*$4H_2O$, pH 2.3, balance DI H_2O to 2.0 liters	120	Most U-Carbonates and hydrated boltwoodite (uranyl silicate minerals)
5	**8 M nitric acid (HNO_3)** at 95°C	2	Dissolved harder U phases

Samples were centrifuged and supernatant solutions ware collected after each step. Additionally, the samples were rinsed with deionized water after each extraction in order to prevent carryover. Following the extraction protocol, the collected supernatant solutions will be analyzed for trace U through KPA to determine the concentration and thus mass of U extracted in each step after executing the sequential extraction experiments to all the unfiltered and filtered samples.

FIU received polished uranium-bearing samples from Pacific Northwest National Laboratory to conduct microprobe analysis at FIU's Florida Center for Analytical Electron Microscopy (FCAEM) facilities.

FIU also completed the sequential extraction experiment for the second set of 12 unfiltered samples with ammonia gas injection as well as to the last set of 12 vacuum-filtered samples. These experiments followed the same protocol adapted from Szecsody (2015) (Table 2-1) as the first set of unfiltered samples, a range from weak extractants such as synthetic groundwater that access highly labile U, to very strong extractants such as 8 M HNO_3 that remove hard-to-extract U. Samples were centrifuged and supernatant solutions were collected after each step. The samples were also rinsed with deionized water after each extraction in order to prevent carry overs.

Additionally, in the month of November, FIU started to analyze the collected supernatant solutions for trace U through KPA to determine the concentration present and thus the mass of U extracted in each step after executing the sequential extraction experiment to the first set of 12 unfiltered samples. A total of 108 supernatant solution samples corresponding to the first set of 12 U-bearing precipitate unfiltered samples were diluted 10 to 100 times in order for the concentrations detected to fall within the limits of the calibration curve (0.5-100 ppb). The uranium analyses are in progress and will be reported in the next monthly report. The same procedure will be repeated for the second and third sets of samples.

During month of December, FIU analyzed the collected supernatant solutions after sequential extraction of mineral-free samples for U(VI) through KPA to determine the concentrations present and calculate mass of U extracted in each step for the first set of 12 unfiltered samples and 12 duplicate unfiltered samples prepared without ammonia gas injection. To accomplish this step, a total of 108 samples were analyzed using the KPA instrument. The results from the uranium analysis were used for mass balance calculations in order to validate U mass measured in each step and to further be able to draw conclusions on the uranium leaching from the precipitates. KPA analyses were conducted using different dilution factors (1:1, 1:10, 1:50 and 1:100). The highest dilution factor was needed for steps 3, 4 and 5. The extractions suggested the highest percentage of uranium extracted for steps 3, 4 and 5.

Figure 2-5 shows the results of uranium detected throughout the different steps of sequential extraction, providing evidence of the arguments previously stated. As a general tendency, step 3, 4 and 5 account for more than 90% of the total uranium extracted in all twelve samples except for sample 1, which might be explained by the fact that the KPA instrument is undergoing maintenance due to low sensitivity. However, analysis for this sample will be repeated to confirm the results obtained for sample 1.

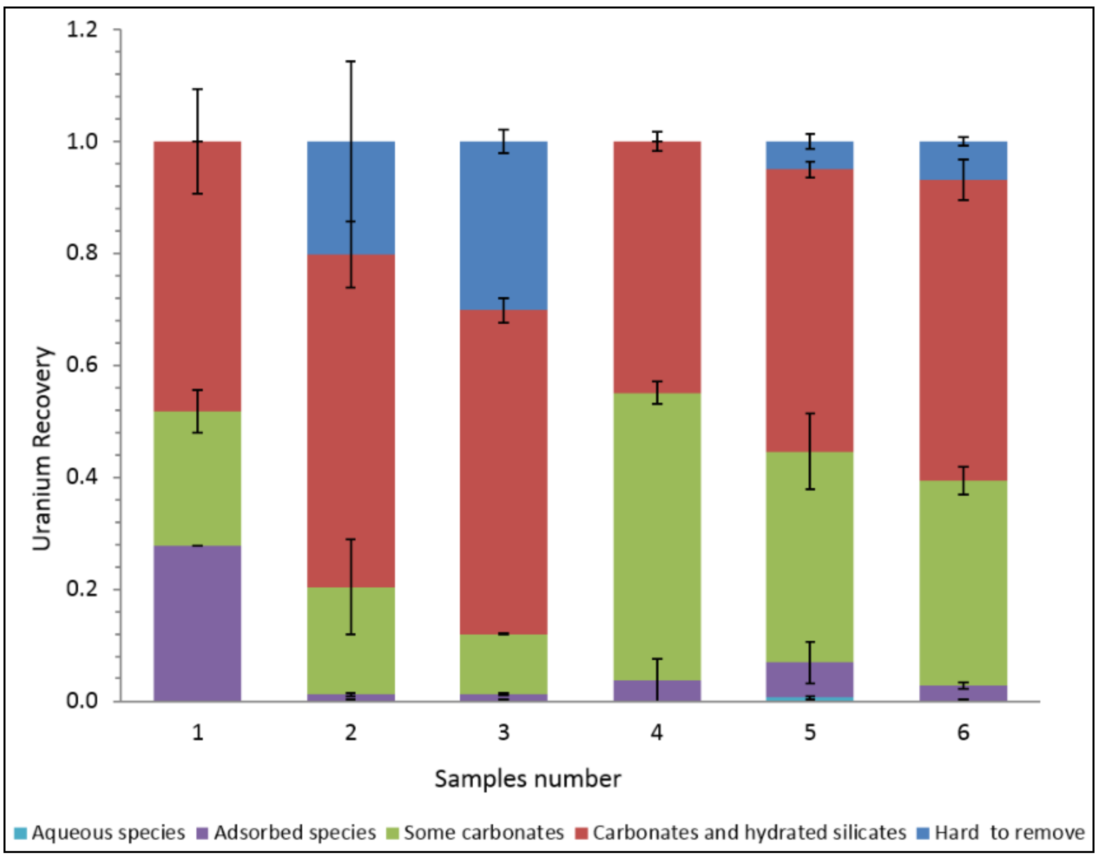

Figure 2-5. Uranium recovery from the first set of unfiltered samples prepared without ammonia gas injection.

The same procedures will be repeated for the second set of unfiltered samples prepared with ammonia gas injection and the third set of vacuum-filtered samples.

FIU conducted electron probe micro-analysis (EPMA) on mineral-free samples that were previously cold mounted in epoxy and shipped to collaborators at Pacific Northwest National Laboratory for cutting, grinding, and polishing steps, which require specialized rad-sample compatible equipment. The EPMA analysis and mapping of elements associated with uranium on the sample surface provided visual comparisons of the elemental associations present in the polished surfaces of uranium-bearing samples through high spatial resolution elemental analysis. A JEOL 8900R Superprobe equipped with 5 two-crystal WDS spectrometers and a single EDS-UTW detector was used to simultaneously detect multiple elements as the beam rastered across the sample surface. Prior to analysis, the polished samples were carbon coated and connected by copper tape to the aluminum sample holder to facilitate electrical conductivity during analysis. The instrument was setup to map a designated area using a 20.0kV accelerating voltage, 5-10 micron spot size, and a 20 ms dwell time. For the majority of the samples, an accumulation of 5 scans was used to create a comprehensive map for each targeted element (Figure 2-6).

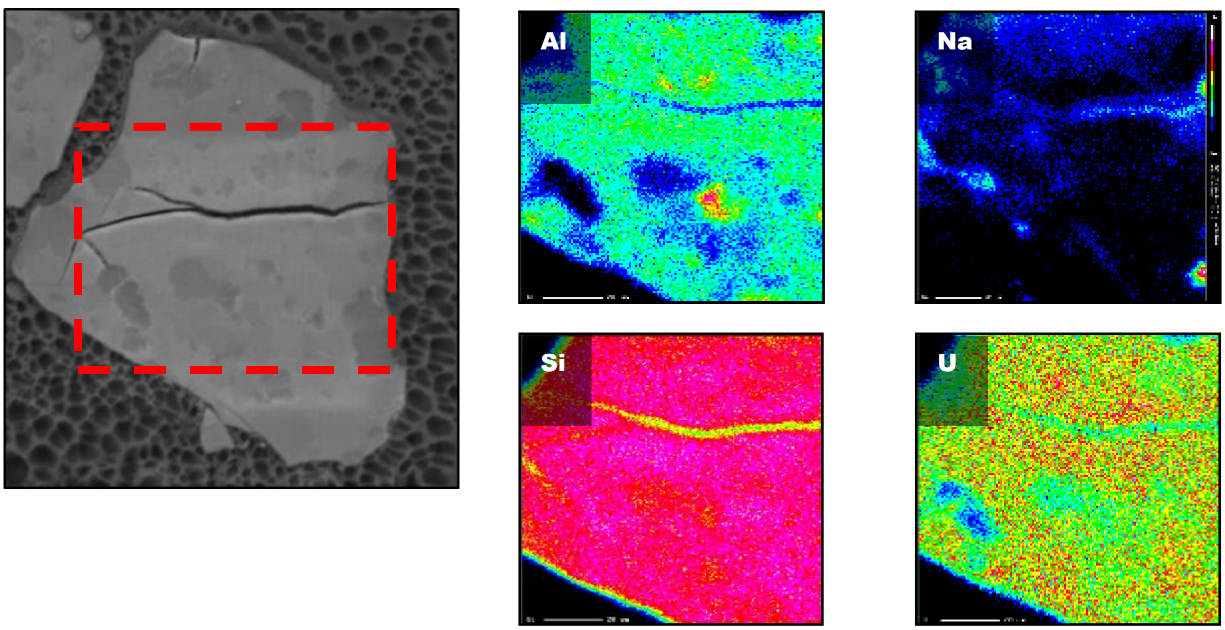

Figure 2-6. EPMA micrograph and corresponding elemental maps. This sample included 500 ppm U(VI), 100 mM Si, 5 mM Al, 50 mM HCO_3 and no calcium.

In the exhibited sample, the elemental distribution maps present the abundance of silica across the entirety of the sample surface. The map for uranium, the analyte of particular interest in this study, shows that it is present at a quantity and distribution that aligns well with that of silica. Evaluation of the EPMA results is still in progress and more data will be presented in the January monthly report.

References

1. Langmuir, D. (1997). Aqueous Environmental Geochemistry. Upper Saddle River, New Jersey, Prentice Hall.

2. Zachara, J. M., C. Brown, J. Christensen, J. A. Davis, E. Dresel, C. Liu, S. Kelly, J. Mckinley, J. Serne and W. Um (2007). "A site-wide perspective on uranium geochemistry at the Hanford Site."

Subtask 1.2. Investigation on Microbial-Meta-Autunite Interactions – Effect of Bicarbonate and Calcium Ions

Collected samples in the mineral-free experiments were evaluated for the cell density via direct count using hemocytometer and cell viability analysis using the spread plate method. The initial inoculation cells density for biotic samples was 10^6 cells/mL (log 6 cells/mL), a similar concentration to the experiment with autunite amended samples.

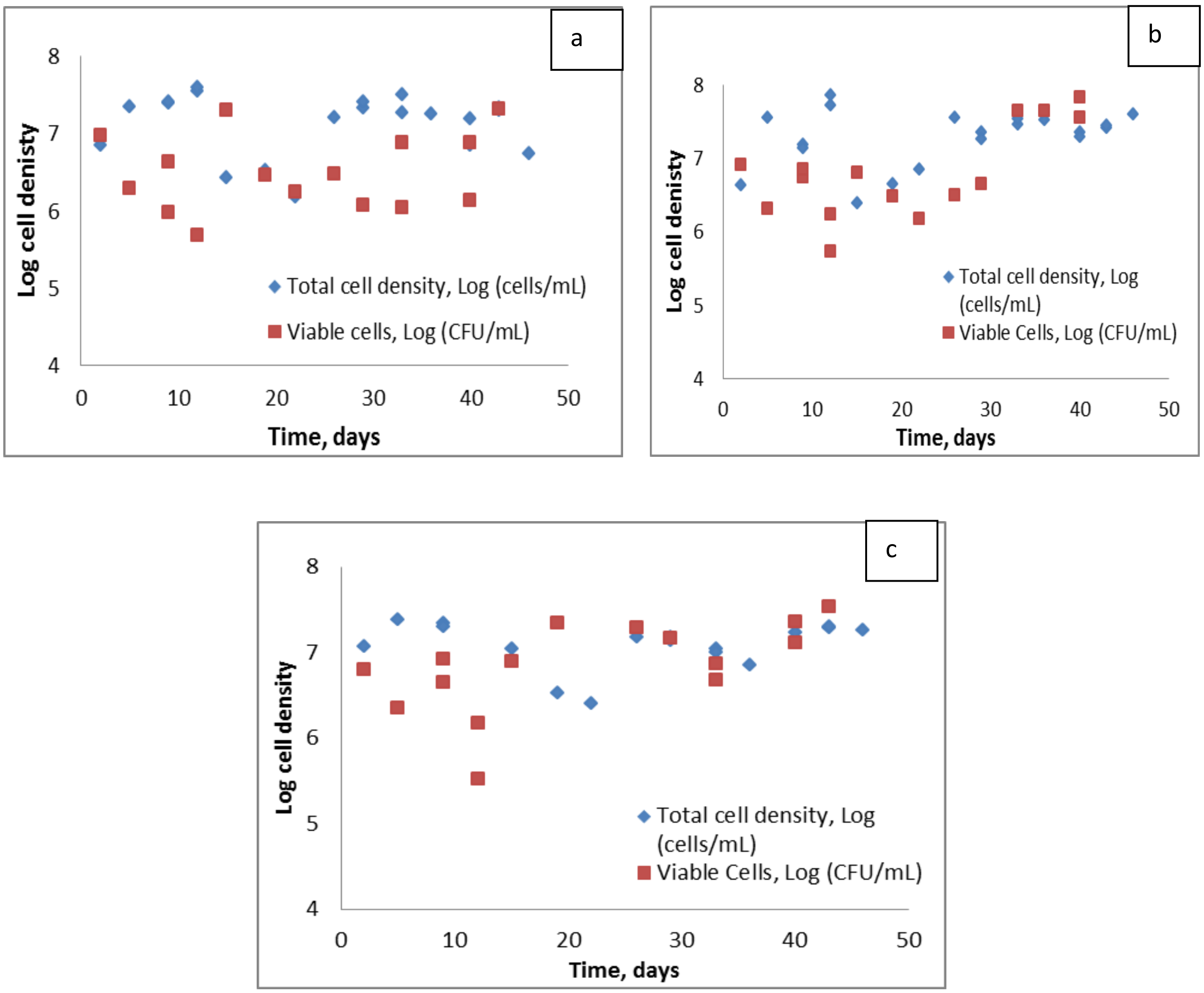

Figure 2-7. Results for the total cell density versus viable cells for mineral-free samples; a) 0 mM HCO_3; b) 3 mM HCO_3; c) 10 mM HCO_3.

In bicarbonate-free samples, total cell densities increased at the beginning of the experiment to log 7.5 cells/mL and then stabilized at the level of log 6.7- 7.2 cells/mL (Figure 2-7a). The cell density values in the mineral-free experiment were observed to be much higher than in the presence of autunite mineral. Samples amended with 3 mM of bicarbonate showed slightly higher results in cell density and values stabilized by the end of experiment in the range of log 7.4 -7.5 cell/mL (Figure 2-7b). The increase in cell density in the solutions amended with 3 mM HCO_3 was noted at higher uranium concentrations compared to bicarbonate-free samples, illustrating the fact that the presence of bicarbonate ions can mitigate uranium toxicity. Cell densities in samples amended with 10 mM HCO_3 were around log 7.2 cell/mL (Figure 2-7c). These cell density values are slightly lower than those observed in samples amended with 3 mM $MHCO_3$. Perhaps the higher uranium concentrations measured in the samples contributed to the slight decrease in cell densities.

Cell viability was determined via counts of colony-forming units (CFU/mL) and values were compared to the cell densities obtained via direct cell counting. At the beginning of the experiment, bicarbonate-free samples yielded an average 3-18% of viable cells out of the total cell density. By the end of the experiments, cell viability increased and stabilized at ~32%. In samples amended with 3 mM and 10 mM HCO_3, the viability of cells in the first 10 days averaged 20% but increased significantly by the end of the experiments at the level of total density concentrations. A similar effect was noted for samples amended with 10 mM HCO_3 but with a larger percentage of cell viability. After 10 days, the viability was noted to be about 32%, and then increased to the level of total cell density concentrations. Overall, mineral-free samples exhibited much higher total cell density and cell viability compared to mineral-amended samples.

In the month of November, FIU continued assessment of samples prepared in the mineral-free experiments. SEM analyses were conducted for the dried precipitates collected from bicarbonate-free samples (Figure 2-8).

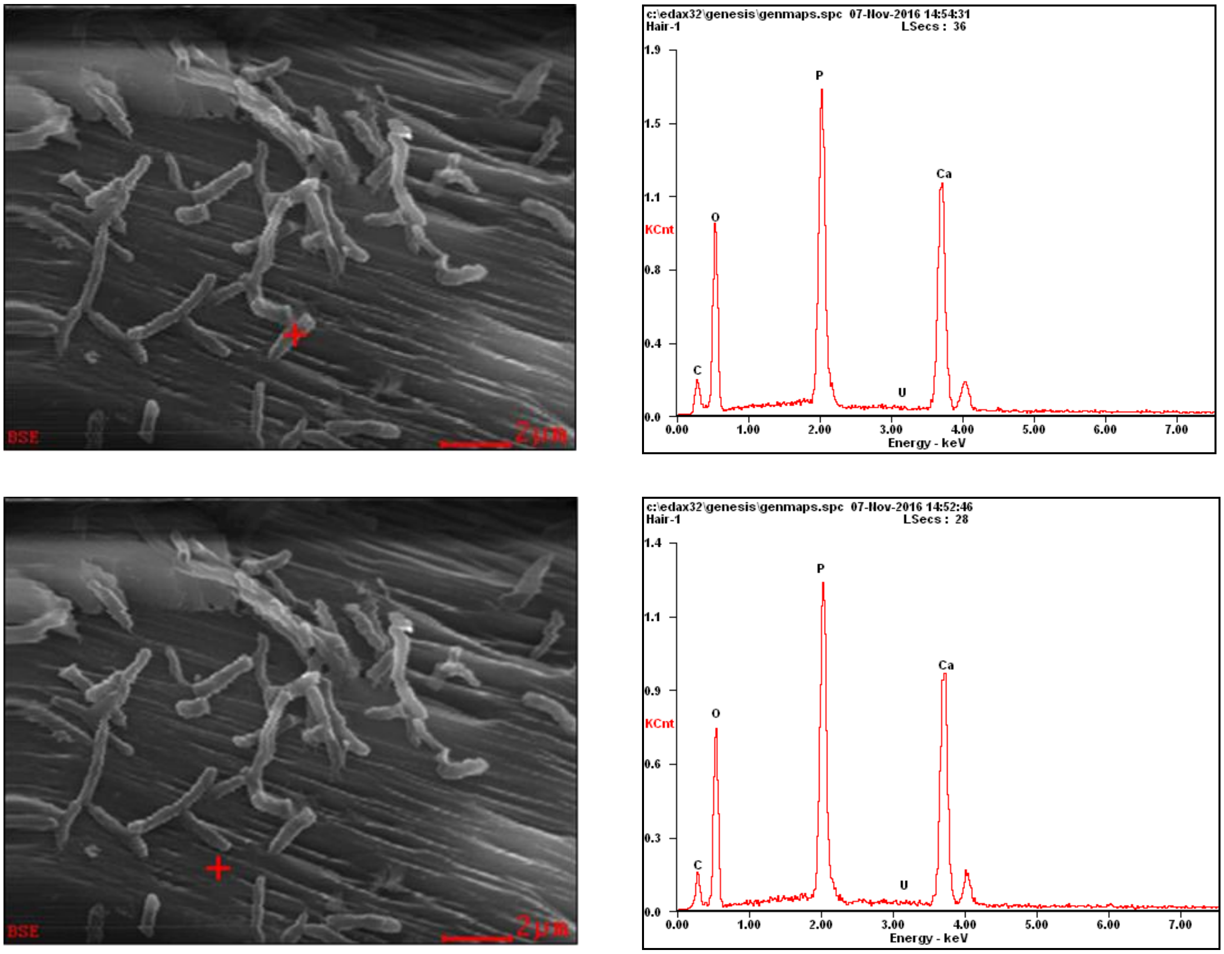

Figure 2-8. Bacteria attached to the surface of calcium phosphate precipitate.

The EDS suggested that the composition of precipitates is composed of calcium and phosphate, which are most likely calcium phosphate solids.

In the month of November, FIU started preparations for a new batch experiment on synthetic autunite dissolution in the presence of anaerobic *Shewanella* bacteria. The bicarbonate media solution was prepared in 1 L of DIW buffered with 0.02 M HEPES buffer with pH adjusted to 7.1 with 0.1 mol/L NaOH. Sodium lactate ($C_3H_5NaO_3$, 60% w/w) was added to the solution with a concentration of 0.024 mol/L. The solution was divided into three bottles and sterilized by autoclaving at 121°C, 15 psi for 15 min and cooled at room temperature. As the experiment is based on the investigation of bacteria interactions in the presence of different bicarbonate concentrations, potassium bicarbonate salt was added to the autoclaved bottles to obtain 3 mM and 10 mM bicarbonate; the remaining bottle was kept bicarbonate-free. This accounts for a total of three concentrations of bicarbonate for the experiment tested. Next, the solutions were filter-sterilized and the sterile bottles were stored in the anaerobic chamber until the beginning of the experiment.

A liquid and hard Luria-Bertani (LB) media was prepared with 10.0 g of tryptone, 5.0 g of yeast extract, and 10.0 g of sodium chloride, with a pH of 7.0. The hard media required an addition of 15.0 g of agar. LB media was prepared, autoclaved, and set in agar plates for future bacterial plating when samples are taken.

In addition, FIU initiated the synthesis of sodium meta-autunite, Na $[UO_2\ PO_4]\ 3H_2O$, via the direct precipitation method using uranyl nitrate, $UO_2(NO_3)2\bullet6H_2O$. The precipitation of Na-autunite via the direct precipitation method was accomplished by mixing uranyl nitrate solution and sodium phosphate dibasic, $Na_2HPO_4\bullet7H_2O$, in a volumetric ratio of 1:7.5 while stirring at 70°C. The overall reaction is as follows:

$$Na_2HPO_4\ 7H_2O + UO_2(NO_3)_2\ 6H_2O \longrightarrow Na[UO_2PO_4]\ nH_2O + NaNO_3 + HNO_3$$

Heating was terminated after a yellowish green precipitate rapidly formed while stirring was continued until the solution returned to room temperature. The solids are currently in a process of curing for 24 hours without stirring. The next step will be recovery of synthetic autunite particles from solution using a disposable 0.45 µm filter. The crystals will be washed with DI water heated to 70° C, then rinsed with isopropyl alcohol.

In the month of December, FIU completed synthesizing of sodium meta-autunite, $Na[(UO_2)(PO_4)]*3H_2O$, via the direct precipitation method using uranyl nitrate, $UO_2(NO_3)_2\bullet6H_2O$, following procedures outlined by Wellman (2005). Autunite particles were dried and FIU weighed 66 samples of 19 mg for each sacrificial sample to be diluted with 10 mL of the solutions containing 0, 3, and 10 mM $KHCO_3$. This amount of autunute correlates to 4.4 mM of U(VI) that was used in all previous experiments.

All sacrificial samples with autunite were autoclaved and kept in the anaerobic glove box prior to initiation of the dissolution experiments. Each set, prepared using a specific bicarbonate concentration, will includes sacrificial biotic vials and abiotic controls. Future work will include labeling all vials and adding 10 mL of media solution augmented with bicarbonate, creating a sampling schedule, and initiating sampling of biotic and abiotic samples.

Reference: Wellman D. M., Catalano J. G., Icenhower J. P., and Gamerdinger A. P. (2005) Synthesis and characterization of sodium meta-autunite, $Na[UO_2PO_4]\bullet3H_2O$. *Radiochimica Acta*, 93, 393-399.

