QUARTERLY PROGRESS REPORT

January 1 to March 31, 2015

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:

U.S. Department of Energy
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 five 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 Year 5 will be May 18, 2014 to May 17, 2015. The information in this document provides a summary of the FIU-ARC's activities under the DOE Cooperative Agreement (Contract # DE-EM0000598) for the period of January 1 to March 31, 2015. Highlights during this reporting period include:

Program-wide:

- From March 31 to April 3, 2015, a program review via VTC was conducted between DOE EM and FIU ARC as part of the DOE Cooperative Agreement. A total of six (6) technical presentations were conducted over the 4-day period. The DOE-FIU program review included participation from colleagues at DOE Headquarters (DC and Maryland Office), DOE national laboratories (Savannah River National Lab, Pacific Northwest National Lab, and Idaho National Lab) and DOE contractors (Washington River Protection Solutions and Savannah River Nuclear Solutions).

ARC scientists/engineers and DOE-EM leadership (Mr. Mark Gilbertson) during the Wrap Up session.

- The presentations included one on the high-level waste/waste processing applied research, two on the soil and groundwater applied research being performed for Hanford and Savannah River Sites, one on the D&D and IT for Environmental Management applied research, and one on the workforce development and training of FIU STEM students (DOE Fellows Program). In addition, 12 DOE Fellows presented during the technical (projects 1-4) and workforce development presentations to highlight the applied research they are performing for DOE EM as part of this Cooperative Agreement. A final Wrap Up presentation was given on Friday to highlight the major applied research accomplishments during the current year and to present the proposed research tasks for the new performance cycle, currently scheduled to start on May 18, 2015. All presentations are available for downloading on FIU's DOE Research webpage at http://doeresearch.fiu.edu and additional information regarding DOE Fellows program can be found at http://fellows.fiu.edu.

Project 1:

- FIU is currently having discussions with DOE-EM to determine how best to reforecast current and future deliverables. Reforecasting is needed for multiple tasks due to changes in personnel and current funding levels.

Project 2:

- Milestone 2014-P2-M1, "completion of solubility measurements of U(VI)-free samples (FIU Year 5 scope)" and "completion of solubility measurements using standards such as calcium chloride and lithium chloride to get better deliquescence predictions at low water activities values (carryover scope)," was completed on January 30, 2015.
- A deliverable, titled, "Progress report on microcosm studies prepared with SRS sediments augmented with molasses and sulfate for subtask 2.2," was also completed and sent to DOE HQ and the SRS site contacts January 30, 2015.
- A deliverable, a progress report on the solubility measurements via isopiestic method (subtask 1.1), was completed and sent to DOE HQ and the PNNL site contacts on February 16, 2015.
- A deliverable, "FIU's Support for Groundwater Remediation at SRS F/H Area (subtask 2.1)," was completed and sent to DOE HQ and the SRNL site contacts on March 31, 2015.
- A manuscript by DOE Fellow Paola Sepulveda-Medina, Dr. Yelena Katsenovich, Dr. Dawn Wellman and Dr. Leonel Lagos titled, "The Effect of Bicarbonate on the Microbial Dissolution of Autunite Mineral in the Presence of Gram-Positive Bacteria" was published in the *Journal of Environmental Radioactivity* (citation: *Journal of Environmental Radioactivity* 144 (2015) 77-85).
- Another manuscript by DOE Fellow Paola Sepulveda-Medina, Yelena Katsenovich, Vishal Musaramthota, Michelle Lee, Brady Lee, Rupak Dua, and Leonel Lagos titled, "The effect of uranium on the bacterial viability and cell surface morphology using atomic force microscopy in the presence of bicarbonate ions," prepared in collaboration with PNNL, was accepted for publication in the *Research in Microbiology* journal.

Project 3:

- Milestone 2014-P3-M4, "completion of Baseline Analysis (Subtask 3.1)" and its associated deliverable "baseline analysis summary (Subtask 3.1)" for the subtask "Sustainability Plan for the A/M Area Groundwater Remediation System" were ompleted and submitted to DOE HQ and SRS site contacts on the due date, February 27, 2015.
- Milestone 2014-P3-M2, a literature review for the surface water modeling of Tims Branch (Subtask 2.2), and the associated summary report deliverable which is entitled

"Literature Review for Surface Water Contaminant Fate and Transport Modeling of Tims Branch" were completed and submitted to DOE and SRNL site contacts on March 31, 2015.

- Milestone 2014-P3-M3, development of preliminary site conceptual model of Tims Branch (Subtask 2.2) was also completed and submitted on March 31, 2015.
- Milestone 2014-P3-M6, meeting and presentation of project progress at SRS which was due March 18, 2015, has been reforecast to April 13, 2015 due to schedule conflicts of both SRNL and FIU personnel.

Project 4:

- Milestone 2014-P4-M3.4, the deployment of the best practices mobile application for D&D KM-IT was sent to DOE for review/testing on January 16, 2015.
- A deliverable on the preliminary metrics progress for outreach and training activities for D&D KM-IT was submitted to DOE on January 16, 2015.
- One deliverable, to host a D&D workshop with the D&D community, was completed on March 16, 2015 during the Waste Management conference.
- Milestone 2014-P4-M3.5, originally due in March, has been reforecast to 5/15/15 due to additional work scope (integration of the Cogentus/NuVision robotics database into D&D KM-IT). This milestone includes the addition/editing of four Wikipedia articles.
- Finally, a milestone for a D&D subtask has been re-defined after discussions with Mike Serrato at SRNL to better meet the research needs of the site. Milestone 2014-P4-M2.2 was re-defined from a draft summary report for SRS 235-F facility on organic semiconductor thin films (subtask 2.1.2) to a draft test plan for incombustible fixatives (subtask 2.1.3) with a due date of 5/15/15.

Project 5:

- Milestone 2014-P5-M4, submission of the student poster abstracts to Waste Management Symposium 2015 was completed by the due date of January 15, 2015.

FIU Year 4 Carryover Work Scope

The activities described in the Continuation Application for FIU Year 4 were planned for a period of performance from September 17, 2013 to May 17, 2014. However, a portion of the funding from Year 4 was provided near the end of the year and scope associated with these carryover funds is being performed in addition to scope associated with FIU Year 5. To differentiate the work scope, the carryover scope activities from FIU Year 4 being performed during FIU Year 5 are highlighted in gray.

The program-wide milestones and deliverables that apply to all projects (Projects 1 through 5) for FIU Year 5 are shown on the following table. The FIU Research Review was held on March 31 to April 3, 2015. Due to difficulties in coordinating the dates for the event with DOE HQ officials, the participating DOE field sites, and FIU, the two planned research reviews for this year were combined into this one research review

Task	Milestone/ Deliverable	Description	Due Date	Status	OSTI
Program-wide (All Projects)	Deliverable	Draft Project Technical Plan	06/18/14	Complete	
	Deliverable	Monthly Progress Reports	Monthly	On Target	
	Deliverable	Quarterly Progress Reports	Quarterly	On Target	
	Deliverable	Draft Year End Report	06/30/15	On Target	OSTI
	Deliverable	Presentation overview to DOE HQ/Site POCs of the project progress and accomplishments (Mid-Year Review)	11/21/14*	Complete	
	Deliverable	Presentation overview to DOE HQ/Site POCs of the project progress and accomplishments (Year End Review)	06/30/15*	Complete	

**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: analysis and development of alternative pipeline unplugging technologies to address potential plugging events; 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 Year 5:

- Task 2: Pipeline Unplugging and Plug Prevention
    - Subtask 2.1.1 – Support for Potential Deployment of the Asynchronous Pulsing System and the Peristaltic Crawler
    - Subtask 2.2.1 – 2D Multi-Physics Model Development
- Task 17: Advanced Topics for Mixing Processes
    - Subtask 17.1.1 – Computational Fluid Dynamics Modeling of Jet Penetration in non-Newtonian Fluids
- Task 18: Technology Development and Instrumentation Evaluation
    - Subtask 18.1.1 – Evaluation of SLIM for Rapid Measurement of HLW Solids on Hanford Mixing Tank Bottoms
    - Subtask 18.1.2 – Testing of SLIM for Deployment in HLW Mixing Tanks at Hanford
    - Subtask 18.2.1 – Development of First Prototype for DST Bottom and Refractory Pad Inspection
    - Subtask 18.2.2 – Investigation of Using Peristaltic Crawler in Air Supply Lines Leading to the Tank Central Plenum
- Task 19: Pipeline Integrity and Analysis
    - Subtask 19.1.1 – Data Analysis of Waste Transfer Components
    - Subtask 19.2.1 – Development of a Test Plan for the Evaluation of Nonmetallic Components

- Subtask 19.2.2 – Preliminary Experimental Testing of Nonmetallic Components

Task 2: Pipeline Unplugging and Plug Prevention

Task 2 Overview

Over the past few years, FIU has found that commercial technologies do not meet the needs of DOE sites in terms of their ability to unplug blocked HLW pipelines. FIU has since undertaken the task of developing alternative methods/technologies with the guidance from engineers at the national laboratories and site personnel. The new approaches that are being investigated include an asynchronous pulsing system (APS) and a peristaltic crawler system (PCS). Both technologies utilize lessons learned from previous experimental testing and offer advantages that other commercially available technologies lack. The objective of this task is to complete the experimental testing of the two novel pipeline unplugging technologies and position the technologies for future deployment at DOE sites. Another objective of this task is to develop computational models describing the build-up and plugging process of retrieval lines. In particular, the task will address plug formation in a pipeline, with a focus on the multi-physical (chemical, rheological, mechanical) processes that can influence the formation.

Task 2 Quarterly Progress

FIU Year 4 Carryover Work Scope

Subtask 2.1: Development of Alternative Unplugging Technologies

The asynchronous pulsing system (APS) effort concentrated on developing a simulant plug with the appropriate strength for our testing. After varying several plug making parameters last month without achieving the desire plug strength, it became apparent that the problem was not with the plug manufacturing techniques but rather with the plaster of Paris material. Therefore, we changed the brand of the plaster of Paris to determine if the original manufacturer (DAP) had changed their recipe, resulting in a weaker plug. We purchased Sheetrock® brand plaster of Paris and made additional plugs. After curing for 24-hours, the plugs were subjected to blowout tests. The blowout test results showed a significant increase in the plug strength from 150 psi to 400 psi. This verified our theory that the weak plugs were a result of the DAP corporation changing the recipe of their plaster of Paris without notification. After verifying the plug strength, we installed a plug on the test loop and attempted to unplug it. The loop was run for over an hour and a half but was unable to unplug it. While conducting the test, one of the piston pumps started to leak hydraulic fluid and water. The test run was stopped and both piston pumps were removed and sent out for repairs.

After the pumps were repaired, they were reinstalled and unplugging tests commenced. Tests were run without air as well as with a half a piston stroke volume of air. Each experiment was run twice for each test scenario. For the unplugging tests without air, the average unplugging duration was 4.5 hours while the average duration for the half stroke volume was 6.5 hours. These verifies tests demonstrated that the system was capable of unplugging the pipeline with and without air entrained.

After all the tests were completed, data from the tests were analyzed. Table 1-1 shows the results from unplugging trials.

Table 1-1. APS Unplugging Trials

Air Quantity	Trail	Unplugged (Y/N)	Time Elapsed (Hrs)	Amplitude (A)	Frequency (Hz)	Wave Type
No Air	1	Y	4	100/150	1,2,3	Square
	2	Y	3	150	1	Square
	3	Y	6	150	1	Square
Half-Stroke	1	Y	4.5	150	1	Sine
	2	Y	8	150	1	Square
	3	Y	5.5	150	1	Square
Full-Stroke	1	Y	9.5	150	1	Square
	2	Y	10	150	1	Square

After analyzing the data, the following observations were realized:

- With no air in the system, the plug was unplugged at an average of 4 hours and 20 minutes.
- With a half stroke or air in the system, the plug was unplugged at an average of 6 hours.
- With a full stroke of air in the system, the plug was unplugged at an average of 9 hours and 45 minutes.

Below are two samples of unplugging data: one includes results from baseline tests with no air and another with a half of stroke of air. Shown in the graphs are pressures from each side of the plug face. The pressures clearly act in an asynchronous and oscillatory manner, maximizing the forces which cause the plug to dislodge. The change in amplitude corresponds to either a breach in the plug or movement of the plug.

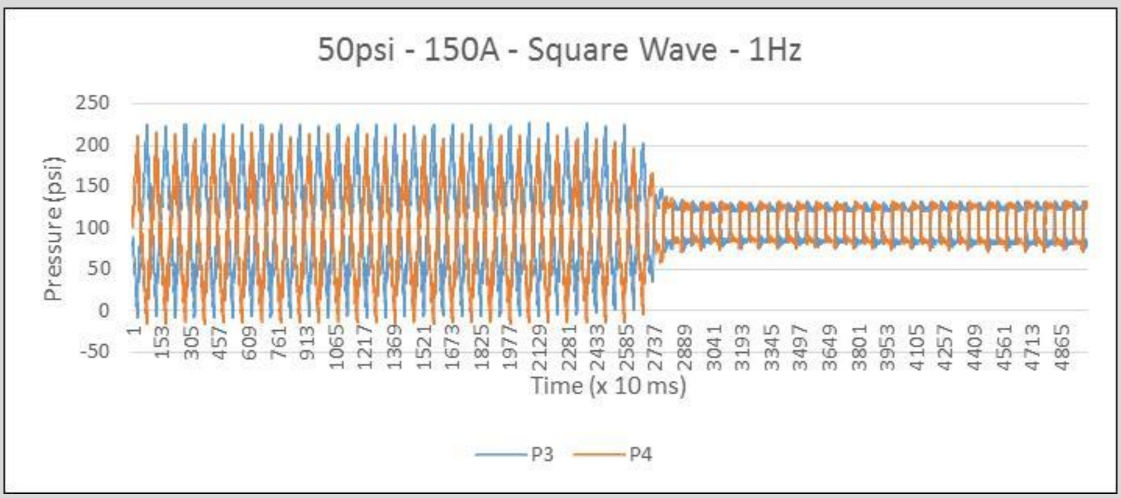


Figure 1-1. No air in system – unplugging results.

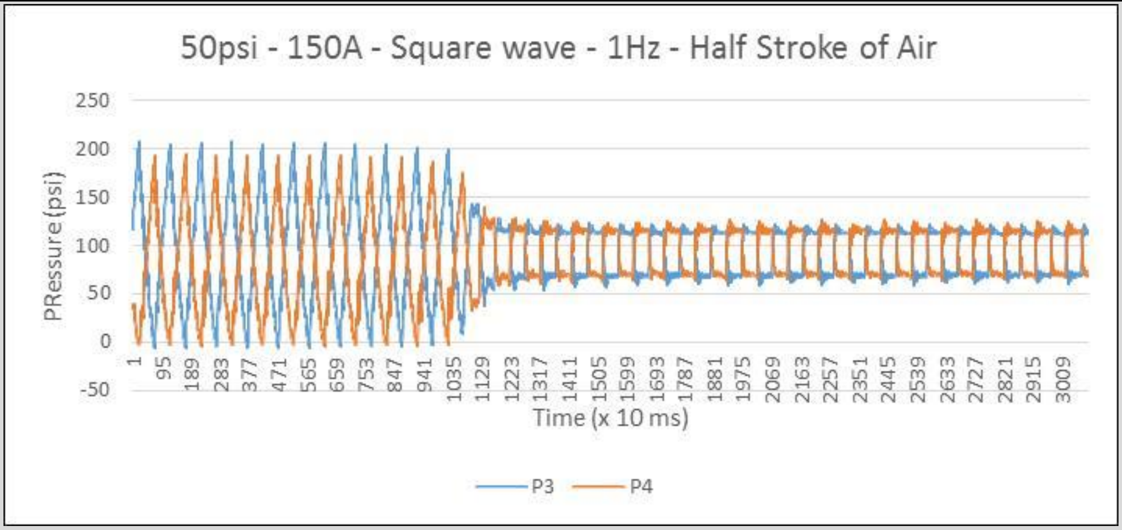


Figure 1-2. Half-stroke of air in system – unplugging results.

For the peristaltic crawler subtask, the primary objective has been to evaluate modifications of the design that could improve the structural reliability of the gripping inflatables at both ends of the crawler. The crawler uses these inflatables to lock, pull and push the device during the operation sequence. The inflatables have to endure the resultant increasing force from dragging the tether, which supplies the device with compressed air, vacuum, water, electric controls and camera signals. Two design modifications were explored. As shown in Figure 1-3, the two possible options include: 1) redesigning the clamps, and 2) replacing the clamps with compressing flanges using inflating bladders.

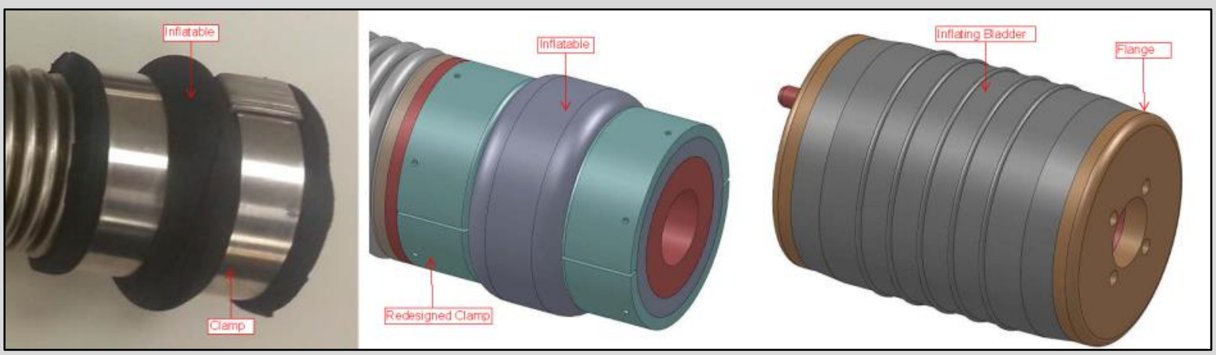


Figure 1-3. Gripping inflatable.

Redesigning the clamps would not require significant changes in the actual rims. The current crawler uses stainless steel clamps that have a very low profile and sharp edges. Using machined clamps with rounded edges have the potential to lower problematic stress risers. Figure 1-4 shows the redesigned clamps developed to be used under the existing clamps. The clamps also could be adapted to be used on the existing rims.

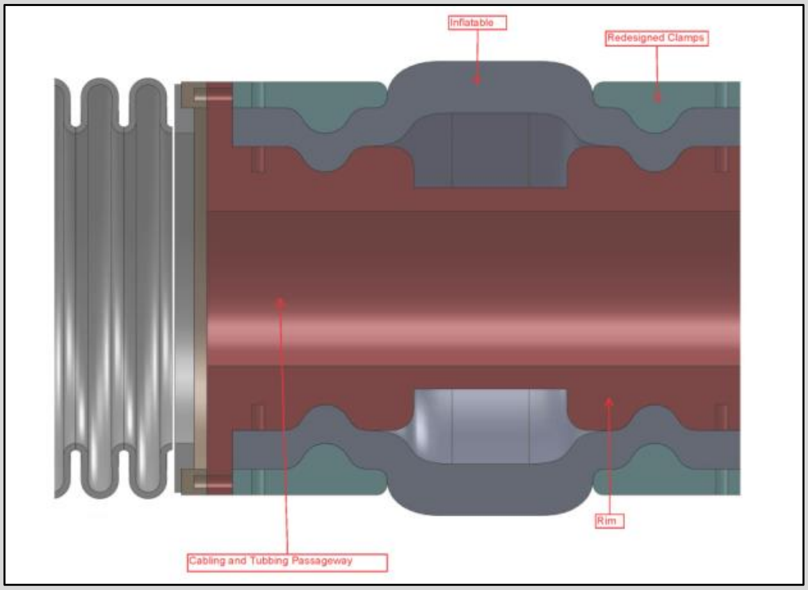


Figure 1-4. Redesigned clamps.

Replacing the clamps with compressing flanges using inflating bladders requires a redesign of the rims (Figure 1-5). However, the redesign increases the contact area of the inflatables, which increases the gripping as well, lowering the required inflating pressure. Also, the clamping stresses would be moved away from the inflating area.

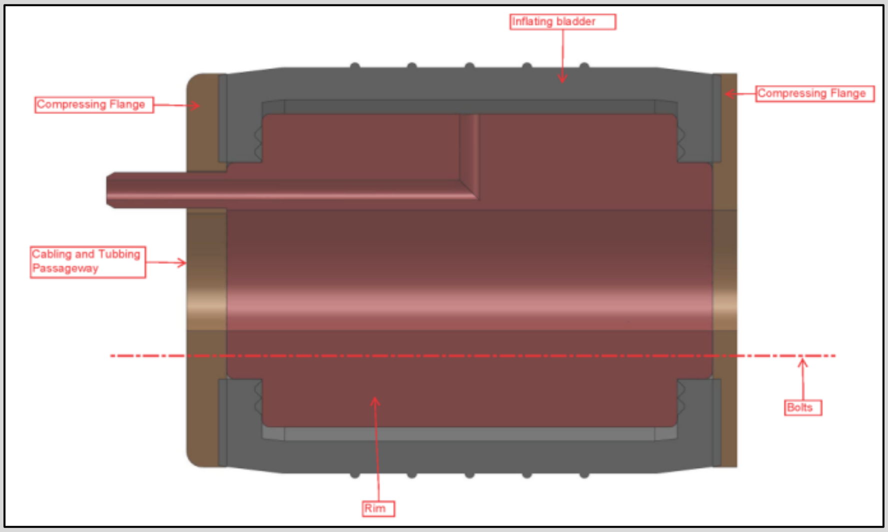


Figure 1-5. Inflating bladder.

Currently, both design modifications are being tested; finite element analyses are being performed in Abacus, and a fatigue test assembly is also being designed. Later on, the vulcanization of rubber to metal and multilayer inflatables will be investigated as a potential improvement to the design.

FIU also developed a hyperplastic finite element model of the crawler's inflatable. As shown in the figures below, the numerical model will help not only in the study of the failure mechanism, but also in the redesign of the current clamping systems.

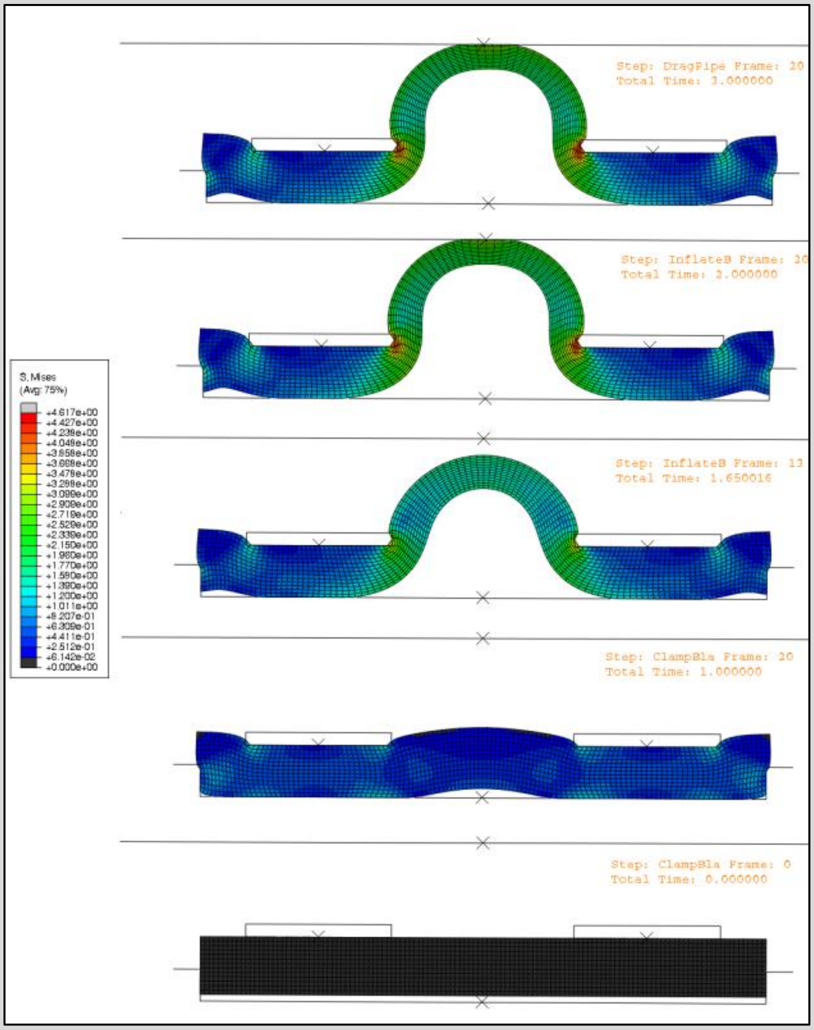


Figure 1-6. Finite element analysis of the crawler's inflatable performing in sequence: clamping, inflating, grabbing and pulling in a 3-inch diameter pipe.

Currently a fatigue test assembly is being constructed for the new designs. Later, new inflatable designs will be investigated and tested as potential improvement to the reliability and durability of the crawler.

FIU Year 4 Carryover Work Scope

Subtask 2.2: Computational Simulation and Evolution of HLW Pipeline Plugs

FIU efforts for this task were directed towards simulating virtual scenarios to understand the behavior of settling as a function of flow velocity by varying particle size, solids density and solids volume fraction. The 3-D multi-phase was developed using the mixture model that is part of the Chemical Engineering module of COMSOL Multiphysics 4.3b.

The base model consisted of a 3D horizontal pipe with a diameter of 0.078 m and a length of 5.2 m. The slurry was modeled as a Newtonian suspension consisting of solids particles dispersed in liquid. The mixture entered through the inlet at velocities characterizing fully developed turbulent flow regimes. The turbulence intensity and length scale were set to 5% and $0.07*r_{in}$ where r_{in} = 0.039 m, the radius of the inlet. The outlet was set to zero pressure, no viscous stress and the dispersed phase flow exited the pipe at mixture velocity. A gravity node was added to account for the gravity force in the negative z-direction over the entire domain. Initially, the velocity as well as the solids phase volume fraction was zero in the entire model domain. The mesh used to partition the model was of tetrahedral type with the coarse element size.

A. Influence of Particle Size

The effect of particle size on the settling dynamics was investigated using 45 μm and 220 μm size solids particles dispersed in water. The solids density was kept constant at 3147 kg/m^3 and the liquid density used was 1000 kg/m^3. The solids volume fraction was 2.9%. The simulations were carried out with entrance velocities ranging from 0.8 m/s to 2 m/s. The 45 μm and 220 μm particle concentrations at different velocities are shown in Figure 1-7 and Figure 1-8. The color legend represents the different solids concentration in the pipe.

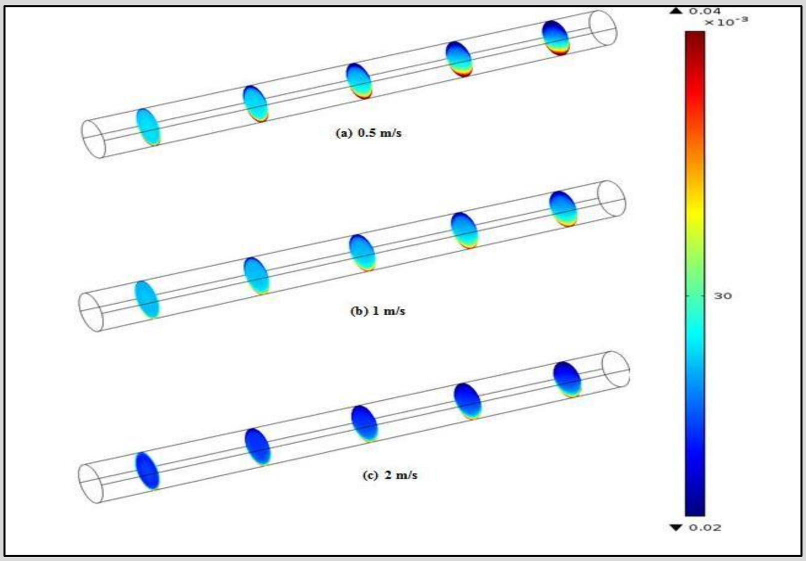


Figure 1-7. A 45 μm particle concentration along the pipe as a function of flow velocity ranging from 0.8 to 2 m/s.

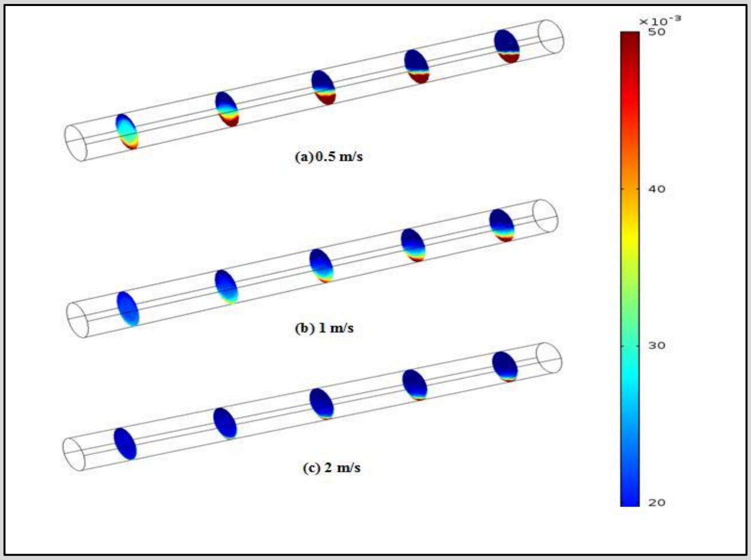


Figure 1-8. A 200 µm particle concentration along the pipe as a function of flow velocity ranging from 0.5 to 2 m/s.

The concentration figures show that the 220 µm larger and heavier particles tend to settle fast on the bottom of the pipe, especially at low flow velocities. The simulations showed that flow velocities of lower than 1.0 m/s will create a stationary bed flow that eventually causes a plug to form. For velocities of greater than 1.0 m/s, the fluid establishes a moving bed regime where the particles move along the bottom of the transfer pipe.

B. Influence of Solids Density

The effect of solids density on the settling dynamics was investigated by running simulations for the 45 µm particle size and 2.9% solids volume fraction at solids densities of 3147 kg/m^3 and 6300 kg/m^3. The entrance velocities used were 0.5 m/s, 1 m/s and 2 m/s and the results of the simulations are shown in Figures 1-9, 1-10 and 1-11, respectively.

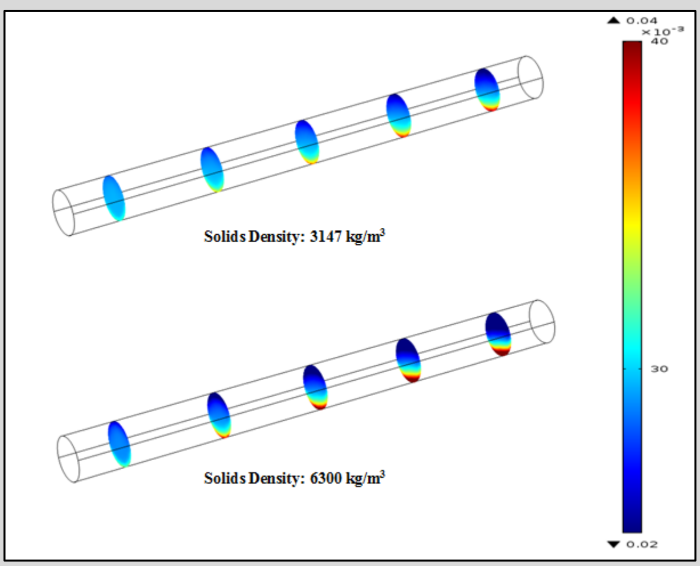


Figure 1-9. Settling of solids as a function of solids density for 45 µm particles at 0.5 m/s.

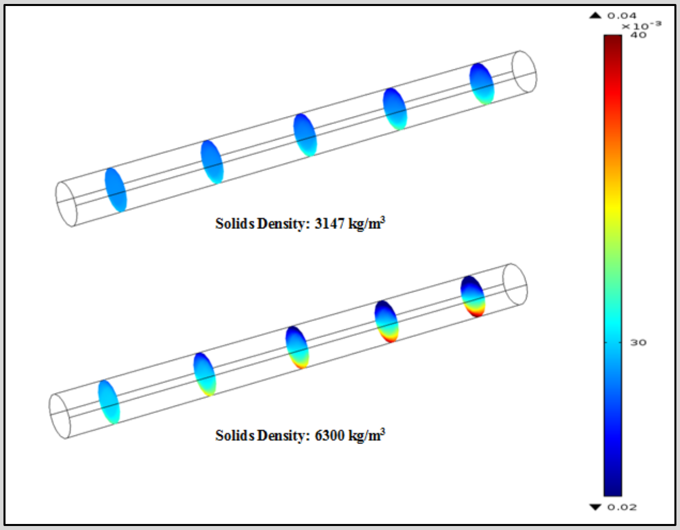


Figure 1-10. Settling of solids as a function of solids density for 45 µm particles at 1 m/s.

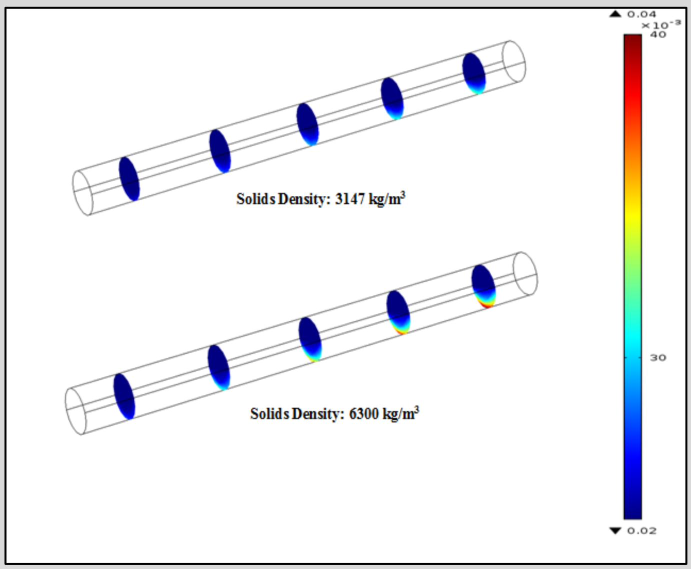


Figure 1-11. Settling of solids as a function of solids density for 45 µm particles at 2 m/s.

The higher density slurries require a higher velocity to keep them suspended and prevent them from settling at the bottom compared to the lower density slurries. The critical velocity for the slurries with density of 3147 kg/m^3 was 0.7 m/s compared to the 4 m/s velocity obtained for the heavier slurries with density of 6300 kg/m^3.

C. Influence of Solids Volume Fraction

The effect of solids volume fraction on the critical velocity was investigated by running simulations for 45 µm particles with a solids density of 3147 kg/m^3. The solids volume fraction values ranged 2.9%, 5.8% and 10% respectively. The liquid density was fixed at 1000 kg/m^{3}The critical velocities were calculated for each case and were numerically assessed as the velocity at which the solids were fully suspended in liquid and hence no settling was observed at the bottom of the pipe. For example, for the slurry consisting of 2.9% volume fraction of solids, the solids were observed to settle at 0.5 m/s, 0.8 m/s, and 1 m/s. This can be seen as an increase in the solids volume fraction from the initial 2.9% to 3.53%, 3.35% and 3.27% at the respective velocities. As the velocity was further increased to 2 m/s, the solids do no settle. They remain fully dispersed across the pipe length as the solids volume fraction stays the same as the initial volume fraction value. i.e., 2.9%. Any increase in the velocity thereafter shows that the solids remain fully suspended. Hence the critical velocity calculated for the case with solids volume fraction of 2.9% is 2 m/s. Table 1-2 below shows the solids volume fraction values highlighted in red color for the cases simulated and their corresponding measured critical velocities.

Table 1-2. Flow Velocity as Function of Solids Volume Fraction

Flow Velocity (m/s)	Solids volume fraction 2.9%	Solids volume fraction 5.8%	Solids volume fraction 10%
0.5	3.53%	6.84%	11.32%
0.8	3.35%	6.57%	10.98%
1	3.27%	6.42%	10.80%
2	2.90%	6.13%	10.44%
4	2.90%	5.90%	10.20%
6	2.90%	5.90%	10.12%

As the solids volume fraction increases, the critical velocity increases, as expected. For instance, for the slurry with solids volume fraction of 2.9%, the critical velocity obtained is 2 m/s compared to the 4 m/s obtained for solids volume fraction of 5.8% and 6 m/s for the slurry with solids volume fraction of 10%.

In the last month of the quarter, efforts were focused on the obtaining 3D velocity and pressure distributions through an elbow to assist in the investigation of flow patterns in pipelines with complex geometries. Single phase laminar flow patterns were studied in a 90° elbow using the COMSOL multi-physics software version 4.4. Results obtained for the velocity (streamline velocity field) and pressure distributions are as shown in Figures 1-12a and 1-12b, respectively. As expected (Figure 1-12a), the velocity gradually changes as the fluid enters the bend and there is a slight increase in the velocity after the bend in the inner core and a reduction in the outer core of the pipe section. Similarly, the pressure distribution in the bend (Figure 1-12b) shows higher stress contours in the bend region.

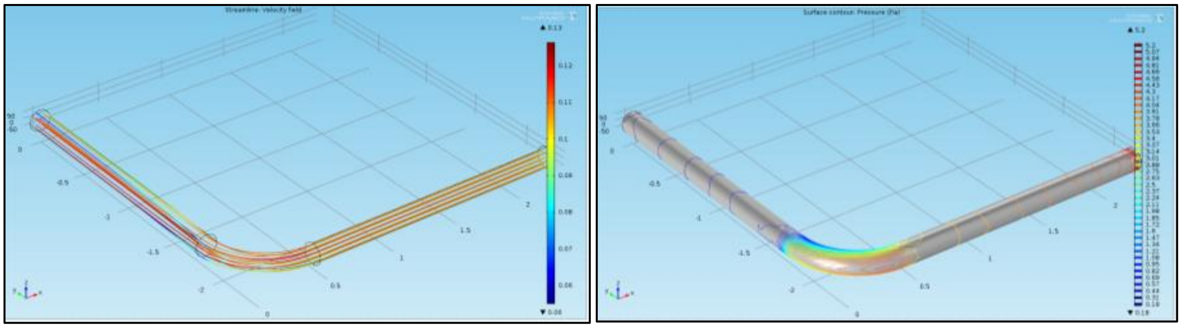


Figure 1-12. 3D elbow simulation results a) velocity distribution, b) pressure distribution.

Additionally, efforts were focused on applying the simulation tool to a practical application with complex geometry. A 3D CAD model of an instrumentation test loop at PNNL was generated in Soildworks and imported into COMSOL. A finite element mesh was generated for the CAD model using tetrahedral elements and the geometry and CAD model are shown in the following figure.

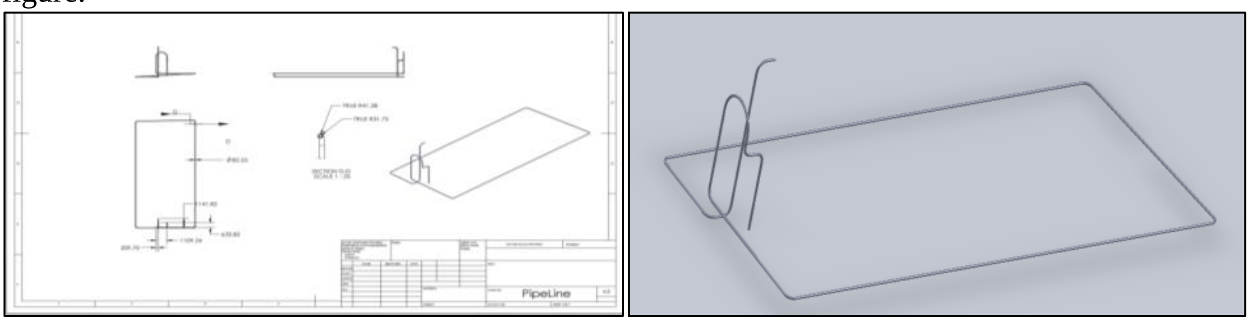


Figure 1-13. Geometry and CAD of PNNL test loop.

Currently, we are investigating the convergence of the model by conducting mesh refinement studies and we are also investigating the possibility of using high performance computing.

Task 17: Advanced Topics for HLW Mixing and Processing

<u>Task 17 Overview</u>

The objective of this task is to investigate advanced topics in HLW processing that could significantly improve nuclear waste handling activities in the coming years. These topics have been identified by the Hanford Site technology development group, or by national labs and academia, as future methods to simulate and/or process waste streams. The task will focus on long-term, high-yield/high-risk technologies and computer codes that show promise in improving the HLW processing mission at the Hanford Site.

More specifically, 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 PJM mixing performance. Focus will be given to turbulent fluid flow in nuclear waste tanks that exhibit non-Newtonian fluid characteristics. The results will provide the sites with mathematical modeling, validation, and testing of computer programs to support critical issues related to HLW retrieval and processing.

Task 17 Quarterly Progress

Subtask 17.1: Multiple-Relaxation-Time, Lattice Boltzmann Model for High-Density Ratio, Multiphase Flows

FIU Year 4 Carryover Work Scope

FIU implemented the algorithm in the 3D LBM MRT code to change the properties of the liquid phase modelled to be of non-Newtonian type in a gas-liquid multiphase system. The viscosity definition in LBM was modified to make the fluid behave in a way different than the linear Newtonian behaviour. Using the Generalized Newtonian Fluids representation an effective viscosity value, μ^{Eff}, was defined to obtain shear-thinning or shear-thickening fluids represented by the Power Law ($\mu_{PL}^{Eff} = \mu_P\,|\dot{\gamma}|^{n-1}$, where μ_P is the flow consistency coefficient and *n* is the Power-law index) or the Bingham plastics ($\mu_{BH}^{Eff} = \mu_B + (1 - e^{-m|\dot{\gamma}|})\frac{\tau_B}{|\dot{\gamma}|}$, where μ_B is the plastic viscosity, τ_B is the Bingham yield stress and *m* is the stress growth exponent).

First, the viscosity definition of the LBM was changed to make the dynamic viscosity a function of the shear rate, $\dot{\gamma} = 2\varepsilon$, where $\varepsilon_{\alpha\beta} = -\frac{1}{2\rho c_s^2 \delta t}\sum_{i=0}^{18}\boldsymbol{e}_{i\alpha}\boldsymbol{e}_{i\beta}\sum_{j=0}^{18}\hat{\Lambda}\left[f_j - f_j^{eq}\right]$ in 3D MRT LBM. The double dot product of the strain rate tensor, ε, gives the following:

$$\varepsilon:\varepsilon = tr\left\{\begin{pmatrix}\varepsilon_{11} & \varepsilon_{12} & \varepsilon_{13}\\ \varepsilon_{21} & \varepsilon_{22} & \varepsilon_{23}\\ \varepsilon_{31} & \varepsilon_{32} & \varepsilon_{33}\end{pmatrix}\begin{pmatrix}\varepsilon_{11} & \varepsilon_{12} & \varepsilon_{13}\\ \varepsilon_{21} & \varepsilon_{22} & \varepsilon_{23}\\ \varepsilon_{31} & \varepsilon_{32} & \varepsilon_{33}\end{pmatrix}\right\}$$

$$= tr\left\{\begin{matrix}\varepsilon_{11}^2 + \varepsilon_{12}\varepsilon_{21} + \varepsilon_{13}\varepsilon_{31} & \varepsilon_{11}\varepsilon_{12} + \varepsilon_{12}\varepsilon_{22} + \varepsilon_{13}\varepsilon_{32} & \varepsilon_{11}\varepsilon_{13} + \varepsilon_{12}\varepsilon_{23} + \varepsilon_{13}\varepsilon_{33}\\ \varepsilon_{21}\varepsilon_{11} + \varepsilon_{22}\varepsilon_{21} + \varepsilon_{23}\varepsilon_{31} & \varepsilon_{22}^2 + \varepsilon_{21}\varepsilon_{12} + \varepsilon_{23}\varepsilon_{32} & \varepsilon_{21}\varepsilon_{13} + \varepsilon_{22}\varepsilon_{23} + \varepsilon_{23}\varepsilon_{33}\\ \varepsilon_{31}\varepsilon_{11} + \varepsilon_{32}\varepsilon_{21} + \varepsilon_{33}\varepsilon_{31} & \varepsilon_{31}\varepsilon_{12} + \varepsilon_{32}\varepsilon_{22} + \varepsilon_{33}\varepsilon_{32} & \varepsilon_{31}\varepsilon_{13} + \varepsilon_{32}\varepsilon_{23} + \varepsilon_{33}^2\end{matrix}\right\}$$

$$= \varepsilon_{11}^2 + \varepsilon_{22}^2 + \varepsilon_{33}^2 + 2(\varepsilon_{12}\varepsilon_{21} + \varepsilon_{13}\varepsilon_{31} + \varepsilon_{23}\varepsilon_{32})$$

Using a D3Q19 lattice structure the components of the above calculation yields: $\mathcal{E}_{11}$ = 10, $\mathcal{E}_{12}$ = 0, $\mathcal{E}_{13}$ = 0, $\mathcal{E}_{23}$ = 0, $\mathcal{E}_{22}$ = 10, and $\mathcal{E}_{33}$ = 10.

This gives $|\dot{\gamma}| = \sqrt{2(\varepsilon_{11}^2 + \varepsilon_{22}^2 + \varepsilon_{33}^2 + 2(0))} = \sqrt{6\varepsilon_{11}^2} = \sqrt{6}\varepsilon_{11} = -\frac{1}{\rho c_s^2\delta t}5\sqrt{6}\sum_{j=0}^{18}\hat{\Lambda}[f_j - f_j^{eq}]$

The effective viscosity for Power-law fluids using the above definition of $|\dot{\gamma}|$ for the required fluid type becomes $\mu_{eff} = \mu_P|\dot{\gamma}|^{n-1}$. When *n<1* this relation results in a shear-thinning fluid, while for *n>1* we obtain a shear-thickening one and *n=0* corresponds to a Newtonian fluid. This effective viscosity definition gives us a shear stress definition for Power-law fluids as, $\mu = \mu_P|\dot{\gamma}|^{n-1}\dot{\gamma}$.