Subtask 1.3. Investigation of Electrical Geophysical Response to Microbial Activity in the Saturated and Unsaturated Environments

FIU continued to perform the column experiments related to the spectral induced polarization (SIP) signatures of microbial activity designed to remediate uranium-contaminated vadose zone sediment. Flow to the columns is powered by a peristaltic pump with a target flow rate of 50 mL/d for each column. There are four separate solutions which are sparged with nitrogen in order to remove any dissolved gases which may form bubbles within the column. Each bottle of solution is connected to a bag full of nitrogen that prevents the solutions from equilibrating with carbon dioxide. The experimental set up shown in Figure 2-9 allows for the collection of SIP measurements and enables correlation of the data with changes in the column pore water geochemical parameters. Initial SIP measurements have been taken and direct sampling of the pore water has been attempted. Difficulties during sampling have been encountered in the form of the port being plugged with sediment which prevents water from being collected. Currently, FIU is investigating ways to clear the ports for more consistent sampling.

Geophysical measurements have also encountered difficulties due to air forming around the current and potential electrodes. One strategy FIU has implemented is leaving syringes within the sample port (Figure 2-9). This has proven moderately effective in preventing sediment from plugging the ports. This strategy, however, has the downside of allowing air into the columns through gaps in between the port and needle; in order to counteract this, FIU has covered the connection between the needle and the port with Parafilm. A reduction in the amount of air entering the columns has increased the reliability of the geophysical measurements; however, some solitary bubbles can cause individual measurements of resistance to be artificially elevated. FIU has elevated the effluent container which has effectively eliminated the majority of air entering the columns through gaps in the ports.

Figure 2-9. Experimental columns with syringe and needles inserted in the sampling ports.

Some initial analysis of the SIP data has been performed. The following graphs are preliminary and require extensive filtering of the data; however, there are noticeable trends available in the data.

The research on this task will continue focusing on laboratory-scale experiments to show the possibilities of using SIP for remote sensing of microbial effects at larger scales. The columns will be inoculated with microbes and monitored over time using geochemical, microbiological, and SIP analyses. In the month of November, FIU continued focusing on laboratory-scale experiments to show the possibilities of using SIP for remote sensing of microbial effects at larger scales by collecting samples from the column ports and taking geophysical measurements. Some initial analysis of the SIP data has been performed. The following graphs on Figure 2-10 are preliminary and require extensive filtering of the data; however, there are noticeable trends available in the data.

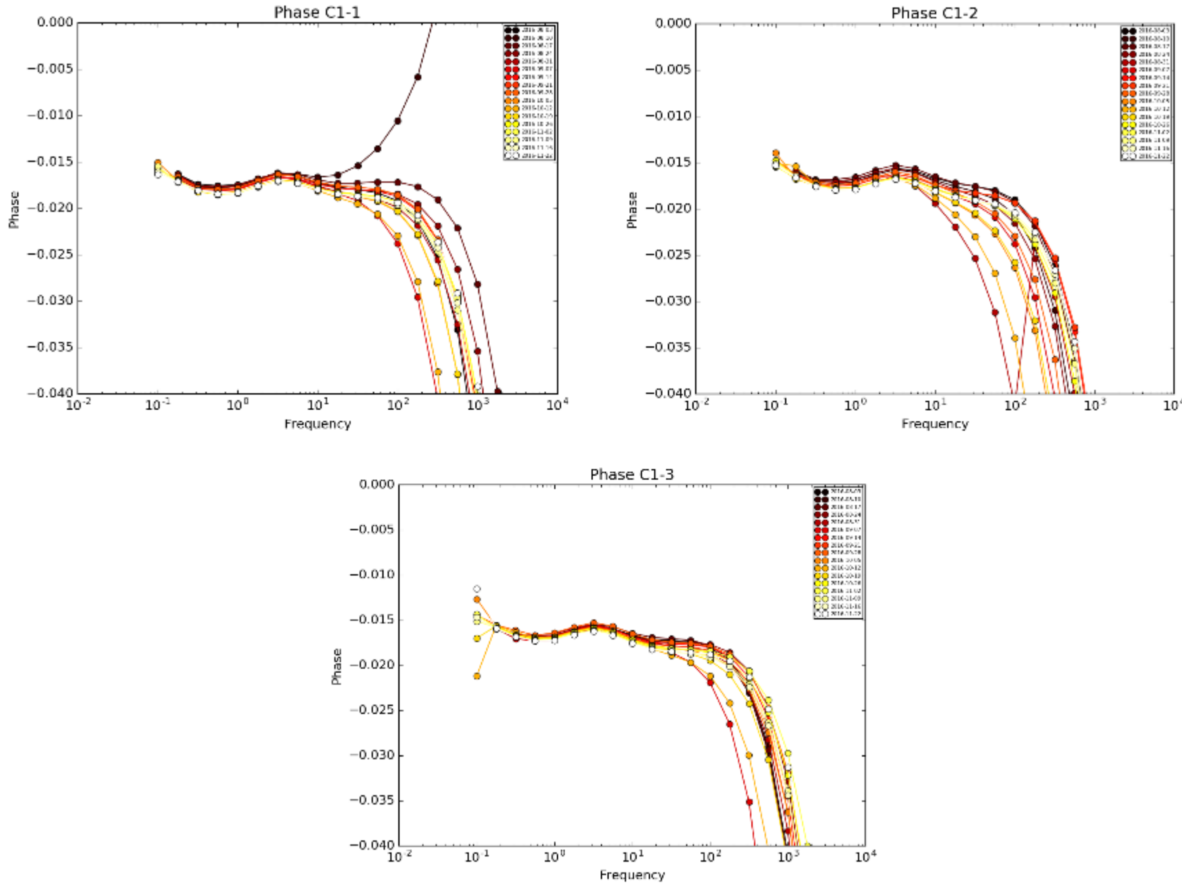

Figure 2-10. Preliminary SIP data for Column 1, sampling ports C1-1, C1-2 and C1-3.

On November 15, a microbial culture was injected into columns five and six. The effect of these will be monitored throughout December. FIU initiated preparation of samples for KPA and ICP-OES analysis.

In the month of December, some initial analysis of the SIP data was performed. The following graphs in Figure 2-11 are preliminary and extra filtering of the data is needed; however, there are noticeable trends shown in the data. Column 2 shows an obvious increase in phase as time passes.

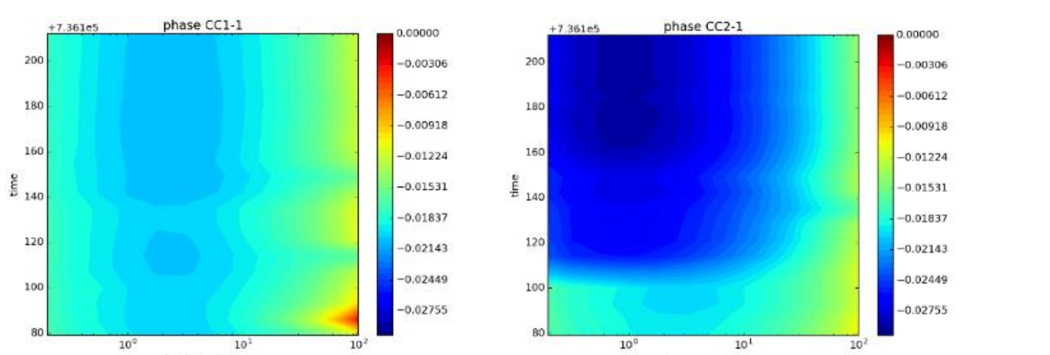

Figure 2-11. Preliminary SIP data for Column 1 (left) and Column 2 (right) for port 1 (time axis is a placeholder).

Changes on the columns are planned for January 2017. These changes will include conversion of columns 1 and 2 into microbe-inoculated columns with higher frequency (daily rather than weekly) measurements. The new data will be compared to the control data presented in the November monthly report. This will allow a greater temporal resolution of chemical and geophysical changes occurring within the columns. Previously this was not feasible due to having 6 active columns.

Subtask 1.4. Contaminant Fate and Transport under Reducing Conditions

The DOE Fellow, involved in this task, Mr. Alejandro Hernandez, prepared a poster for the DOE Fellows Poster Competition entitled "*In-situ Precipitation of AgCl for Removal of Iodide from Groundwater*" and an oral presentation under the title "*Sodium silicate treatment to attenuate uranium mobility in acidic groundwater plumes - In-situ Precipitation of AgCl for Removal of Iodide from Groundwater"* for the 2016 DOE Fellows Induction Ceremony, highlighting his experimental findings during the year that he has been a part of the program.

The Hanford Site in Washington State was one of the major sites for the production of nuclear materials during the cold war period and it is considered the most contaminated nuclear site in the United States due to past practices in waste management and disposals operations. Contaminants include U, ^{99}Tc, ^{3}H, ^{129}I, NO_3^- and CCl_4, all present in concentrations exceeding the drinking water standards.

Tc-99 with a half-life of $2.13 \cdot 10^5$ years is of special interest because of its chemical properties under oxidizing and reducing conditions. Under oxidizing condition, it is found as pertechnetate (TcO_4^-) or Tc(VII), which is highly mobile in oxidizing conditions. Under reducing conditions, it can be found as Tc(IV), which has been thought to sorb to sediments, or precipitate as insoluble $TcO_2 \cdot nH_2O$. At Hanford, the presence of a deep vadose zone and, consequently, reducing conditions, as well as the presence of carbonates, raise questions on the mobility of Tc due to potential complexation of Tc(IV) with carbonates. This would practically indicate mobility of technetium, even under reducing conditions in the form of Tc-carbonates. Although research has been conducted to investigate the fate and transport of Tc(IV) under reducing conditions, mobility of Tc(IV) in the presence of carbonates is still not well understood.

The goal of the first experimental set up will be to identify the range of carbonate concentrations under which previously immobilized Tc(IV) may re–enter the aqueous phase and, hence, re-mobilize. To this end, an anaerobic glove box will be purged with a mixture of hydrogen and nitrogen to induce reducing conditions. Hanford soil suspensions spiked with Tc(VII) will be equilibrated and the concentration of Tc(VII) in the aqueous phase will be monitored until it is reduced to Tc(IV). Then, the samples will be re-suspended in different concentrations of bicarbonates solutions to investigate the potential re-mobilization of insoluble Tc (IV). Furthermore, experiments will involve Hanford soil suspensions in Tc(IV)-carbonate aqueous phase (pH 7.5); the sample will be introduced into the anaerobic glovebox, where oxygen levels will be recorded and the partitioning of Tc between the two phases as a function of time will be recorded. Different levels of Tc(IV) and carbonate will be considered as well.

Technetium standards solutions will be provided by Pacific Northwest National Laboratory (PNNL) and University of Nevada Las Vegas (UNLV). PNNL will provide a standard solution of Tc(VII) 1,000 µg/mL, whereas UNLV will provide a Tc(IV)-carbonate standard solution of 1 mCi activity and carbonate concentration of 1M. For the separations between Tc(IV) and Tc(VII), chloroform and tetraphenylphosphonium chloride (TPPC) reagents have been purchased. Once TPPC is in contact with the aqueous phase, it dissociates to give $(C_6H_5)_4P^+$ and Cl^- which complex with Tc(VII), giving very stable complexes. Hence, tetravalent technetium ends up in the aqueous phase whereas heptavalent technetium ends up in the organic phase (Kopunec et al. 1998; Yalcintas 2015). Trial and error experiments will be conducted on the arrival of the standard solutions in order to determine the recovery of Tc(VII) and Tc(IV).

FIU has also conducted a literature research on the geochemistry of technetium under conditions related to the Hanford Site (Icenhower et al. 2008, Um et al. 2010), as well as the mineralogy of the site (Xie et al., 2003); the literature research is going to continued with relevant papers and reports.

Tc-99 will be determined by means of liquid scintillation counting (LSC). To this end, FIU hosted a LSC training webinar entitled "Liquid Scintillation Counting – Theory and Applications," which encompassed topics such as scintillation basics, performance optimization and statistics. The training was attended by DOE Fellows that will be involved in this task as well as FIU ARC staff.

Preliminary experiments also included sieving of the soil and identifying the major fractions: 567 g of Hanford soil was sieved in the lab and the results are presented at Figure 2-12. In the future, elemental analysis by means of SEM-EDS will be performed and the mineralogy will be identified by means of XRD. These preliminary results will assist in identifying the appropriate fraction of soil to be used for the experiments. The largest soil fraction has a mean particle diameter of 500 µm<d< 2mm, making up approximately 35 % of the soil, followed by the soil fraction 300 µm<d< 500 µm with approximately 33% of the soil. The remainder of the fractions was combined to make the remaining 32% of the soil with d< 300 µm.

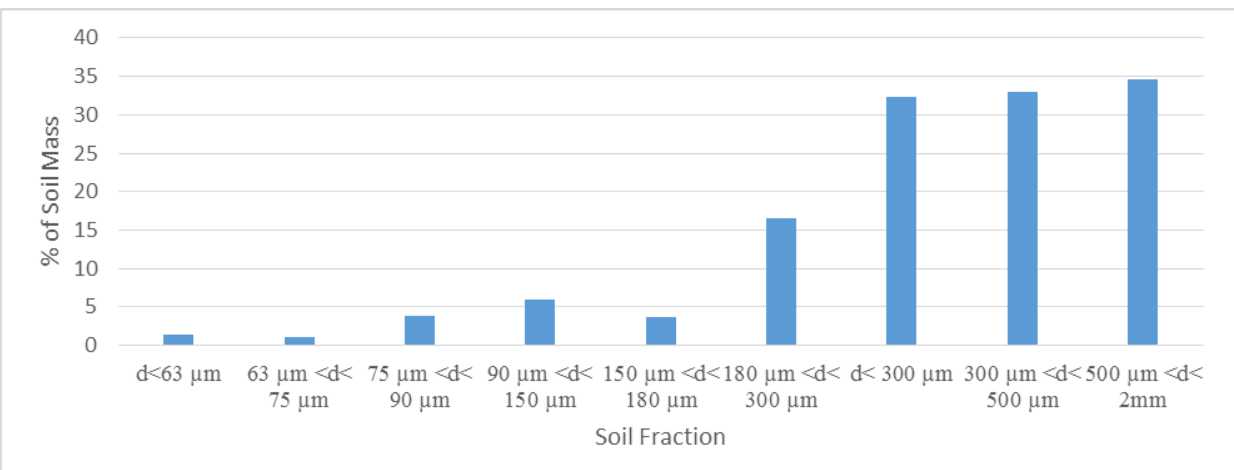

Figure 2-12. Presence of soil mass by soil fractions

BET results are shown in Table 2-2; as expected, the fine fraction d< 300 µm is double the surface area and pore volume of the remaining fractions. Conversely, the bulk fractions are similar in surface area and pore volume, suggesting the existence of only two soil fractions.

Table 2-2. Specific Surface Area Analysis (BET)

Soil Fraction	Surface Area (m^2/g)	Pore Volume (cm^2/g)
d<300 µm	10.67	0.0144
300 µm<d<500 µm	5.36	0.0075
500 µm<d<2 mm	5.73	0.0082

* Constant Sample Density (2.65 g/cm^2)

Future experiments will be conducted with the two significantly different soil fraction (d< 300 µm, and 300 µm<d< 2 mm).

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

Task 2 Overview

The acidic nature of the historic waste solutions received by the F/H Area seepage basins caused the mobilization of metals and radionuclides, resulting in contaminated groundwater plumes. FIU is performing basic research for the identification of alternative alkaline solutions that can amend the pH and not exhibit significant limitations, including a base solution of dissolved silica and the application of humic substances. Another line of research is focusing on the evaluation of microcosms mimicking the enhanced anaerobic reductive precipitation (EARP) remediation method previously tested at SRS F/H Area.

Task 2 Quarterly Progress

Subtask 2.1. Investigation on the Properties of Acid-Contaminated Sediment and its Effect on Contaminant Mobility

The DOE Fellow involved in this task, Ms. Awmna Rana, prepared a poster for the DOE Fellows Poster Competition entitled "*Study of the Fate & Transport of Irrigated Tritium Waste Water in Various Biological Species*," highlighting the experimental findings during her summer internship at Savannah River Ecology Lab (SREL). Ms. Rana gave a short oral presentation on the same topic at the McNair Scholars Research Conference that took place at FIU on October 20-21.

Furthermore, literature related to the determination of ion exchange capacity in soils has been considered (Pansu and Gautheyrou 2006 – Handbook of Soil Analysis, Sposito 2008 – The Chemistry of Soils, van Reeuwijk 2002 – Procedures for Soil Analysis). DOE Fellow Awmna Rana also studied the Year End Report for the FIU Performance Year 6 in order to transition smoothly to this new task and gain perspective on the conditions and challenges of the SRS F/H Area.

During November, FIU initiated the experiments for the creation of different profiles of acidified soil. A triplicate of SRS background soil (mean particle diameter 0.18<d<2mm) suspensions in HNO_3, pH 2.5 were created (Table 2-3). An aliquot was isolated from the supernatant on a daily basis for the determination of Si, Al and Fe in the aqueous phase. Si, Al and Fe leachates in the aqueous phase are associated with kaolinite and goethite in the soil, respectively. The goal is to create a graph of the percentage of Al and Fe leached in the aqueous phase as a function of time. The percentage of the Si, Al and Fe will be calculated as follows: concentration of Si, Al and Fe in the supernatant is going to be converted to mass and will be divided by the initial mass of elements in the soil (determined during last year's experiments by means of EDS elemental analysis). This will allow the evaluation of the extent of soil corrosion and will allow re-creating different acidified soil profiles (e.g. 1%, 5% and 15% of leaching-these are arbitrary numbers which serve plainly as an example), which will be consequently characterized and used for sorption experiments.

Table 2-3. Soil Mass and Volume in the Triplicate SRS Soil Suspensions (mean particle diameter of the soil is 0.18<d<2mm)

Soil mass (g)	HNO_3, pH 2.5 volume(mL)
4.2264	130
4.2395	130
4.2439	130

The samples are left undisturbed for 30 minutes and then 0.5 ml of the supernatant is isolated and diluted with 1% HNO_3 up to a final volume of 2 ml (1:4 dilution); the samples are stored in the fridge (4ºC) until analysis. Al and Fe will be determined by means of ICP-OES or spectrophotometrically. Currently, the daily sampling has been ongoing for 3 weeks and the pH of the supernatant has remained similar to the initial value, approximately 2.5.

After consultation with the SRS site contacts, FIU has decided to use a batch experimental approach to acidify the soil. Compared to using columns, a batch system approach is a quicker and simpler method to obtain initial data and to more quickly reach the targeted soil acidification point. A batch approach also provides homogeneity of the system. The analysis of the collected samples from this experimental setup will determine if the soil samples have leached enough Fe, Al and Si or if the experiment needs to be continued to the point that the soil is acidified enough to make a difference in the following U sorption experiments.

During December, FIU continued the sampling of the batch experiments, containing SRS F/H area soil of mean particle diameter 0.18<d<2 mm and HNO_3, pH 2.5. Al, Fe and Si will be determined by means of ICP-OES. During December, the servicing of the ICP-OES took place, which included changing the chilling system and other preventive maintenance service. FIU prepared two sets of standards: one containing both Al and Fe and a set that contains only Si, in a range of 25 ppb-1 ppm. Measurements are expected to take place in early January.

The hypothesis behind the proposed experimental course is to assess the morphological alterations to the soil (e.g., specific surface area, pore distribution, etc.) as a consequence of the impact of the acidification, which will eventually affect the interaction of the soil with uranium and, hence, affect uranium mobility.

Future work includes:

a. Conclude the Al, Fe and Si determination after long exposure of the soil to acid.
b. Determine if the presence of Si in the supernatant is stoichiometric to kaolinite dissolution.
c. Evaluate the morphological characteristics of distinct acidified soil samples (e.g., 1%, 5% and 15% of Fe leached) and analyze the characterization (e.g., specific surface area, pore distribution).
d. Perform sorption experiments of uranium by different acidified soil samples and compare to background soil sorption results as well as actual acidified soil from the site (if applicable).
e. Develop a manuscript for publication in which the morphological and physico-chemical characteristics of background (clean) soil are compared to those of different degree acidified soil, as expressed in terms of kaolinite and goethite dissolution (mass tracking of Fe, Al and Si) and correlate the physico-chemical characteristics to the sorptive properties of each type of soil.

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

During the month of October, DOE Fellow Alexis Smoot prepared a poster titled "*Synergetic Interactions between Uranium, Humic Acid, Silica Colloids and SRS Sediments at Variable pH*" based on the experimental data obtained for batch experiments conducted with 30 ppm of humic acid and presented at the FIU McNair Scholars Research Conference held at the main FIU campus on October 20-21, 2016.

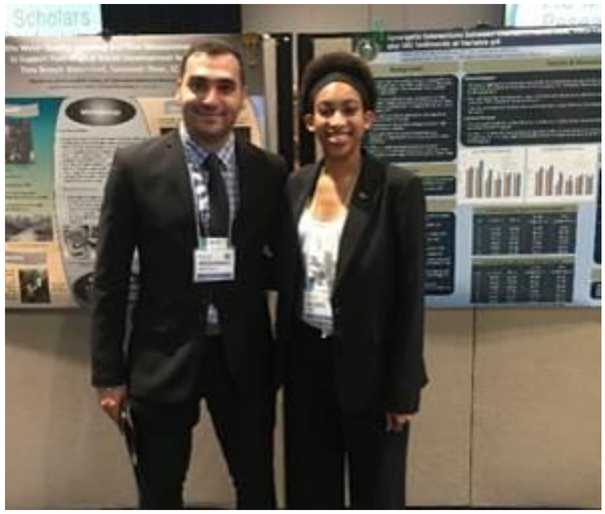

Figure 2-13. DOE Fellows Alexis Smoot and Mohammed Albassam at the FIU McNair Scholars Research Conference.

Previously, FIU tested the influence of various concentrations (10, 30 and 50 ppm) of humic acid in the presence of 3.5 mM colloidal silica, 0.5 ppm uranium and sediment on uranium removal. FIU is planning on testing the influence of varying uranium concentrations (10-50 ppm) on uranium removal at a constant humic acid concentration. To initiate the next phase of the synergy experiments, FIU prepared fresh stock solutions of 30 ppm humic acid, 3.5 mM of silica and 25 ppm uranium. Triplicate samples of batches containing 30 ppm humic acid, 3.5 mM of silica, 400 mg of sediment and 25 ppm uranium at pH 3 were prepared by mixing known amounts of the various constituents, except uranium, as shown in Table 2-4; the uranium was added prior to pH adjustment. The pH of the samples was adjusted with a stock solution of 0.01M HCl and 0.1M NaOH to pH 3 (Table 2-5); afterwards, the samples were placed on a platform shaker. The pH of each sample was measured daily and adjusted if different from pH 3.0 (Table 2-6). This experiment is complete, samples will be processed once the ICP-OES is serviced and working.

Table 2-4. Matrix of pH 3 Batch Samples

PH 3 Adjusted Set	***Constituents***					
	SiO_2	Humic Acid (HA)	Sediments	Uranium U(VI)	Water H_2O	Total Volume
	ml	ml	mg	ml	ml	ml
Batch No. 2	2.1	6		0.5	11.4	20
Batch No. 3	0	6		0.5	13.5	20
Batch No. 5	2.1	6	400	0.5	11.4	20
Batch No. 6	0	6	400	0.5	13.5	20

Table 2-5. Sample Matrix of pH 3 Batch Samples

pH 3 Adjusted Set		Constituents							
		SiO2	Humic Acid (HA)	Sediments	Uranium, U (VI)	Volume of acid/ base	DIW, H2O	pH	
		ml	ml	mg	ml	ml	ml	Initial	Final
Batch No. 2	2.1	2.1	6	0	0.50	4.10	9.00	1.85	3.00
	2.2					3.50	9.00	1.77	3.00
	2.3					3.44	9.00	1.80	2.97
Batch No. 3	3.1	0	6	0	0.50	5.75	11.00	1.65	2.94
	3.2					4.60	11.00	1.66	2.89
	3.3					5.55	11.00	1.63	2.96
Batch No. 5	5.1	2.1	6	400	0.50	3.70	8.00	1.77	3.03
	5.2					4.50	8.00	1.76	3.00
	5.3					3.70	8.00	1.76	2.97
Batch No. 6	6.1	0	6	400	0.50	4.25	10.00	1.64	3.01
	6.2					4.90	10.00	1.68	2.87
	6.3					4.65	10.00	1.66	2.94

Table 2-6. Daily Change in pH of Samples

Sample #		pH 3						
		Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
Batch No. 2	2.1	1.85	3.09	3.10	3.33	3.11	3.04	3.00
	2.2	1.77	2.95	2.94	3.20	3.10	3.07	3.00
	2.3	1.80	2.30	2.89	3.24	3.10	3.10	2.97
Batch No. 3	3.1	1.65	3.71	3.08	3.31	3.27	3.10	2.94
	3.2	1.66	3.04	3.03	3.38	3.10	3.13	2.89
	3.3	1.63	3.69	3.08	3.33	3.00	3.17	2.96
Batch No. 5	5.1	1.77	2.98	3.00	3.24	3.10	3.07	3.03
	5.2	1.76	2.95	3.11	3.31	3.13	3.05	3.00
	5.3	1.76	2.97	2.96	3.25	3.09	3.07	2.97
Batch No. 6	6.1	1.64	3.10	3.07	3.39	3.10	3.07	3.01
	6.2	1.68	3.14	3.11	3.42	3.11	3.14	2.87
	6.3	1.66	2.89	3.06	3.40	3.10	3.14	2.94

The pH 4 batch samples are currently being prepped for pH adjustments using the same amount of components as the pH 3 batch samples. The data for these samples is being collected will be reported in the next monthly report. FIU is in the process of retrofitting the KPA instrument; once the instrument is ready, samples will be processed for uranium measurement.

Subtask 2.3: Humic Acid Batch Sorption and Column Experiments with SRS Soil

During the month of October, a literature review was conducted on the possible effects of a sample matrix that can cause quenching on the measurement of uranium concentrations in aqueous solutions using kinetic phosphorescence analyzer (KPA). Six samples were prepared with various compositions as shown in Table 2-7. For the dilution with HNO_3, 2.7 mL of 1% HNO_3 was added to 0.5 mL of sample. For samples 2 and 6 that were prepared in DI water without dilution in 1% HNO_3, the results had an error higher than 10%. This probably can be explained by the sample matrix effect or uranium change in speciation in DI water. For samples 3, 4, and 5, since the sample matrix is the same as the standards, the error is less than 3%.

Table 2-7. Sample Composition to Investigate a Quenching Effect of Humic Acid on Uranium Measurements

Sample #	Sample	Results
1	10 ppb U + 10 ppm HumaK in DI water (10x dilution in HNO_3)	11.55
2	10 ppb U + 10 ppm HumaK in DI water (no dilution)	7.14
3	100 ppb U + 100 ppm HumaK in DI water (10x dilution in HNO_3)	96.12
4	10 ppb U + 10 ppm HumaK in 1%HNO_3 (no dilution)	10.14
5	10 ppb U in 1% HNO_3 (no dilution)	10.22
6	10 ppb U in DI water (no dilution)	12.44

During the month of November, new samples containing Huma-K and uranium were prepared. The samples were treated by dry- and wet-ashing to investigate if the presence of humic acid can interfere with the uranium readings of the KPA instrument. In the wet-ashing treatment, an aliquot of the sample was mixed with 0.5 ml of HNO_3 and 0.5 ml of H_2O_2. The mixture was heated to just below boiling until evaporation was complete. The samples were cooled and then wet-ash-treated in the same manner two more times. After that, the samples were placed in the oven at 450°C for 15 minutes and then allowed to cool. Lastly, the samples were dissolved in 1M HNO_3. The effect of wet-ashing is shown in the table below.

Table 2-8. Effect of Wet Ashing

	Sample undisturbed	Sample centrifuged	Wet ashing
	U conc (ppb)	U conc (ppb)	U conc (ppb)
10ppb U (control)	10.15	9.82	54.51
100ppb U (control)	96.33	96.03	143.93
10ppb U + 10ppm HumaK	9.40	9.40	67.76

Some effects were observed from wet-ashing: the uranium concentration in all of the samples was higher than the amount spiked. Also in wet-ashing, there were several manipulation steps of the samples and this can introduce errors compared to samples that were not treated (shown in Table 2-8 as sample undisturbed and sample centrifuged). Based on these results, it was decided that treatment of the samples containing Huma-K by wet-ashing is not recommended.

During the month of December, uranium sorption kinetic experiments at pH 4 were conducted with SRS sediments with and without Huma-K coating. For the sediments coated with Huma-K, a known concentration of Huma-K (200 ppm) was pipetted into different tubes containing SRS sediments. The pH of the mixture was adjusted to pH 4, and the final volume in each tube was corrected to 20 mL. The samples amended with Huma-K were left on the shaker for five days to reach equilibrium. After equilibration, the supernatant solution was removed and replaced by DI water with pH adjusted to 4 and spiked with 500 ppb of uranium. Samples containing non-coated SRS sediments were also spiked with 500 ppb of uranium. Both types of uranium-bearing samples containing SRS sediments with and without Huma-K coating were placed on the shaker. At predetermined time intervals, samples were withdrawn and centrifuged. An aliquot of the sample was transferred to KPA vials containing 1% of HNO_3 to keep the samples ready for uranium analysis. The KPA instrument requires maintenance and replacement of the laser cartridge to increase the sensitivity. FIU is in the process of creating a purchase order for the KPA retrofit. Samples will be processed once the laser cartridge is replaced and the KPA is ready for analysis.

FIU is in a process of developing a new manuscript on the Huma-K characterization studies. In the month of January, the Huma-K manuscript will be sent to the co-authors at SRS and FIU's Chemistry Department for their review and input.

During this performance period a new DOE Fellow, Ripley Raubenolt, was hired to work on the column experiments and is currently reviewing the technical reports that detail the experimental results of FIU Performance Year 6.

FIU planned to initiate a control column experiment without Huma-K to estimate the influence of sorbed Huma-K. It was noticed that the electrode used for measuring bromide in the samples collected during the tracer test is not functioning properly. Two possible alternatives are being considered to replace the bromide electrode: i) use rhenium as an potential alternative as a non-reactive tracer and use in-house ICP-OES for analyzing the samples collected; or ii) use bromide as a non-reactive tracer and analyze the samples using IC at FIU's chemistry department. FIU initiated trials with rhenium as a potential alternative for the non-reactive tracer. A column was filled with oven-dried SRS sediment and is being saturated with DIW water; the flow rate is being monitored. The pump was recalibrated to 2 mL/min (same flow rate used in previous experiments). 1000 ppm of rhenium will be injected for two minutes and samples will be collected; the concentration of rhenium will be measured via ICP-OES to develop breakthrough curves.

Task 3: Surface Water Modeling of Tims Branch

<u>Task 3 Overview</u>

This task will perform modeling of surface water, and solute/sediment transport specifically for mercury and tin in Tims Branch at the Savannah River Site (SRS). This site has been impacted by 60 years of anthropogenic events associated with discharges from process and laboratory facilities. Tims Branch provides a unique opportunity to study complex systems science in a full-scale ecosystem that has experienced controlled step changes in boundary conditions. The task effort includes developing and testing a full ecosystem model for a relatively well defined system in which all of the local mercury inputs were effectively eliminated via two remediation actions (2000 and 2007). Further, discharge of inorganic tin (as small micro-particles and nanoparticles) was initiated in 2007 as a step function with high quality records on the quantity and timing of the release. The principal objectives are to apply geographical information systems and stream/ecosystem modeling tools to the Tims Branch system to examine the response of the system to historical discharges and environmental management remediation actions.

<u>Task 3 Quarterly Progress</u>

Subtask 3.1. Modeling of Surface Water and Sediment Transport in the Tims Branch Ecosystem

Last quarter, the saturated zone module of the MIKE SHE model was completed, and this as well as any additional work accomplished during the period July – September, 2016 was used to update a technical progress report for this task that was originally submitted on June 30, 2016. The updated technical report was included as an appendix to the FIU Performance Year 6 YER deliverable which was submitted at the beginning of this quarter on October 14, 2016.

This task is a work-in-progress and is still in the preliminary stages of development. FIU will continue to modify the MIKE SHE model by performing simulations under different conditions and various parameters to understand the calibration factors and the relative effect of the hydrological modules on the simulation results, and then making adjustments to the input parameters as necessary.

One of the modifications includes revision of the model grid element size which was initiated in order to capture more detail of the surface topography and manmade structures such as roads or dams. An alternative hydrological unstructured mesh high resolution flow and transport model using SMS/RiverFlow2D was also implemented in Tims Branch watershed (Figure 2-14). Having a high resolution model will allow comparing results with the MIKE SHE model and provide higher reliability on the simulation results. In addition, with the SMS/RiverFlow2D model, ARC researchers and students will be able to develop new model capabilities to better represent some of the pollutant transport characteristics of SRS.

Figure 2-15 shows the refined model where the mesh cells have been decreased in size to increase resolution and accuracy along the main streams of the Tims Branch drainage network. The resulting refined mesh has 76,278 triangular cells, and 38344 nodes.

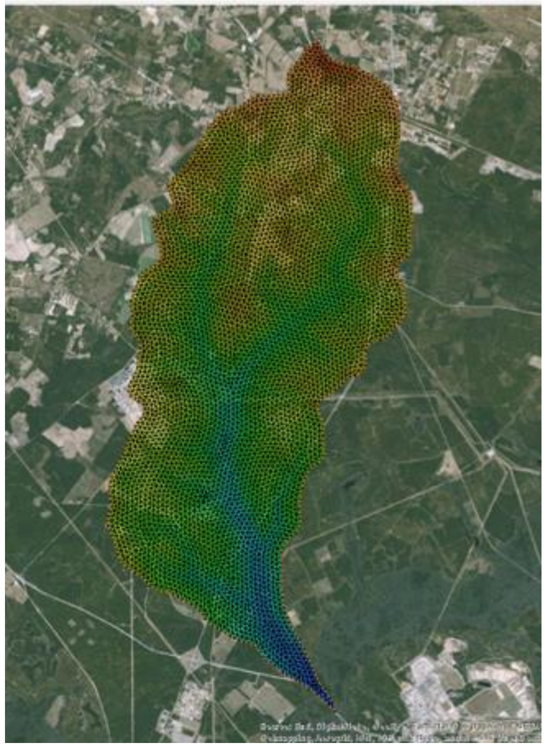

Figure 2-14. Preliminary Unstructured mesh developed on Tims Branch Watershed as part of the implementation of the alternative hydrologic flow and transport model.

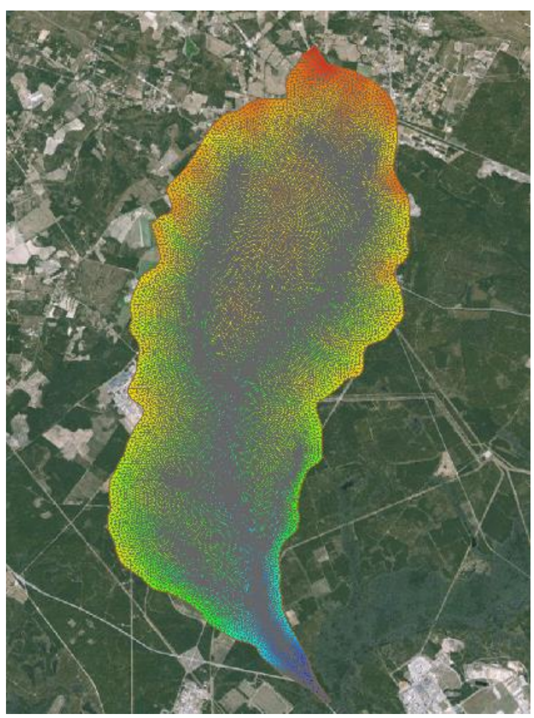

Figure 2-15. General view of the hydrologic model refined mesh. Number of nodes: 38344. Number of triangular cells 76,278. The mesh was refined using smaller cells to increase accuracy along the drainage network.

Figure 2-16 presents a detailed area of the watershed and overlaps the model mesh.

Figure 2-16. Detail of the hydrologic model refined mesh. Note that the mesh has higher resolution (smaller cells) on areas of more interest, while cells are larger along the boundaries.

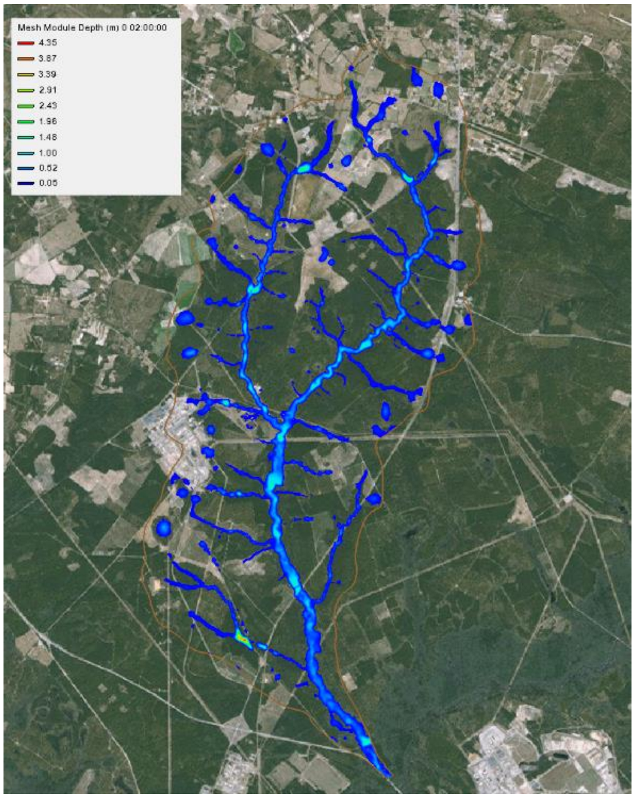

Figure 2-17. Preliminary results of the alternate hydrologic model. Colors indicate water depth along the streams of the watershed drainage network.

Figure 2-17 shows preliminary results for a rainfall runoff simulation to assess the model performance without considering infiltration loses. A uniform 24 hour rainfall event was simulated and the results indicate that the model correctly represents the drainage network and flow to the lower end of the watershed.

This quarter, a preliminary MIKE 11 model for the A-014 outfall tributary was also initiated for simulation of stream flow in this channel. In October, data derived from the field work conducted at SRS in the first week of August 2016 was entered into spreadsheets for QA/QC review prior to implementation into the hydrology/hydraulic model as initial and boundary conditions. The *in situ* data was collected from Tims Branch to support model development and enhance model performance.

During the month of November, continuous progress was made to the MIKE 11 model setup for the Tims Branch A-014 outfall tributary stream simulation. A new MIKE 11 cross section file was implemented using some of the data measurements collected. The four essential files required to set up a MIKE 11 simulation are: River Network, Cross Section, Boundary Condition, and Hydrodynamic Parameters. These files were created based on the MIKE 11 model setup reference file. GIS and time series data were used to build each of these files. The process to generate the River Network file (.nwk11) includes digitizing the river network and branch connections, defining hydraulic structures (weirs, culverts, etc.), and defining inflow points. Figure 2-18 illustrates the stream flow network for A-014 and sampling locations in MIKE 11.

Figure 2-18. Stream network and sample location layers viewed in MIKE 11.

In order to process the stream network, MIKE 11 generates a chainage sequence to connect branches to the main stream. Figure 2-19 shows the chainage and network connectivity in MIKE 11.

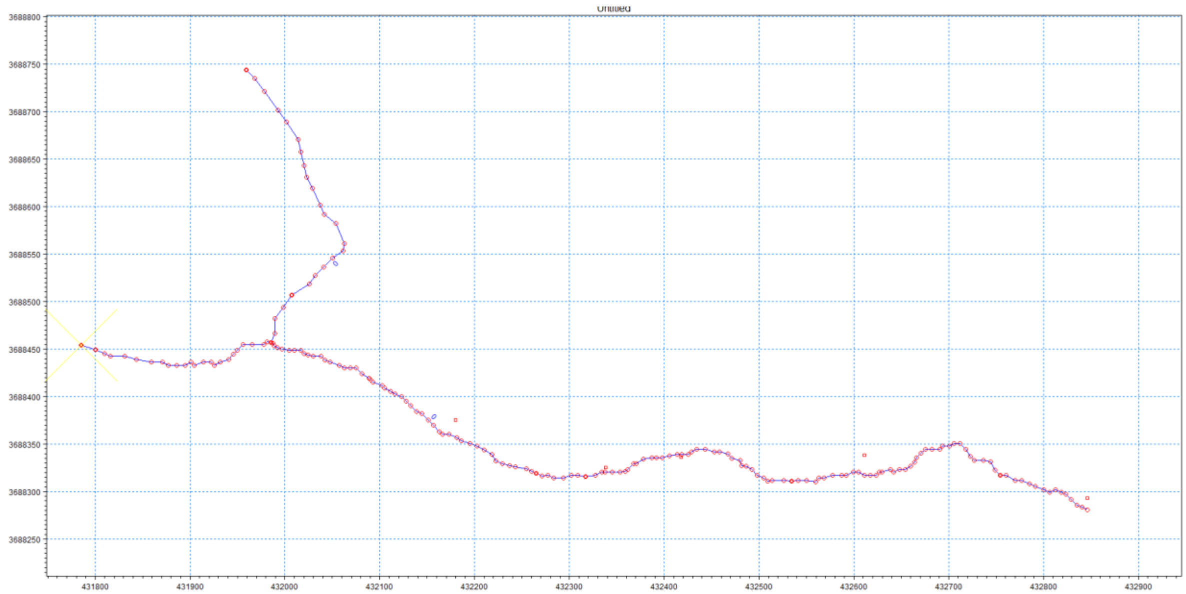

Figure 2-19 Final river network in MIKE 11. Each red dot indicates the starting point of a chainage within the stream/branch.

Cross sections were input manually and the cross section file (.xns11) was generated. Cross section data was manually input into the river network file at each sampling location (Figure 2-20).

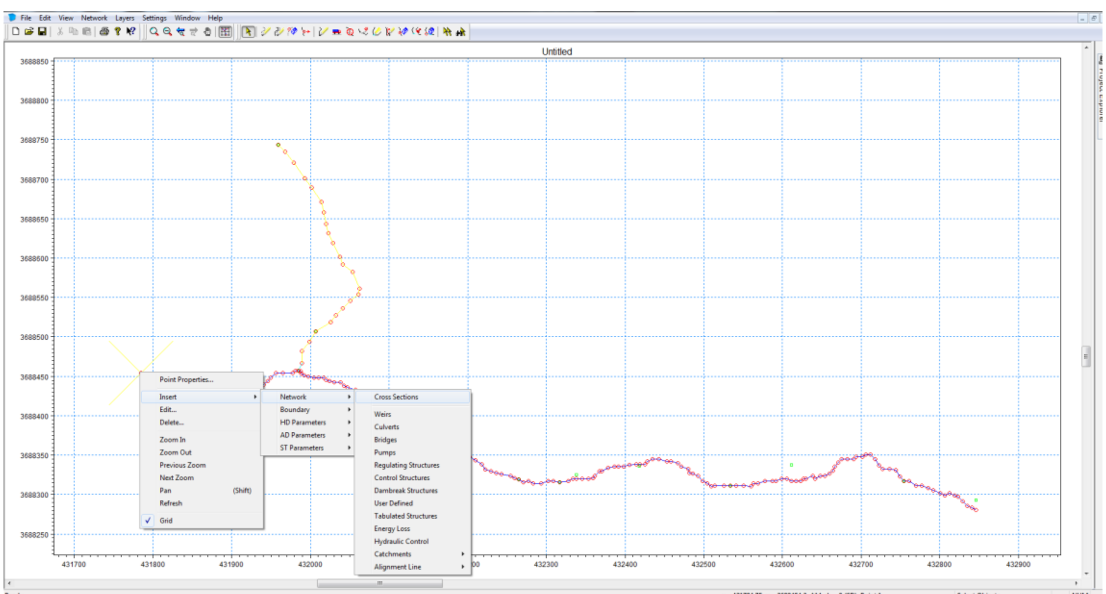

Figure 2-20. Manual insertion of the cross section data into the MIKE 11 network file.

To ensure the accuracy of the cross section profile, the data was graphed in an Excel spreadsheet. Figure 2-21 shows the Excel cross section profile that is identical to the MIKE 11 profile in Figure 2-22.

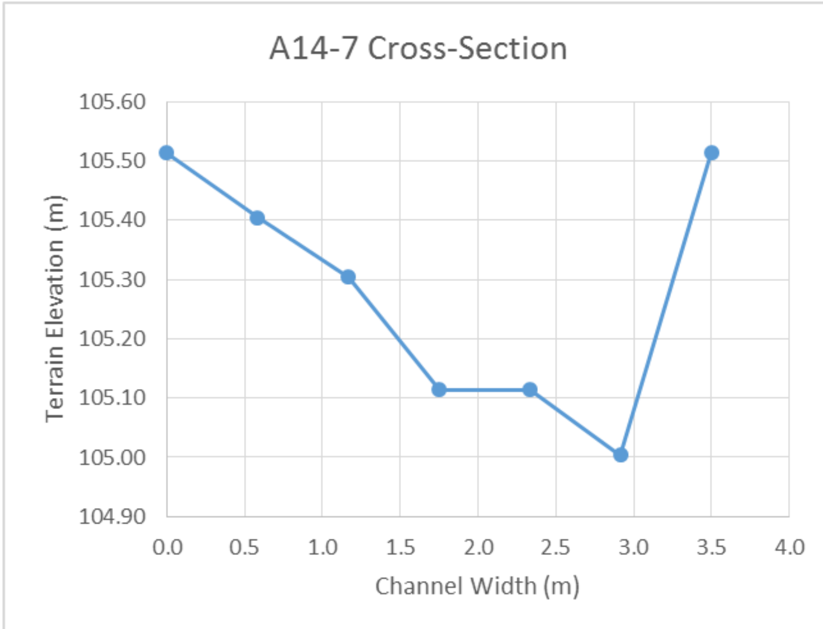

Figure 2-21. Processed cross section data in Excel.

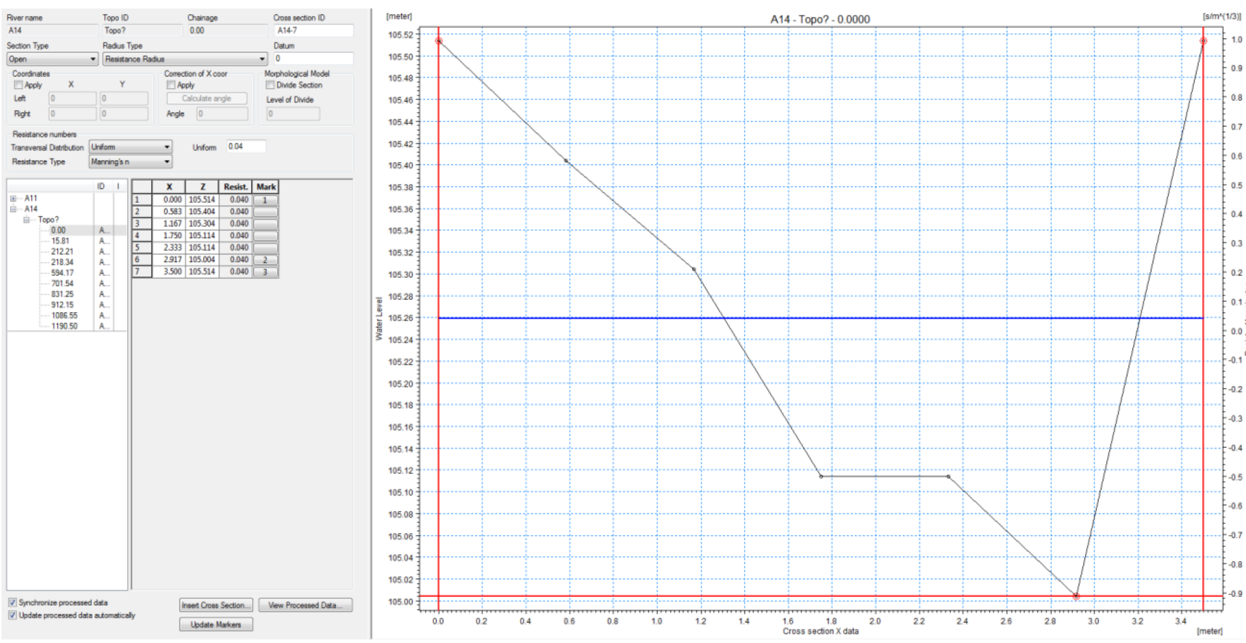

Figure 2-22. Processed cross section data in MIKE 11.

When creating cross sections in MIKE 11, it is necessary to input certain parameters that are characteristic of the stream, such as resistance type and the associated Manning's number (Table 2-9). At this stage of model development, a Manning's n (i.e., 1/M) value of 0.04 was assigned to all the cross sections. This number is in the range recommended for these types of stream characteristics by the United States Department of Transportation – Federal Highway Administration (Schall, Richardson, & Morris, 2008).