For the case of a Bingham plastic the definition for effective viscosity becomes $\mu_{eff} = \mu_B + \left(1 - e^{-m|\dot{\gamma}|}\right)\frac{\tau_B}{|\dot{\gamma}|}$. When τ_B*=0*, the Newtonian fluid is obtained. This effective viscosity definition results in the shear stress definition for Bingham plastics given as,

$$\begin{cases} \tau = \dfrac{\tau_B}{|\dot{\gamma}|} + \mu_B, & |\tau| > \tau_B, \\ \dot{\gamma} = 0, & |\tau| < \tau_B, \end{cases}$$

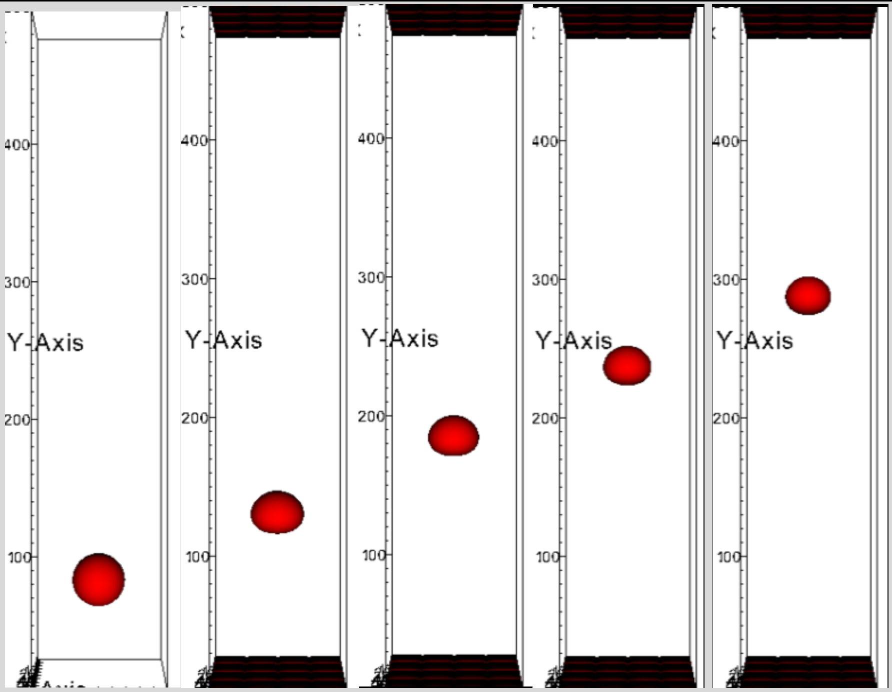
where τ_B is the Bingham yield stress.

The effective viscosity was related to the relaxation parameter using the definition of viscosity in Lee-Lin approach, $\mu_H = \rho_H \tau_H / 3$, where ρ_H is the density of the heavy fluid and τ_H is the relaxation parameter for the heavy fluid. If this is replaced in the equation for effective viscosity, we obtain:

$$\tau_{Eff} = \tau_H + \left(1 - e^{-m|\dot{\gamma}|}\right) \frac{3\tau_B}{\rho_H |\dot{\gamma}|}.$$

Once the relaxation parameter was calculated then the relaxation factor s_7 was obtained using the relation, $\tau = \left(\frac{1}{s_7}\right)$.

FIU also conducted 3D simulations using the LBM code for Newtonian and Non-Newtonian fluids. The test case was for a single bubble rising simulation. A circular bubble of diameter 40 lu is placed at rest at the bottom of the computational domain of size 100x500x100 in x,y and z dimensions, respectively. A gravitational acceleration was imposed in the negative y direction of magnitude 5×10^{-6} to create the buoyancy effect. The density ratio between the fluid and the gas phase was 10. Figure 1-14 shows the transition of the bubble shown in red during the rise. The bubble is seen to have an ellipsoid shape with a flatter bottom as expected. The same scenario was used to conduct a simulation of a bubble rise in a fluid that behaves as a Bingham plastic using the modified LBM code. Here, we change the viscosity definition for the surrounding fluid and make it depend on the shear rate induced by the buoyancy forces. The results were found to be identical with the Newtonian results; this is unexpected. The fluid properties imposed for the Bingham fluid was observed to create a difference in the 2D implementation of the LBM code; however, a similar effect was missing in the 3D implementation. FIU is currently investigating possible reasons.



T= 0 T=2000 T=4000 T=6000 T=8000

Figure 1-14. Bubble rising simulation in a Newtonian fluid.

Subtask 17.2: Computational Fluid Dynamics Modeling of HLW Processes in Waste Tanks

In order to gain experience with the Quasi- Direct Numerical Simulation capabilities (Q-DNS) of Star CCM+, a case study in a published work (Shams, et al. 2011) which performs Q-DNS of flow through a pipe using Star CCM+ will be replicated. The flow will have a Reynolds shear stress of 360 and the entire computational domain will use a polyhedral mesh in combination with a prism off-set layer to produce about 3.7 million grid points. Once the pipe flow simulation is executed, the velocity contours, mean velocity profiles, and their fluctuations in the principle direction will be compared to that of those shown in the published work. Accomplishing similar results will entail knowledge on the proper use of Q-DNS parameters in addition to basic meshing and simulation interface proficiency in Star CCM+.

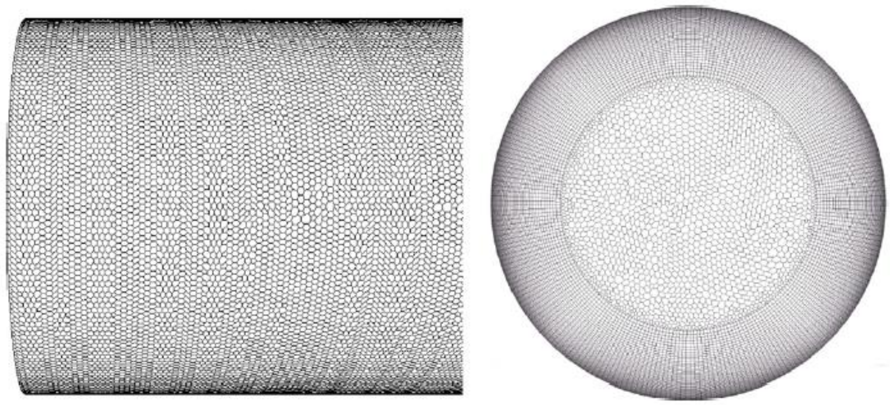


Figure 1-15. Target polyhedral mesh with prism off-set layer (Shams et al., 2011).

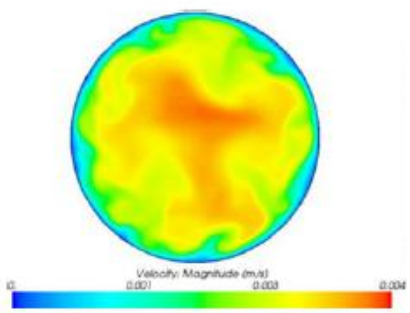


Figure 1-16. Target velocity field magnitude at mid cross section (Shams et al., 2011).

Reference: Shams, A., Roelofs, F., Komen, E.M.J., Baglietto, E., 2011. Optimization of a pebble bed configuration for quasi-direct numerical simulation. Nucl. Eng. Des. 242, 331–340.

FIU started utilizing the Star-CCM+ software for the analysis of turbulent flow of a Newtonian fluid through a pipe using the quasi-DNS method. The particular conditions of the test case are set by replicating the procedures given in Shams et al. (2012) where two DNS results, performed by J. G. M. Eggels (1993) and F. Unger and R. Friedrich (1993), for the same flow conditions were presented. Both DNS results are validated against a Digital Particle Image Velocimetry (DPIV) experiment performed by Westerweel et al. (1996). Below are the target flow properties:

Table 1-3. Mean Flow Quantities of the Simulations Being Replicated (1994, Eggels et al). [DNS(e) is performed by Eggels while DNS(u) is performed by F. Unger and R. Friedrich. DPIV lab experiment is performed by Westerweel (1996).]

	DNS(e)	DNS(u)	DPIV
$Re_c = (V_z)_c D/v$	6950	6950	7044
$Re_b = (V_z)_b D/v$	5300	5300	5327
$Re_* = \mu_* D/v$	360	360	362
$(V_z)_c/\mu_*$	19.31	19.29	19.43
$(V_z)_b/\mu_*$	14.73	14.74	14.70
$(V_z)_c/(V_z)_b$	1.31	1.31	1.32

The mesh characteristics of the pipe have been successfully created. A polyhedral mesh with prism offset layers was used on Star-CCM+ to obtain a total of 3 million grid points. The target of 3.7 million grid points will be achieved through further grid refinement. Below is a mesh comparison shown for the cross sections of the pipe.

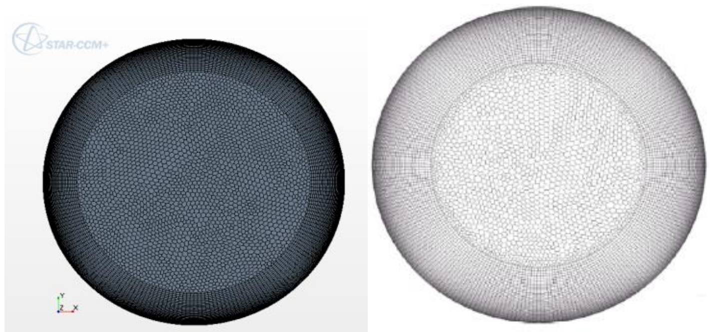


Figure 1-17. View of the mesh from front of the pipe: 3.7 million elements (left), 2.9 million elements (right).

In Figure 1-17, the mesh developed using STAR-CCM+ at FIU is shown on the left while the mesh on the right is the one created by Shams et al. (2012). The meshing quality has also been ascertained. Normalized values such as cell quality, face validity and volume change of our mesh greatly surpassed the minimum thresholds established by the STAR-CCM+ user's manual.

As described by Shams et al. (2012), the pipe was assigned a mass flow rate at the inlet of 0.165 kg/s and pressure outlet boundaries. A periodic interface was assigned for the inlet and outlet boundaries. The Sub-grid Viscosity Coefficient in LES parameters were set sufficiently low to enable Quasi-DNS capability in STAR-CCM+. Finally, a second order central scheme with 5% boundedness spatial discretization with a second order implicit scheme for time integration was set.

With the meshing and physics complete, the Q-DNS was performed. Figure 1-18 is a u+ vs Y+ profile comparison of our simulation against the DNS being replicated and the DPIV experiment:

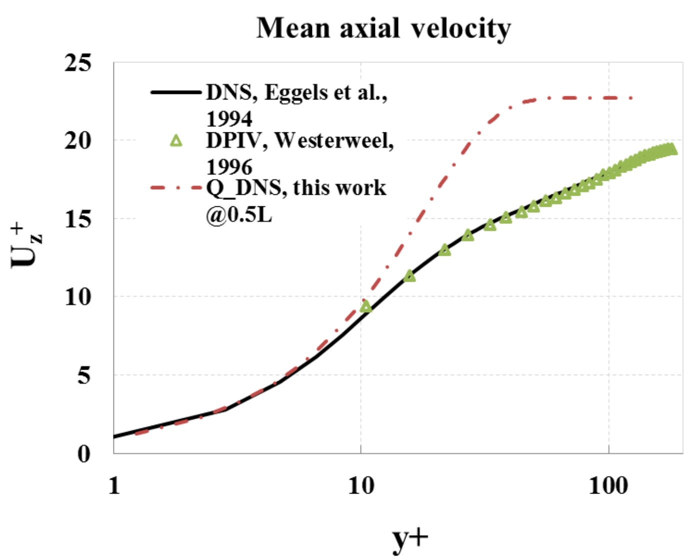


Figure 1-18. Mean axial velocity comparison for turbulent pipe flow.

Currently, FIU is conducting additional simulations to improve the agreement between the current results and the validation data for the u+ vs Y+ profiles. In the literature, small values of dynamic viscosity were recommended to avoid dampening initial values of turbulence intensities. Once the full turbulence is established in the domain, the viscosity can be increased to its original value. The Q-DNS performed used values of $\mu=1/18\mu_{real}$ and then increased it to 0.5 μ_{real}. This is a possible cause of the error seen on the u+ vs Y+ profile comparison. Original values of the viscosity must be used in order to match the physical characteristics of the flow. An insufficient number of grid points might also play a role on the error of the results obtained. Lastly, the wall treatment method is not mentioned in the works replicated; therefore, different wall treatments must be attempted. The wall treatment method used was an "All wall values" option, which is an advanced wall treatment scheme that blends the high and low wall functions. Refined simulation results will be presented for the next reporting period.

Task 18: Technology Development and Instrumentation Evaluation

<u>Task 18 Overview</u>

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, FIU is assisting in the evaluation of using a sonar (SLIM) developed at FIU for detecting residual waste in HLW tanks during pulse jet mixing (PJM). This effort would provide engineers with valuable information regarding the effectiveness of the mixing processes in the HLW tanks. Additionally, the Hanford Site has identified a need for developing inspection tools that provide feedback on the integrity of the primary tank bottom in DSTs. Recently, waste was found to be leaking from the bottom of the primary tank in AY-102. FIU will assist in the development of a technology to provide visual feedback of the tank bottom after traversing through the refractory pad underneath the primary tank.

Task 18 Quarterly Progress

FIU Year 4 Carryover Work Scope

Subtask 18.1: Evaluation of SLIM for Rapid Measurement of HLW Solids on Tank Bottoms

Previously, FIU carried out experimental tests of the 3-D sonar for its ability to image solids on the tank floor while solids are beings mixed (suspended) in a tank. Kaolin clay with a diameter of 1 micron is an excellent surrogate for the rheology and settling of solids in Hanford high-level radioactive waste tanks.

Testing was completed for 0%, 1% and 3% volume of Kaolin. Data was collected for both 30 degree and 60 degree swath arcs with scans taking 29 seconds and 42 seconds, respectively. There were two primary results of this testing: (1) the pump used is insufficient in power to keep all Kaolin suspended; and (2) the sonar experienced a major decrease in imaging quality with a major increase in "transmit breakthrough." It is normal for the sonar to have a small amount of transmit breakthrough near to the origin caused by the transmit pulse bouncing around in the sonar dome due to the impedance mismatch between the transducer/oil/PEEK/water interfaces. FIU is working with the sonar manufacturer to discover why there was a sudden, permanent increase in the level of the breakthrough during January testing.

FIU looked at various options for a bigger pump and possible reconfiguration of the nozzles to ensure suspension of up to 1000 pounds of Kaolin clay particles in the tank, including the purchase of a used or new pump or the use of a much larger pump already at FIU.

FIU also worked with the manufacturer, Marine Electronics, from the United Kingdom to assist in understanding and troubleshooting the system. Some of the initial troubleshooting included: 1) testing the electrical current within the electrical processing units in order to determine if the device is receiving accurate signals, and 2) testing of the electrical pins on the umbilical cord connecting the electrical processing unit to the remote commercial sonar head. FIU completed these diagnostic tests on the sonar; the result of diagnostic tests was that the sonar needs repairs and FIU shipped the system to the manufacturer. A 6-week delay is expected for repairs and shipping with mixing experiments now likely in May.

Due to the need for a larger mixing pump in the test set up, all sonar imaging tests during mixing will be redone with the new setup. The new experimental setup will include a bigger pump and a modified configuration of nozzles to ensure suspension of up to 1000 pounds of Kaolin clay particles in the tank.

FIU performed an initial study to analyze how powerful (horsepower) a pump was required to suspend up to 1000 pounds of Kaolin clay in the upcoming experiments. FIU has a 1 HP and a 1.5 HP pump and the 1.5 HP pump was selected for installation into the test tank. The shape and the orientation of the nozzles in the test tank are also being studied for improved mixing.

FIU has two 2-D sonars that were also built for deployment in a high-level radioactive waste environment. These sonars are from Imaginex, another manufacturer, and have not been used at FIU for 5 years. FIU staff and 1 student obtained the sonar imaging software from the manufacturer and read the manual and have begun to learn this new sonar graphic user interface (GUI) and imaging software. In upcoming months, FIU will be able to run the 2D sonar and test its performance in imaging Kaolin clay particles in mixing tanks with quick (20-30 seconds) scans. Past mixing tests with the 2D sonar always required several minutes for excellent images. These short scans will be the first such tests on this 2D sonar. If successful, then results from the 2D sonar for the current test tank and test matrix can be compared to that of the 3D sonar when it is tested in May 2015.

Subtask 18.2: Development of Inspection Tools for DST Primary Tanks

This task involves developing a miniature, motorized inspection tool with the capability of providing live video feedback. Its intended path of inspection is that of the cooling channels of tank AY-102, located at the Hanford Site. The engineers on-site have communicated several capabilities that the tool must possess in order to complete its task, and will provide regular feedback throughout the different design iterations.

A model of the inspection tool was designed, assembled and reported. Areas of potential performance improvement were observed; these areas are the basis of the following design, as seen in Figure 1-19. The previous generation employed 4 wheels, driven directly by the respective motors; whereas this generation proposes the use of 4 additional, free-rolling wheels. The addition of these wheels will help emulate a continuous track, improving the tool's stability and ability to overcome possible obstacles, such as debris due to tank corrosion. These additional wheels will also address structural stress created by a bending moment caused from the reaction forces on the wheels, effectively decreasing the stresses experienced by ~50%. Another modification made through this revision was shaving the hub of the wheels; in doing so, the total width of the tool was reduced by 2.6 mm (0.0394 in.), or 7.6%.

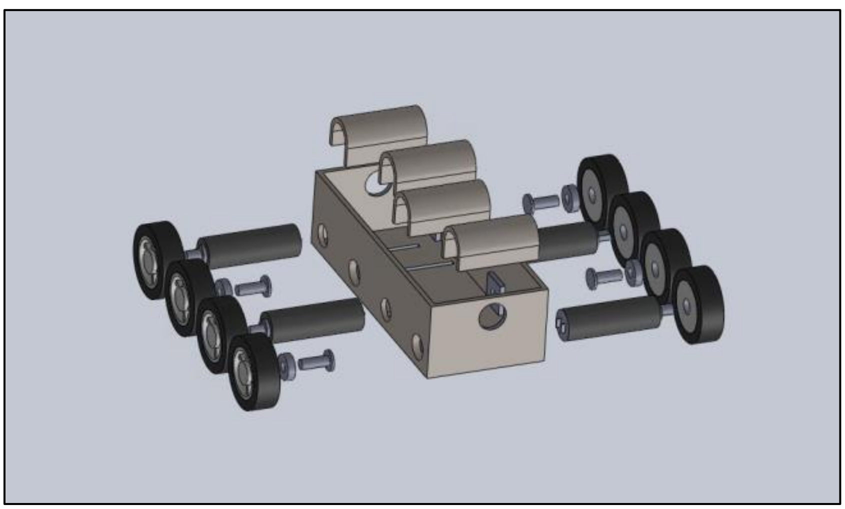


Figure 2-19. Exploded view of the revised design.

A few structural changes have also been incorporated into the design. The gap between the magnet and the surface is very small, allowing small objects to become wedged into the edge of the body and magnet. To overcome this possible problem, the bottom surface of the tool is now lofted, such that it is smoothly pitched from the edge of the body to the edge of the magnet. As seen in Figure 1-20, the structure of the body has also been modified to house the camera in preparation for a later generation in which protection from radiation will be required.

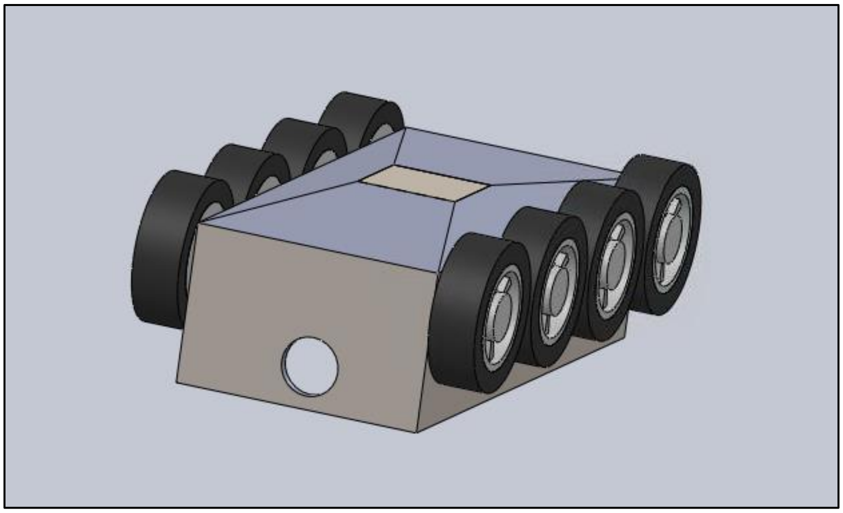


Figure 1-20. Underside view of the revised design.

During February, additional design modifications were made and were 3D printed. These modifications were a valuable change to the inspection tool; however, further modification was made in pursuit of a more robust design. The various 3D prints can be seen in Figure 1-24. The leftmost print is the previously proposed design; a couple observations were made, such as having weaker resistance to elastic deformation than expected, partly due to the body printing with a gap in the middle. The 3D printer was set up with a resolution of 0.007", making it incapable of printing a solid wall of such small width. We were able to print at its finest resolution, 0.005", by interchanging the printer tip, and the result of this change alone is the 3D print in the middle of Figure 1-21. The aforementioned change made a significant increase in the strength of the body, but further strengthening was pursued.

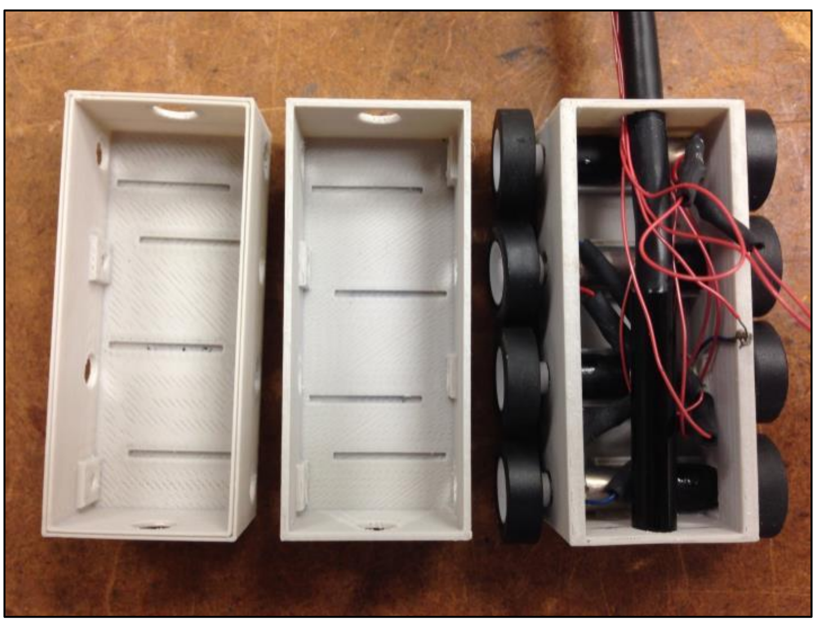


Figure 3-21. Side by side comparison of various design iterations.

The rightmost 3D print in Figure 1-21 is the result of increasing the body width by 1 mm, and redesigning the motor mount. The previous motor mount required ridges in the bottom, causing it to be weaker. As can be seen in Figure 1-22, the mount is now integrated into the body, increasing its strength, and increasing the clearance from above the motor. It was decided to attempt assembly of the most recent design iteration. All parts were a snug fit into the body and some preliminary testing was done to revise the practicality and functionality of the design.

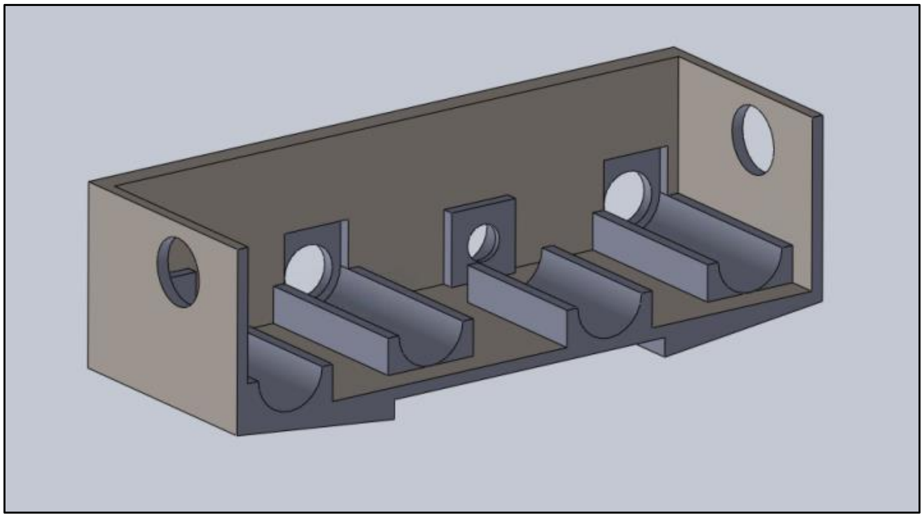


Figure 4-22. Section view of the most recent design iteration.

The preliminary testing of the inspection tool involved mounting the tool upside-down and stretching out the tether 17 feet (Figure 1-23). These conditions serve as an idea of what the inspection tool will face after traveling 17 feet down the first slot. The tool was able to pull the tether approximately 4 feet, while traveling upside down, with a starting drag force of 17 feet of tether. The tool did not fail after 4 feet, but simply ran out of space to travel. This preliminary test served the purpose of proving capability, and further testing will be conducted that will better simulate expected conditions. In the coming month, further testing will be conducted as well as investigating and acquiring test bed materials to closely emulate the cooling channel dimensions.

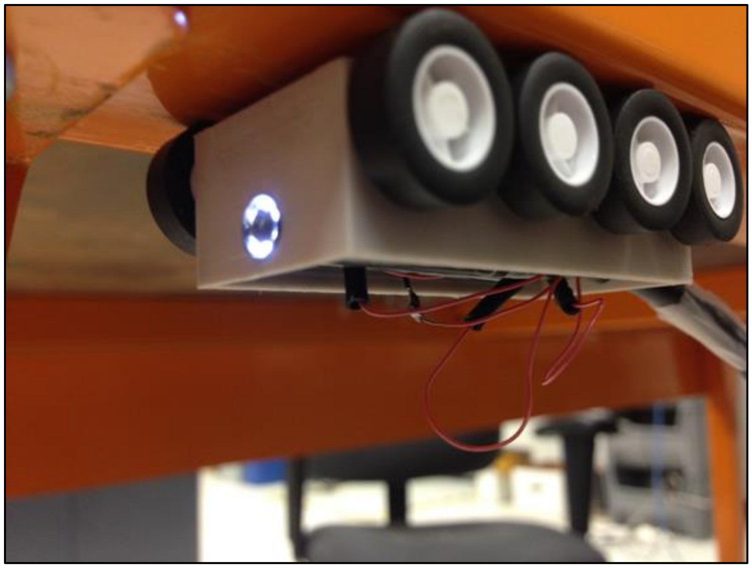


Figure 1-23. Inspection tool mounted upside down, video feedback on bottom-left.

During the feasibility test conducted, the tool produced enough power at 5 volts to travel inverted with a load due to 17ft of tether directly behind with an additional 13 ft after turning a corner. Further testing was conducted in March, focusing on the maximum force the inspection tool could produce. The purpose of this test is to verify the torque output of each motor and to test the maximum power out and traction force. The dimensions of the tool are the limiting factor and, consequently, the size of the motors available is highly constrained. This places a ceiling on the amount of torque available, making it a priority that the motors stall before the inspection tool loses traction. However, a magnet that is too strong will impose a large rolling resistance on the motors.

The testing conducted was a maximum force test on the tool with bare weight, as can be seen on the left of Figure 1-24, and with the weight of the camera and drag of 3 ft. of tether, as can be seen on the right of Figure 1-24. The results from the aforementioned testing can be seen in Table 1-4. The results show that the tool is capable of a very high power to weight ratio and, during testing, the motors were successfully stalled prior to traction loss using a 3.4 lb. magnet.

Figure 1-24. Maximum force testing of inspection tool.

Table 1-4. Maximum Force Values of Inspection Tool

	Bare weight	Camera and tether added
Inspection tool weight	16.8 gf	24.7 gf
Max. force – from start	213.4 gf	199.1 gf
Max. force – to stall	268.4 gf	254.1 gf
Power:weight – from start	12.7	8.1
Power:weight – to stall	16.0	10.3

An additional effort for this task is focusing on developing an inspection tool that can navigate and provide visual feedback through the 4” air supply pipe that leads to the tank central plenum of AY-102. The idea is to utilize lessons learned from previous devices created at FIU and apply the concepts to the new effort. For the initial design phase, two options are being explored:

- modifying the existing crawler developed by FIU, and
- developing a new crawler design

Modifying the existing crawler, designed for a 3” diameter pipe, would not require major modifications to the current design. As shown in Figure 1-25, the only necessary modification would be the redesign of the inflatables, located at both ends of the crawler, to grip 4” diameter pipe.

The drag force produced by the tether on the new inspection tool will be considerably lower, due to a shorter crawling distance and the absence of the unplugging water hose. A straightforward modification would be the usage of balloon type inflatables without any modifications to the current rims, as shown in Figure 1-25.

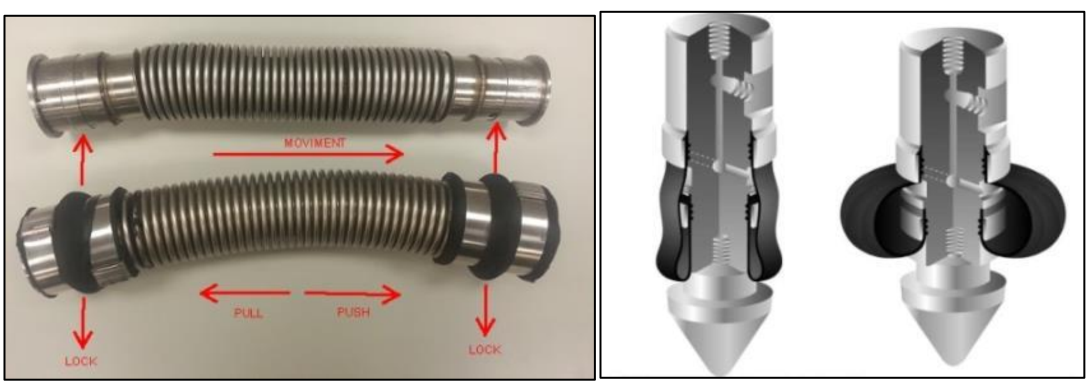


Figure 1-25. The existing crawler (left) and an example of a balloon type inflatable (right).

Also since the new inspection tool will be required to traverse through a dry environment with considerably lower radiation levels, the use of actuators instead of inflatables is being considered. FIU is currently investigating a gripping mechanism design that is capable of gripping on different pipe diameters, as show in Figure 1-26. Additionally, a crawler with a modular design is being considered, as illustrated in Figure 1-26.

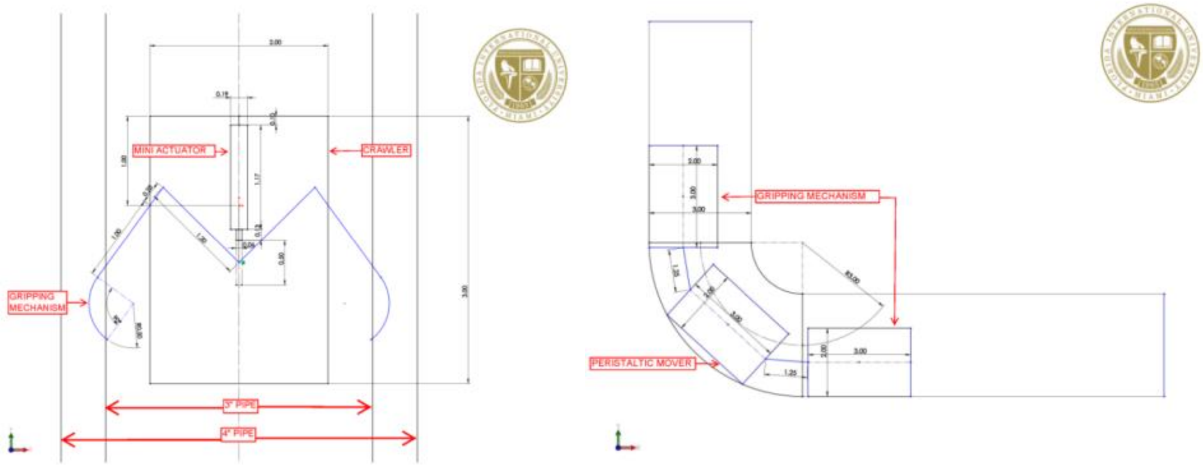


Figure 1-26. New gripping mechanism (left) and modular design (right) schematics.

During February, a new pipeline inspection tool was designed, considering the lessons learned from previous crawlers developed at FIU. As shown in Figure 1-27, the new conceptual design uses pneumatic actuators to emulate the peristaltic movement of the existing FIU crawler.

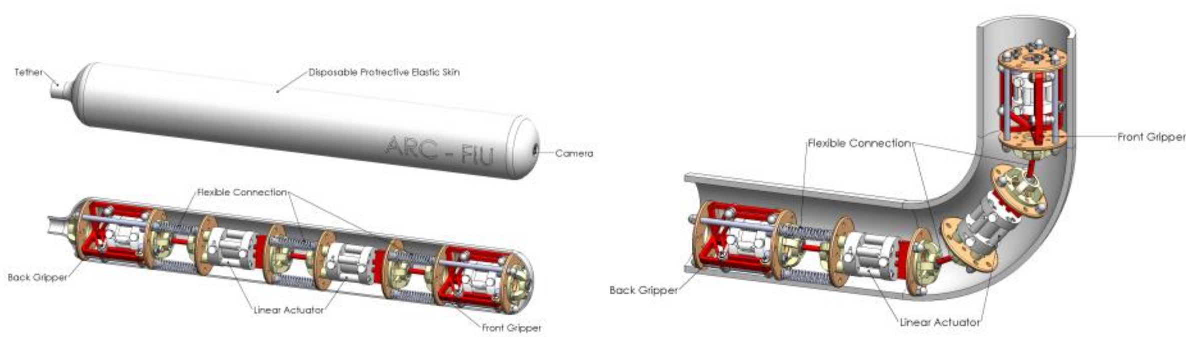


Figure 1-27. New conceptual design.

The main advantage of using a peristaltic locomotion in the design of inspection tools is that the device can crawl inside a pipeline without using any external moving parts, such as wheels and continuous tracks. Therefore, the device can be fully encapsulated with a disposable protective skin, which is suitable for decontamination in harsh environments and critical applications.

The new inspection tool has a modular design. The device is composed of interchangeable modules connected with flexible connections. The modular approach has the potential to be customized for specific tasks with the addition of extra modules; for instance, adding instrumentation, material sampling, and pipe repair.

As shown in Figure 1-28 as well, the new design is composed of linear actuators, which propel the device using gripping mechanisms located at both ends of the crawler.

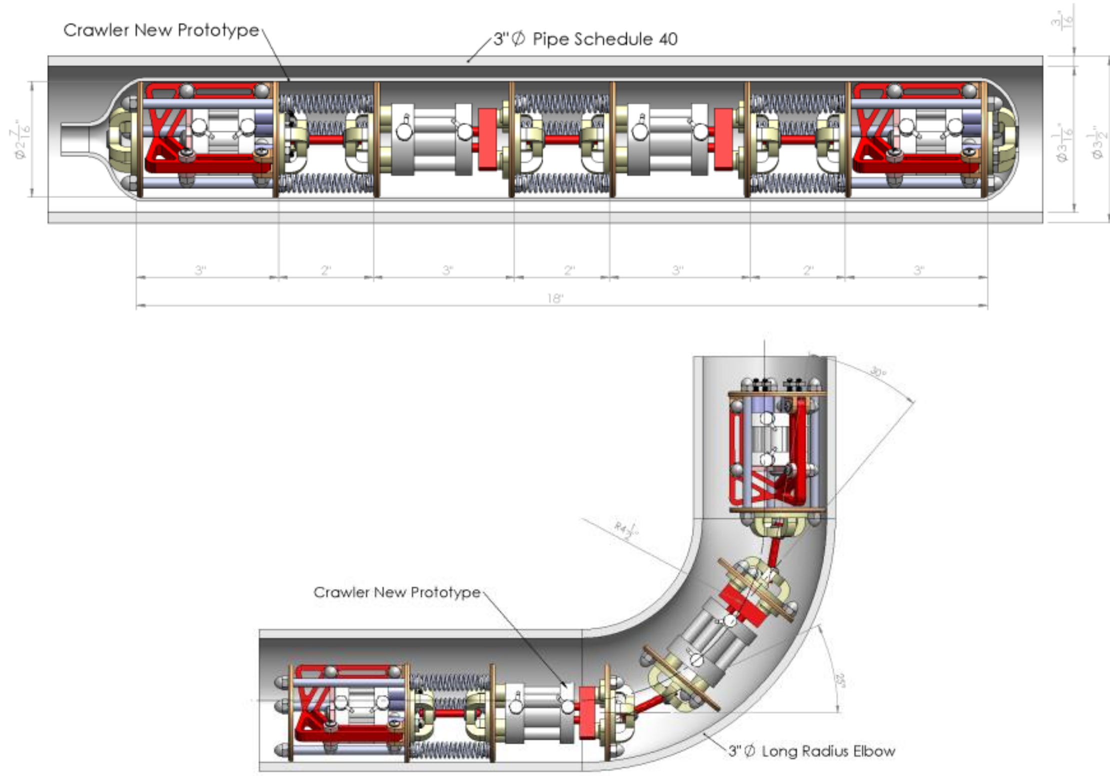


Figure 1-28. Inspection tool with modular design.

The gripping mechanism was designed to grip pipes with internal diameters varying from 3 to 4 inches, as illustrated in Figure 1-29. The mechanism was also designed to be self-locking, possibly allowing gripping forces greater than the one provided by the pneumatic actuator (40 lbs.). In that case, the actuator will only open and close the mechanism, the locking would be carried out by the body of the module. As a proof of concept, a gripping mechanism was 3D printed. The prototype is shown in Figure 1-30.

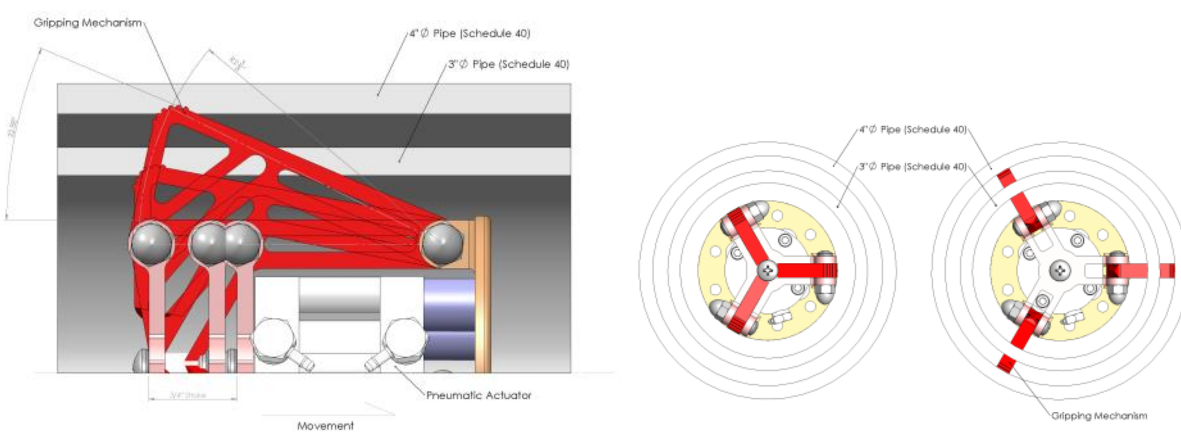


Figure 1-29. Rendering of designed gripping mechanism.

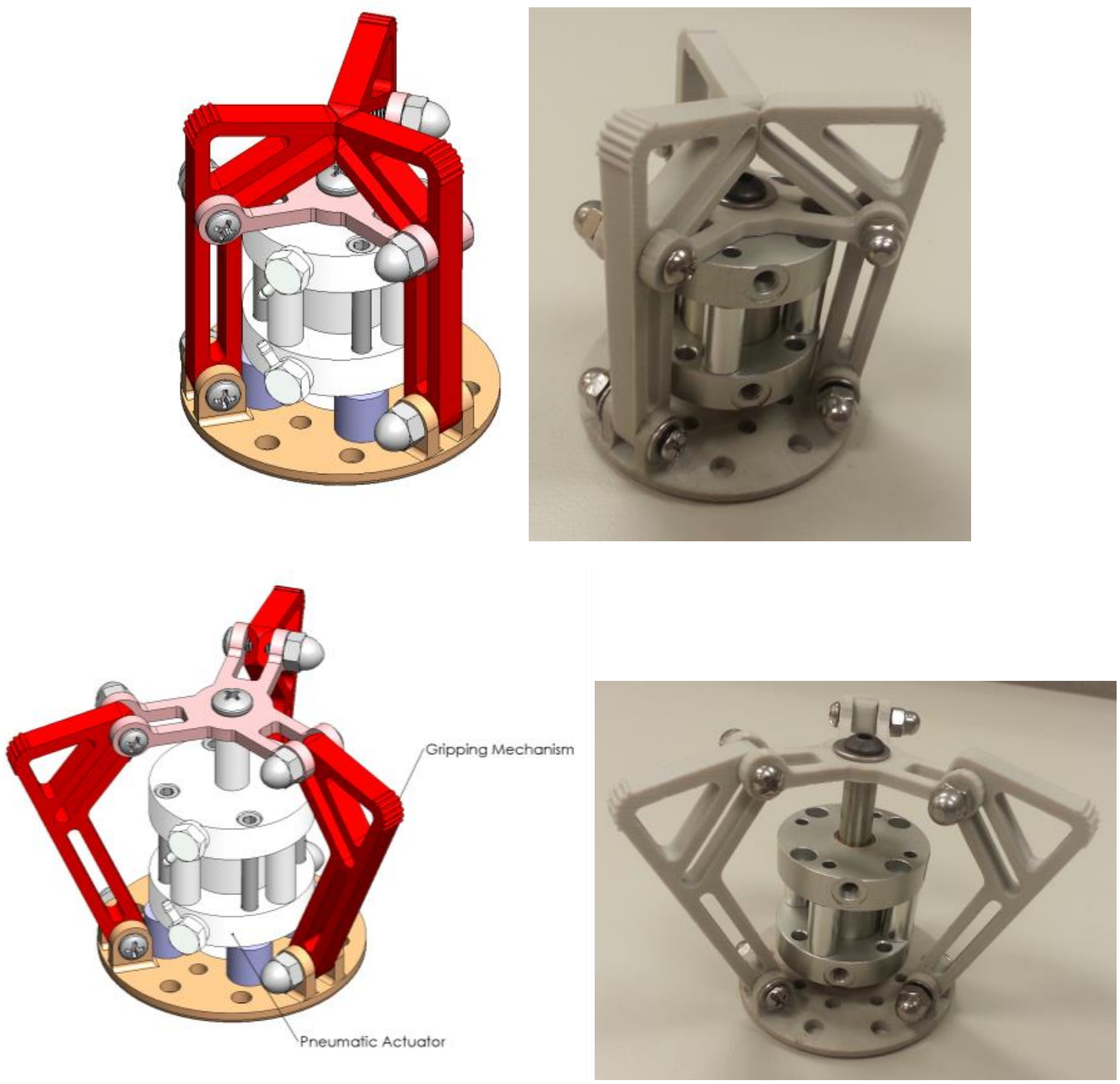


Figure 1-30. Designed gripping mechanism prototype.

Currently, a kinematics analysis of the gripping mechanism is being conducted to determine the maximum gripping forces and its relation with the pipe diameter. Also, an inter-module flexible connection design using ball joints and stabilizing compression strings are being investigated. The use of ball joints would provide a pivot point without losing compression or traction, which is ideal for straight runs and elbow turns.

Task 19: Pipeline Integrity and Analysis

<u>Task 19 Overview</u>

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. This includes primary piping, encasements, and jumpers. It has been recommended that at least 5% of the buried carbon steel

DSTs waste transfer line encasements be inspected. Data has been collected for a number of these system components, but the data still needs to be analyzed to determine effective erosion/corrosion rates so that a reliable life expectancy of these components can be obtained. 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

Engineers at Hanford provided FIU with real-time data of thickness measurements taken from components in the POR 104 Valve Pit. The results were found to be unreliable and it was hypothesized that the difficulty with the sensors was based on installation procedures. FIU has been asked to assist in the evaluation of the installation procedures of these sensors. Hanford engineers were able to provide a report to FIU detailing the mounting process for the sensors and possible options for use. It was determined that a new mounting system is needed to provide more consistent readings.

Operation specifications include:

1. Ability to permanently mount onto a 2-inch schedule 40 pipe (90° elbow and straight).
2. 100% duty cycle in a 200°F environment.
3. Measures to an accuracy of 0.001 inches.
4. Operates in a 50-250 rad/hour environment.
5. Preferably utilizes a dry couplant solution.

The system originally implemented by WRPS is Pipe Wrap™ manufactured by Sigma Transducers. This system includes a silicone substrate that has cables attached to the ultrasonic transducers (UT) embedded within and covered with a thin layer silicon serving as an acoustic couplant. The silicon is wrapped around the 2-inch schedule 40 pipe and held into place with a pipe clamp (Figure 1-31).

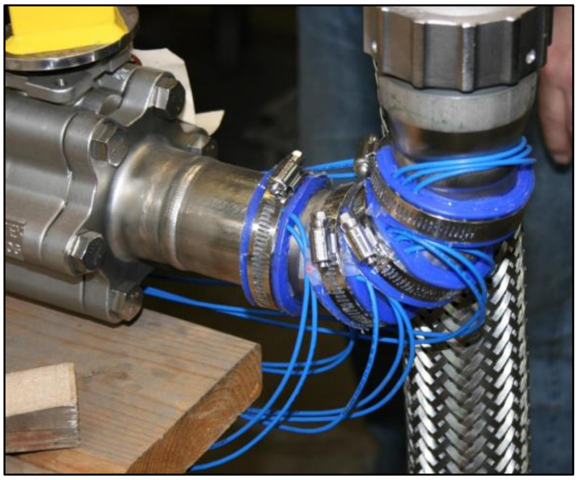


Figure 1-31. Installed Pipe Wrap™.

The Pipe Wrap™ system, although efficient, poses a few problems:

1. Excessive tightening of the pipe clamp could damage the UT
2. Contains loose cabling and exposed features
3. Cable leads may detach from the silicon through excessive compressive force
4. Pipe clamps could damage the silicon
5. Pipe clamp makes it difficult to fine tune the pressure on individual UT
6. Future degradation due to environmental conditions

In an effort to explore other options available, WRPS contacted several manufacturers to determine if any other viable options exist. ClampOn® offers a system that attaches the UT by a metallic band to the pipe and encloses it with another metallic case. However, ClampOn® only offers this product for a pipe with a minimum diameter of 3 inches. It should be noted that this technology uses acoustically guided lambda waves.

Sigma Transducers was also contacted regarding the installation issue. Sigma was open to working with WRPS to tailor the Pipe Wrap™ system to their specific needs.

Another option available is an ultrasonic system by Olympus. A report supplied by WRPS indicated that implementation of these UT along with a custom mechanical frame for mounting onto a 2-inch pipe would be optimal. A conceptual solution was modeled to demonstrate the possible features of a custom made alternative. Manufacturing of the transducer support cage may prove to be difficult due to the complexity of the structure.