Table 2-9. Recommended Manning's n Values

Channel Characteristics	Manning's n
Bottom: gavels, cobbles, and few boulders	0.030 - 0.050
Bottom: cobbles with large boulders	0.040 - 0.070

The processed data created by the program was later used for calculating some of the boundary condition parameters. The Boundary Editor is used to specify boundary conditions in the MIKE 11 model. It is used not only to specify common boundary conditions, such as water levels and inflow hydrographs, but also for the specification of lateral flow along river reaches, solute concentrations of the inflow hydrographs, various meteorological data and certain boundary conditions used in connection with structures applied in a MIKE 11 model (DHI, 2003). The Boundary Condition file (.bnd11) was set for each inflow point at the A-014 and A-011 outfalls. The boundary conditions need to be specified at each upstream and downstream end of the branches that are not connected at a junction. For this model, the locations of the boundary conditions are: 1) the start point of the A-011 branch, 2) the start point of the A-014 branch, and 3) the end point of the A-014 branch. Boundary conditions are manually input into the river network file as unconnected points.

For the starting points of both branches, the type of boundary condition specified was constant flow. The volumetric flow values were calculated from the data collected during the field survey using the velocity flow measured and the cross-sectional areas of the actual outfalls. The estimated discharge values were 0.03 m^3/s for the A-014 outfall, and 0.04 m^3/s for the A-011 outfall. For the end point of the A-014 branch, the Q/h rating curve was used for the boundary condition. The rating curve was obtained theoretically by applying Manning's equation:

$$Q = \frac{1}{n} A R^{2/3} S^{1/2}$$

Where:

$Q = discharge \left({}^{m^3}/_{s} \right)$

$n = Manning's\,roughness\,coefficient \left({}^{s}/_{m^{1/3}} \right)$

$A = cross-sectional\ area\ (m^2)$

$R = hydraulic\,radius\,(m)$

$S = friction\,slope\,({}^{m}/_{m})$

Manning's roughness of 0.04 was used to calculate the rating curve. Stream slope was estimated to be approximately 0.03. The theoretical rating curve values used in this model setup are shown in Table 2-10.

Table 2-10. Theoretical Rating Curve Values

Level (m)	Q (m^3/s)	Level (m)	Q (m^3/s)	Level (m)	Q (m^3/s)	Level (m)	Q (m^3/s)
69.948	0	70.038	0.012	70.143	0.09	70.258	0.31
69.956	0	70.046	0.013	70.152	0.11	70.268	0.34
69.963	0.0002	70.053	0.018	70.162	0.12	70.278	0.37
69.971	0.0002	70.061	0.022	70.171	0.13	70.288	0.4
69.978	0.0006	70.068	0.026	70.18	0.15	70.298	0.43
69.986	0.001	70.077	0.032	70.19	0.16	70.308	0.46
69.993	0.002	70.087	0.038	70.199	0.18	70.318	0.5
70.001	0.003	70.096	0.046	70.209	0.2	70.328	0.53
70.008	0.004	70.106	0.053	70.218	0.22	70.338	0.57
70.016	0.006	70.115	0.06	70.228	0.24	70.358	0.65
70.023	0.007	70.124	0.07	70.238	0.26	70.378	0.73
70.031	0.01	70.134	0.08	70.248	0.29		

The hydrodynamic parameter editor (.hd11) is used for setting supplementary data used for the simulation. Most of the parameters in this editor have default values and in most cases these values are sufficient for obtaining satisfactory simulation results.

This stream model will be coupled with the MIKE SHE overland flow model to complete the surface hydrology model development. A short description of the model will be prepared to submit for an upcoming milestone due by December 8, 2016.

Preliminary Results

The preliminary simulation was set to start at 1/1/2014 and end at 1/1/2015. Figure 2-23 shows preliminary results of the water level time series within the A-014 outfall tributary.

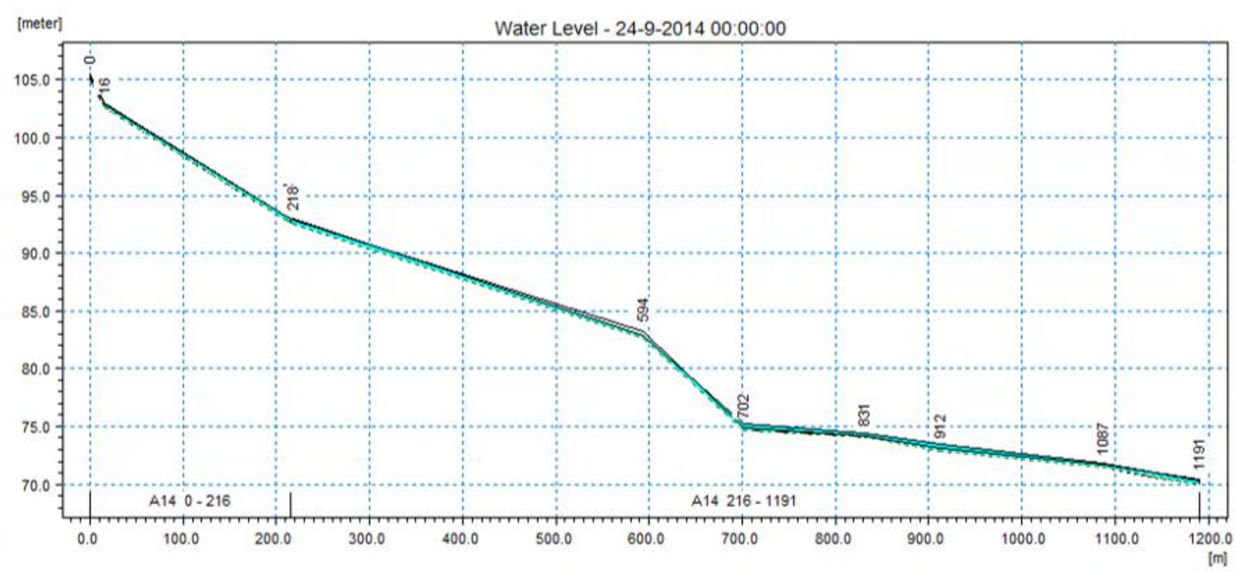

Figure 2-23. Water level profile along A-014 outfall tributary.

Figures 2-24 and 2-25 illustrate the water levels at two cross sections in the A-014 outfall tributary. These figures visualize how the model produces results that can represent the natural hydrology within the channel. It should be taken into consideration that these results are inconclusive since the model is still under construction.

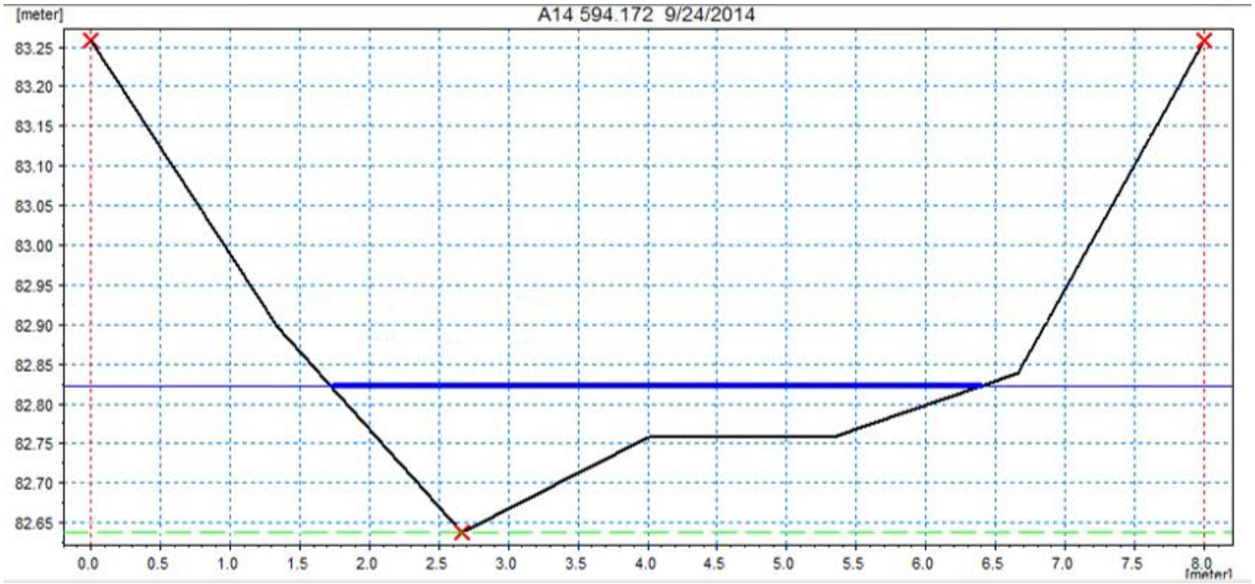

Figure 2-24. Water level simulation in cross section 1.

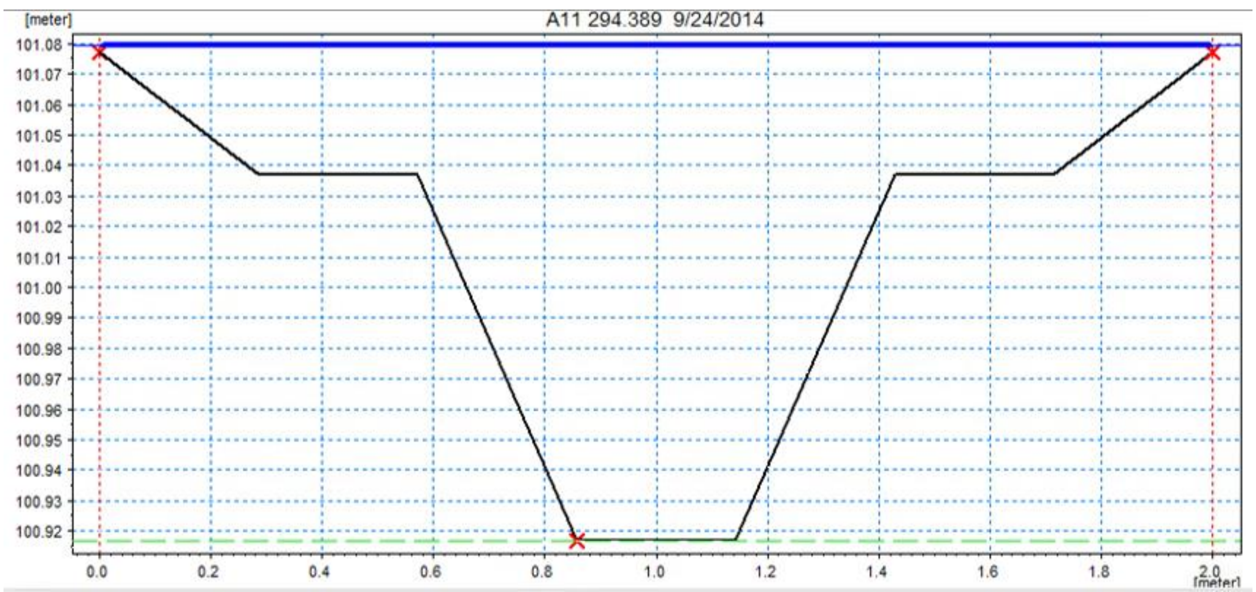

Figure 2-25. Water level simulation in cross section 2.

It is important to note that the A-014 stream contains a culvert and a weir that were not included in the model. These engineered structures need to be added to the model before the calibration process. Calibration will involve modification of input parameters in an attempt to match field conditions within acceptable criteria.

During this quarter, the months of November and December were also spent training the students on GIS as well as MIKE SHE and MIKE 11 to support this DOE research project. Two of the

DOE Fellow students who were recently inducted in November and joined the hydrology modeling team at ARC received individual instruction and training to understand the background and goals of the project. They are being mentored by members of the hydrology modeling group. Further training on both MIKE SHE and MIKE 11 was then provided in December to the entire team of students involved in the project to develop their knowledge and experience in hydrology and hydrogeology. DOE Fellow Natalia Duque, who has worked on the development of the MIKE 11 model of the A-014 outfall tributary, trained the other students, teaching them how to create the stream network and cross sections using a combination of GIS and MIKE 11 geoprocessing tools. In addition, a new graduate level course has been added to the Civil and Environmental Engineering Department's curriculum entitled, "Sediment Transport Theory, Practice, and Application." The course will be taught by Dr. Noosha Mahmoudi and was designed to train graduate STEM students on the development and utilization of transport models. A few of the DOE Fellows currently supporting ARC's hydrological modeling research have registered for this course for the spring 2017 semester. This course, although not part of the project work scope, will be of benefit to these fellows who will receive project/research-relevant training while fulfilling some of their graduate program credit requirements.

Figure 2-26. MIKE SHE/11 and GIS training of students being conducted in the Modeling, Simulation and GIS Research Lab at the Applied Research Center, FIU.

Several of the DOE Fellows supporting this research graduated in December 2016. Mohammed Albassam graduated with a Bachelor of Science (BS) in environmental engineering and will continue supporting ARC research as a DOE Fellow while continuing his education towards a master's (MS) degree in engineering management. Recently inducted DOE Fellow, Ron

Hariprashad, also graduated with a BS degree in environmental engineering and now intends to pursue an MS degree in geosciences (hydrogeology track) as well as a second BS degree in biochemistry at FIU. Ron will also remain in the DOE Fellows program and support ARC's DOE-related research. Natalia Duque graduated with an MS degree in environmental engineering. Natalia has provided research support over the past three years to various tasks conducted by the Soil & Groundwater research group including GIS, hydrological modeling, field sampling and sustainability analysis.

During the month of December, the Modeling, Simulation and GIS Research Lab was relocated to another room within the ARC facilities; however, ARC's IT personnel managed to conduct the transition with minimal downtime in an effort to reduce the impact on the progress of model development.

Subtask 3.2. Application of GIS Technologies for Hydrological Modeling Support

The use of GIS tools remains a continuous integrated component of the hydrological model development. The field data collected during the SRS visit in August was used to generate georeferenced GIS shapefiles of the sample locations along Tims Branch and the A-014 outfall tributary, which were then used in MIKE 11 to generate the river network file. A combination of GIS and MIKE 11 tools were also used to generate the cross sections based on the field measurements taken in Tims Branch.

By the end of this quarter, FIU successfully completed preliminary development of the MIKE 11 model of the Tims Branch A-014 outfall tributary and began running test simulations. As described above under Subtask 3.1, the process involved delineation of the Tims Branch watershed stream network from a digital elevation model (DEM) (3 m resolution) to create a GIS shapefile in ArcMap using ArcHydro. ArcGIS tools were then used to clip the shapefile and simplify the dense network generated to be representative of the A-014 outfall tributary only, which was then imported into MIKE 11. MIKE 11 tools were then used to generate the branches and nodes of the stream network.

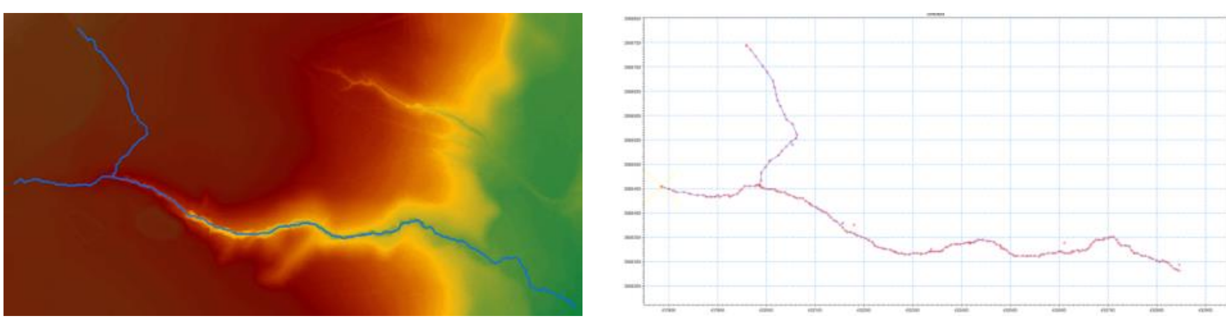

Figure 2-27. Delineated stream network generated from DEM using ArcHydro within the ArcMap interface (left) and imported in to MIKE 11 (right).

ArcGIS was also used to create a point feature class (shapefile) containing the field sampling locations using the UTM coordinates obtained during the field sampling exercise conducted at SRS in August 2016. This file was later used in MIKE 11 to map the exact cross-section locations. Cross-section data was then manually input into the river network file at each sampling location where measurements were taken. The raw data collected was pre-processed using MS Excel by subtracting the measured water elevations at the different points along the width to the base elevation derived from the DEM. The processed cross-section data was then imported into MIKE 11 to create each of the cross-sections. Other relevant input parameters were then added to set the boundary conditions.

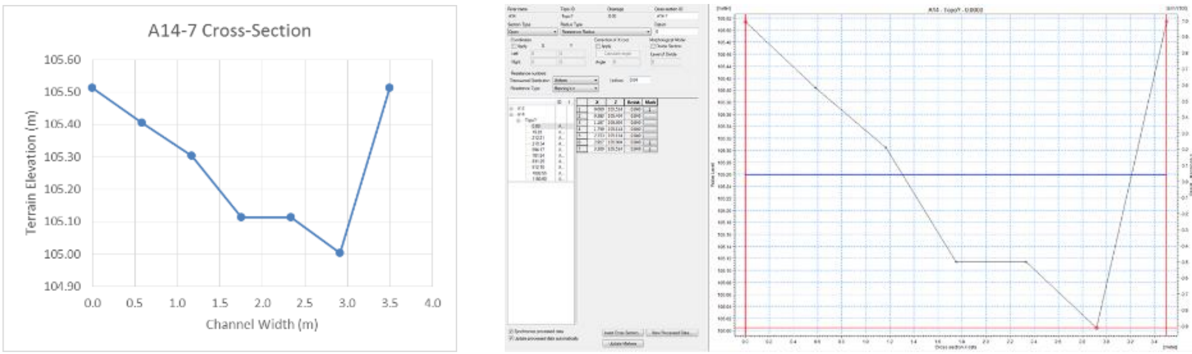

Figure 2-28. Processed cross-section in MS Excel (left) and MIKE 11 (right).

Subtask 3.3. Biota, Biofilm, Water and Sediment Sampling in Tims Branch

To support the flow and contaminant transport modeling research, FIU staff and DOE Fellows conducted fieldwork at SRNL which included in situ data collection including flow velocity, water quality parameters, and cross section profiles from Tims Branch stream, its major tributary, A-014 outfall, and joining outfall A-11. FIU is planning another site visit in order to conduct seasonal sampling and data collection within Tims Branch and the A-014 outfall, including plans to measure the cross section along Tims Branch where it is accessible.

These field exercises provide FIU undergraduate and graduate STEM students with an opportunity to receive technical training on various field and laboratory procedures for collecting water samples, measuring flow velocity, quantifying water quality parameters (pH, turbidity, temperature, etc.), and generating multiple stream cross section profiles. The data derived from their fieldwork will be implemented into the hydrology/hydraulic model as initial and boundary conditions.

Proposed plans for follow-up sampling and data collection at SRS, as outlined in the project technical plan submitted to DOE, were discussed during a teleconference in December with the SRNL lead for this task, Dr. Brian Looney. The possibility of establishing fixed monitoring stations at several locations along Tims Branch was discussed. The purpose of these monitoring stations would be to collect timeseries data of flow discharge and water quality. Future plans are to conduct additional field work and data collection to improve the model calibration and validation; however, the timing and scope will be based on budget availability of both FIU and SRNL personnel.

Sampling and analysis for a biofilm study, potentially as part of a student summer 2017 internship, was also discussed. A former DOE Fellow, Amaury Betancourt, conducted a preliminary study entitled “Tin Distribution and Fate in Tims Branch at the Savannah River Site” under Dr. Looney’s mentorship; hence, there was discussion of possibly tailoring a student internship to conduct a follow-up study.

A draft highlight was submitted to DOE HQ for review and possible incorporation in an upcoming DOE EM Update newsletter. The article is based on the SRS field study performed by

FIU in August 2016 from the DOE Fellow perspective. The intent is to highlight that DOE Fellows are conducting research on EM-related problems, which they are able to integrate into their coursework, and that the research they are conducting at the site is relevant at the sites and/or labs for potential real-world application. In addition, the Fellows intern to conduct fieldwork at the sites/labs/HQ as an integral part of the program.

Task 5: Remediation Research and Technical Support for WIPP

Task 5 Overview

This task is in collaboration with research scientists Donald Reed and Timothy Dittrich in support of Los Alamos National Laboratory's field office in Carlsbad, New Mexico. This research center has been tasked with conducting experiments in the laboratory to better understand the science behind deep geologic repositories for the disposal of nuclear waste. The majority of their work is conducted in high ionic strength systems relevant to the Waste Isolation Pilot Plant (WIPP) located nearby. WIPP is currently the only licensed repository for the disposal of transuranic (TRU) defense waste in the world. FIU-ARC is supporting the basic research efforts requested to update risk assessments for the WIPP site as it moves towards restarting operations.

The objective of this task is to support LANL researchers in the basic science research required to address concerns in risk assessment models for the re-opening of the WIPP site for acceptance of defense waste.

Task 5 Quarterly Progress

During the month of October, DOE Fellow Zengotita presented a poster on this task at the FIU McNair conference. Furthermore, DOE Fellow Zengotita submitted a student poster abstract to be presented at the Waste Management Symposia in Phoenix, AZ in March 2017.

ICP-MS analysis was completed for Nd in both batch (2 and 5 M IS) and column (0.1 M IS) experiments at CEMRC-LANL with the help of Dr. Timothy Dittrich. Batch kinetics data is presented below for 20 ppb Nd sorption to variable dolomite concentrations at 0.01 – 5.0 M IS. The collection of data from the 0.1 and 5 M IS columns was also continued during the months of October through December and have been ongoing for approximately 8 and 6 months, respectively.

Batch sorption of Nd to dolomite

As shown in Figure 2-29 and Table 2-11, the sorption of Nd appears to increase slightly with increasing ionic strength. This is likely due to changes in the speciation of Nd and their effect on sorption processes. The pC_{H+} is calculated based on the empirical equation developed previously (Borkowski, Lucchini et al. 2009). Furthermore, the data is presented only up to 300 minutes because data collected after this period for 2 and 5 M ionic strength is below the limits of detection (LOD).

The LOD was estimated based on the following equation:

$$LOD = 3.2x\frac{SE}{m}$$

Where SE = standard error as calculated based on a linear regression of the calibration and m=slope of a linear fit of a graph of instrument response (counts) versus the known concentration of the standard.

In order to keep the high ionic strength from interfering with the ICP-MS, samples were diluted at least 250 times to keep the total dissolved solids (TDS) below 0.2%. The instrument detection limit (without dilution correction) is 0.022 ppb for both ^{144}Nd and ^{146}Nd.

Previous work has suggested that the trivalent actinides and lanthanides may sorb to carbonate minerals through ion exchange with Ca^{2+}, surface complexation, and surface precipitation. Brady et al. (1999) postulated that Am^{3+} and Nd^{3+} may exchange with Ca^{2+} on the surface due to their similar ionic radii, and their team showed a decrease in Ca/Mg adsorption to the surface at increased ionic strength. However, their results did not report a change in Nd/Am sorption to dolomite with ionic strength (0.005 to 0.5 M NaCl). Nor did previous work investigating sorption of Eu to natural clay samples above pH 8 for Eu (up to 4.37 m NaCl) (Schnurr, Marsac et al. 2015).

Although it is possible that these experiments did not reach a high enough ionic strength for the Na^{+} ion to compete for exchangeable sites with Nd^{3+}, an ionic strength effect for this type of process would result in a decrease in sorption with ionic strength (the opposite of the current results). Therefore, it is most likely that ion exchange is not the primary mechanism leading to sorption in this system. Furthermore, the nearly quantitative sorption reported above neutral pH for both experiments indicates that further experiments are needed to understand if there is a sorption dependence on ionic strength that could be attributable to other processes (Brady, Papenguth et al. 1999, Schnurr, Marsac et al. 2015).

Previous sequential extraction experiments showed that Am^{3+} is most likely to be associated with exchangeable and carbonate sites in the presence of a natural clay (with 20-34% calcite) (Lujanienė, Beneš et al. 2012). Their experimental protocols could not differentiate between exchangeable and carbonate sites. However, based on the above discussion, it is assumed that interactions with carbonate minerals not including exchange processes control the behavior of Nd/Am^{3+} in the system as well as the Lujaniene et al. (2012)'s experiments.