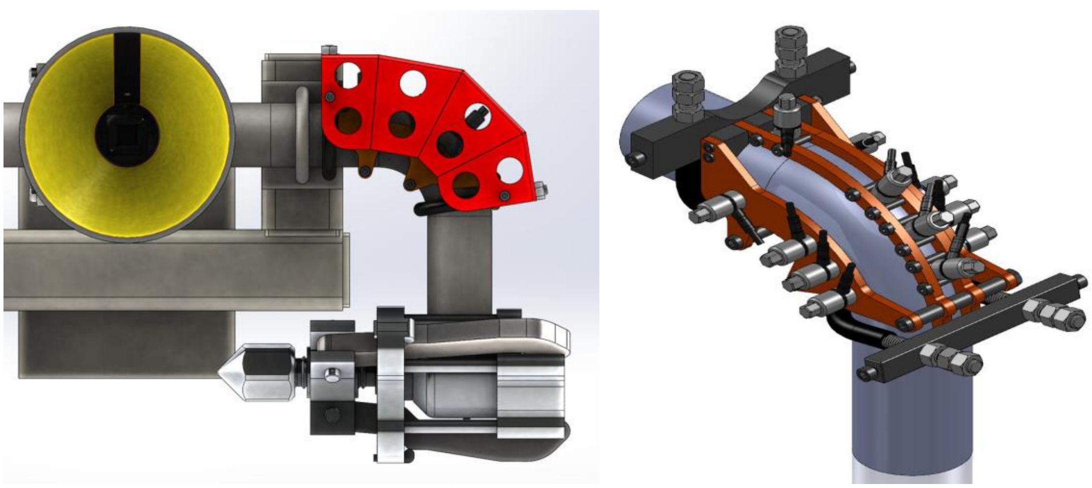


Figure 1-32. Rendering of proposed support structure for the ultrasonic transducers.

FIU continued to investigate the use of ultrasonic transducers used for measuring the thickness of pipes in real time. FIU spoke with vendors and had discussions that indicate other models from the manufacturer might be better suited for our applications. We will discuss this issue with Hanford engineers and decide on a path forward. We also have become more familiar with the issues that need to be resolved including choice of couplant and adhesive for affixing the transducer to the pipe. Selection of these materials is important in terms of maximizing the quality of the measurement.

During this period of performance, FIU prepared a presentation and gave an oral presentation at the Waste Management Conference in March, providing an overview of thickness measurements obtained from the 241-SY, AW and AP Farms, 242-A Evaporator Pump Room, the 241-AW02E Pit and the POR104 Valve Box. DOE Fellow Brian Castillo also prepared a student poster presentation based on this research that was presented during the Waste Management Symposia (Figure 1-33). The information was also presented during the DOE EM research review of FIU's cooperative agreement.

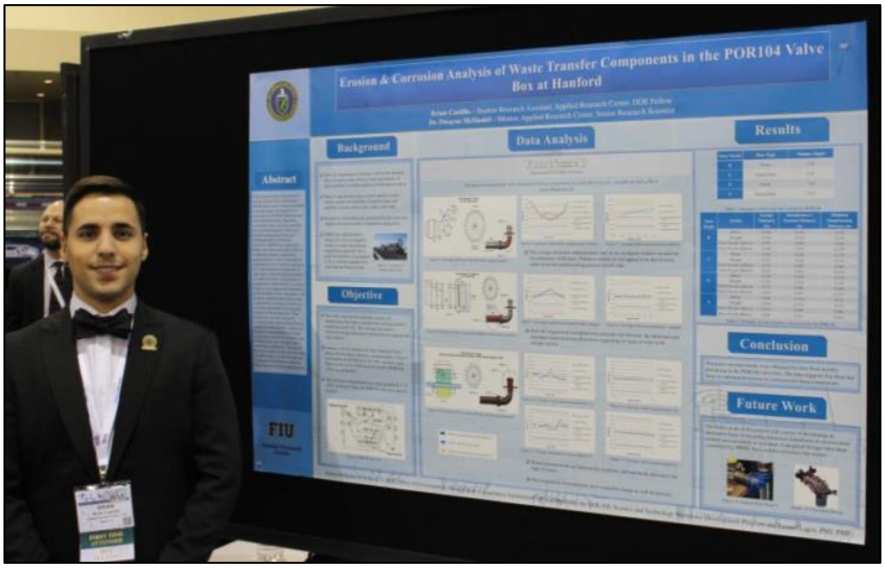


Figure 1-33. DOE Fellow Brian Castillo at Waste Management.

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

The purpose of this task is to support the integrity assessment of hose-in-hose transfer lines (HIHTL) and Teflon gaskets to improve the existing technical basis. This work has been focused on component selection of the aging flow loop. After a conference call with site personnel, it was decided that a high flow rate was not required in the aging flow loop. Pumps are being selected that will provide a flow rate that is enough to maintain the caustic solution circulating through the test specimens. In addition, FIU reviewed the vendor quotes from MTS, Instron and Test Resources for the tensile testing machine to be used for testing the material properties of the samples. The quotes are based upon a dual column configuration and the peripherals for testing plastics and rubber materials. FIU completed a purchase request to obtain an MTS machine that will be used to measure the material properties of baseline and aged materials. These properties will be used to determine the level of degradation of the aged materials.

Hanford engineers have identified an inner hose sample that can potentially be used in our testing. The hose is 2 inches in diameter and 864 inches in length but does contain some kinks. It was set aside after being kinked during testing in the MARS system. This should provide FIU with a sufficient amount of hose to manufacture 3-foot sample sections.

FIU presented this task during the DOE EM research review of FIU's cooperative agreement. Below is a flow diagram of the test loop that has been proposed for in-service configuration aging. Three loops will be created, each with a different operating temperature. Three specimens will be tested for each parameter set including time of exposure (90, 180 and 365 days).

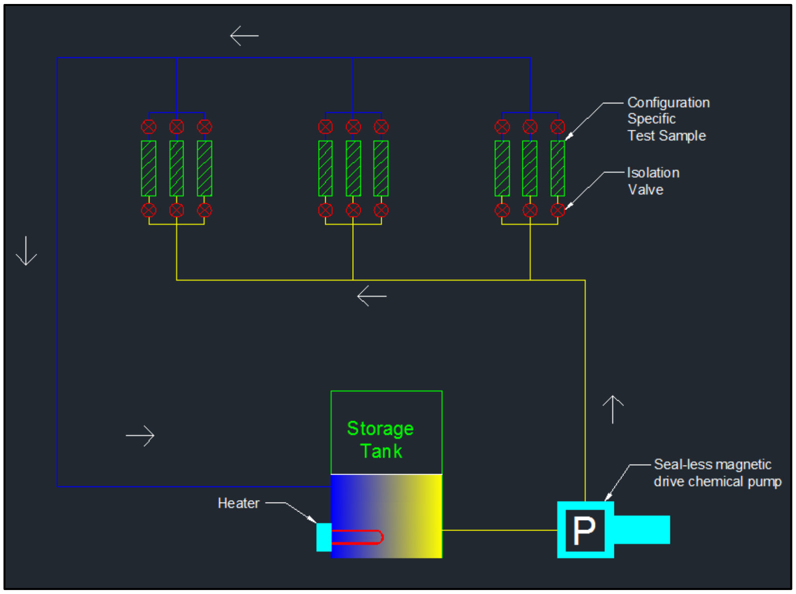


Figure 1-34. Aging test loop for in-service configurations.

Milestones and Deliverables

The milestones and deliverables for Project 1 for FIU Year 5 are shown on the following table. FIU is currently in discussions with DOE-EM to determine how best to reforecast current and future deliverables.

FIU Year 5 Milestones and Deliverables for Project 1

Task	Milestone/ Deliverable	Description	Due Date	Status	OSTI
Task 2: Pipeline Unplugging	2014-P1-M2.2.1	Complete 2D multi-physics simulations evaluating the influence of piping components on the plug formation process	03/02/15	To be Reforecast	
	Deliverable	Draft summary report for subtask 2.2.1	04/01/15	To be Reforecast	OSTI
Task 17: Advanced Topics for Mixing Processes	2014-P1-M17.2.1	Complete computational fluid dynamics modeling of jet penetration in non-Newtonian fluids	05/11/15	On target	
	Deliverable	Draft topical report for subtask 17.2.1	05/15/15	On target	OSTI
Task 18: Technology Development and Instrumentation Evaluation	2014-P1-M18.2.1	Complete development of first prototype of the inspection tool	12/19/14	Complete	
	Deliverable	Draft summary report for first prototype (subtask 18.2.1)	01/30/15	To be Reforecast	OSTI
	2014-P1-M18.1.1	Complete pilot-scale testing of SLIM to assess imaging speed and ability to estimate volume of solids on tank bottom during mixing operations	02/20/15	To be Reforecast	
	Deliverable	Draft summary report of pilot scale testing of SLIM (subtask 18.1.1)	03/13/15	To be Reforecast	OSTI
	2014-P1-M18.2.2	Complete analysis design and	03/20/15	To be	

		modifications to the peristaltic crawler		Reforecast	
	Deliverable	Final Deployment Test Plan and Functional Requirements for SLIM (subtask 18.1.2)	05/15/15	To be Reforecast	
Task 19: Pipeline Integrity and Analysis	2014-P1-M19.2.1	Complete test plan for the evaluation of nonmetallic components	11/14/14	Complete	
	Deliverable	Draft experimental test plan for subtask 19.2.1	11/14/14	Complete	OSTI
	2014-P1-M19.1.1	Complete data analysis of the C-Farm POR 104 Valve Box	05/01/15	On target	
	Deliverable	Draft summary report for subtask 19.1.1	05/01/15	On target	OSTI

Work Plan for Next Quarter

- Project-wide:
    - Draft the Year End Report for FIU Year 5 (May 2014 to May 2015).
- Task 2:
    - For the APS, data analysis from the unplugging testing will continue. General data trends will be determined and a year-end report will be written.
    - For the peristaltic crawler, a new clamp system adaptable to the existing crawler will be designed using finite element modeling. Additionally, a bladder type inflatable will be investigated as an alternate solution. A fatigue test apparatus is being built, and will be able to stress test the crawler's cavities under cyclic loading. The test will simulate the peristaltic movement of the crawler under controlled conditions dragging a long tether. Fatigue testing will be conducted on the actual clamps and the redesigned gripper, and improvements in the design will be quantified.
    - Schematics for the PNNL test loop have been provided and FIU has started the process of developing solid works modules to incorporate into Comsol. During the next quarter, we will complete the 2D simulations, ultimately showing the effects of geometry on plug formation. If possible, this will be validated against experimental data.
- Task 17:
    - FIU will use STARCCM+ to run DNS and RANS simulation cases of a pipe flow with different Reynolds numbers. An H-B viscosity model will be utilized in the simulations. Results of the RANS will be compared with DNS in terms of shear rate at small scales. From the DNS results, a more precise viscosity model based on shear rate is expected to be obtained. We will then implement the modified viscosity model in a second set of RANS simulations for the same flow conditions and compare with published data.
- Task 18:
    - For the SLIM subtask, the pump and the flow design for the experimental setup was modified from experiments in January to ensure that solids at 1-20% vol. of

Kaolin clay particles will remain suspended and not settle on the floor during mixing. Calculations and empirical tests will be performed in May to confirm that the pump flow field is over designed for the mixing and suspension. The 3D sonar at FIU was sent for repairs to the manufacturer in late February. The sonar will be repaired in April and sent back to FIU by early May. Final experiments of mixing kaolin clay up to 20% by volume will be completed by the end of May.

- The inspection tool being designed to travel through the refractory cooling channels will be tested through a full scale test bed built to accurately simulate the cooling channel dimensions and tether drag force that is expected. Kaolin 2200 will be used in the test bed to simulate the drag forces created by the refractory pad. The full scale test bed will also aid in making design modifications necessary to navigate through a 90-degree turn.
- The designed grip mechanism will be tested under several conditions that include various pipe and fittings configurations. If necessary, the mechanism will be redesigned to maximize gripping forces and durability. Also other gripping methods using inflatables and electromagnets will be investigated as alternative possibilities. A full prototype of the new proposed design is being built, and the pneumatic controls will also be incorporated to the device. Functional tests will be conducted and the inspection tool will be tested under controlled conditions.

- Task 19:
  - FIU will determine optimal sensors for the application in HLW lines. Sensors will be procured and design concepts will be explored with the intention of permanently mounting the sensors on pipelines.
  - For the non-metallic materials task, FIU will acquire a hose-in-hose sample which will allow for the design of the fittings that will attach to the samples. This design selection is critical as we need to avoid premature failure at the fittings. Additionally, the design and assembly of the test loop should be completed.

Project 2
Rapid Deployment of Engineered Solutions to Environmental Problems

Project Manager: Dr. Leonel E. Lagos

Project Description

In FIU Year 5, Project 2 includes three tasks. Each task is comprised of subtasks that are being conducted in close collaboration with Hanford and SRS site scientists. FIU ARC continues to provide research support on uranium contamination and remediation at the Hanford Site with subtasks under Task 1 and Task 3 as well as conducted remediation research and technical support for SRS under Task 2. The following tasks are included in FIU Year 5:

- Task 1: Sequestering Uranium at the Hanford 200 Area Vadose Zone by *in situ* Subsurface pH Manipulation using NH_3 Gas
    - Subtask 1.1 – Sequestering Uranium at the Hanford 200 Area Vadose Zone by in situ Subsurface pH Manipulation using NH3 Gas
    - Subtask 1.2 – Investigation on Microbial-meta-autunite Interactions – Effect of Bicarbonate and Calcium Ions
- Task 2: Remediation Research and Technical Support for the Savannah River Site
    - Subtask 2.1 – FIU Support for Groundwater Remediation at SRS F/H Area
    - Subtask 2.2 – Monitoring of U(VI) Bioreduction after ARCADIS Demonstration at F-Area
    - Subtask 2.3 - Sorption Properties of the Humate Injected into the Subsurface System
- Task 3: Evaluation of Ammonia Fate and Biological Contributions during and after Ammonia Injection for Uranium Treatment
    - Subtask 3.1 – Investigation on NH3 Partitioning in Bicarbonate-Bearing Media
    - Subtask 3.2 – Bacteria Community Transformations before and after NH_3 Additions

Subtask 1.1: Sequestering Uranium at the Hanford 200 Area by *In Situ* Subsurface pH Manipulation using Ammonia (NH_3) Gas Injection

<u>Subtask 1.1 Overview</u>

The objective of Subtask 1.1 is to evaluate the stability of U-bearing precipitates created after NH3 (5% NH3 in 95% nitrogen) pH manipulation in the synthetic solutions mimicking conditions found in the vadose zone at the Hanford Site 200 Area. The study will examine the deliquescence behavior of formed uranium-bearing solid phases via isopiestic measurements and investigate the effect of environmental factors relevant to the Hanford vadose zone on the solubility of solid phases. Solubility experiments will be conducted at different temperatures up to $50^{o}C$ using multicomponent samples prepared with various bicarbonate and calcium ion concentrations. In addition, studies will continue to analyze mineralogical and morphological characteristics of precipitates by means of XRD and SEM-EDS. An additional set of samples will be prepared with the intention of minimizing nitratine (NaNO3) formation in order to lessen the obtrusive peaks that shadowed the peaks of the less plentiful components found in the sample XRD patterns.

Subtask 1.1 Quarterly Progress

FIU Year 4 Carryover Work Scope

During the month of January, a new measurement from the isopiestic chamber was taken after adding 50 ul of pure water to the standard samples. Water activities and osmotic coefficient measurements were calculated for the multicomponent precipitates and standard samples using the previous equations already reported. The obtained value had a similar trend as previous data for the standard and multicomponent precipitates samples. $CaCl_2$ had an increase in the water activities, from 0.840 to 0.848; however, the osmotic coefficients slightly decreased from 1.458 to 1.429. Similarly, LiCl water activity increased from 0.832 to 0.834. However, the osmotic coefficient showed an incremental increase from 1.430 to 1.458. Table 2-1 and Table 2-2 display the new values for water activities and osmotic coefficients for $CaCl_2$ and LiCl (highlighted in yellow) and graphical representations are presented in Figure 2-1 and Figure 2-2. Results with both standards suggested that multicomponent precipitate mixtures containing Na_2SiO_3, Al $(NO_3)_3$, $KHCO_3$, and $CaCl_2$ will deliquescence at relative humidity greater than 81% at a temperature of 25^{o}C.

The results presented in Table 2-1 and Table 2-2 as well as Figure 2-1 and Figure 2-2 complete the FIU Year 4 carryover scope of work to investigate the deliquescence behavior of uranium-free multicomponent samples.

Table 2-1. Values for Water Activities, a_w, and Osmotic Coefficients, Ø, for $CaCl_2$ and Multicomponent Samples

a_w $CaCl_2$	Na_2SiO_3+ $Al(NO_3)_3$+ KHCO3 (3mM)	Na_2SiO_3+ $Al(NO_3)_3$+ $KHCO_3$ (50mM)	Na2SiO3+ $Al(NO_3)_3$+ $KHCO_3$* (3mM) + $CaCl_2$ (5mM)	Na_2SiO_3+ $Al(NO_3)_3$+ $KHCO_3$* (50mM) + $CaCl_2$ (5mM)	Na_2SiO_3+ $Al(NO_3)_3$+ $KHCO_3$* (3mM) + $CaCl_2$ (10mM)	Na_2SiO_3+ $Al(NO_3)_3$+ $KHCO_3$* (50mM) + $CaCl_2$ (10mM)	Ø $CaCl_2$
0.755	1.519	1.795	3.685	2.519	2.863	3.004	1.755
0.787	1.498	1.856	3.469	2.47	2.754	2.958	1.648
0.786	1.485	1.82	3.499	2.462	2.803	2.961	1.652
0.798	1.436	1.861	3.424	2.426	2.727	2.929	1.607
0.8	1.303	1.755	3.336	2.331	2.643	2.902	1.602
0.808	1.319	1.803	3.199	2.341	2.585	2.951	1.573
0.808	1.3	1.814	2.47	2.229	2.489	2.881	1.575
0.811	1.259	1.811	1.852	2.235	2.428	2.91	1.564
0.825	1.38	2.05	1.953	2.407	2.592	3.141	1.515
0.834	1.475	2.405	2.084	2.77	2.819	3.566	1.483
0.84	1.587	2.645	2.192	3.029	2.978	3.894	1.458
0.848	1.682	2.985	2.266	3.377	3.193	4.328	1.429

Table 2-2. Values for Water Activities, a_w, and Osmotic Coefficients, Ø, for LiCl and Multicomponent Samples

a_w LiCl	Na_2SiO_3+ $Al(NO_3)_3$+ (3mM) $KHCO_3$	Na2SiO_3+ $Al(NO_3)_3$+ (50mM) $KHCO_3$	Na2SiO_3+ $Al(NO_3)_3$+ (3mM) $KHCO_3$+ (5mM)Ca Cl_2	Na2SiO_3+ $Al(NO_3)_3$+ (50mM) $KHCO_3$+ (5mM)Ca Cl_2	Na2SiO_3+ $Al(NO_3)_3$+ (3mM) $KHCO_3$+ (10mM)Ca Cl_2	Na2SiO_3+ $Al(NO_3)_3$+ (50mM) $KHCO_3$+ (10mM)Ca Cl_2	Ø LiCl
0.735	1.668	1.972	4.048	2.768	3.146	3.301	1.695
0.768	1.651	2.045	3.822	2.721	3.034	3.259	1.596
0.768	1.621	1.987	3.82	2.688	3.06	3.233	1.601
0.795	1.466	1.901	3.497	2.478	2.786	2.991	1.465
0.795	1.33	1.792	3.408	2.381	2.7	2.964	1.47
0.798	1.347	1.841	3.268	2.392	2.64	3.015	1.493
0.799	1.328	1.853	2.523	2.277	2.542	2.943	1.502
0.8	1.286	1.85	1.892	2.282	2.48	2.973	1.509
0.824	1.409	2.094	1.995	2.459	2.648	3.209	1.379
0.829	1.507	2.457	2.129	2.83	2.879	3.643	1.41
0.832	1.621	2.702	2.239	3.094	3.041	3.978	1.43
0.834	1.718	3.049	2.315	3.449	3.262	4.421	1.458

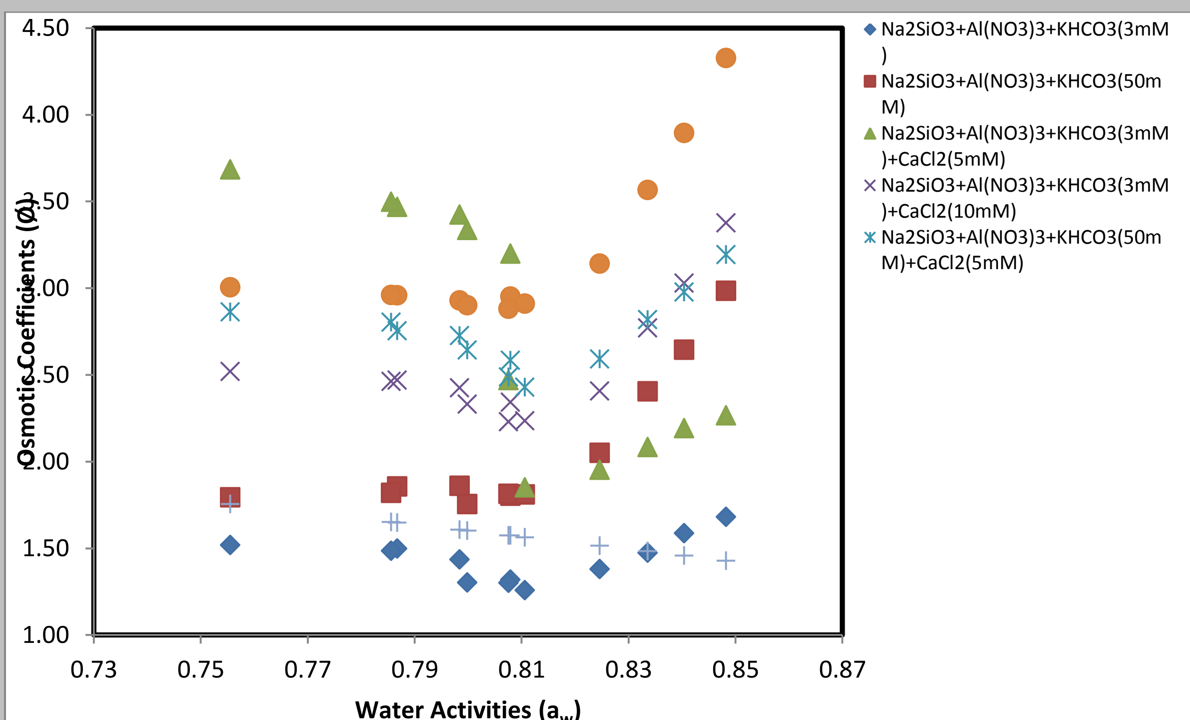


Figure 2-1. Osmotic coefficient for multicomponent samples as a function of water activities, a_w, using $CaCl_2$ as a standard.

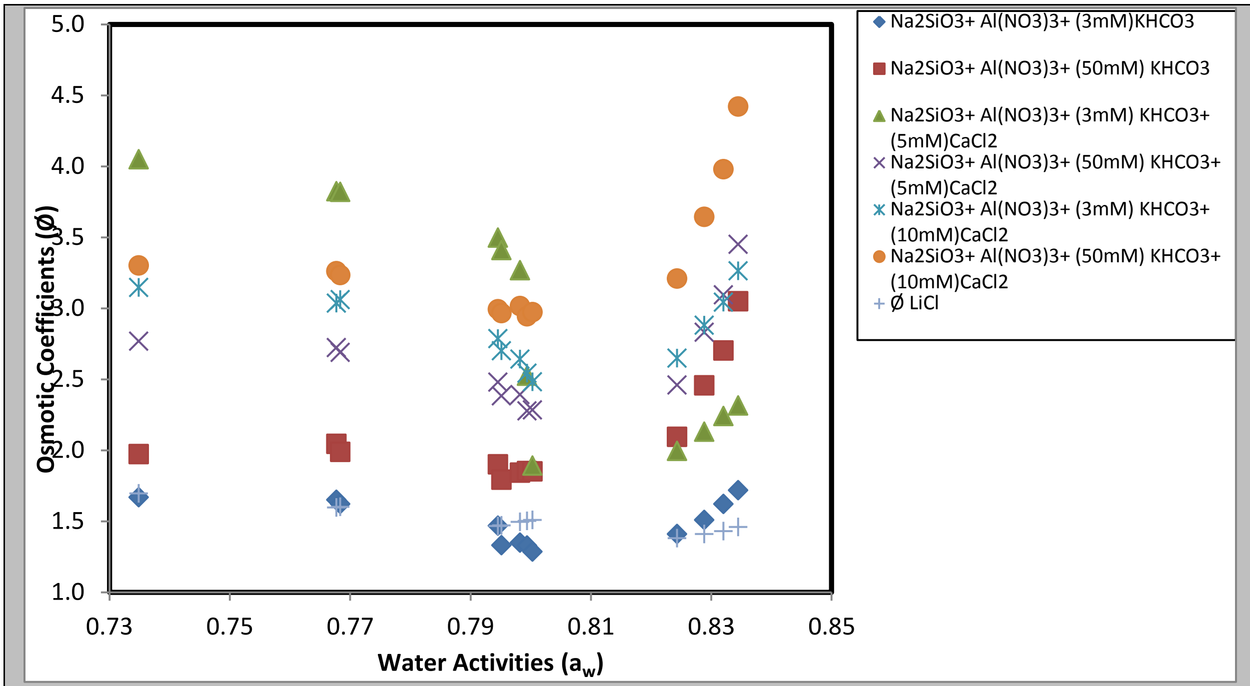


Figure 2-2. Osmotic coefficient for multicomponent samples as a function of water activities, a_w, using LiCl as a standard

FIU started preparations for the next round of experiments using the isopiestic chamber in January. It is expected that lowering the chamber's head space would help to reach equilibrium faster. A drawing for a new isopiestic chamber that is being fabricated in the FIU-ARC machine shop is shown in Figure 2-3.

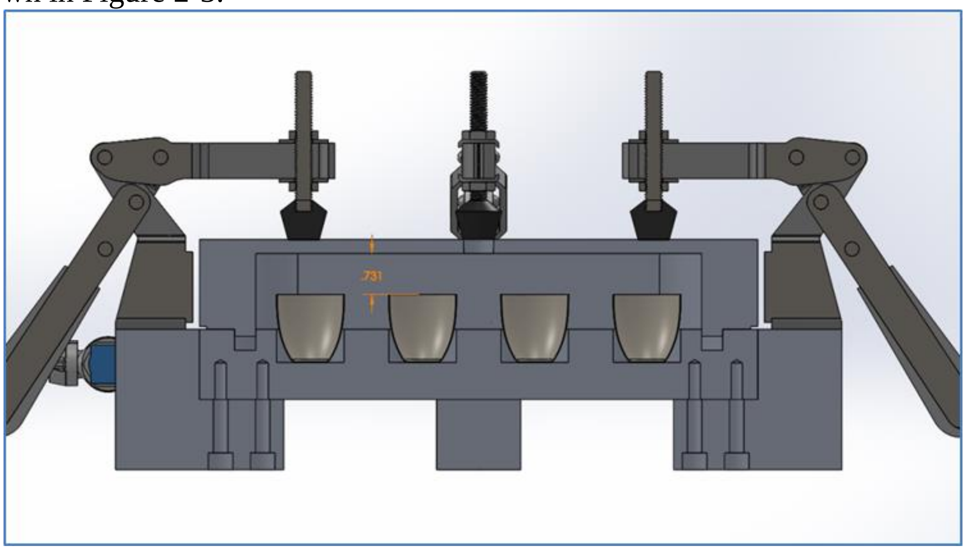


Figure 2-3. A drawing of a new isopiestic chamber being fabricated in the FIU-ARC machine shop.

- The characterization of the solid uranium-phases formed after treatment of a synthetic pore water solution with NH_3 gas has continued using the X-ray diffraction (XRD). Two samples were analyzed for XRD analysis:Sample 1 was combined with 50 mM of $Na_2SiO_3.9H_2O$, 5 mM of $Al(NO_3)_3.9H_2O$, 3 mM of $KHCO_3$, and 10 mM of $CaCl_2$

- Sample 2 was combined with 50 mM of $Na_2SiO_3.9H_2O$, 5 mM of $Al(NO_3)_3.9H_2O$, 3 mM of $KHCO_3$, and 5 mM of $CaCl_{2.}$

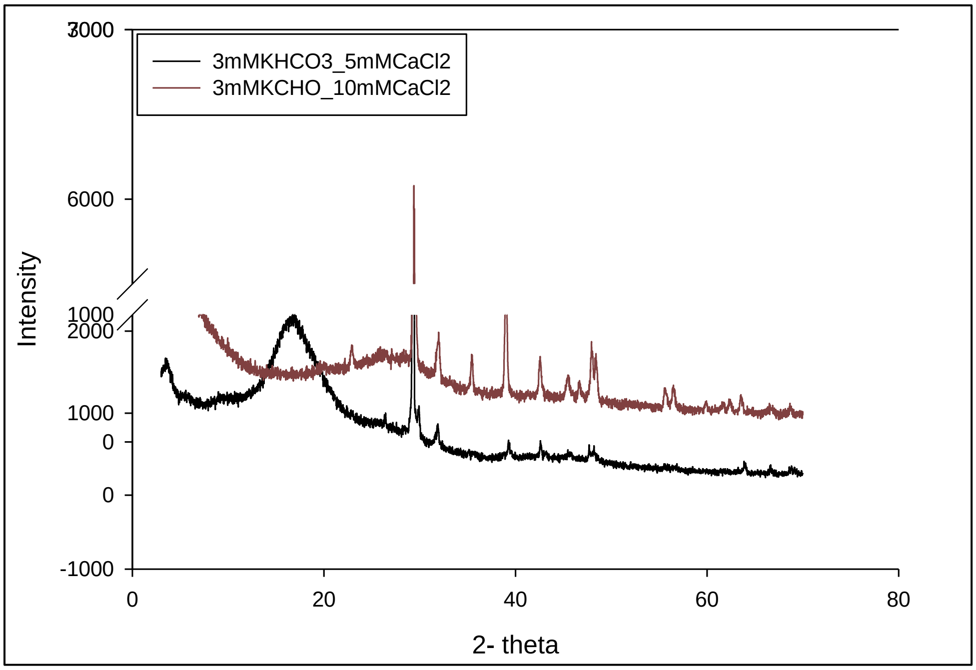


Figure 2-4. XRD data for two samples prepared with 5 mM and 10 mM of Ca.

The analysis of the uranium bearing solid phases produced by applying the ammonia (NH_3) gas remediation method to a synthetic pore-water solution continued with analysis by transmission electron microscope (TEM). This method was proposed as an alternative to the bulk powder XRD method that produced inconclusive results for the majority of prior samples. Sample preparation involved determining the solution that would best serve as a suspending agent for the uranium containing samples without dissolving the uranium phase. Following a brief extraction study using methanol, ethanol, and isopropanol as the test solutions, ethanol was selected for the suspension.

For the initial TEM samples, crushed precipitates were added to ethanol in sealed glass vials. The mixtures were sonicated for 2 hours in order to break down the insoluble solids in the suspension (Figure 2-5). A drop of this suspension was then deposited onto a copper micro-grid with a carbon mesh for TEM analysis (Figure 2-6). This grid was allowed to dry overnight, an important step to avoid evaporation of the solution in the TEM system.

Figure 2-5. Sonication of TEM suspensions.

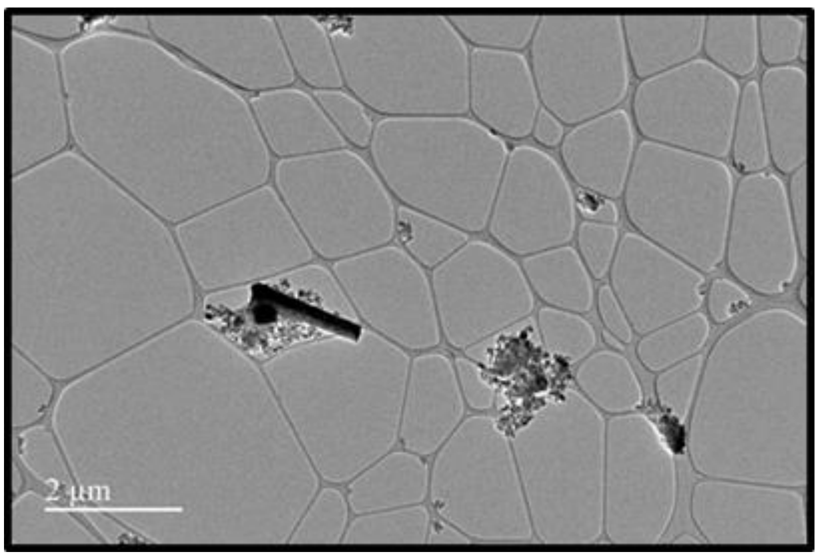


Figure 2-6. Sample particulates on the carbon mesh of a TEM grid.

The selective area electron diffraction (SAED) of the crystalline areas (Figure 2-7) revealed a polycrystalline pattern that is currently being evaluated to identify the crystal structure present in the sample. This will be done with a comparison of the d-spacings, based on the concentric rings of the diffraction pattern, with those of predicted minerals from the *Match!* XRD database.

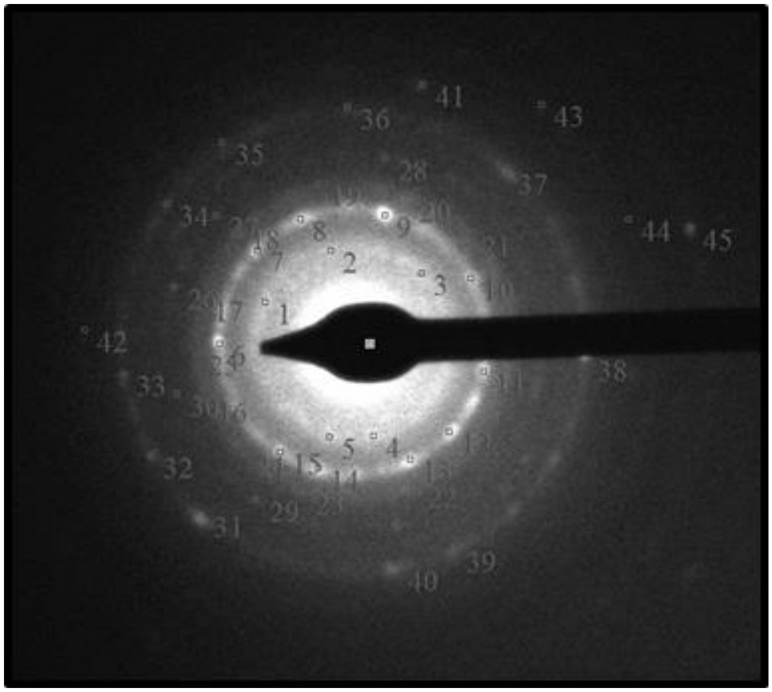


Figure 2-7. Electron diffraction pattern for selected crystalline area of sample.

In the month of February, FIU completed a progress report on the solubility measurements via isopiestic method that summarizes results from isopiestic measurements of the deliquescence behavior of no-uranium multicomponent precipitates combined from major pore water constituencies such as Na^+, SiO_3^-, Al^+, NO_3^-, K^+, HCO_3^-, Ca^{2+}, and Cl^- .

The study was continued to compare the experimental results with theoretical calculations. Literature was searched for the theoretical thermodynamic parameters related to the multicomponent precipitates of our interest. The literature review showed information on the binary systems and some of the ternary systems; however, parameters for higher-order multicomponent systems similar to those analyzed in the current study are scarse or practically nonexistent. Therefore, based on the available data, a direct modeling for the mixture of compounds included in our multicomponent precipitates is currently not possible to perform. The theoretical estimation of these parameters will be performed through binary and/or ternary systems using the major components that are included in the studied precipitates.

Sodium metasilicate (Na_2SiO_3) is one of the major components of the studied dried precipitates; its content based on the molar fraction is between 77% and 97%. A theoretical osmotic coefficient using the Pitzer's equation was calculated for only this compound and compared with the osmotic coefficient values obtained experimentally via the isopiestic method. Only three parameters ($\boldsymbol{\beta}_{\boldsymbol{ca}}^{(\mathbf{0})}$, $\boldsymbol{\beta}_{\boldsymbol{ca}}^{(\mathbf{1})}$, and $\boldsymbol{C}_{\boldsymbol{ca}}^{(\emptyset)}$) were considered for the modeling of the Na_2SiO_3 binary system. These parameters were obtained from Park and Englezos [1], who investigated the osmotic coefficient and water activity for a Na_2SiO_3 aqueous solution at 25 ^oC by using an isopiestic method. Pitzer found the best results to calculate the osmotic coefficients of a binary system at 25^{o}C as [2]:

$$\text{Ø} = \mathbf{1} - \frac{|z_M z_X| A_{\text{Ø}}\sqrt{I}}{\mathbf{1} + b\sqrt{I}} + \left(\mathbf{2}\frac{v_M v_X}{v}\right) m \left(\beta_{M,X}^{(0)} + \beta_{M,X}^{(1)}{}^{-\alpha_1\sqrt{I}}\right) + \left[\mathbf{2}\frac{(v_M v_X)^{3/2}}{v}\right] m^2 C_{MX}^{\text{Ø}}$$

Where:

M and X: Cation and Anion respectively

m: Stoichiometric molality

b: A constant of 1.2 $kg^{1/2}.mol^{-1/2}$ and is independent of temperature and pressure

$A_{\text{Ø}}$: Debye-Huckel liming slope for Ø and its value is 0.3915 $kg^{1/2}$ $m^{-1/2}$ @ 25^oC

I: Stoichiometric ionic strength (molality based), $I = \frac{1}{2}\left(\sum_i m i z_i^2\right)$

z_M and z_X: Valences of ions M and X

v_M and v_X : The number of M and X ions formed by complete dissociation of one molecule of the solute

$v = v_M + v_X$: Total stoichiometric ionization number of the electrolyte

α_1 : Usually its values is 2.0 $kg^{1/2}mol^{-1/2}$, which is independent of temperature and pressure

The Pitzer's binary and mixing parameters ($\beta_{MX}^{(0)}, \beta_{MX}^{(1)}$ and $C_{MX}^{(\text{Ø})}$) for $Na_2S_iO_3$ at 25^oC were taken as follows [1]:

Table 2-3. The Pitzer's Binary and Mixing Parameters for the Pitzer Equation

Binary and Mixing Parameters	Value	Standard Deviation
$\beta_{NaSiO_3}^{(0)}$	0.0577	0.0039
$\beta_{NaSiO_3}^{(1)}$	2.8965	0.0559
$C_{NaSiO_3}^{\text{Ø}}$	0.00977	0.00176

The number of ions formed by complete dissociation of one molecule and the valance of ions for Na_2SiO_3 to plot in the Pitzer equation are displayed in Table 2-4.

Table 2-4. Valence and the Number of Ions Formed by the Dissolution of One Molecule

Na_2SiO_3 Number of ions formed/valence of ions	Value
v_M	2
v_X	1
v	3
z_M	1
z_X	-2

The theoretical osmotic coefficients were calculated as 0.7671, 0.6383, 0.6897, 0.6322, 0.6447, and 0.6279 for the assumed equilibrium isopiestic molalities of 2.407, 1.159, 1.786, 1.024, 1.267, and 0.799 moles*kg^{-1}, respectively.

Bibliography used to conduct these calculations:

1. The Binary Coefficients for Na_2SiO_3 from Osmotic Coefficient data for Na_2SiO_3 and Na_2SiO_3-NaOH by an isopiestic method and modeling using Pitzer's Model, Hyeon Par and Peter Englezos. Fluid Phase Equilibria 153 (1998)-87-104

2. Determination and Modeling of the Solubility of $Na_2SiO_3 \cdot 9H_2O$ in the NaCl−KCl−H_2O System, Yan Zeng,† Zhibao Li,*,† and George P. Demopoulos. Key Laboratory of Green Process and Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China. Department of Mining and Materials Engineering, McGill University, 3610 University Street, Montreal, Quebec H3A 2B2, Canada

3. Review of Thermodynamics Proprietaries of Mg(NO3)(aq) and their Representation with the standard and extended Ion-Interaction (Pitzer) Models at 298.15K, J.A Radar, A.M. Wijessinghe, and T.J. Wolery, March 2004. Energy and Environment Directorate, LLNL, University of California, Livermore, California.

FIU completed the fabrication of the two new isopiestic chambers in the FIU-ARC machine shop. The chamber is shown in Figure 2-8.

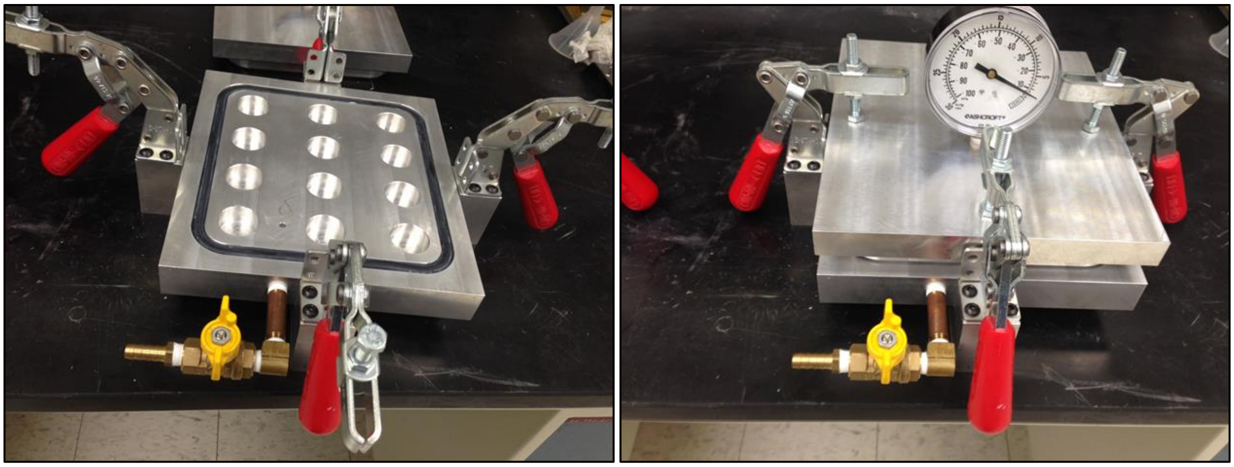


Figure 2-8. A new isopiestic chamber fabricated in the FIU-ARC machine shop.

The analysis of the uranium bearing solid phases produced by applying the ammonia (NH_3) gas remediation method to a synthetic pore-water solution continued with analysis by transmission electron microscope (TEM). The analysis of the data produced by selective area electron diffraction (SAED) was complicated and required review of reference material and consulting of more experienced users. The d-spacings of selected samples, as determined by the average distance from the outer ring of reflections to the center, were compared to reference values for the uranium minerals believed to be most likely to precipitate. Particular attention was paid to cejkaite, $Na_4(UO_2)(CO_3)_3$, which was previously reported to be a tentative identity for the crystalline phase evaluated by x-ray diffraction. The comparison revealed that, in the case of cejkaite, all calculated d-spacings fell within 5% of the corresponding values for reference mineral data. Continued analysis is required before a tentative conclusion can be drawn. Additional TEM runs for further samples are on ongoing.

During March, the study of the solubility of multicomponent solids via isopiestic method has continued. New standard solutions containing the major constituents mimicking Hanford Site pore water composition have been prepared. The new multicomponent precipitate samples will include 2 ppm of uranium added to the sample as $UO_2(NO_3)_2$, 100 mM of sodium metasilicate (Na_2SiO_3), 5 mM of aluminum nitrate $Al(NO_3)_3$, three concentrations of $CaCl_2$ (0, 5, and 10 mM), and two concentrations of $KHCO_3$ (3 and 50 mM). In addition, four crucibles containing $NaNO_3$, Na_2SiO_3, $UO_2(NO_3)_3$, and $Al(NO_3)_3$ salts will be placed in the isopiestic chamber to be able to model experimental results using the extended Pitzer's equation. The comparison of the theoretical and experimental results will allow us to verify the reliability of the experimental data. Again, the multicomponent precipitate samples will be analyzed to find the deliquescence point to compare it with previously obtained data on samples prepared without uranium.

In addition, the new isopiestic chamber set-up that includes an environmental chamber, vacuum pump and balances was moved to the radiation lab to allow for the conduction of experiments with uranium- bearing samples (Figure 2-9).

The current results of the ongoing efforts to characterize the products of the laboratory scale application of the ammonia gas remediation method were organized for presentation in poster form. Robert Lapierre, a DOE Fellow, presented a poster "Characterization of the Uranium-Bearing Products of the Ammonia Injection Remediation Method" in the WM15 symposia student poster section. During the presentation, experienced scientists familiar with the Hanford Site and uranium chemistry were consulted on their opinions regarding the planned experiments. Some contributions, determined to be suitable for application, were discussed with PNNL contacts in order to decide how they could be implemented to facilitate reaching the project objectives. New sample preparation methods were discussed with adjustments to improve the representativeness of and ability to characterize the samples. These changes include:

1. Replacing a decanting step with vacuum filtration to ensure that no solubilized uranium species are precipitated out with drying

2. Analysis using FIB to mill out a section of analyte

3. Electron microprobe analysis using polished samples fixed in epoxy

Also, the accomplishments for Task 1.1 were summarized and presented in the DOE EM research review for the FIU cooperative agreement.

Figure 2-9. A new isopiestic chamber set up in the FIU-ARC radiation laboratory.

Subtask 1.2: Investigation on Microbial Meta-Autunite Interactions – Effect of Bicarbonate

<u>Subtask 1.2 Overview</u>

The goal of experimental activities under subtask 1.2 is to investigate the bacteria interactions with uranium by focusing on facultative anaerobic bacteria and study their effect on the dissolution of the uranyl phosphate solid phases created as a result of sodium tripolyphosphate injections into the subsurface at the 300 Area. The Columbia River at the site exhibits water table fluctuations, which can vary up to 3 m seasonally. This rising water table over the extent of its annual vertical excursion creates an oxic-anoxic interface that in turn, due to activates of facultative anaerobic bacteria, can affect the stability of uranium-bearing soil minerals. Previous assessments noted the decline in cultivable aerobic bacteria in subsurface sediments and suggested the presence of facultative anaerobic bacteria in sediment samples collected from the impacted area (Lin et al, 2012). Therefore, understanding the role of anaerobic bacteria as one of the factors affecting the outcome of environmental remediation is very important.

Subtask 1.2 Quarterly Progress

On January 26 and 27, researchers from PNNL, Brady Lee and Sabrina Saurey, visited ARC. Dr. Leo Lagos presented a program overview and Dr. Yelena Katsenovich presented a summary of the research results for this project. In addition, DOE Fellows Claudia Cardona, Robert Lapierre and Sandra Herrera presented updates on their research projects. Dr. Lee and Ms. Saurey toured ARC's facilitates and laboratories and visited the FIU molecular biology laboratory. The discussion on microbial tasks was extended to the renewal application for the FIU DOE proposed scope for 2015-2020.

During January, FIU evaluated the control samples that were not inoculated with bacteria and found growth in a control for the no-bicarbonate samples and a control sample that contained 10 mM of bicarbonate (Figure 2-10).

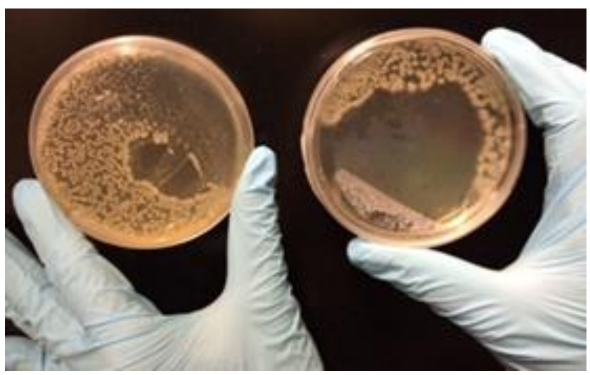


Figure 2-10. Bacterial contamination in the control samples with no-bicarbonate and amended with 10 mM bicarbonate.