Previous TRLFS measurements at pH 8.1 at 0.01 M IS (as $NaClO_4$) identified two surface species for Cm^{3+} interacted with calcite including: (1) a surface adsorbed species, and (2) an incorporated species (Fernandes, Stumpf et al. 2008). Moreover, sorption of Am on calcite was previously found to be largely irreversible, suggesting surface precipitation (Shanbhag and Morse 1982, Higgo and Rees 1986). Surface precipitation would result in incorporation of Nd^{3+} within the solid phase as observed by Fernandes et al. (2008). Therefore, it is likely that both of these sorption processes may be occurring in the system.

However, the effect of ionic strength on surface adsorption and precipitation processes is not well understood for the trivalent actinides and lanthanides especially in the presence of carbonate minerals. Previous experiments investigating the adsorption of Np(V) to halophilic bacterium reported an increase in sorption with increasing ionic strength which was attributed to increasing aqueous ion activity (Ams, Swanson et al. 2013). The increases in aqueous ion activity predicted an increase in hydrolysis and carbonate complexation constants for 2 and 4 M ionic strength solutions of Np(V).

The different hydrolysis and carbonate species likely have differing sorption behavior and may explain the overall increase in sorption of Nd with ionic strength. However, $NdCl_x^{3-x}$ species must also be taken into account when considering speciation changes with respect to ionic strength. Previous work reported that $NdCl^{2+}$ species were significant above 1 mM Cl^- concentrations (Brady, Papenguth et al. 1999). Future work will include modeling of speciation changes with respect to ionic strength to explain this phenomenon.

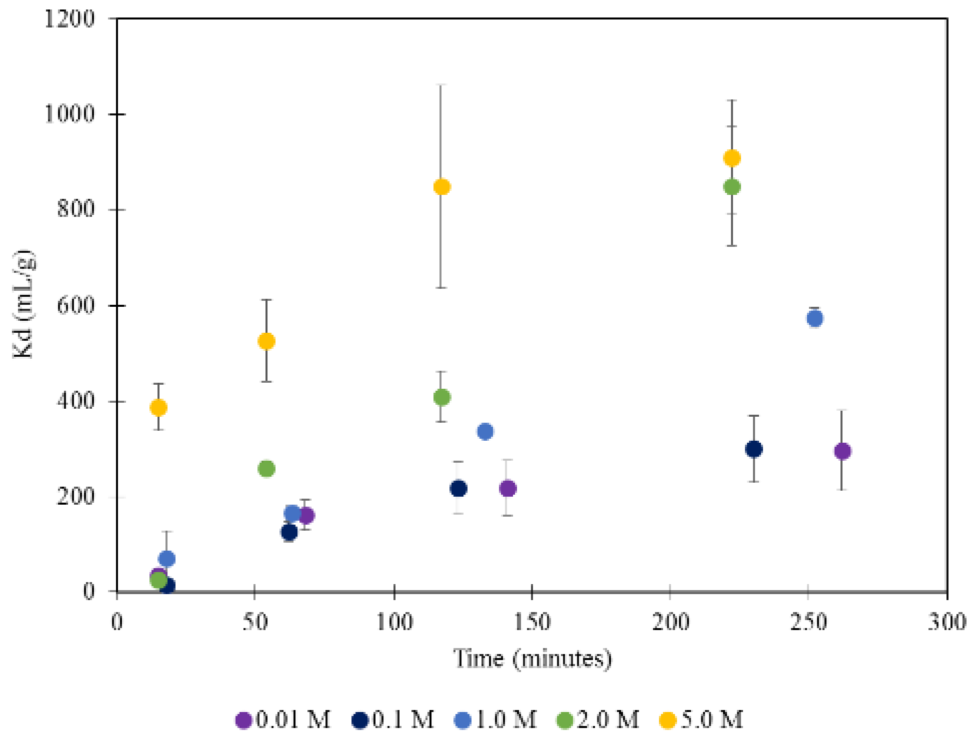

Figure 2-29. Sorption of 20 ppb Nd to 0.01 to 2.0 M ionic strength (as NaCl + 3 mM $NaHCO_3$) dolomite with respect to time.

Table 2-11. Summary of pH and pCH throughout the Batch Experiments and Comparison of K_d Coefficients at 24 Hours

	pH	**pC_{H+}**	**K_d (mL/g)**	**K_d (m^2/g)**
5.0 M	7.42±0.11	8.28±0.38	6380±3060	3750±1800
2.0 M	7.92±0.23	8.22±0.43	1180±450	695±262
1.0 M	8.29±0.08	8.41±0.38	819±225	482±132
0.1 M	8.64±0.08	8.59±0.38	724±105	426±62
0.01 M	8.67±0.11	8.60±0.39	503±129	296±76

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4. Higgo, J. J. and L. V. Rees (1986). "Adsorption of actinides by marine sediments: effect of the sediment/seawater ratio on the measured distribution ratio." Environmental science & technology **20**(5): 483-490.
5. Lujanienė, G., P. Beneš, K. Štamberg and T. Ščiglo (2012). "Kinetics of plutonium and americium sorption to natural clay." Journal of environmental radioactivity **108**: 41-49.
6. Schnurr, A., R. Marsac, T. Rabung, J. Lützenkirchen and H. Geckeis (2015). "Sorption of Cm (III) and Eu (III) onto clay minerals under saline conditions: Batch adsorption, laser-fluorescence spectroscopy and modeling." Geochimica et Cosmochimica Acta **151**: 192-202.
7. Shanbhag, P. and J. W. Morse (1982). "Americium interaction with calcite and aragonite surfaces in seawater." Geochimica et Cosmochimica Acta **46**(2): 241-246.

Milestones and Deliverables

The milestones and deliverables for Project 2 for FIU Performance Year 7 are shown on the following table. To complete milestone 2016-P2-M1, three draft papers were submitted to Waste Management Symposia by 11/4/16 to be published in the WM Symposia proceedings: 1) Removal of U(VI) in the Alkaline Conditions Created by NH3 Gas (abstract #17288); 2) Iron Behavior in Microcosms Simulating Bioreduction in Savannah River Site Sediments (abstract #17389); and 3) Ammonia Gas Treatment for Uranium Immobilization at DOE Hanford Site (abstract #17067). In addition, milestone 2016-P2-M2 was completed with the submission of an abstract entitled, "Effects of Ammonia and Variable Redox Conditions on Mineral Dissolution," to the ACS Spring Conference on November 30, 2016. A summary of the work completed to date on subtask 2.1 for the acidification of SRS F/H Area soil and, more specifically, to the creation of different profile acid-impacted soil samples through monitoring of the concentrations of Fe, Al and Si in the leachates, was sent to DOE and the SRS points-of-contact on December 15, 2016 (FIU milestone 2016-P2-M4); completion of this milestone has been reforecasted to May 8, 2017. Finally, preliminary development of the MIKE 11 stream flow model for the A-014 outfall tributary (subtask 3.1, milestone 2016-P2-M3) was completed and a summary of the work was sent to DOE and SRS on December 8, 2016.

FIU Performance Year 7 Milestones and Deliverables for Project 2

Task	Milestone/ Deliverable	Description	Due Date	Status	OSTI
Project	2016-P2-M1	Submit three draft papers to Waste Management 2017 Symposium	11/4/16	Completed	
Task 1: Hanford Site	2016-P2-M2	Submit abstract to ACS Spring Conference (Subtask 1.1)	11/30/16	Completed	
	2016-P2-M5	Complete training on LSC analytical technique and trial-and-error experiments for separations and determination of Tc(IV) and Tc(VII) (Subtask 1.4)	1/27/17	On Target	

	Deliverable	Technical report on the results of columns monitoring using geochemical and SIP analyses (Subtask 1.3)	1/30/17	On Target	
Task 2: SRS	2016-P2-M4	Complete the creation of acid-impacted soil samples through conditioning of SRS F/H Area soil with acidified water in columns (Subtask 2.1)	12/15/16	Reforecasted to 5/8/17	
	Deliverable	Technical report on the Investigation on the Properties of Acid-Contaminated Sediment and its Effect on Contaminant Mobility (Subtask 2.1)	2/13/17	On Target	
	2016-P2-M6	Complete batch experiments of uranium removal by Huma-K sorbed on SRS sediments (Subtask 2.3)	2/15/17	On Target	
	2016-P2-M7	Complete a set of column experiments using modified humic acid (Subtask 2.3)	2/28/17	On Target	
	Deliverable	Technical report on the synergy between colloidal Si and HA on the removal of U(VI) (Subtask 2.2)	3/31/17	On Target	
	Deliverable	Technical report on the Investigation of the Removal of Uranium by Huma-K Sorbed on SRS Sediments via Batch Experiments (Subtask 2.3)	4/3/17	On Target	
Task 3: Tims Branch	2016-P2-M3	Complete development of MIKE 11 stream flow model for A-014 outfall (Subtask 3.1)	12/8/16	Completed	
	2016-P2-M8	Complete calibration of MIKE SHE and MIKE 11 models (Subtask 3.1)	3/1/17	On Target	
	2016-P2-M9	Complete batch experiments on the biodissolution of Na-autunite (Subtask 1.2)	3/20/17	On Target	
	2016-P2-M10	Complete coupling of MIKE SHE and MIKE 11 models (Subtask 3.1)	5/5/17	On Target	
	Deliverable	Technical report on the surface water modeling of Tims Branch (Task 3)	6/15/17	On Target	
Task 5: WIPP	Deliverable	Technical report on the effect of ionic strength on the sorption of neodymium to dolomite (Task 5)	5/12/17	On Target	

Work Plan for Next Quarter

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

Subtask 1.1 – Remediation Research with Ammonia Gas for Uranium

- Initiate experiments at low Si/Al ratios and variable HCO_3^-/Ca/Mg/Fe to determine the minimum concentration of Si in the system that causes coagulation reactions with U after ammonia gas applications. Continue EMPA sample analysis to characterize the uranium-bearing solid phases produced by the application of the ammonia gas injection method.
- Initiate sample preparation for continuous flow reactors (CFR) to measure the release of U(VI) from U(VI)-bearing multicomponent precipitates created in conditions mimicking ammonia gas applications for the Hanford Site vadose zone.
- Continue analysis of samples from DOE Fellow Di Pietro's summer internship to quantify the rate of mineral dissolution following base treatment.
- Begin experiments with ammonia gas to compare with NaOH and NH_4OH treatment with a focus on the changes in redox conditions with gas versus liquid treatment.
- Prepare two posters (one student and one professional session) for the WM-2017 symposia.

Subtask 1.2. Investigation on Microbial-Meta-Autunite Interactions - Effect of Bicarbonate and Calcium Ions

- Initiate Na-autunite solids biodissolution experiments by anaerobic bacteria.
- Collect samples for U(VI) and Na, P analysis. Initiate samples processing via KPA and ICP-OES instruments.

Subtask 1.3. Investigation of Electrical Geophysical Response to Microbial Activity in the Saturated and Unsaturated Environments

- Convert columns 1 and 2 into microbe-inoculated columns.
- Initiate higher frequency sampling of these columns.
- Inject a microbial culture into columns 1 and 2.
- Analyze data and produce a higher resolution visualization of processes occurring within columns after microbial culture injection.
- Perform chemical analysis on samples.

Subtask 1.4: Contaminant Fate and Transport Under Reducing Conditions

- Implement the SOP for Tc(IV)/Tc(VII) separation.
- Commence experiments with Tc and Hanford soil (batch).
- Continue reading literature on the Tc environmental behavior.

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

Subtask 2.1. FIU's Support for Groundwater Remediation at SRS F/H –Area

- Create different profile acidic soil samples, taking into consideration the preliminary kinetic experiments that identify the time necessary to reach equilibrium conditions.
- Initiate measurement of specific surface area (BET) of acidified soil.
- Initiate SEM analysis of the samples.

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

- Continue experiments by preparing batch samples containing 10 ppm of uranium and 30 ppm humic acid with colloidal silica and study the synergetic effect of humic acid and silica on uranium removal in the pH range of 4-8.
- Prepare a student poster to be presented at WM-17.

Subtask 2.3. Humic Acid Batch Sorption and Column Experiments with SRS Soil

- Perform potentiometric titrations of modified and refined humic acid to compare results with Huma-K.
- Perform FTIR studies on modified and refined humic acid.
- Analyze samples collected from the kinetic experiments using KPA.
- Continue with the sorption experiments of uranium on sediments with and without Huma-K coating.
- Complete rhenium tracer test and initiate the control column experiment to study the sorption of uranium onto sediment with specific pH to be able to compare the data with previous column data to study the effect of Huma-K.
- Start experiments with modified humic acid obtained from SRNL.
- Prepare a student poster to be presented at WM-17.

Task 3: Surface Water Modeling of Tims Branch

Subtask.3.1. Modeling of surface water and sediment transport in the Tims Branch ecosystem

- Although the preliminary MIKE 11 model for the A-014 branch was successfully created, it is important to note that the A-014 stream contains a culvert and a weir that were not included in the model. Future plans include the incorporation of these engineered structures into the model before the calibration process.

- FIU will begin refinement of the existing model grid in MIKE SHE to a smaller grid element size in order to capture more detail of the surface topography and man-made structures such as roads and the features described above (culvert and weir). Optimum grid element size will be established by performing simulations with various element sizes while observing the model runtime. Simulations will also be performed to understand the calibration parameters and the relative effect of the hydrological modules on the simulation results, and then make adjustments to the input parameters as necessary.

- Future work over the next three months includes:
    - Calibration of the MIKE 11 model of the A-014 outfall tributary. Calibration consists of changing the values of input parameters in an attempt to match field conditions within acceptable criteria.
    - Calibration of the MIKE SHE model. FIU will continue to modify the MIKE SHE model by performing simulations under different conditions and various parameters to understand the calibration factors and the relative effect of the hydrological modules on the simulation results and then making adjustments to the input parameters as necessary.
    - FIU will also begin the development of a MIKE 11 model of the main Tims Branch stream following the same methodology described above to add it to the current A-014 stream network. This will begin with delineation of the main Tims Branch stream network using ArcHydro.

Subtask 3.2. Application of GIS technologies for hydrological modeling support

- The use of GIS tools remains a continuous integrated component of the hydrological model development. Over the next few months, a review of the existing GIS and time series data derived from the various federal agencies will be conducted to determine if any updates are necessary. The aim is to always use the most current data available to ensure greater model accuracy. Any changes required will be updated in the SRS geodatabase and subsequently in the MIKE SHE and MIKE 11 models being generated.

Subtask 3.3. Biota, biofilm, water and sediment sampling in Tims Branch

- In order to conduct an accurate model calibration, additional in situ field data (e.g., water level stage and discharge timeseries) will be necessary. Proposed plans for follow-up sampling and data collection at SRS, as outlined in the Project Technical Plan submitted to DOE, still requires further discussion. The timing and scope will be based on budget availability of both FIU and SRNL personnel. Incorporation of the sampling and analysis as part of a student summer 2017 internship is also being considered.

Task 5: Remediation Research and Technical Support for WIPP

- Continue collaboration with LANL on parallel experiments including mini-columns and batch experiments with Nd(III) for 0.01 – 5 M NaCl.
- Begin model development for mini-column experiments in PHREEQC.
- Investigate and apply kinetic models to fit batch sorption data.

Project 3
Waste and D&D Engineering & Technology Development

Project Manager: Dr. Leonel E. Lagos

Project Description

This project focuses on delivering solutions under the decontamination and decommissioning (D&D) and waste areas in support of DOE EM. This work is also relevant to D&D activities being carried out at other DOE sites such as Oak Ridge, Savannah River, Hanford, Idaho and Portsmouth. The following tasks are included in FIU Performance Year 7:

Task No	Task
Task 1: Waste Information Management System (WIMS)	
Subtask 1.1	Maintain WIMS – database management, application maintenance, and performance tuning
Subtask 1. 2	Incorporate new data files with existing sites into WIMS
Task 2: D&D Support to DOE EM for Technology Innovation, Development, Evaluation and Deployment	
Subtask 2.1	D&D Technology Demonstration & Development and Technical Support to SRS's 235-F Facility Decommissioning
Subtask 2.2	Technology Demonstration and Evaluation
Subtask 2.3	Support to DOE EM-4.11 and the D&D Community
Task 3: D&D Knowledge Management Information Tool	
Subtask 3.1	Web and Mobile Application for D&D Decision Model
Subtask 3.2	Mobile Applications/Platforms for DOE Sites
Subtask 3.3	Development & Integration of International KM-IT Pilot for UK Collaboration
Subtask 3.4	Outreach and Training (D&D Community Support)
Subtask 3.5	Data Mining and Content Management
Subtask 3.6	D&D KM-IT Administration and Support

Task 1: Waste Information Management System (WIMS)

<u>Task 1 Overview</u>

This task provides direct support to DOE EM for the management, development, and maintenance of a Waste Information Management System (WIMS). WIMS was developed to receive and organize the DOE waste forecast data from across the DOE complex and to automatically generate waste forecast data tables, disposition maps, GIS maps, transportation details, and other custom reports. WIMS is successfully deployed and can be accessed from the web address http://www.emwims.org. The waste forecast information is updated at least annually. WIMS has been designed to be extremely flexible for future additions and is being enhanced on a regular basis.

Task 1 Quarterly Progress

The Waste Information Management System (WIMS) was developed to receive and organize the DOE waste forecast data from across the DOE complex and to automatically generate waste forecast data tables, disposition maps, GIS maps, transportation details, and other custom reports. WIMS is successfully deployed and can be accessed from the web address http://www.emwims.org. During this reporting period, FIU performed database management, application maintenance, and performance tuning to the online WIMS in order to ensure a consistent high level of database and website performance.

FIU developed and submitted a paper on WIMS to the Waste Management 2017 Symposia. The abstract was accepted for an oral presentation at the conference:

> **Abstract**: 17246 Waste Information Management System with 2016-17 Waste Streams
> **Session**: Decisionmaking Tools and Frameworks that Enhance Communication for ER Cleanup Programs
> **Date/Time**: Tuesday March 07, 2017, 3:20 PM - 5:00 PM

Task 2: D&D Support to DOE EM for Technology Innovation, Development, Evaluation and Deployment

Task 2 Overview

This task provides direct support to DOE EM for D&D technology innovation, development, evaluation and deployment. For FIU Performance Year 7, FIU will assist DOE EM-4.11 in meeting the D&D needs and technical challenges around the DOE complex. FIU will expand the research in technology demonstration and evaluation by developing a phased approach for the demonstration, evaluation, and deployment of D&D technologies. One area of focus will be working with the Savannah River Site to identify and demonstrate innovative technologies in support of the SRS 235-F project. FIU will further support the EM's International Program and the EM-4.11 D&D program by participating in D&D workshops, conferences, and serving as subject matter experts.

Task 2 Quarterly Progress

Task 2.1.1: Adaptation of Intumescent Coatings
This research task will be presented to the Waste Management 2017 Symposia by SRNL in collaboration with FIU:

> **Abstract**: 17107 Environmental and Radiological Response of Fixatives and Intumescent Coatings for D&D Applications
> **Session**: D&D of US DOE Facilities
> **Date/Time**: Tuesday March 07, 2017, 1:30 PM - 3:15 PM

The objective of this research task is to improve the operational performance of fixatives to mitigate the release of radioisotopes during fire and/or extreme heat conditions. FIU is currently performing a series of tests to subject test coupons of intumescent coatings (IC) to increasing temperatures using a muffle furnace along with adhesion and impact testing of these test coupons on various types of substrates, both before and after exposure to extreme heat conditions.

FIU continued to perform bench-scale experiments on the two intumescent coatings being considered as standalone fixatives. Testing first focused on stainless steel coupons that were prepared and cured under adverse environmental conditions (temperatures greater than 90 degrees F and humidity ranging from 60-90%). FIU performed adhesion testing using the ASTM D3359 (Standard Test Methods for Measuring Adhesion by Tape Test) standard protocol in order to quantify the ability of two selected intumescent coatings (FX and FD) to adhere to stainless steel substrates under various conditions. These tests will serve as the basis for future testing efforts designed to determine the impacts of fixatives / intumescent coatings on the airborne release fraction (ARF) and respirable fraction (RF) coefficients in the source term formula used to calculate a facility's safety basis.

The stainless steel substrates were placed outdoors in ARC's hot cell mock up for 1-week to acclimatize them to the environmental conditions. Temperatures during this period averaged approximately 94 F and 78% humidity. The FX and FD intumescent coatings were then applied to the stainless steel coupons in the hot cell, to the manufacturer's thickness specifications, under the same environmental conditions (no primer was applied) and allowed to cure. The coupons remained outdoors under these conditions for a period of two months, at which time they were collected from the hot cell mock up and ASTM D3359 adhesion tests were conducted.

As noted in the photographs below, FX exhibited no noticeable degradation in terms of adhesion to the stainless steel substrate (0% removal from the substrate during the adhesion stress test). These results mirror those encountered when testing was executed under ideal, laboratory conditions. However, some discoloration was noted, and special attention will be paid to determine if any operational impact on fire resistance has occurred when the coupons are subjected to high heat in the muffle furnace. FD intumescent coating did not perform as well, with the adhesion stress tests resulting in an approximate 55% removal of the coating from the substrate (see 2nd series of 3 photos). This result is almost identical to the results received under ideal, laboratory conditions. No discoloration was noted.

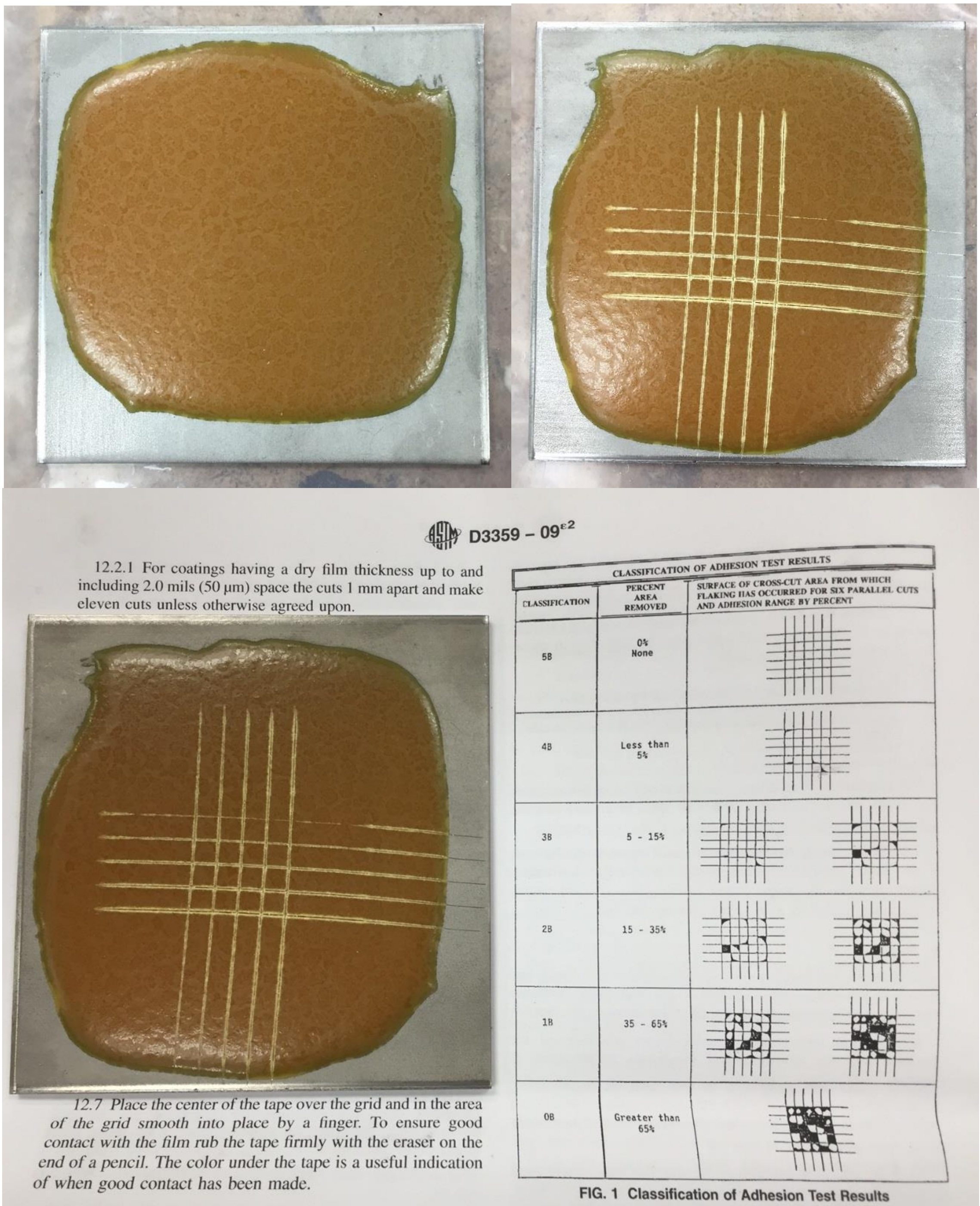

Figure 3-1. FX intumescent coating test coupon (top left), cross-cuts into IC (top right), classifying the adhesion test results per ASTM D3359 (bottom).