In comparison, petri dishes inoculated from the control bottle amended with 3 mM of bicarbonate and 5 mM bicarbonate presented no evidence of bacterial contamination (Figure 2-11).

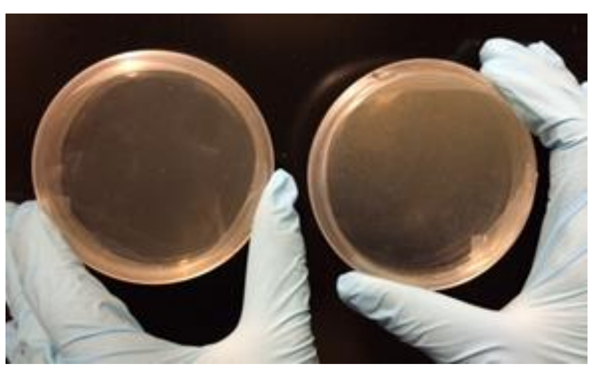


Figure 2-11. Clear plates and no evidence of contamination in the control bottle amended with 3 mM and 5 mM of bicarbonate.

FIU continued sampling of control and experimental bottles after inoculation of bacteria and conducted uranium analysis on collected samples via the KPA instrument. The results for the no-bicarbonate amended bottles are presented in Figure 2-12.

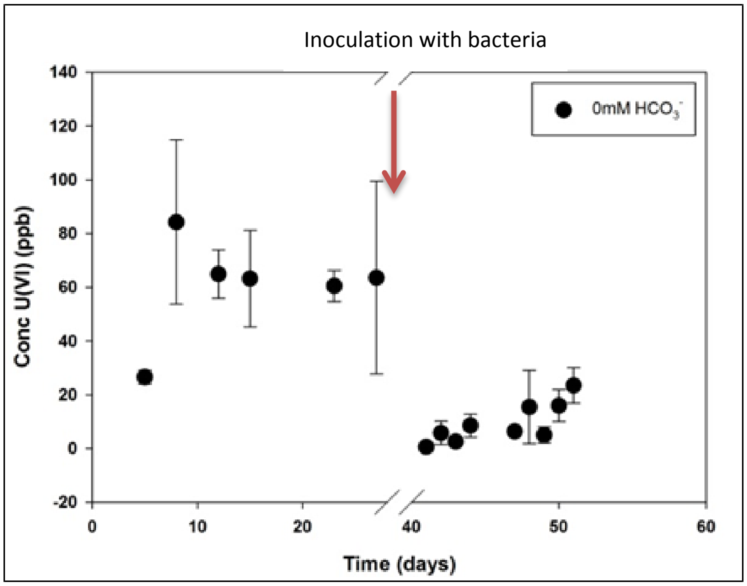


Figure 2-12. Changes for aqueous U (VI) concentrations as a function of time for the natural autunite dissolution experiments inoculated with *Shewanella Oneidensis* MR1.

The data suggest that before the inoculation with bacteria, there was an incremental increase in U(VI) concentration until autunite equilibrated with the media solution. After bacteria inoculation, the concentration of uranium sharply decreased for some samples to no detectable levels. Data analysis for the bicarbonate amended bottles is in progress and the results will be presented in the next report.

The processed results for the uranium biorelease from autunite minerals are presented in Figure 2-13 and Figure 2-14.

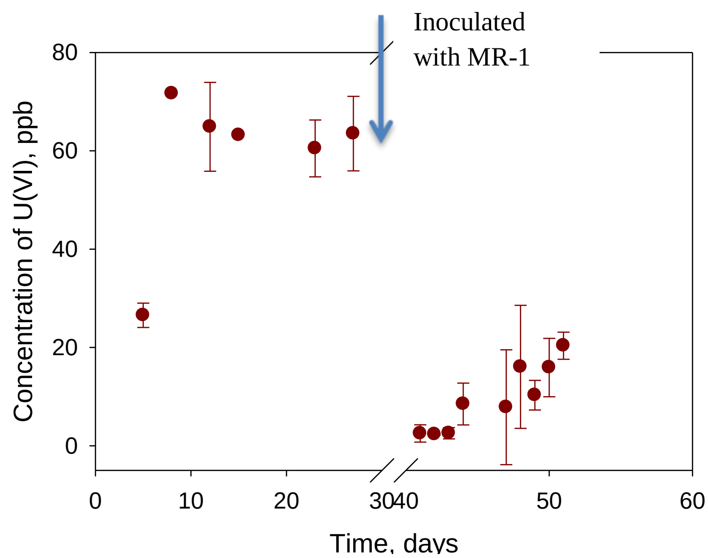


Figure 2-13. The concentration of uranium (VI) released in the aqueous phase as a function of time in bicarbonate-free media solution.

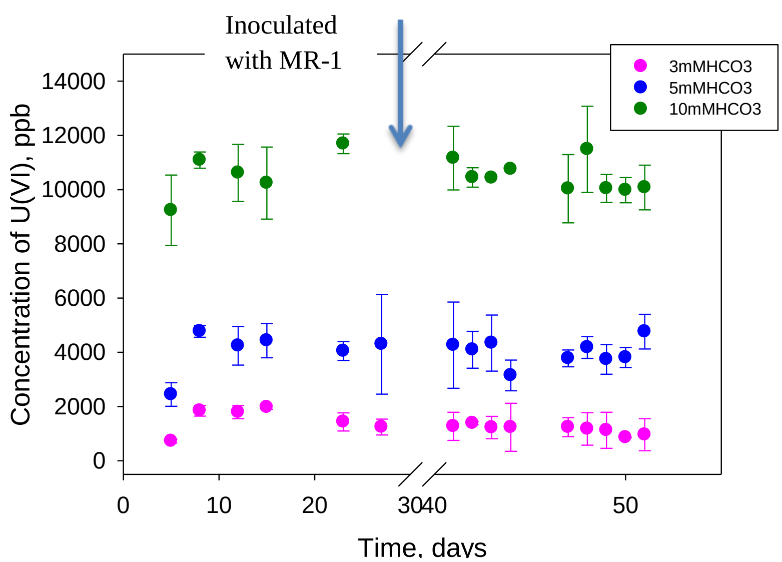


Figure 2-14. The concentration of uranium (VI) released in the aqueous phase as function of time under three different bicarbonate concentrations: 3,5 and 10 mM.

For the group of samples amended with bicarbonate, some of the values obtained from the results of measured concentration of U (VI) via KPA were out of range and the samples were reprocessed several times. The results suggest that in bicarbonate-free solutions (Figure 2-13), there was a decrease in uranium (VI) concentration after the inoculation with metal reducing bacteria *Shewanella Oneidensis* MR1. In solutions amended with bicarbonate, there was no significant difference in uranium (VI) concentration before and after inoculation with bacteria (Figure 2-14).

FIU started preparations for a new round of autunite dissolution experiments using *Shewanella Oneidensis* MR1. In the month of February, a new sample of *Shewanella Oneidensis* MR1 was obtained from PNNL. Cells were grown in the LB media and preserved in 25% glycerol at -80C. A new freezer (TermoScientific) was ordered and received to preserve bacterial cells. In addition, FIU ordered and received polycarbonate and GFF filters which are needed for future experiments in order to prepare samples for live/dead assay. To quantify the total protein in a bacterial sample, FIU obtained a BCA Protein Assay Kit.

In the month of March, FIU obtained preliminary results from the inductively coupled plasma (ICP) instrument for the calcium and phosphorous biorelease from autunite minerals. The results are presented in Figure 2-15 and 2-16.

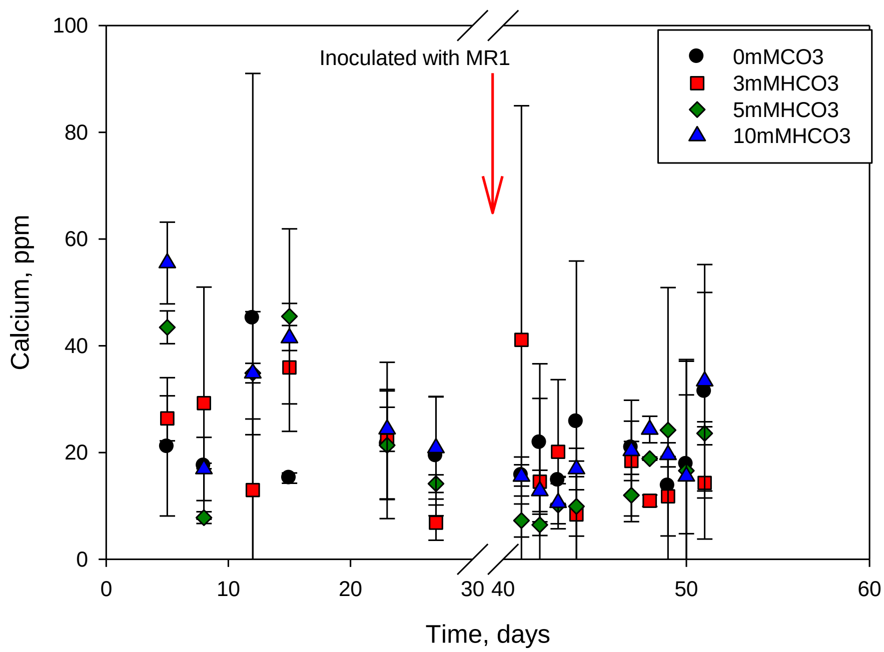


Figure 2-15. Concentration of calcium released to the aqueous phase as a function of time in the presence of different bicarbonate concentrations: 0, 3, 5 and 10 mM.

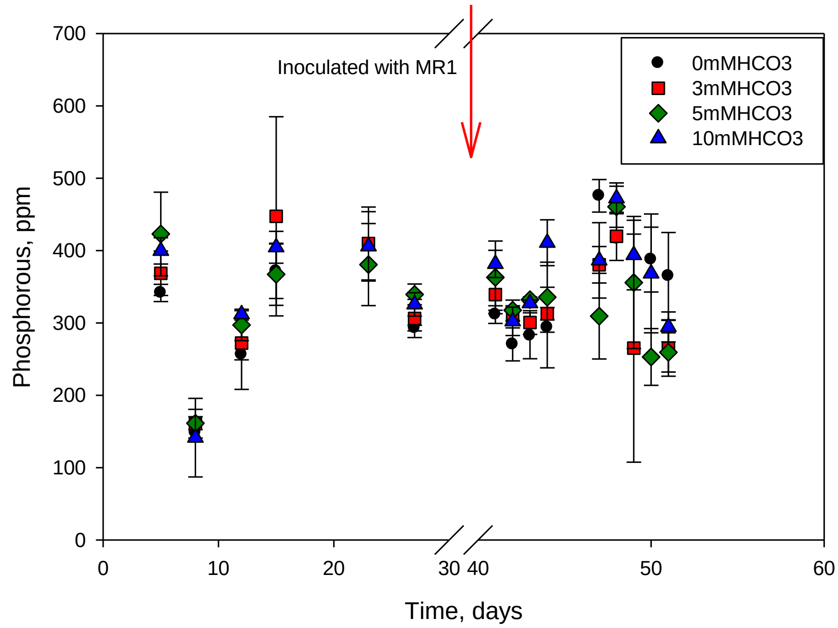


Figure 2-16. Concentration of phosphorous released to the aqueous phase as a function of time in the presence of different bicarbonate concentrations: 0, 3, 5 and 10 mM.

The results suggested that the concentration for calcium (Ca) released before inoculation was higher than the concentrations obtained after inoculation with facultative anaerobic bacteria Shewanella *Oneidensis MR1*. It might be a reduction in soluble Ca content in the media solution caused by the formation of insoluble secondary calcium phosphate phases. In the case of phosphorous (P), the measured concentrations had a slight decrease during the second week before inoculation but stabilized and even slightly increased after bacteria inoculation for batches augmented with 0 mM and 3 mM of HCO_3.

FIU obtained all necessary materials and supplies to repeat this experiment with more emphasis on bacteria protein analysis and Live and Dead assay. FIU initiated the first phase by preparing autoclaving and filter-sterilizing all media solutions that will be used in the experiment.

During the Waste Management Conference in the third week of March (Phoenix, Arizona), Sandra Herrera, a graduate student, presented a poster titled, “A Study of Autunite Dissolution in the Presence of Shewanella Oneidensis MR1 and Different Bicarbonate Concentrations” in the student poster section of the conference.

A manuscript by DOE Fellow Paola Sepulveda-Medina, Dr. Yelena Katsenovich, Dr. Dawn Wellman and Dr. Leonel Lagos titled, “The Effect of Bicarbonate on the Microbial Dissolution of Autunite Mineral in the Presence of Gram-Positive Bacteria,” was published in the *Journal of Environmental Radioactivity* with the citation *Journal of Environmental Radioactivity* 144 (2015) 77-85.

Another manuscript by DOE Fellow Paola Sepulveda-Medina, Yelena Katsenovich, Vishal Musaramthota, Michelle Lee, Brady Lee, Rupak Dua, and Leonel Lagos titled, “The effect of uranium on the bacterial viability and cell surface morphology using atomic force microscopy in the presence of bicarbonate ions," prepared in collaboration with PNNL, was accepted for publication in the *Research in Microbiology* journal.

Task 2 Quarterly Progress

Subtask 2.1: FIU's support for groundwater remediation at SRS F/H Area

In the previous experiment, the effect of sodium silicate on the pH of a solution was analyzed in order to determine the optimal concentration of sodium silicate required to elevate pH values close to neutral. The solution contained Savannah River Site (SRS) soil and synthetic ground water (acidified to a pH of 3.6) with the following chemical concentrations to replicate the site's natural groundwater composition (Table 2-5).

Table 2-5. The Composition of the SRS Synthetic Groundwater

Compound	**$CaCl_2$**	**Na_2SO_4**	**$MgCl_2$**	**KCl**	**NaCl**
Amount (g)	5.4771	1.0727	3.0943	0.3997	2.6528

The results of that experiment presented evidence that a concentration of between 40-70 ppm of sodium silicate was successful in creating a neutral pH, where 40-50 ppm appeared optimal. A sequential experiment was then conducted specifically using a 40-50 ppm concentration of sodium silicate with the SRS soil, synthetic groundwater, and uranium (VI) in order to investigate the removal of uranium concentrations in the aqueous phase via precipitation.

In the following experiment, nine samples were created using 400 mg of SRS soil, 20 mL of synthetic SRS groundwater, uranium with a concentration of 0.5 ppm, and sodium silicate with a concentration of 40 and 50 ppm. Three of the samples acted as control samples with no sodium silicate present. The samples were equilibrated on a platform shaker at 110 RPM for different time intervals. Two sets of 150 µL were extracted from each of the original samples: one set was filtered through 0.45µm PTFE filters and the other was not. Non-filtered samples, as well as filtrates were then diluted 1:10 with 1% nitric acid. All samples were analyzed with a kinetic phosphorescence analyzer (KPA). The results are shown in Figure 2-17 and Figure 2-18.

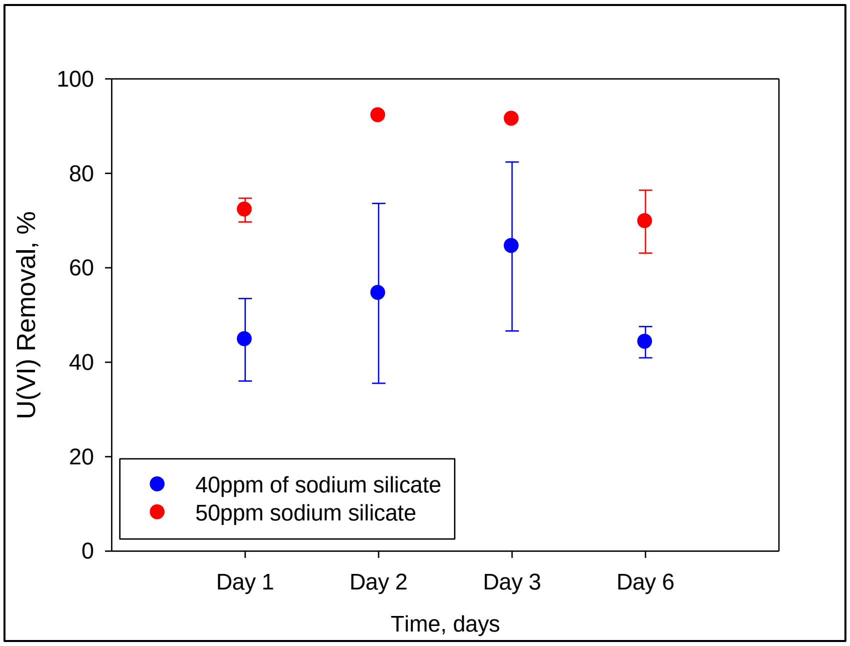


Figure 2-17. U(VI) percent removal as a function of time for filtered samples for two different conditions: 40 and 50 ppm sodium silicate.

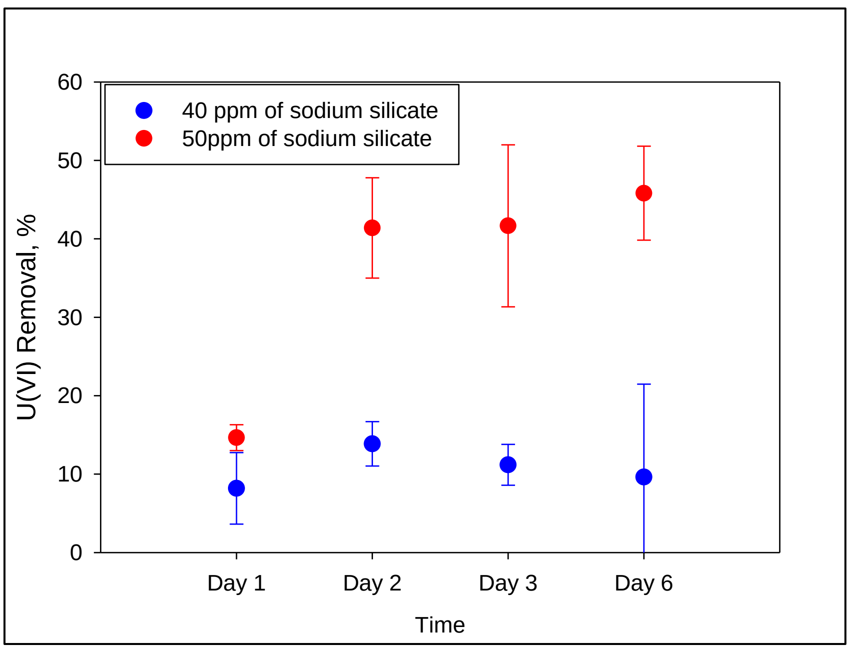


Figure 2-18. U(VI) percent removal as a function of time for non-filtered samples for two different conditions: 40 and 50 ppm sodium silicate.

Results revealed that the addition of 50 ppm sodium silicate is more efficient in the removal of uranium from aqueous phase compared to the addition of 40 ppm, which resulted in a lower removal. A big difference between the removal of filtered and non-filtered samples from the same day was observed, for both sodium silicate concentrations tested, indicating that there is a substantial amount of uranium species that are retained in the filter.

The experiment is going to be repeated with more sodium silicate concentrations tested and pH monitoring in parallel, so that a better understanding of the phenomenon is achieved.

In February, an experiment was conducted to continue the investigation of the influence of sodium silicate on the removal of uranium concentrations in the aqueous phase via precipitation. A total of 14 samples were created consisting of Savannah River Site soil and synthetic groundwater, with the addition of sodium silicate. The concentrations of sodium silicate that were analyzed during this experiment included: 40, 50, 60, and 70 ppm. Over the course of three days, the pH values of each sample were collected ensuring the pH value correlated with the concentration of sodium silicate present in each sample. From each sample, two additional samples were extracted and categorized as filtered and non-filtered to conduct a kinetic phosphorescence analysis. As uranium precipitation was achieved, the precipitate was removed via filtration. The amount of precipitation was directly influenced by the amount of sodium silicate present in each sample. The percent of uranium removal can be observed in the Figure 2-19.

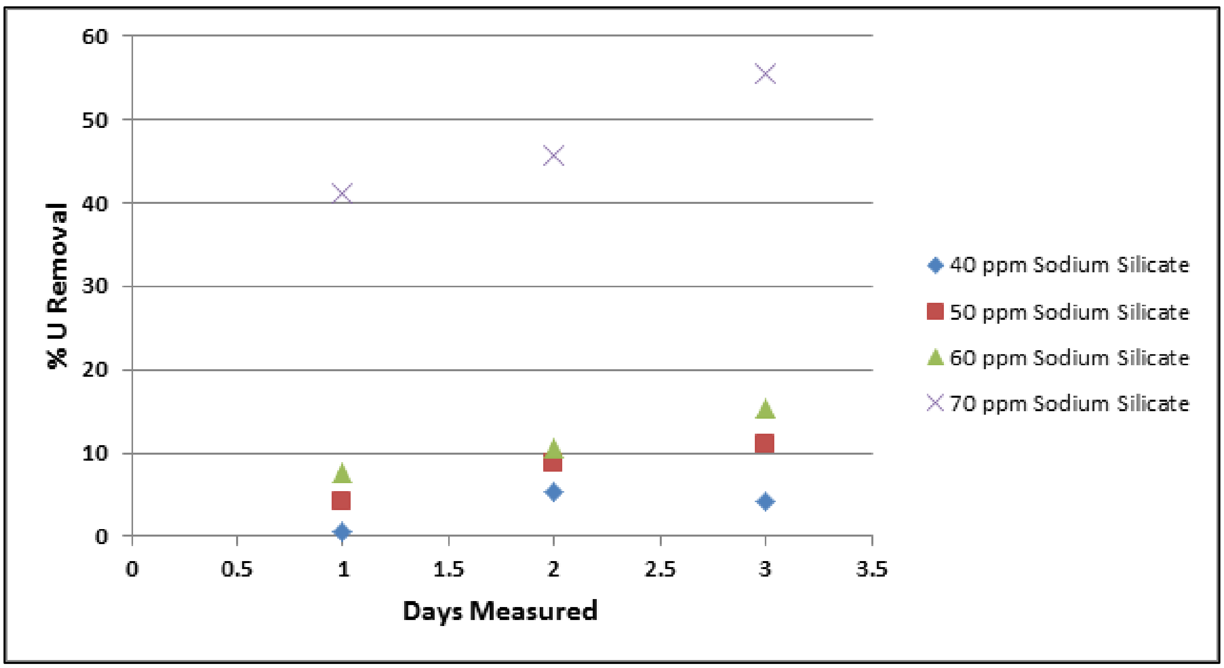


Figure 2-19. Percent of uranium removal as a function of time for non-filtered samples for 40, 50, 60, and 70 ppm of sodium silicate.

In the filtered samples, the percent of uranium removed was found to be higher. Overall, the 70 ppm sample appeared to have the highest percent of uranium removed. The variation between 40, 50, and 60 ppm appeared limited compared to 70 ppm (Figure 2-20). Day 2 for the filtered samples presented values slightly lower than expected due to what appeared to be an experimental error; therefore, those values were retested at a later date.