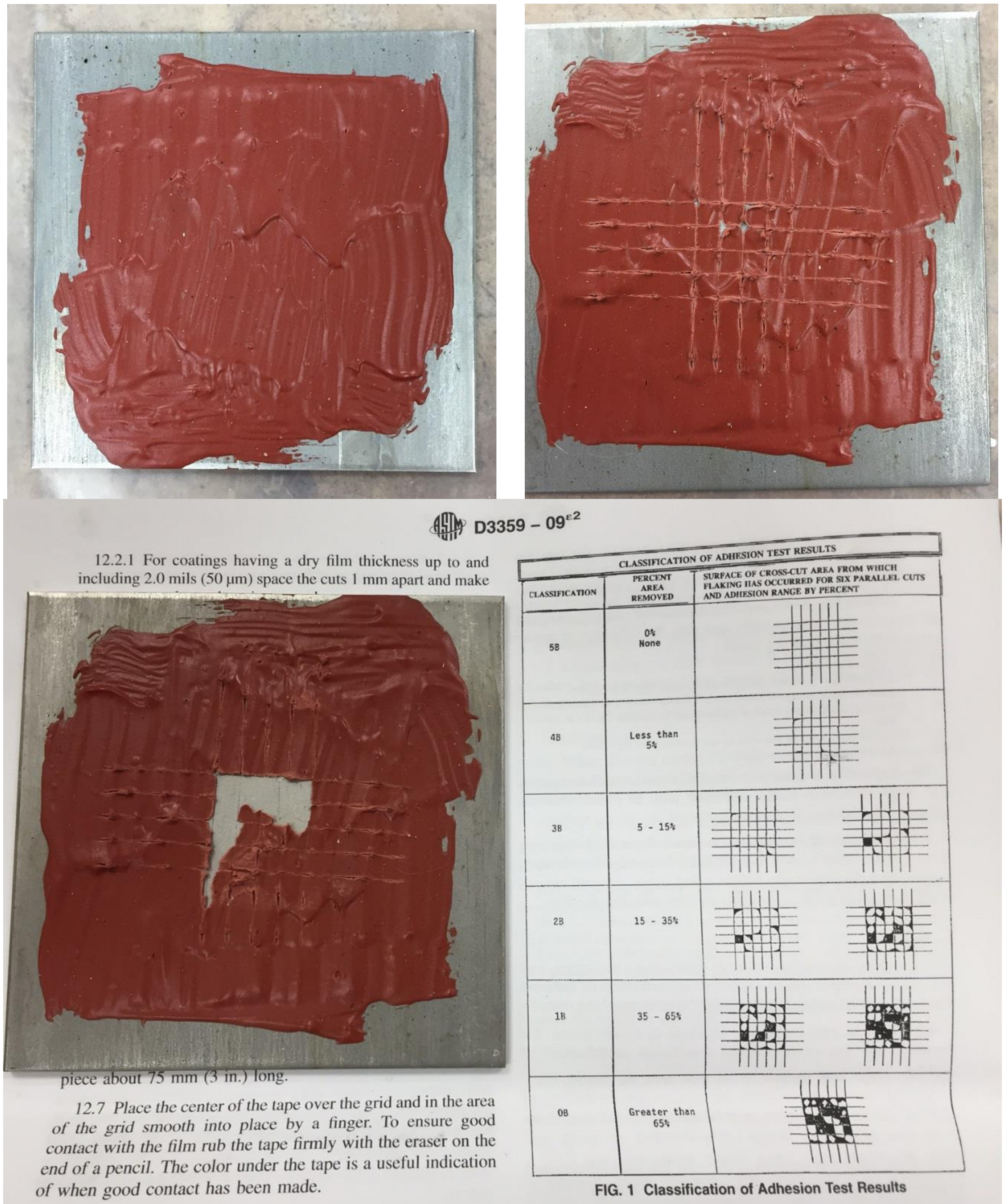

Figure 3-2. FD intumescent coating test coupon (top left), cross-cuts into IC (top right), classifying the adhesion test results per ASTM D3359 (bottom).

Subtask 2.1.2: Application of Intumescent Coatings to other DOE EM Problem Sets

This is a new subtask for FIU Performance Year 7. Discussions with DOE site and DOE EM HQ personnel have highlighted the potential of intumescent coatings to have much broader applications at other sites. FIU will be engaging other DOE sites to share the results of the intumescent coatings research and its applications at SRS 235-F and to identify specific applications of intumescent coating technology to satisfy other problem sets and challenge areas related to fire / extreme heat conditions.

Subtask 2.1.3: Robotic Technologies for D&D Applications

As part of this subtask during FIU Performance Year 6, FIU performed research to identify robotic technology systems applicable to the challenges and needs of the SRS 235-F Facility. Research utilized the Robotic Database in D&D KM-IT to search and identify potential robotic technologies and compiled a spreadsheet of all of the available robotic technologies in the database.

During FIU Performance Year 7, FIU will leverage the research already completed to begin identifying cross-cutting applications of robotic technologies being developed at FIU in the high-level waste research area that could potentially be used in support of D&D activities. On December 1, FIU conducted a teleconference with Mike Serrato and Connor Nicholson at SRNL to begin identifying the potential requirements for robotic applications in support of D&D activities at SRS 235-F. FIU briefly presented the robotic technologies currently being developed under the high level waste activities (Project 1) and opened the discussion to ways in which one or more of these technologies could be used in support of D&D activities at the site.

Task 2.2: Technology Demonstration and Evaluation

The primary objective of this task is to standardize and implement proven processes to refine and better synchronize DOE-EM technology needs, requirements, testing, evaluation, and acquisition by implementing a three-phased technology test and evaluation model.

Subtask 2.2.1: Uniform Testing Protocols and Performance Metrics for D&D

The development of uniformly accepted testing protocols and performance metrics is an essential component for testing and evaluating D&D technologies. During FIU Performance Year 6, an FIU representative obtained official membership on ASTM International's E10 Committee on Nuclear Technologies and Applications and was selected to lead the ASTM International E10.03 Subcommittee. In this position, FIU oversaw the development of two new draft standard specifications for removable/strippable coatings and permanent coatings/fixatives.

FIU performed detailed planning for the ASTM International E10.03 Subcommittee meeting on standards development for D&D technologies, scheduled for January 29-31, 2017 in Norfolk, VA. The focus of this meeting will be on modifying the two draft specifications for strippable coatings and permanent fixatives based on feedback received from stakeholders. The Committee will address specific comments related to incorporating ARF and RF characteristics into the performance metrics of the standard specifications, with a desired end state of staffing for formal review and vote by the E10 Committee. A detailed agenda is being developed to support the meeting. Additionally, as requested, ARC is moving forward with drafting a DOE newsletter article on this initiative and will submit to DOE EM for review in January.

Subtask 2.2.2: Technology Demonstration under Nonradioactive Conditions at FIU

Leveraging the research being performed on intumescent coatings as part of subtask 2.1.1 and including close coordination with DOE EM, SRNL, and SRS, FIU will conduct a cold demonstration / test and evaluation of applying intumescent coatings in a full-scale SRS 235-F hot cell mock-up at the FIU Hot Cell Test Bed during FIU Performance Year 7.

FIU revised four (4) separate design options for consideration for the planned test and evaluation ARC based on discussions with SRS 235-F site personnel. These options included: 1) a single corner cell; 2) a single middle cell; 3) a consolidated corner and middle cell design; and 4) all 3 designs with the incorporation of a 3' raised floor. These design options were briefed to SRNL representatives and a final design was selected.

The design phase for the full-scale SRS 235-F hot cell mock-up testbed was completed, reviewed, and approved by the project task stakeholders (SRS 235-F site personnel, SRNL, and ARC). The decision was made to pursue a combination middle and corner cell design (figures below) using the actual hot cell dimensions from the site's schematics. A raised floor will also be incorporated to best mirror the operational conditions experienced at the site. Detailed blue prints were developed for approval by the ARC Senior Engineer.

Based on the stakeholder approval received on October 28 as well as a follow-on site visit and phone conversation on November 15 with SRS 235-F site personnel and SRNL research scientists, the SRS 235-F Hot Cell Test Bed design was reaffirmed and construction began in December 2016. The construction of the test bed is being conducted at FIU ARC's outdoor test facility. As of the end of December, the 3' raised floors for both the middle and corner cells were completed and framing of the walls was commenced (figures below). Pending funding and available resources, construction is expected to be completed no later than the end of April 2017.

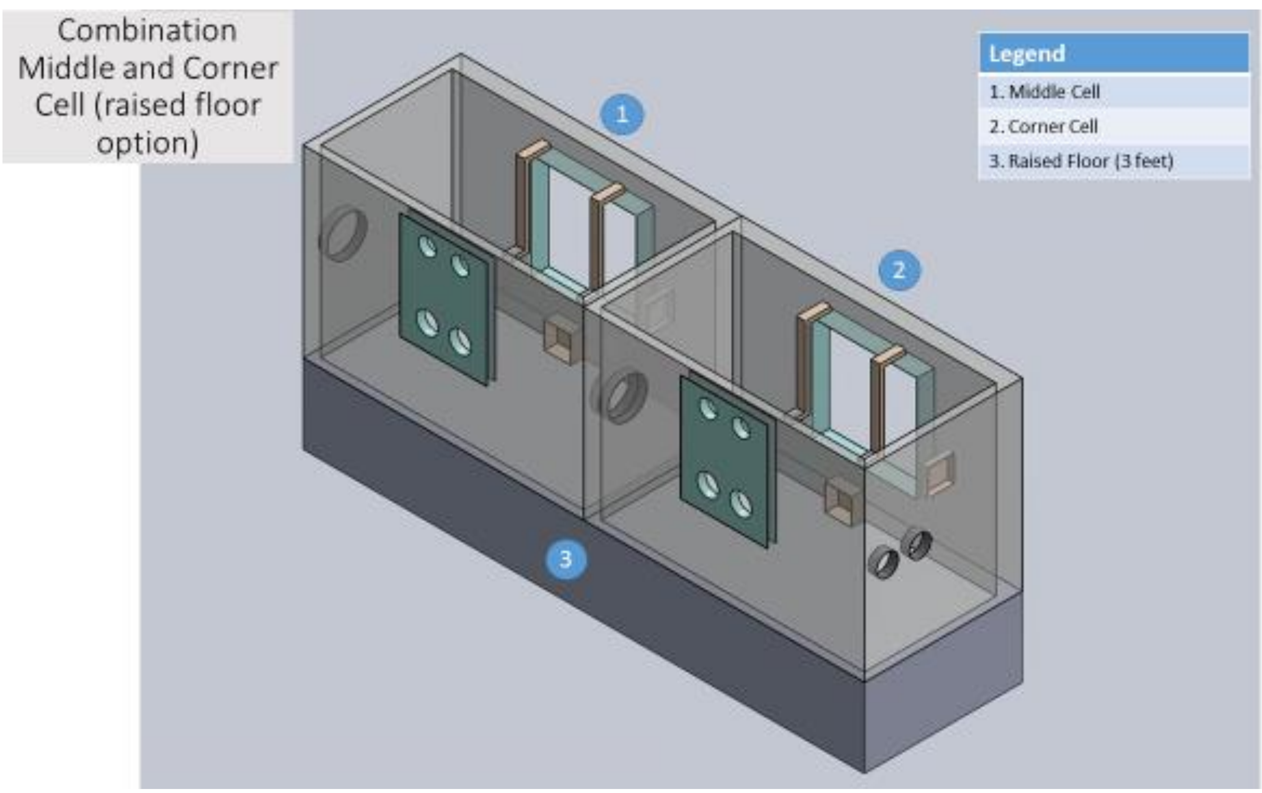

Figure 3-3. Selected design for the hot cell mock-up testbed showing the combination of a middle and corner hot cell.

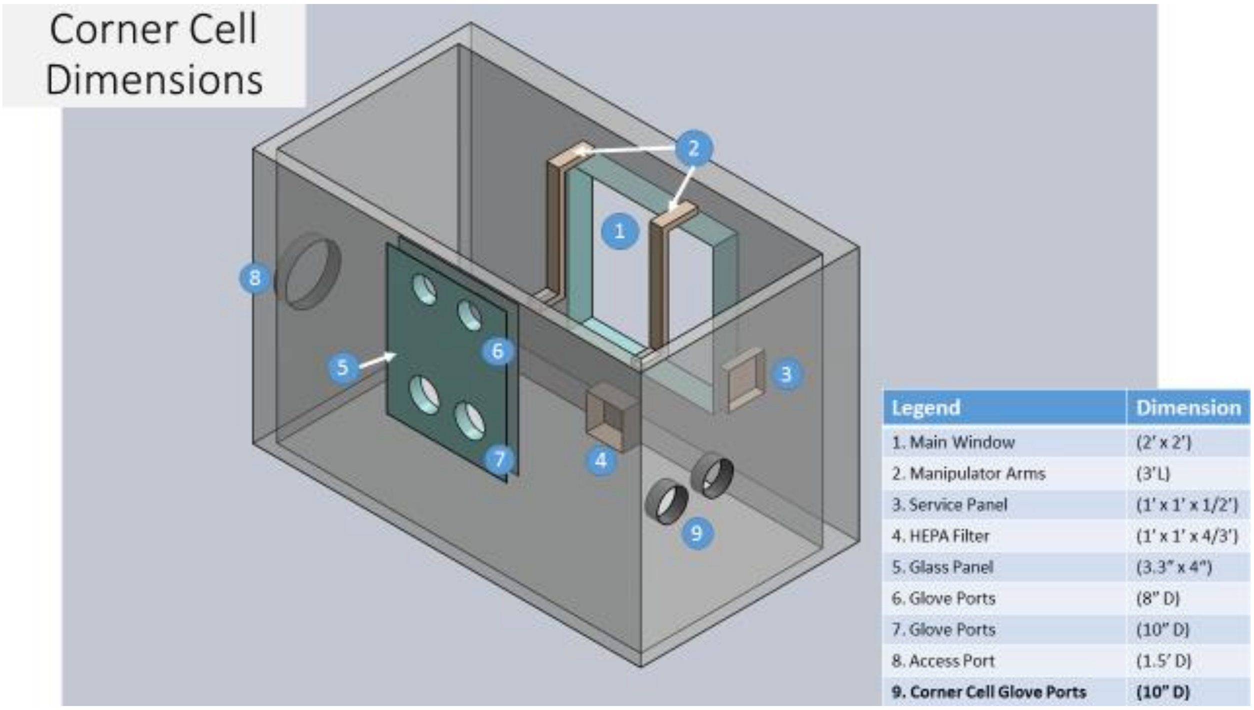

Figure 3-4. Schematic illustrating the dimensions for the corner hot cell mock-up.

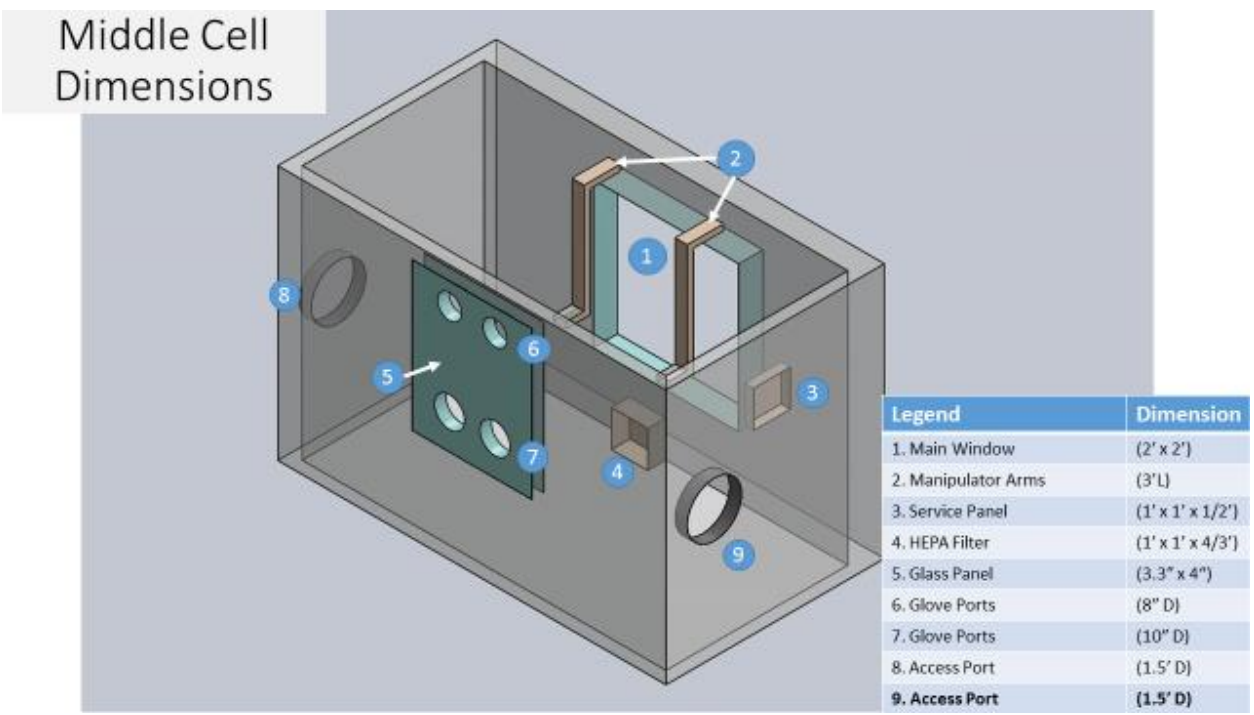

Figure 3-5. Schematic illustrating the dimensions for the middle hot cell mock-up.

In addition, FIU completed the draft test plan to support the objective of this subtask: to advance the testing, evaluation, and possible deployment of intumescent coating (IC) technologies as fire resilient fixatives to mitigate the potential release of radioisotopes during postulated fire scenarios highlighted in the Basis for Interim Operations (BIO) and contingency planning documents in support of D&D activities at SRS 235-F, with a particular emphasis on the 235-F PuFF Facility Cells 6-9. This test plan addresses Phase II of the overall research effort, with the first main objective centered on constructing a to-scale SRS 235-F Hot Cell Test Bed on site at ARC that mirrors the operating environment encountered in an adjoining corner and middle hot cell configuration at the SRS 235-F facility. The second main objective involves an evaluation on the mechanics and processes associated with applying the selected intumescent coatings in the hot cell configurations using: 1) the approved tools as identified in the 235-F Risk Reduction Tooling List, Rev 0, dated 26 January 2015; and 2) alternative application methods, such as airless sprayers, recommended by the IC manufacturer. Based on discussions with site personnel, if the alternative application methods prove optimal, then it is possible to have them added to the next revision of the 235-F Risk Reduction Tooling List. Development of the draft test plan is on schedule and will be forwarded to SRNL and SRS 235-F stakeholders for review and comment no later than January 6, 2017.

Figure 3-6. Construction begins on selected hot cell mockup design - DOE Fellows constructing raised floor.

Figure 3-7. Raised floor height of 3 ft (left) and hot cell height of 7 ft (right).

Figure 3-8. Hot cell width of 5 ft (left) and middle cell lower glove port (right).

Subtask 2.2.3 Support to SRNL and SRS 235-F for Onsite Demonstration

This is a new subtask for FIU Performance Year 7 under which FIU will coordinate with SRNL and SRS 235-F to support a possible onsite intumescent coating demonstration on a contaminated apparatus (i.e., hot demonstration). The objective of this subtask is to select and validate operational performance of fire resilient fixative coating material(s) for residual surface contamination after gross decontamination is completed.

Task 3: D&D Knowledge Management Information Tool (KM-IT)

Task 3 Overview

The D&D Knowledge Management Information Tool (KM-IT) is a web-based system developed to maintain and preserve the D&D knowledge base. The system was developed by Florida International University's Applied Research Center (FIU-ARC) with the support of the D&D community, including DOE-EM (EM-4.11 & EM-5.12), the former ALARA centers at Hanford and Savannah River, and with the active collaboration and support of the DOE's Energy Facility Contractors Group (EFCOG). The D&D KM-IT is a D&D community driven system tailored to serve the technical issues faced by the D&D workforce across the DOE Complex. D&D KM-IT can be accessed from web address http://www.dndkm.org.

Task 3 Quarterly Progress

FIU developed and submitted a paper to the Waste Management 2017 Symposia. The abstract was accepted for an oral presentation at the conference:

> **Abstract**: 17249 Application of Robotics Technology to D&D
> **Session**: Robotics and Remote Systems – Nuclear Environments: International Applied D&D Operations Cleanup Programs
> **Date/Time**: Thursday March 09, 2017, 1:30 PM - 5:00 PM

FIU held regular bi-weekly teleconferences with DOE on the status and progress of the activities on this task.

A strategic plan document for D&D KM-IT titled, *D&D Knowledge Management Information Tool – A Strategic Approach for the Long-Term Sustainability of Knowledge*, offers a strategic vision for the long-term sustainability of knowledge through the D&D KM-IT by applying the system's assets together with good web practices; thereby, promoting and enhancing the collaborative sharing of knowledge and work experiences across the D&D community. FIU developed a quarterly update document for this document and submitted it to DOE on October 5, 2016. The strategic plan for D&D KM-IT is a living document and the projected schedule and status evolve over time as the recommended strategic approaches are implemented. The update document, developed on a quarterly basis, provides an update to the table of recommended actions contained in the original document.

FIU has engaged in several discussions with DOE related to social media integration on D&D KM-IT for the purpose of outreach and marketing. Social media has been identified as a platform that should be targeted to increase visibility of D&D KM-IT among the community and other EM related areas. FIU-ARC is approaching this integration using DOE's *social media policy and best practices* as a guideline for the following two tasks: 1) Provide social integration on KM-IT to allow Like/Share/Pin to Facebook, Twitter, LinkedIn, and Pinterest; and 2) Create pilot to utilize YouTube as platform for D&D KM-IT Videos. During October, FIU created a sample to demonstrate how the videos hosted on YouTube and embedded into KM-IT will be displayed on D&D KM-IT. FIU uploaded a couple of videos to the FIU-ARC channel on YouTube and embedded these videos in the sample page. The link to the sample page was sent to DOE on October 27 for review and discussion purposes.

FIU also began making revisions to the infographic on Knowledge Management based on comments received from DOE. FIU also discussed potential topics for the next infographic with DOE. Ideas included: 1) the standards development work being conducted under Task 2 of this project as they apply to national labs, sites, and industries; and 2) mobile technologies as they apply to environmental remediation issues.

FIU completed the development of a Google Web Analytic report for D&D KM-IT for the second quarter of 2016 (April to June) and submitted it to DOE on October 25, 2016. This report included information from Google Analytics (GA) and Google Web Master Tools (GWT) and a narrative to explain the results. The figure below shows an infographic of the web analytics for the second quarter of 2016. Some of the highlights of this report include:

- Better than expected results were seen for the second quarter. Typically, there is a significant dip in the web analytics after the first quarter. However, an increase in some of the metrics was reflected in the analytics.
- There were a total of 5,346 combined session (GA + GWT) by 2,489 users (GA), generating 9,674 page views (GA).
- Looking at the GA figures alone, there were double digit increases in the number of sessions (15.77%), users (15.50%) and page views (10.71%). The only decreases from previous second quarters were relatively small. These included pages/session (4.37%), average session duration (0.64%) and bounce rate (5.17%).
- Google Chrome is used by about half of the users who visit the site.
- Canada is back in the top 5 countries that visit D&D KM-IT after falling from the top 5 last quarter.
- The top document on the site continues to be the "NITON XL-800 Series Multi-Element Spectrum Analyzer (Alloy Analyzer)" from the Innovative Technology Summary Reports (ITSRs) category.
- "Mobile Systems" continues to be the top query impression for D&D KM-IT.
- The top 3 visited modules included Technology, Vendors and Fixatives (a new module added to D&D KM-IT during the first quarter) with traffic to the Technology module increasing by 9.14%.
- Referral traffic doubled this period from 5.9% to 10.4% of all traffic to the site.
- Wikipedia is one of the top domains linking a referring visitor to D&D KM-IT this period.
- A closer look at Wikipedia traffic reveals research activity. Traffic from Wikipedia quadrupled, increasing the pages per session and the average time per page.

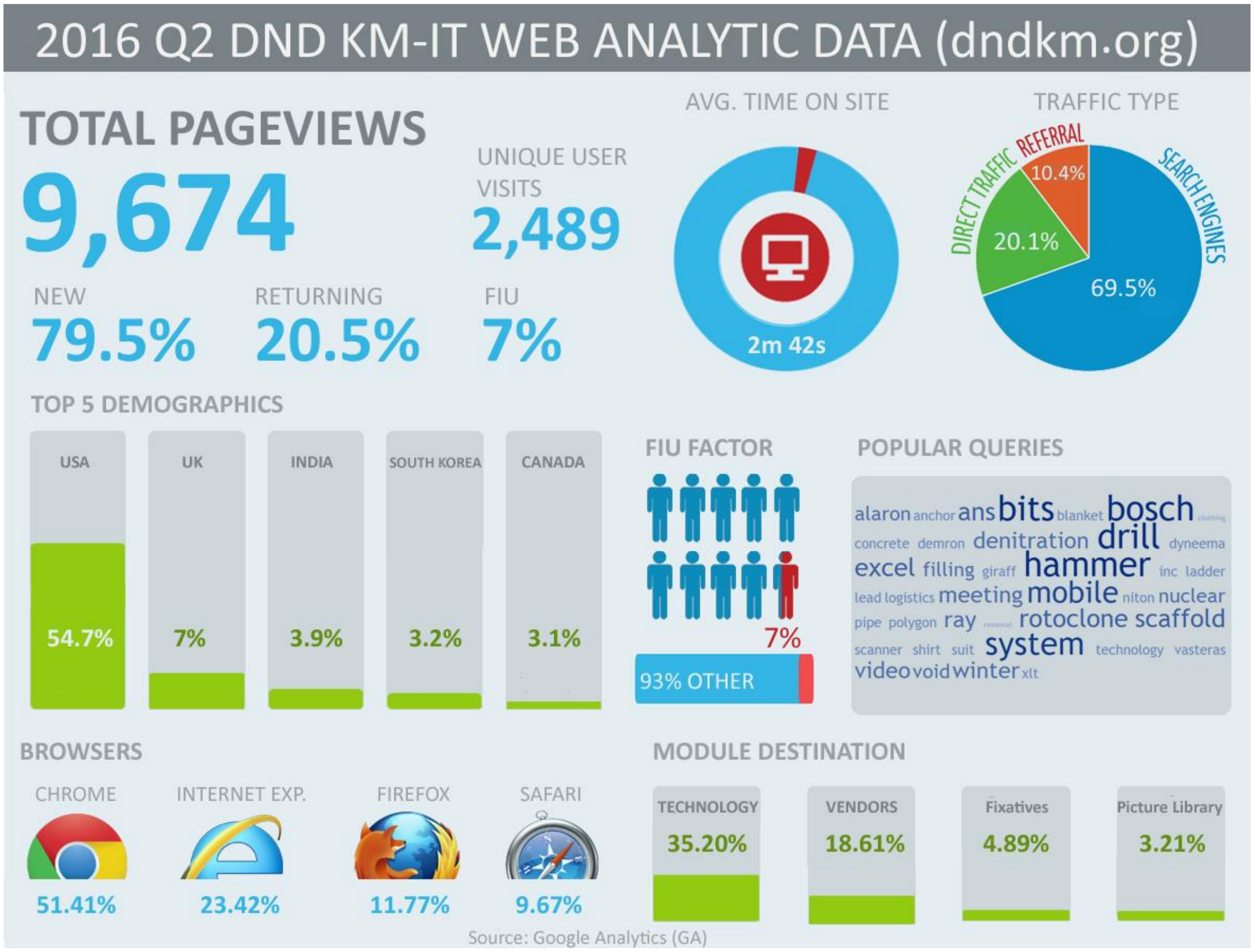

Figure 3-9. Web analytic infographic for 2nd quarter of 2016.

FIU also completed the development of a Google Web Analytic report for D&D KM-IT for the third quarter of 2016 (July to September) and sent it to DOE on December 29. This report includes information from Google Analytics (GA) and Google Web Master Tools (GWT) and a narrative to explain the results. Highlights from this report include:

- The major metrics (including pageviews and average session duration) were down from the previous quarter but up from the same quarter of the previous year.
- There were a total of 5,351 combined sessions (from GA and GWT) by 2,221 Users (GA) that generated 6,719 pageviews (GA).
- Despite the drop from last quarter in major metrics as mentioned in the first bullet, the combined sessions were similar to the previous quarter; in fact, there were 5 more combined sessions (5,351 vs. 5,346).
- There is an improvement of 14.6% in combined visits when compared to the same period last year.
- A total of 53.33% of users use Google Chrome to access the site, a gain of another 2%.
- The top document on the site continues to be the "NITON XL-800 Series Multi-Element Spectrum Analyzer (Alloy Analyzer)" from the Innovative Technology Summary Reports (ITSRs) category.

- ITSRs managed to keep 5 of its document in the top 10 documents accessed. Last quarter was the first time ITSRs dropped after averaging 8 since being added to the D&D KM-IT.
- There was only one new document in the top 10 list, titled Copper Cable Recycling Technology.
- "Mobile Systems" continues to be the top query impression for D&D KM-IT.
- The top 3 visited modules included Technology, Vendors and Document Library.
- There was a significant increase in traffic from New Mexico which started at the end of last period and continued during this period. Isolating the network traffic revealed that users from Waste Control Specialists increased their visits to the site after the newsletter was sent out on August 15, 2016.

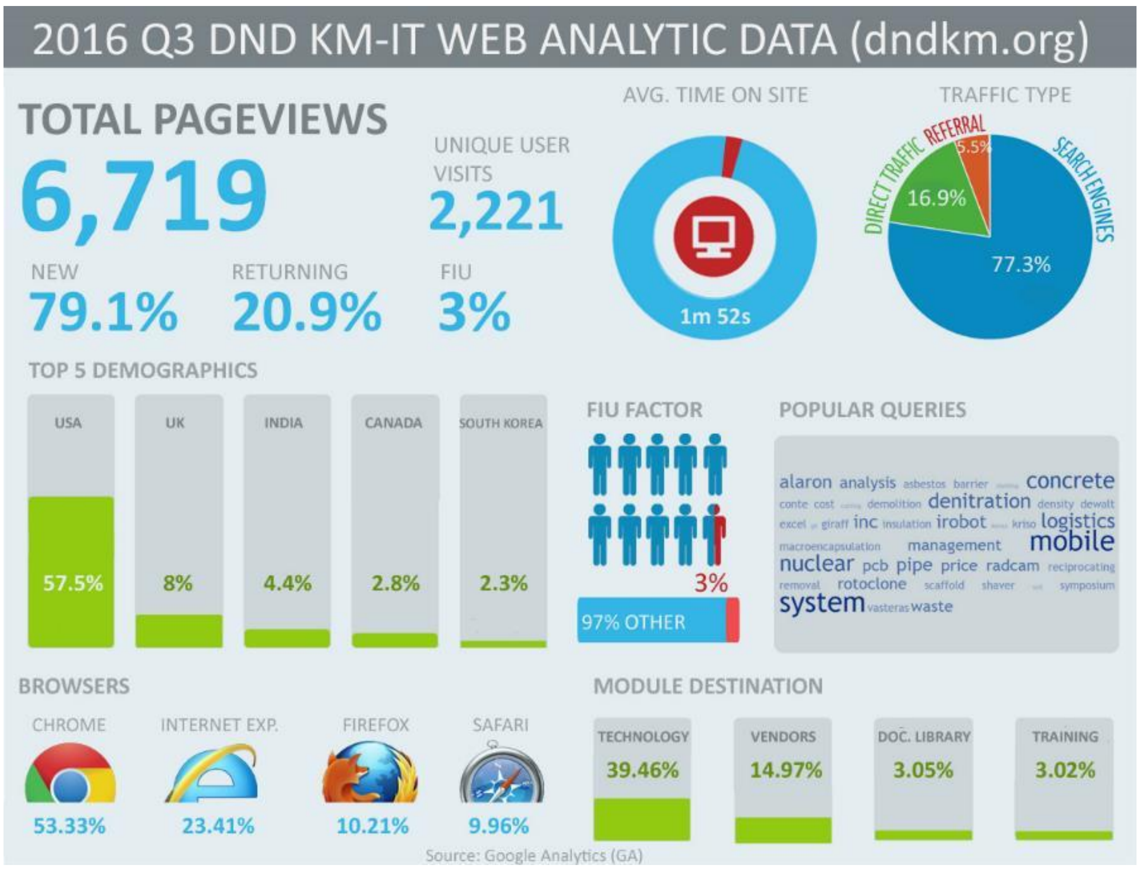

Figure 3-10. Infographic for 2016 Q3 Based on Web Analytic Data

FIU continued revisions to the infographic on Knowledge Management based on comments received from DOE. FIU also discussed potential topics for the next infographic with DOE. Ideas included: 1) the standards development work being conducted under Task 2 of this project as they apply to national labs, sites, and industries; and 2) mobile technologies as they apply to environmental remediation issues.

DOE Fellows are supporting D&D KM-IT by reviewing the information in the vendor and technology modules and researching new vendors and technologies for adding to the system. As of December 28, the system included a total of 1310 technologies and 948 vendors. In addition, there were 935 registered users and 102 subject matter specialists. The top ten areas of expertise for the registered subject matter specialists is shown in Table 3-1. Figure 3-11 shows a couple of the technologies recently added to the system.

Table 3-1. Top Ten Areas of Expertise for Registered Subject Matter Specialists in D&D KM-IT

Expertise Area	SMS Registered
Decontamination	47
Characterization	42
Dismantlement	39
Demolition	35
Deactivation Planning	31
Radiation Controls	30
Large Scale Decon & Demolition	27
ALARA Controls	24
Computer Modeling	24
Sampling	24

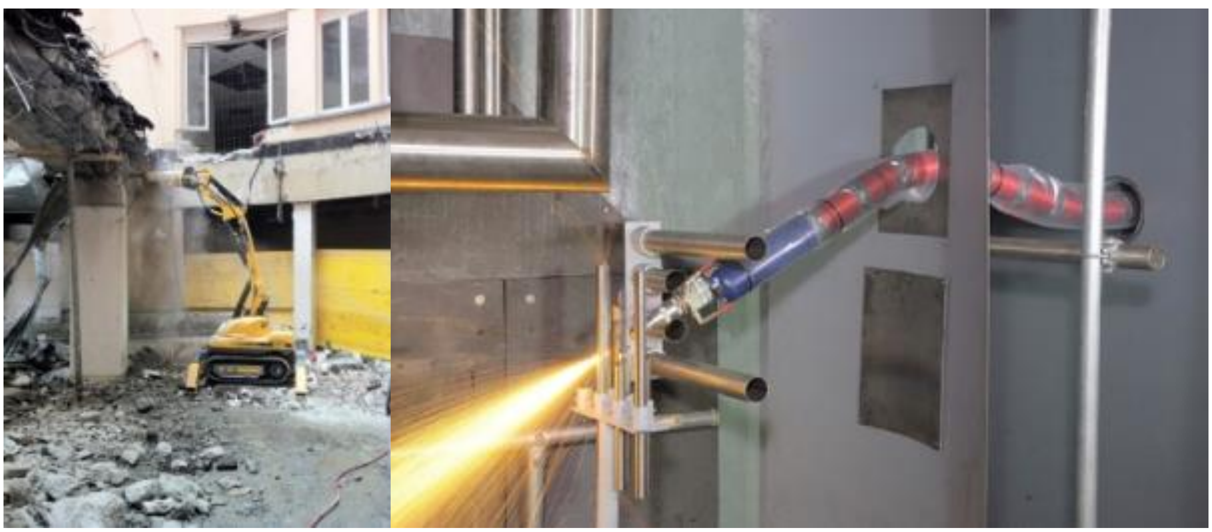

Figure 3-11. Brokk 100 remote controlled demolition robot (left) and OC Robotics LaserSnake remote controlled laser cutter (right).

Milestones and Deliverables

The milestones and deliverables for Project 3 for FIU Performance Year 7 are shown on the following table. Milestones 2016-P3-M1.2 and 2016-P3-M3.1, completion of draft papers on WIMS and D&D KM-IT for submission to the Waste Management Symposium, was completed in November.

FIU Performance Year 7 Milestones and Deliverables for Project 3

Task	Milestone/ Deliverable	Description	Due Date	Status	OSTI
Task 1: WIMS	2016-P3-M1.1	Import 2017 data set for waste forecast and transportation data	Within 60 days after receipt of data from DOE	On Target	
	2016-P3-M1.2	Waste Management Symposium 2017 Draft Paper	11/04/16	Complete	
Task 2: D&D	Deliverable	Draft Test Plan for IC Demo / Test & Evaluation at FIU (subtask 2.2.2)	1/6/17	On Target	OSTI
	2016-P3-M2.1	Participate in ASTM E10 Committee Meeting to coordinate effort to develop standardized testing protocols and performance metrics for D&D technologies (subtask 2.2.1)	2/28/17	On Target	
	2016-P3-M2.2	Complete demonstration / test and evaluation of IC on FIU hot cell test bed (subtask 2.2.2)	4/28/17	On Target	
	Deliverable	Decision brief to DOE EM on recommended D&D technologies to test for FIU Performance Year 8 using the 3-phased model	4/28/17**	On Target	
	Deliverable	Draft summary report of robotic technologies for D&D (subtask 2.1.3)	5/31/17	On Target	OSTI
	Deliverable	Draft progress report on the adaptation of IC to enhance fire resiliency (subtask 2.1.1)	6/30/17	On Target	OSTI
	2016-P3-M2.3	Participate in ASTM International's Executive Steering Committee Meeting to coordinate effort to develop standardized testing protocols and performance metrics for D&D technologies (subtask 2.2.1)	7/31/17	On Target	
	Deliverable	Draft progress report on the identification of IC applications to other DOE EM problem sets (subtask 2.1.2)	7/31/17	On Target	OSTI
	Deliverable	Draft technical reports for demonstrated technologies	30-days after evaluation/ demo	On Target	OSTI
	Deliverable	Draft Tech Fact Sheet for technology evaluations/ demonstrations	30-days after evaluation/ demo	On Target	
Task 3: D&D KM-IT	2016-P3-M3.1	Waste Management Symposium Draft Paper	11/4/16	Complete	
	Deliverable	D&D KM-IT Workshop to DOE EM staff at HQ	2/28/17**	On Target	
	Deliverable	Preliminary Metrics Progress Report on Outreach and Training Activities	3/10/17	On Target	
	Deliverable	Unclassified summary report on the status and findings of the KM-IT audits	3/24/17	On Target	
	2016-P3-M3.2	Four Wikipedia integration edits/articles	3/31/17	On Target	
	Deliverable	First D&D KM-IT Workshop to D&D community /DOE Site	3/31/17	On Target	
	Deliverable	First infographic to DOE for review	3/31/17	On Target	
	2016-P3-M3.3	Deployment of pilot video onto YouTube platform	4/28/17	On Target	

	2016-P3-M3.4	Deployment of pilot native mobile application for D&D Fixatives Module	5/31/17	On Target	
	Deliverable	Second infographic to DOE for review	7/31/17	On Target	
	Deliverable	Metrics Progress Report on Outreach and Training Activities	8/18/17	On Target	
	Deliverable	Unclassified summary report on the status and findings of the KM-IT audits	8/25/17	On Target	
	Deliverable	Second D&D KM-IT Workshop to D&D community / DOE Site	8/25/17	On Target	
	Deliverable	D&D KM-IT Web Analysis Report	Quarterly	On Target	
	Deliverable	Draft Tech Fact Sheet for new modules or capabilities of D&D KM-IT	30-days after deployment of new module or capability	On Target	

***Completion of this deliverable depends on scheduling and availability of DOE EM staff*

Work Plan for Next Quarter

Task 1: Waste Information Management System

- Perform database management, application maintenance, and performance tuning to WIMS.
- Submit final technical paper on WIMS and present at WM17.
- Receive 2017 data set for waste forecast and transportation data from DOE and begin integration into WIMS.

Task 2: D&D Support

- Continue testing for evaluating intumescent coatings.
- Complete construction of the SRS 235-F hot cell mock-up and submit the draft test plan for the cold demonstration / test & evaluation of intumescent coatings at FIU to SRNL collaborators for review. Continue purchasing of equipment and materials needed to complete construction and execute the test plan.
- Continue leading the working group in for ASTM International's E10 Committee on Nuclear Technologies and Applications and Subcommittee E10.03 - Radiological Protection for Decontamination and Decommissioning of Nuclear Facilities and Components to support the initiative of developing and promulgating uniform testing protocols and performance metrics for D&D technologies across the stakeholder community. Participate in the January 2017 conference in Norfolk, VA.

Task 3: D&D Knowledge Management Information Tool

- Submit final technical paper on D&D KM-IT and present at Waste Management 2017 Symposia.
- Develop quarterly website analytics report and submit to DOE for review.
- Develop website analytics report for calendar year 2016 and submit to DOE for review.

- Develop preliminary metrics progress report on outreach and training activities and submit to DOE for review.
- Perform outreach and training, community support, data mining and content management, and administration and support for the D&D KM-IT system, database, and network.
- Complete first D&D KM-IT Workshop to DOE EM staff at HQ, based on scheduling and availability of DOE EM staff.
- Complete four new Wikipedia integration edits/articles in support of D&D topics.
- Develop a new infographic and submit to DOE for review.
- Perform outreach and training, community support, data mining and content management, and administration and support for the D&D KM-IT system, database, and network.

Project 4
DOE-FIU Science & Technology Workforce Development Initiative

Project Manager: Dr. Leonel E. Lagos

Project Description

The DOE-FIU Science and Technology Workforce Development Initiative has been designed to build upon the existing DOE/FIU relationship by creating a "pipeline" of minority engineers specifically trained and mentored to enter the Department of Energy workforce in technical areas of need. This innovative program was designed to help address DOE's future workforce needs by partnering with academic, government and DOE contractor organizations to mentor future minority scientists and engineers in the research, development, and deployment of new technologies, addressing DOE's environmental cleanup challenges.

Project Overview

The main objective of the program is to provide interested students with a unique opportunity to integrate course work, Department of Energy (DOE) field work, and applied research work at ARC into a well-structured academic program. Students completing this research program would complete the M.S. or Ph.D. degree and immediately be available for transitioning into the DOE EM's workforce via federal programs such as the Pathways Program or by getting directly hired by DOE contractors, other federal agencies, and/or STEM private industry.

Project Quarterly Progress

FIU STEM (Science, Technology, Engineering, and Math) students are actively supporting the research efforts under the DOE-FIU Cooperative Agreement during FIU Performance Year 7. The following DOE Fellows are supporting the research under Projects 1-3:

Project 1: Gene Yllanes (undergraduate, electrical engineering), John Conley (undergraduate, mechanical engineering), Max Edrei (graduate, M.S., mechanical engineering), Sebastian Zanlongo (graduate, Ph.D., computer science), Clarice Davila (undergraduate, mechanical engineering), Ryan Sheffield (undergraduate, mechanical engineering), and Michael DiBono (undergraduate, mechanical engineering).

Project 2: Alejandro Garcia (graduate, M.S. geoscience), Alejandro Hernandez (undergraduate, chemistry), Alexis Smoot (undergraduate, environmental engineering), Awmna Kalsoom Rana (undergraduate, chemistry), Christine Wipfli (undergraduate, environmental engineering), Christopher Strand (undergraduate, civil & environmental engineering), Claudia Cardona (graduate, PH.D., environmental engineering), Hansell Gonzalez (graduate, Ph.D., chemistry), Natalia Duque (graduate, M.S., environmental engineering), Robert Lapierre (graduate, M.S., chemistry), Sarah Bird (undergraduate, environmental engineering), Silvina Di Pietro (graduate, Ph.D., chemistry), Sarah Solomon (undergraduate, environmental engineering), Mohammed Albassam (undergraduate, environmental engineering), Frances Zengotita (undergraduate, chemistry and health), Juan Morales (graduate, M.S., public health), Ripley Raubenolt (undergraduate, environmental engineering), and Ron Hariprashad (undergraduate, environmental engineering).

Project 3: Jesse Viera (undergraduate, mechanical engineering), Alexander Piedra (undergraduate, mechanical engineering), Andres Cremisini (undergraduate, computer science), and Daniel Khawand (undergraduate, computer science).

Fellows continue their support to the DOE-FIU Cooperative Agreement by actively engaging in EM applied research and supporting ARC staff in the development and completion of the various tasks. The program director continues to work with DOE sites and HQ to fully engage DOE Fellows with research outside ARC where Fellows provide direct support to mentors at DOE sites, DOE-HQ, and DOE contractors. All Fellows also participated in a weekly meeting conducted by the program director, a conference line has been established to enable DOE Fellows conducting internship to join to weekly meeting and update program director on their internship. During each of these meetings, one DOE Fellow presents the work they performed during their summer internship and/or EM research work they are performing at ARC.

The DOE Fellows Fall 2016 selection process was completed. A total of twenty-five (25) applications were received. FIU students' applications were reviewed and ten (10) candidates were interviewed by the DOE Fellows selection committee during the month of October. Four (4) new DOE Fellows were selected and hired for the program.

Table 4-1. New DOE Fellows from Spring and Fall 2016 Recruitment

New DOE Fellows	Degree	Major Area of Study	Recruitment
Mohammed Albassam	B.S.	Environmental Engineering	Spring 2016
Andres Cremisini	B.S.	Computer Science	Fall 2016
Clarice Davila	B.S.	Mechanical Engineering	Spring 2016
Michael DiBono	B.S.	Mechanical Engineering	Spring 2016
Ron Hariprashad	B.S.	Environmental Engineering	Fall 2016
Daniel Khawand	B.S.	Computer Science	Fall 2016
Juan Morales	M.S.	Public Health	Spring 2016
Alexander Piedra	B.S.	Mechanical Engineering	Spring 2016
Ripley Raubenolt	B.S.	Environmental Engineering	Fall 2016
Sarah Solomon	B.S.	Environmental Engineering	Spring 2016
Francis Zongotita	B.S.	Chemistry And English	Spring 2016

Four (4) DOE Fellows (Alexis Smoot, Awmna Kalsoom Rana, Frances Zengotita and Mohammed Albassam) presented their research at the FIU McNair Scholars Research Conference held at the main FIU campus on October 20-21, 2016. An oral presentation was given by DOE Fellow Awmna Rana titled "Tritium Partitioning in the Biosphere at Savannah River Site, Aiken, SC" Poster presentations were given by all four DOE Fellows. **Mohammed was awarded second place for his performance in the McNair poster presentations.**

- Alexis Smoot: Synergetic Interactions between Uranium, Humic Acid, Silica Colloids and SRS Sediments at Variable pH
- Awmna Rana: Study of the Fate and Transport of Irrigated Tritium Waste Water in Biological Receptors
- Frances Zengotita: Role of Ionic Strength on Sorption of Neodymium on Dolomite
- Mohammed Albassam: In-Situ Water Quality Sampling and Flow Measurement to Support Hydrological Model Development for Tims Branch Watershed, Savannah River Site, SC

Figure 4-1. DOE Fellows participated at FIU's McNair Research Conference

DOE Fellow Hansell Gonzalez prepared and submitted a paper for a student paper competition with the 9th International Conference on Remediation and Management of Contaminated Sediments, to be held in New Orleans on January 9-12, 2017. The title of his paper is "Unrefined humic substances as a potential low-cost remediation method for groundwater contaminated with uranium in acidic conditions."

The DOE Fellows completed their technical reports based on their summer 2016 internships with DOE sites, DOE national laboratories, DOE contractors, and DOE-HQ. A total of 10 DOE Fellows interned this summer as detailed in the following table. The reports are available on the DOE Fellows website (https://fellows.fiu.edu/internships-reports).

Table 4-2. Summer 2016 Internships

DOE Fellow	Location	Internship Mentor	Report Title
Erim Gokce	WRPS	Ruben Mendoza/ Dennis Washenfelder	Transfer Line Reliability for the Waste Feed Delivery Operations Research Model Phase 2
Max Edrei	NETL	Chris Gunter	Investigation of Ethanol as a Feasible Tracer in the Experimental Investigation of a Non-Newtonian Fluid Undergoing Pulse Jet Mixing
Sebastian Zanlongo	LANL	David Mascarenas	Artificial Personality Synthesis
Alejandro Hernandez	SRNL	Miles Denham	In Situ Precipitation of Silver Chloride for Treatment of I-129 Contaminated Groundwater
Alexis Smoot	DOE HQ	Skip Chamberlain	Sustainability Index
Awmna Rana	REU/SREL	John Seaman (SREL)	Tritium Partitioning in the Biosphere
Christopher Strand	LANL	Bill Foley	Calculating the Retention Storage Volume of Surface Water within a Predetermined Contour Area in Los Alamos County
Hansel Gonzalez	SRNL	Miles Denham	Study of an Unrefined Humate Solution as a Possible Remediation Method for Groundwater Contamination
Sarah Bird	DOE HQ	Skip Chamberlain	Sustainability Index
Silvina Di Pietro	PNNL	Jim Szecsody/ Nik Qafoku	Effects of Base Treatment and Redox Conditions on Mineral Dissolution

In addition, DOE Fellow Christine Wipfli continued a one year internship at the International Atomic Energy Agency (IAEA) in the Waste Technology Section, Division of Nuclear Fuel Cycle & Waste Technology at IAEA's Headquarters in Vienna, Austria.

FIU conducted the 10th annual DOE Fellows Poster Exhibition and Competition on November 2, 2016. The purpose of this event was to showcase the DOE Fellows' research accomplishments for the past year as a result of their participation in various DOE EM related applied research projects. A total of 19 posters were exhibited. Some of the projects showcased by the students were a result of their summer internship assignments at DOE sites, national laboratories, and DOE HQ in Washington, DC. Additional posters reflected the DOE Fellows' DOE EM applied research that they conduct at ARC as part of the DOE-FIU Cooperative Agreement sponsored research. For some of the graduate students, these projects are also a part of their thesis towards a master's or Ph.D. degree. This year's panel of judges included Dr. Jeff Griffin (Associate Laboratory Director, Environmental Stewardship, SRNL), Dr. Hope Lee (Manager, Soil and Groundwater Program, PNNL), Dr. Yong Cai (Professor & Chair, FIU Dept. of Chemistry & Biochemistry/ S.E. Environmental Research Center), Dr. Michael Sukop (Professor, FIU Arts & Sciences, Dept. of Earth & Environment), and Dr. Inés Triay (ARC Executive Director). The poster titles and DOE Fellow presenters were:

1. **Alejandro Garcia:** The influence of biofilm formation on the SIP response of Hanford vadose zone sediment
2. **Alejandro Hernandez:** In-situ Precipitation of AgCl for Treatment of I-129 Contaminated Groundwater
3. **Alexander Piedra:** Baseline Adhesion Testing of Intumescent Coatings
4. **Awmna Rana:** Study of the Fate and Transport of Irrigated Tritium Waste Water in Biological Receptors
5. **Christopher Strand:** Calculating the Retention Storage Volume of Surface Water within a Predetermined Contour Area
6. **Clarice Davila:** Thermal management and modeling of nuclear waste in DST's at Hanford using miniature sensors
7. **Frances Zengotita:** Role of Ionic Strength on Sorption of Neodymium on Dolomite
8. **Gene Yllanes:** Robotic Platform for Inspection of Highly Radioactive Areas
9. **Hansell Gonzalez:** Unrefined humate solution as a potential low-cost remediation method for groundwater contaminated with heavy metals
10. **John Conley:** Nonmetallic Material Testing of Hanford's HLW Transfer System
11. **Juan Morales:** Watershed Toxicology Management approach analyzing point source pollutants in Tims Branch, Savannah River Site, SC
12. **Maximiliano Edrei:** Investigation of Mixing Times of Sparged Bingham plastic type fluids as applied to the Pulse Jet Mixing Process
13. **Michael DiBono:** Miniature Motorized Inspection Tool for DOE Hanford Site Tank Bottoms
14. **Mohammed Albassam:** In-Situ Water Quality Sampling and Flow Measurement to Support Hydrological Model Development for Tims Branch Watershed, Savannah River Site, SC
15. **Natalia Duque:** Development of a Flow Model to Simulate Discharge in Tims Branch, Savannah River Site
16. **Ryan Sheffield:** Pneumatic pipe crawler for Hanford DOE site double-shell tanks
17. **Sarah Bird:** Sustainability Index for Comparison of Environmental Remediation Technologies
18. **Sarah Solomon:** Shewanella oneidensis MR1 Interaction with U(VI) in Bicarbonate Media

19. **Silvina Di Pietro:** Ammonia Gas Treatment for Uranium Immobilization at DOE Hanford's Site

Figure 4-1. 2016 Poster Competition and Exhibition Participants and Judges

On November 3, 2016, FIU conducted the tenth (10th) annual DOE Fellows Induction Ceremony. This year, eleven (11) FIU STEM students were inducted as DOE Fellows. Ms. Stacy Charboneau (Associate Principal Deputy Secretary for Field Operations, DOE EM) was one of the keynote speakers for the ceremony. Other distinguished guests from DOE EM included Mr. Barton Barnhart (Director, Office of Infrastructure Management & Disposition Policy), Mr. Kurt Gerdes (Director, Office of Subsurface Closure), and Mr. Andrew Szilagyi (Director, Office of Infrastructure and D&D). Additional distinguished guests Dr. Terry Michalski (Executive Vice President of SRNS and Director of SRNL), Dr. Jeff Griffin (Associate Laboratory Director, Environmental Stewardship, SRNL), Dr. Hope Lee (Manager, Soil and Groundwater Program, PNNL), Mr. Jose E. Sanchez (Director, Coastal and Hydraulics Laboratory, US Army Engineer Research & Development Center (ERDC), US Army Corps of Engineers), and Dr. Carlos Ruiz (Senior Research Scientist, ERDC, Army Corps of Engineers).

FIU was represented at the event by Mr. Steve Sauls (FIU Former Vice President of Governmental Relations), Dr. Inés Triay (ARC Executive Director) and Dr. Leonel E. Lagos (Principal Investigator for DOE-FIU Cooperative Agreement and Director, DOE Fellows Program), as well as FIU faculty, staff, and students. Former DOE Fellows who participated in the event included Dr. Stephen Wood (DOE Fellow Class of 2008, Computational Engineer, University of Tennessee/PRNL Joint Institute for Computational Sciences) and Ms. Melina Idarraga-Istambouli (DOE Fellow Class of 2008, Engineer, Miami Dade County Permitting and Inspection Center).

Ms. Stacy Charboneau and the other distinguished guests had the opportunity to participate in morning tours of the ARC research laboratories and listen to DOE Fellows presenting their research work. Presentations were given by Dr. Lagos and DOE Fellows Michael DiBono and Alexandro Hernandez. Dr. Lagos presented an overview of the DOE Fellows program. DOE Fellow Michael DiBono presented his DOE EM research on developing a miniature motorized inspection tool for DOE Hanford Site tank bottoms. DOE Fellow Alexandro Hernandez presented his DOE EM research on sodium silicate treatment to attenuate uranium mobility in acidic groundwater plumes. Tours of the ARC facilities included: 1) the robotics and sensors laboratory for a demonstration of the inspection tools being developed for double-shell tanks at the Hanford Site as well as the technologies being investigates for pipeline corrosion and erosion evaluation; 2) the materials testing laboratory where non-metallic materials are undergoing testing and evaluation for multiple stressors in support of the high level waste research; 3) the soil and groundwater laboratory for an overview of the research being performed in support of SRS and PNNL; 4) the radiological laboratory; 5) the ARC test and evaluation facility for a demonstration on the incombustible fixatives research; and 6) the modeling, simulation & GIS laboratory.

Figure 4-2. Induction ceremony guests touring ARC's laboratory facilities.

Figure 4-3. New DOE Fellows at the 2016 Induction Ceremony.

During this year's induction ceremony, 11 new FIU STEM students were inducted as DOE Fellows:

Table 4-1. DOE Fellows Class of 2016 Inducted into Program

New DOE Fellows	Degree	Major Area of Study
Mohammed Albassam	B.S.	Environmental Engineering
Andres Cremisini	B.S.	Computer Science
Clarice Davila	B.S.	Mechanical Engineering
Michael DiBono	B.S.	Mechanical Engineering
Ron Hariprashad	B.S.	Environmental Engineering
Daniel Khawand	B.S.	Computer Science
Juan Morales	M.S.	Public Health
Alexander Piedra	B.S.	Mechanical Engineering
Ripley Raubenolt	B.S.	Environmental Engineering
Sarah Solomon	B.S.	Environmental Engineering
Francis Zongotita	B.S.	Chemistry And English

In addition, awards were presented to the DOE Fellows that won the DOE Fellows Poster Exhibition and Competition held on the previous day. First place was awarded to Mr. Michael DiBono for his poster titled, "Miniature Motorized Inspection Tool for DOE Hanford Site Tank Bottoms." Second place went to Mr. Maximiliano Edrei for his poster titled, "Investigation of

Ethanol as a Feasible Tracer in the Experimental Investigation of a Non-Newtonian Fluid Undergoing Pulse Jet Mixing.” Third place was awarded to Mr. Alejandro Hernandez for his poster titled, “In-Situ Precipitation of AgCl for Treatment of I-129 Contaminated Groundwater.”

For the eight year, the DOE Fellow of the Year Award and the Mentor of the Year Award were presented at the ceremony. DOE Fellows were requested to nominate their ARC mentors and ARC mentors were requested to nominate the DOE Fellows. An ARC committee was established to review and select the winners from the submitted nominations. The 2016 Mentor of the Year Award went to Research Scientist Anthony Abrahao. The 2016 DOE Fellow of the Year Award was awarded to Mr. Maximiliano Edrei (DOE Fellows Class of 2014).

The four (4) new DOE Fellows hired during the fall recruitment were assigned to an ARC staff member to act as their mentor and supervise their research work. The following table lists the new DOE Fellows as well as their ARC mentor and DOE related project.

Table 4-2. New DOE Fellows from Fall Recruitment

New DOE Fellows	Degree	Major Area of Study	ARC Mentor	Project Support
Andres Cremisini	B.S.	Computer Science	Dr. Himanshu Upadhyay	D&D KM-IT
Daniel Khawand	B.S.	Computer Science	Dr. Himanshu Upadhyay	D&D KM-IT
Ripley Raubenolt	B.S.	Environmental Engineering	Dr. Ravi Gudavalli	Modeling of the Migration and Distribution of Natural Organic Matter Injected into Subsurface Systems
Ron Hariprashad	B.S.	Environmental Engineering	Dr. Noosha Mahmoudi	Surface Water Modeling of Tims Branch

The new DOE Fellows also completed the required environmental health and safety (EH&S) training prior to engaging in laboratory work, including:

- Laboratory Hazard Awareness Training
- HazCom: In Sync with GHS
- Fire Safety
- Environmental Awareness Part II
- Small Spills and Leaks
- EPA Hazardous Waste Awareness and Handling
- Personal Protective Equipment
- Safe Use of Fume hoods
- Radiation Safety

Dr. Lagos conducted orientation sessions for the new class of DOE Fellows and discussed the expectations of the program, including program components such as hands-on research on DOE related challenges, summer internships, and potential future employment with DOE EM, national laboratories and DOE contractors.

In addition, DOE Fellows completed development of abstracts on their research to be presented at Waste Management 2017 during the student poster session. Submitted student abstracts include:

1. Laboratory Analysis of the Spectral Induced Polarization Response of Biofilm Formation within Hanford Sediment **- Alejandro Garcia**
2. In Situ Precipitation of Silver Chloride for Treatment of 129I-Contaminated Groundwater - **Alejandro Hernandez**
3. Baseline Adhesion Testing of Intumescent Coatings - **Alexander Piedra**
4. Study of Synergetic Interactions between Uranium, Humic Acid, Silica Colloids and SRS Sediments at Variable pH - **Alexis Smoot**
5. Cross-Platform Mobile App for KM-IT Fixatives Module - **Andres Cremisini**
6. Promoting the Creation of a Global Inventory for Radioactively Contaminated Sites - **Christine Wipfli**
7. Thermal Measurement and Modeling of Nuclear Waste in the Double Shell Tanks at Hanford Nuclear Waste Site Using Miniature Sensors - **Clarice Davila**
8. Role of Ionic Strength on Sorption of Neodymium on Dolomite - **Frances Zengotita**
9. T-Rex: A Multipurpose All-Terrain Robotic Platform - **Gene Yllanes**
10. Study of an Unrefined Humate Solution as a Possible Remediation Method for Groundwater Contamination - **Hansell Gonzalez Raymat**
11. Accumulated Metal Analysis for Watershed Toxicology Management in Tims Branch, Savannah River Site, Aiken, SC - **Juan Morales**
12. Miniature Motorized Inspection Tool For DOE Hanford Site Tank Bottoms - **Michael DiBono**
13. In-Situ Water Quality Sampling and Flow Measurement to Support Hydrological Model Development for Tims Branch Watershed, Savannah River Site, SC - **Mohammed Albassam**
14. Investigating the Effect of Sorbed Humic Acid on the Mobility of Uranium - **Ripley Raubenolt**
15. “Shewanella oneidensis” MR1 Interaction with U(VI) in Bicarbonate Media - **Sarah Solomon**
16. Low-Cost Robotic Platform for D&D Activities - **Sebastian Zanlongo**
17. Fate of U and Mineral Dissolution upon Treatment with NaOH or NH_4OH - **Silvina Di Pietro**

Four DOE Fellows graduated from FIU and participated during FIU’s fall 2016 graduation ceremony held during December 11 - 14, 2016:

- Mohammed Albassam (Class of 2016) - B.S., Environmental Engineering
- Natalia Duque (Class of 2013) - M.S., Environmental Engineering

- Ron Hariprashad (Class of 2016) - B.S., Environmental Engineering
- Ryan Sheffield (Class of 2014) - B.S., Mechanical Engineering

Starting in the spring semester of 2017, Mohammed and Ron will begin their graduate degree programs, majoring in water resources engineering and geoscience, respectively. Ryan has accepted an employment offer with the applied physics laboratory at Johns Hopkins University and will start his new job in January 2017.

Figure 4-1. DOE Fellows Natalia, Mohammed and Ron during FIU's Fall 2016 graduation ceremony.

DOE Fellows Ripley and Ron attended hands-on radiation safety training offered by FIU's radiation safety officer on December 12, 2016, and have successfully completed and passed the training evaluation, enabling them to participate in the radiological experiments being carried out as a part of DOE-FIU cooperative agreement.

Each semester, DOE Fellows pursuing graduate degrees (Master's and Ph.D.) present their DOE-EM related research activities that is part of their thesis/dissertation during grad reviews, this will enable mentors and the program director to evaluate the students' progress towards their thesis/dissertation goals. During December 12-14, FIU conducted graduate reviews for DOE Fellows Sebastina, Silvina, Alejandro, Juan, Hansell and Maximilliano, who participated and presented their accomplishments.

Dr. Annie Kersting (Director of university relations and science and education, Lawrence Livermore National Laboratory) visited FIU on December 15 and presented "Plutonium in the Environment: Can we Predict its Subsurface Behavior?" to the DOE Fellows and ARC staff as part of the DOE Fellows lecture series. Dr. Kersting also toured the FIU-ARC facilities and participated in technical discussions with ARC researchers about potential future collaborations.

FIU continued working with DOE Fellows interested in federal jobs. FIU supports the Fellows with identifying federal entry-level career opportunities within DOE and other federal agencies on USA Jobs and forward those vacancy announcements to the DOE Fellows. FIU also continues to identify those DOE Fellows who are preparing to transition from academia to the workforce within the next year for conducting focused mentoring sessions with those Fellows on resume preparation and the USA Jobs application process.

In addition, FIU is providing a DOE Fellows Professional Development seminar series that is aligned with DOE's mentoring program in terms of goals and objectives. The intent of this effort is to round out the technical mentoring the Fellows are already receiving. The initial seminar offerings will include four presentations and discussions centered on challenges entry-level personnel will encounter as they enter the federal workforce:

- Establishing Your Professional Reputation (held in September 28, 2016)
- Workforce Communication Techniques
- Successfully Adapting to and Navigating Organizational Cultures
- Emotional Intelligence and the Leadership Spectrum

The DOE Fellows who participated in a spring/summer 2016 internships are preparing and presenting an oral presentation at the weekly DOE Fellows meetings. The schedule for these presentations is provided below.

Table 4-3. Research Presentation Schedule for DOE Fellow Meetings

DOE Fellow	DOE Site	Date
Alexis Smooth & Sarah Bird	HQ/DOE EM - Washington DC	08/31/16
Erim Gokce	WRPS - Richland, Washington State	09/07/16
Alejandro Hernandez	SRNL - Aiken, South Carolina	09/16/16
Alejandro Garcia	PNNL - Richland, Washington State	09/28/16
Natalia Duque, Mohammed Albassam, & Juan Morales	Savannah River Site, SC	10/19/16
Maxmiliano Edrei	NETL - Morgantown, West Virginia	11/16/16
Sebastian Zanlongo	LANL - Los Alamos, New Mexico	11/30/16
Silvina Di Pietro	PNNL - Richland, Washington State	01/25/17
Hansell Gonzalez	SRNL - Aiken, South Carolina	02/01/17
Awmna Rana	REU/SREL - Aiken, South Carolina	02/08/17
Christopher Strand	LANL - Los Alamos, New Mexico	02/15/17

During this month, the Fellows continued their research in the DOE EM applied research projects under the cooperative agreement and research topics identified as part of their summer internships at DOE sites, national labs, and/or DOE HQ. Each DOE Fellow is assigned to DOE EM research projects as well as ARC mentors. A list of the current Fellows, their classification, areas of study, ARC mentor, and assigned project task is provided below.

Table 4-4. Project Support by DOE Fellows

Name	Classification	Major	ARC Mentor	Project Support
Alejandro Garcia	Graduate - B.S.	Geoscience	Dr. Yelena Katsenovich	The influence of microbial activity on the corresponding

Name	Classification	Major	ARC Mentor	Project Support
				electrical geophysical response after ammonia injections in the vadose zone
Alejandro Hernandez	Undergrad - M.S.	Chemistry	Dr. Vasileios Anagnostopoulos	Contaminant Fate and Transport Under Reducing Conditions
Alexander Piedra	Undergrad – B.S.	Mechanical Eng.	Mr. Joseph Sinicrope	Database of Robotic Technologies for D&D Activities
Alexis Smoot	Undergrad - B.S.	Envr. Eng.	Dr. Ravi Gudavalli	Synergistic Effects of Silica and Humic Acid on U(VI) Removal
Andres Cremisini	Undergrad – B.S.	Computer Science	Dr. Himanshu Upadhyay	D&D KM-IT
Awmna Kalsoom Rana	Undergrad - B.S.	Chemistry	Dr. Vasileios Anagnostopoulos	Investigation on the Properties of Acid-Contaminated Sediment and its Effect on Contaminant Mobility
Christine Wipfli	Undergrad - B.S.	Envr. Eng.	Dr. Vasileios Anagnostopoulos	Groundwater Remediation at SRS F/H Area
Christopher Strand	Undergrad - B.S.	Civil & Env. Eng.	Dr. Noosha Mahmoudi	Surface Water Modeling of Tims Branch
Clarice Davila	Undergrad - B.S	Mechanical Eng.	Dr. Aparna Aravalli	Investigation Using an Infrared Temperature Sensor to Determine the Inside Wall Temperature of DSTs
Claudia Cardona	Graduate - Ph.D.	Envr. Eng.	Dr. Yelena Katsenovich	Sequestering Uranium at the Hanford 200 Area Vadose Zone
Daniel Khawand	Undergrad - B.S.	Computer Science	Dr. Himanshu Upadhyay	D&D KM-IT
Frances Zengotita	Undergrad - B.S.	Chemistry & Health	Dr. Hilary Emerson	Absorption of Neodymium into the Dolomite Mineral
Gene Yllanes	Undergrad - B.S.	Electrical Eng.	Mr. Anthony Abrahao	Development of Inspection Tools for DST Primary Tanks
Hansell Gonzalez	Graduate - Ph.D.	Chemistry	Dr. Yelena Katsenovich	Sorption Properties of Humate Injected into the Subsurface System
Jesse Viera	Undergrad - B.S.	Mechanical Eng.	Mr. Joseph Sinicrope	Incombustible Fixatives
John Conley	Undergrad - B.S.	Mechanical Eng.	Mr. Anthony Abrahao	Development of Inspection Tools for DST Primary Tanks
Juan Morales	Graduate – M.S.	Public Health	Ms. Angelique Lawrence / Dr. Reinaldo Garcia	Development of Flow and Contaminant Transport Models for SRS
Maximiliano Edrei	Graduate – M.S.	Mechanical Eng.	Dr. Dwayne McDaniel	Computational Fluid Dynamics Modeling of a Non-Newtonian Fluid Undergoing Sparging for Estimating PJM Mixing Times

Name	Classification	Major	ARC Mentor	Project Support
Michael DiBono	Undergrad - B.S.	Mechanical Eng.	Mr. Anthony Abrahao	Development of Inspection Tools for DST Primary Tanks
Mohammed Albassam	Graduate – M.S.	Envr. Eng.	Dr. Noosha Mahmoudi	Environmental Remediation and Surface Water Modeling of Tims Branch Watershed at SRS
Natalia Duque	Graduate – M.S.	Envr. Eng.	Dr. Noosha Mahmoudi	Surface Water Modeling of Tims Branch
Ripley Raubenolt	Undergrad - B.S.	Envr. Eng.	Dr. Ravi Gudavalli	Modeling of the Migration and Distribution of Natural Organic Matter Injected into Subsurface Systems
Robert Lapierre	Graduate – M.S.	Chemistry	Dr. Yelena Katsenovich	Sequestering Uranium at the Hanford 200 Area Vadose Zone
Ron Hariprashad	Undergrad - B.S.	Envr. Eng.	Dr. Noosha Mahmoudi	Surface Water Modeling of Tims Branch
Ryan Sheffield	Undergrad - B.S.	Mechanical Engineering	Dr. Dwayne McDaniel	Development of Inspection Tools for DST Primary Tanks
Sarah Bird	Undergrad - B.S.	Envr. Eng.	Dr. Noosha Mahmoudi	Surface Water Modeling of Tims Branch
Sarah Solomon	Undergrad - B.S.	Envr. Eng.	Dr. Yelena Katsenovich	Investigation on Microbial-Meta-Autunite Interactions - Effect of Bicarbonate and Calcium Ions
Sebastian Zanlongo	Graduate - Ph.D.	Computer Science	Dr. Dwayne McDaniel	Cooperative Controls for Robotic Systems
Silvina Di Pietro	Graduate - Ph.D.	Chemistry	Dr. Hilary Emerson	Evaluation of Ammonia for Uranium Treatment

Milestones and Deliverables

The milestones and deliverables for Project 4 for FIU Performance Year 7 are shown on the following table. Milestone 2016-P4-M1 was completed with the development of the draft summer internship reports. These deliverables are available on the DOE Fellows website. FIU also completed milestone 2016-P4-M2 and associated deliverable with the final selection and recruitment of the DOE Fellow Class of 2016. Milestone 2016-P4-M3 was completed with the conduction of the induction ceremony for the DOE Fellows Class of 2016, held on November 3, 2016.

FIU Performance Year 7 Milestones and Deliverables for Project 4

Milestone/ Deliverable	Description	Due Date	Status	OSTI
2016-P4-M1	Draft Summer Internships Reports	10/14/16	Complete	
Deliverable	Deliver Summer 2016 interns reports to DOE	10/31/16	Complete	OSTI
Deliverable	List of identified/recruited DOE Fellow (Class of 2016)	10/31/16	Complete	
2016-P4-M2	Selection of new DOE Fellows – Fall 2016	10/31/16	Complete	
2016-P4-M3	Conduct Induction Ceremony – Class of 2016	11/04/16	Complete	
2016-P4-M4	Submit student poster abstracts to Waste Management Symposium 2017	1/16/17	On Target	
Deliverable	Update Technical Fact Sheet	30 days after end of project	On Target	

Work Plan for Next Quarter

- Continue research by DOE Fellows in the four DOE-EM research projects under the cooperative agreement and research topics identified as part of their summer internships.
- Coordinate travel for DOE Fellows to attend Waste Management 2017 Symposium.
- DOE Fellows will develop posters on their research and present during the student poster session at WM17.
- Begin Spring 2017 campaign to recruit DOE Fellows into the program.
- Begin coordination of internship placements for summer 2017 at DOE sites, national laboratories, DOE HQ, and DOE contractor locations.