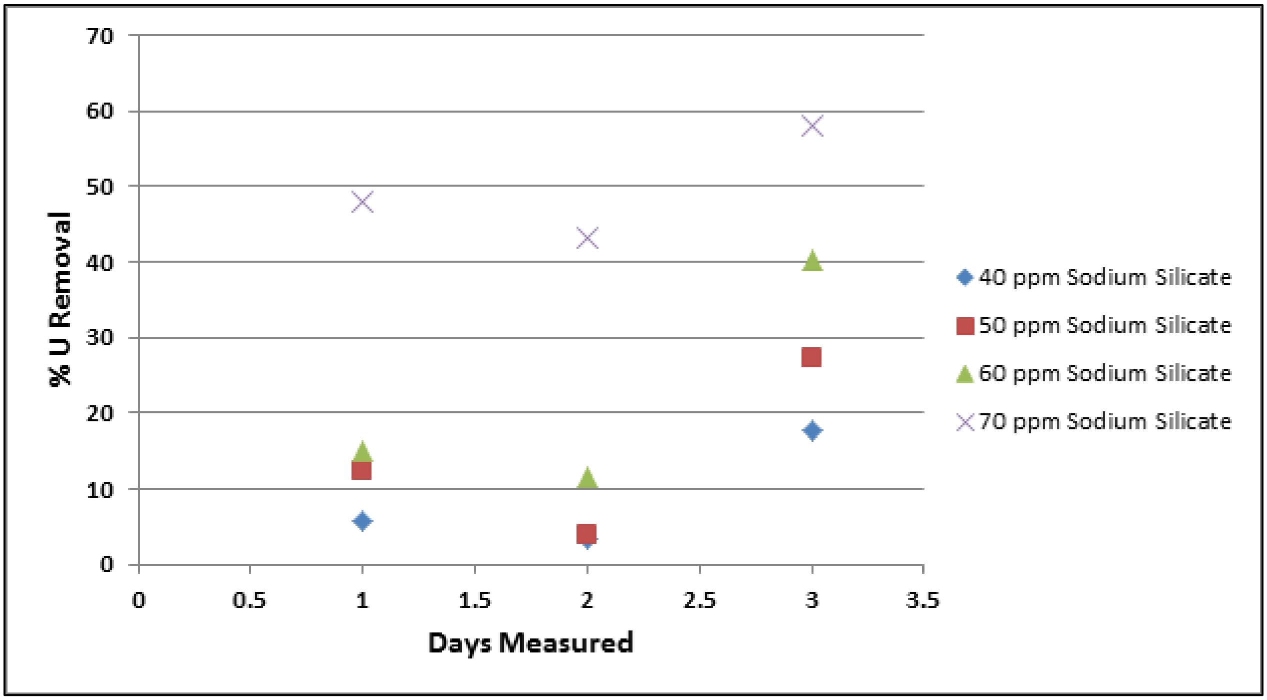


Figure 2-20. Percent of uranium removed as a function of time for filtered samples for 40, 50, 60, and 70 ppm of sodium silicate.

To continue the investigation of the influence of sodium silicate on the removal of uranium concentrations in the aqueous phase via precipitation, a sequential experiment was conducted with 60, 70, 80, and 90 parts per million of sodium silicate solution. The batch samples consisted of soil from SRS, synthetic ground water, 0.5 ppm of uranium (VI), and the four aforementioned sodium silicate concentrations. In total, 14 samples were created, including two control samples where no silicates were introduced, and monitored for a period of three days.

Over the course of the three days, the pH values were collected to ensure the pH value correlated with the concentration of sodium silicate present in each sample. Each day, additional aliquots were extracted from the original samples and the residual silica in the supernatant was determined in unfiltered and filtered samples (0.45 micrometer filter). In this experiment, the percentage of silica and iron present in each sample was obtained using inductively coupled plasma- optical emission spectrometer (ICP-OES); the results of the analysis are presented below in Figure 2-21 and Figure 2-22:

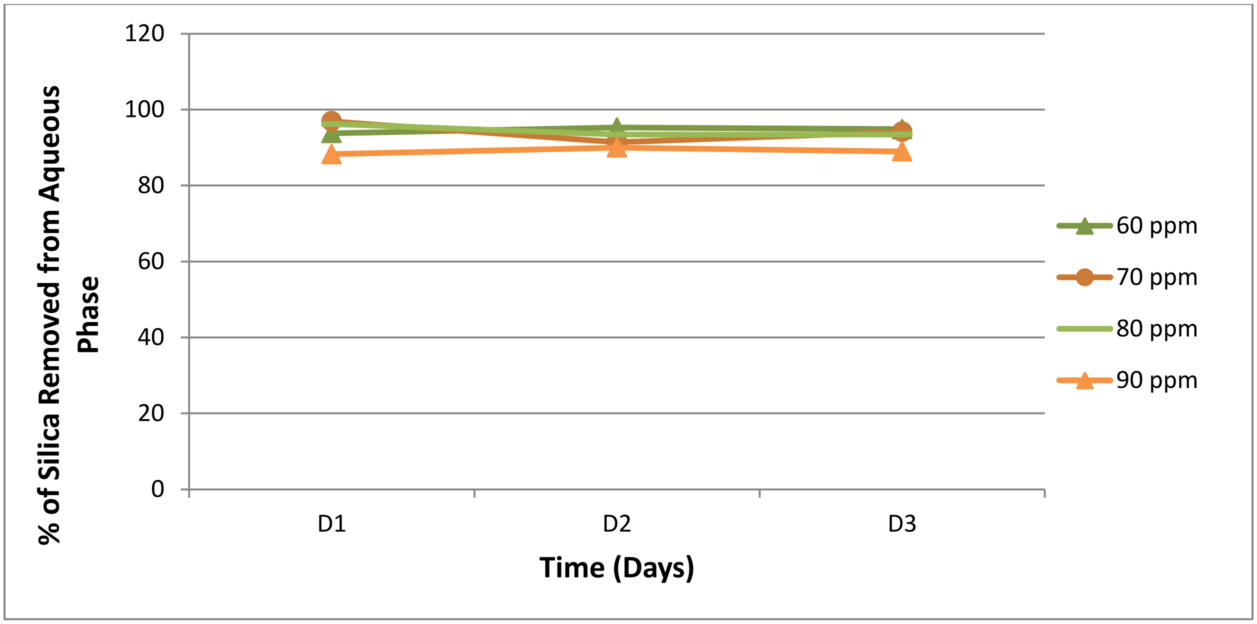


Figure 2-21. The percent of silica precipitate present in the non-filtered samples for the three days in which data was collected.

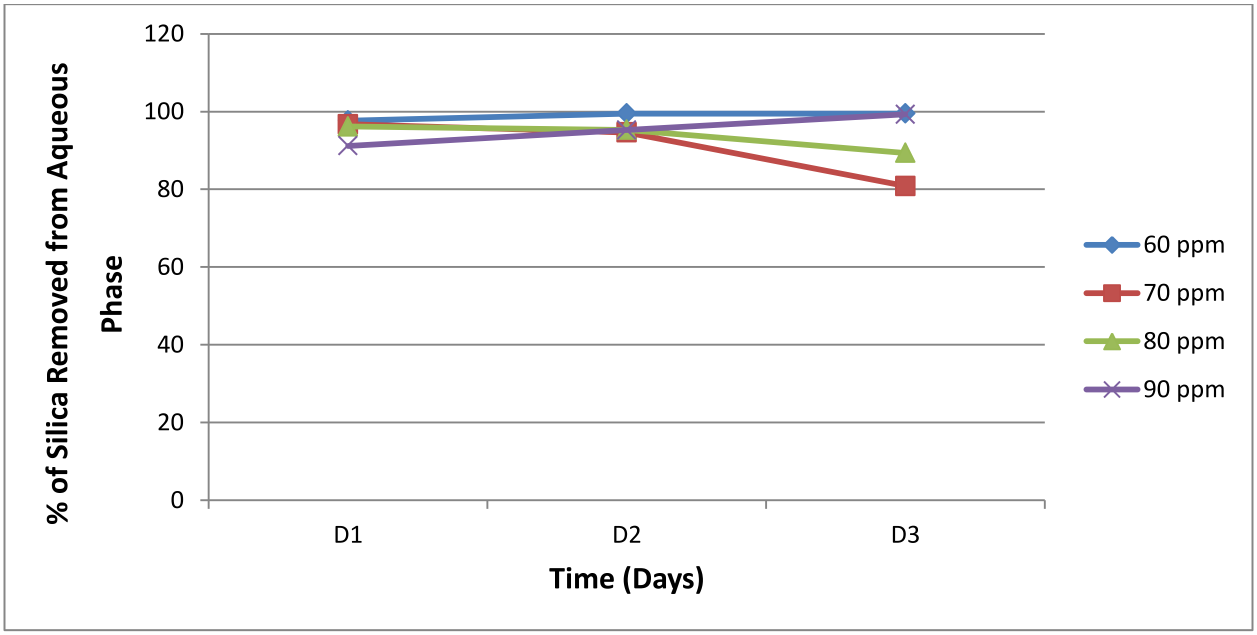


Figure 2-22. The percent of insoluble silica present in the filtered samples for the three days in which data was collected.

The results from this experiment show that the silica concentrations are relatively consistent throughout the 3-day experiment in both the filtered and non-filtered samples, with a range between 80-100%. The values for the non-filtered samples were only slightly higher due to the presence of both colloidal and soluble silica, but the difference between the values was insignificant. In addition to silica, iron concentrations will also be measured and analyzed in this same format to observe levels throughout the duration of the experiment.

A poster titled, "Sodium Silicate Treatment for Uranium (VI) Bearing Groundwater Systems at F/H Area at Savannah River Site," was presented in the student poster section of the WM conference by DOE Fellow Christine Wipfli. She won first prize for the student poster competition. An image of this poster is provided in the Workforce Development section of this report (Project 5). Christine will also be preparing a poster presentation for the 2015 STEM Undergraduate Research Symposium, which will take place at Indian River State College in Port St. Lucie, Florida.

FIU Year 4 Carryover Work Scope

During January, batches 5 and 6 containing 50 ppm of HA, 3.5 mM colloidal silica, 0.5 ppm U and 400 mg of SRS sediment were analyzed with a KPA. The percent removal of uranium (VI) concentration was calculated from U remaining in the supernatant solutions and results are presented in Table 2-6.

Table 2-6. Percent Removal of Uranium

pH	Batch	Uranium Removal
3	5	83.83
	6	79.16
4	5	65.36
	6	70.06
5	5	49.59
	6	52.18
6	5	43.08
	6	45.82
7	5	39.26
	6	44.8
8	5	41.57
	6	43.52

Figure 2-23 shows the results for batch 5 and 6 alongside the results determined for batches 2 and 3.

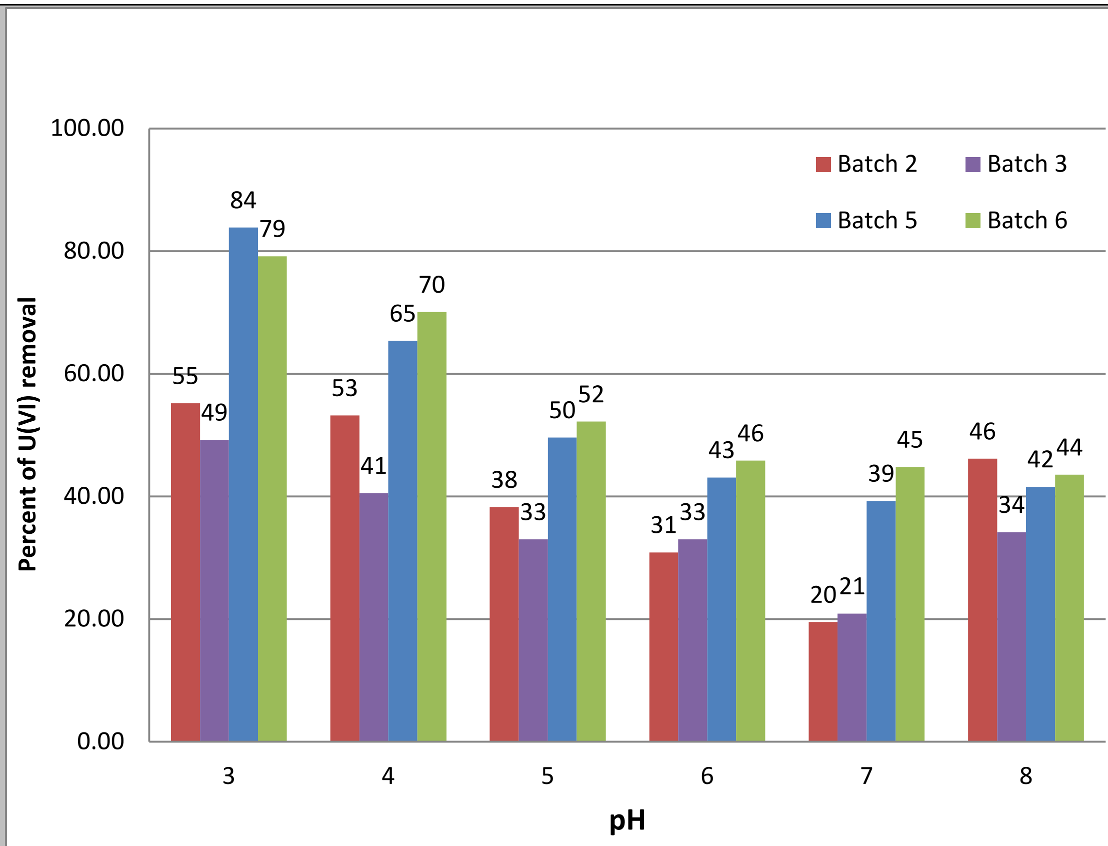


Figure 2-23. Results for uranium removal for the filtered samples.

Relative to batches 2 and 3, which contain no sediment, batches 5 and 6 show a significant increase in U(VI) removal though with the same overall trend of percent removal decreasing as pH increases. At acidic pH, the humic acid and uranium aggregate together due to attraction of their opposite charges. This aggregation in conjunction with soil create more binding sites, which seems to allow for a high removal of U(VI). As the pH increases, less aggregation will occur due to the humic acid becoming insoluble and creating less possibility for interaction to occur; though batches 5 and 6 still show a higher percent removal of U(VI), which is due to the sediment in solution. The silica as seen previously does not seem to cause a significant impact on U(VI) removal.

During February, ICP analysis for Si and Fe was completed for batches 2, 3, 5 and 6. These samples were previously analyzed to measure uranium concentrations via KPA and data was reported during the month of January. The data for Si and Fe is currently under processing and will be reported in the next monthly report; this will help further explain the synergistic interactions between U(VI) ions, humic acid and silica and also explain the influence of HA and Si on the sorption of U(VI) onto sediments. A progress report on batch experiments conducted with 50 ppm HA is being prepared as a deliverable under the carryover scope of this task.

During March, data analysis was completed for batches 2, 3, 5 and 6 processed through ICP-OES. The data is presented in Table 2-7 and Figure 2-24.

Table 2-7. Average Percent Removal of Elements for All Batches

Sample-Description, pH 3	U(VI) Avg Removal, %	Std.	Si Avg Removal, %	Std Deviation	Fe, ppm	Std Deviation
Batch 2	55.17	4	87.86	3.35	No Sediment	
Batch 3	49.22	6.5	No Si	0.63	No Sediment	
Batch 5	83.83	1.97	85.28	0.15	0.31	0.02
Batch 6	79.16	2.9	No Si	0.43	0.37	0.07
Sample-Description,	**U(VI) Avg Removal, %**	**Std.**	**Si Avg Removal, %**	**Std Deviation**	**Fe, ppm**	**Std Deviation**
Batch 2	53.2	3.93	83.41	1.19	No Sediment	
Batch 3	40.52	4.28	No Si	2.39	No Sediment	
Batch 5	65.36	2.39	86.44	1.56	0.3	0.06
Batch 6	70.06	0.42	No Si	3.32	0.41	0.02
Sample-Description, pH 5	**U(VI) Avg Removal, %**	**Std.**	**Si Avg Removal, %**	**Std Deviation**	**Fe, ppm**	**Std Deviation**
Batch 2	38.25	3.08	86.01	2.91	No Sediment	
Batch 3	32.98	4.12	No Si	0.59	No Sediment	
Batch 5	49.59	1.98	86.2	0.66	0.42	0.03
Batch 6	52.18	1.43	No Si	0.67	0.48	0.02
Sample-Description, pH 6	**U(VI) Avg Removal, %**	**Std.**	**Si Avg Removal, %**	**Std Deviation**	**Fe, ppm**	**Std Deviation**
Batch 2	30.87	5.66	79	4.67	No Sediment	
Batch 3	32.98	5.82	No Si	1.42	No Sediment	
Batch 5	43.08	0.94	85.05	1.65	0.48	0.03
Batch 6	45.82	0.84	No Si	1.07	0.59	0.07
Sample-Description, pH 7	**U(VI) Avg Removal, %**	**Std.**	**Si Avg Removal, %**	**Std Deviation**	**Fe, ppm**	**Std Deviation**
Batch 2	19.51	3.64	77.08	3.79	No Sediment	
Batch 3	20.89	1.03	No Si	2.05	No Sediment	
Batch 5	39.26	1.91	85.12	0.91	0.48	0.03
Batch 6	44.8	1.66	No Si	1.61	0.68	0.18
Sample-Description, pH 8	**U(VI) Avg Removal, %**	**Std.**	**Si Avg Removal, %**	**Std Deviation**	**Fe, ppm**	**Std Deviation**
Batch 2	46.14	2.62	63.36	12.63	No Sediment	
Batch 3	34.17	5.75	No Si	2.27	No Sediment	
Batch 5	41.57	0.54	84.52	0.47	0.46	0.03
Batch 6	43.52	1.34	No Si	0.46	0.58	0.03

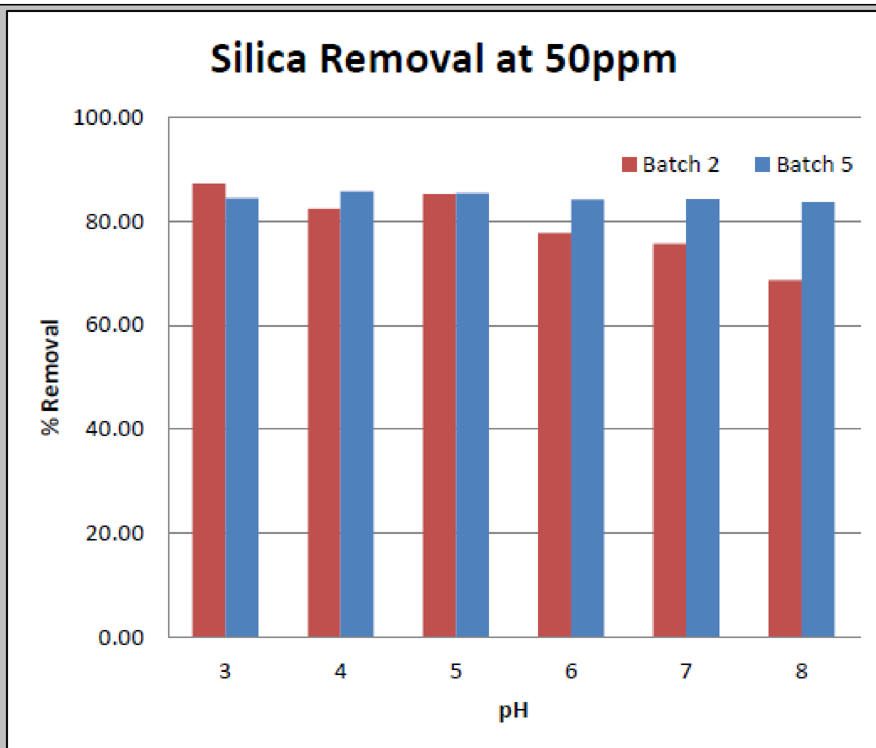


Figure 2-24. Silica Removal for Batch 2 and 5.

Upon completion of analysis, the silica percent removal remained fairly constant through all pH ranges for batch 5 and showed a slight decrease for batch 2. Batch ranges from 87.86% at pH 3 to 63.36% at pH 8; while batch 5 remained constant at ~85%. When comparing these results to the percent removal seen for U(VI), colloidal silica does not seem to have a significant effect.

The presentation for the DOE EM research review for the FIU cooperative agreement was completed and presented on March 31. A technical progress report on batch experiments conducted with 50 ppm HA titled, "FIU's Support for Groundwater Remediation at SRS F/H Area," was prepared as a deliverable under the carryover scope of this task. FIU also initiated preparation of analysis of unfiltered samples for batches 2, 3, 5 and 6.

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

During the month of January, XRD analyses were conducted on sub-samples collected from the Batch 1 samples used in the microcosm experiment. The experimental patterns were compared against the known patterns for siderite and pyrite using Sigma Plot software (Figures 2-25 through 2-28); no matches were found in this instance. It is presumed that iron will be found as ferrous iron in the soluble form. The iron concentration in the supernatant solution will be measured via ICP-OES.

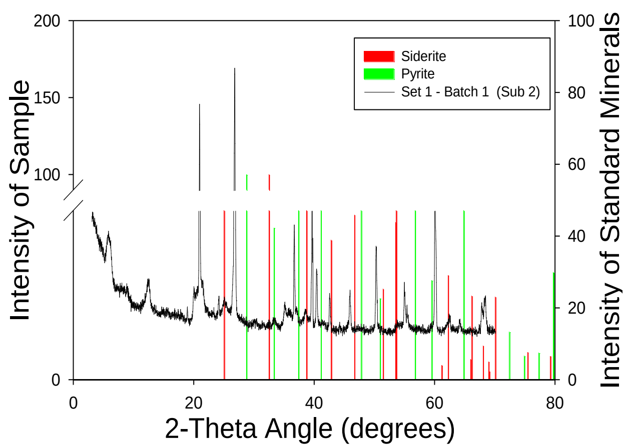


Figure 2-25. Set 1 vs. siderite and pyrite.

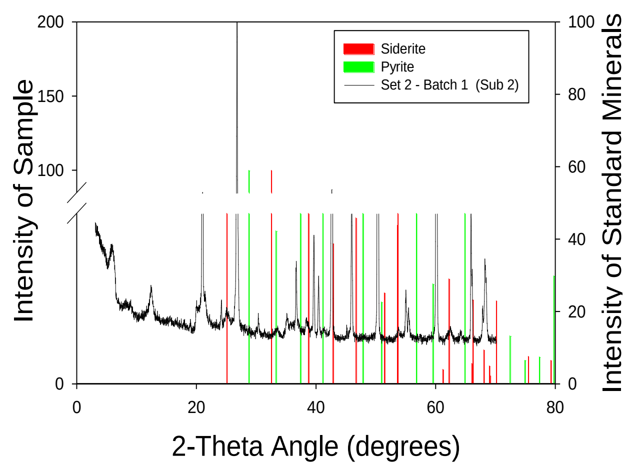


Figure 2-26. Set 2 vs. siderite and pyrite.

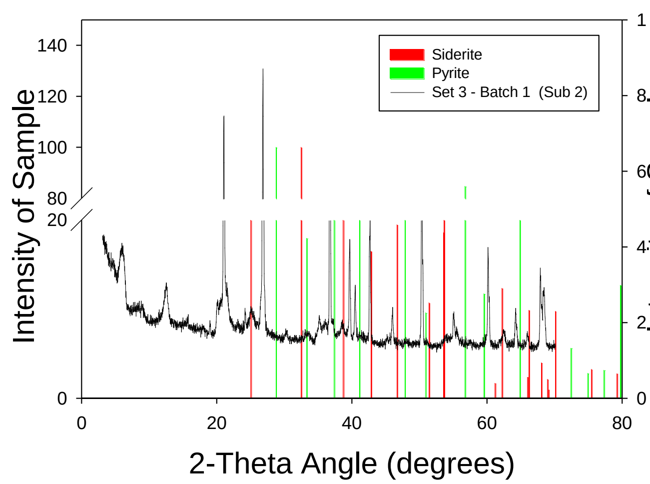


Figure 2-27. Set 3 vs. siderite and pyrite.

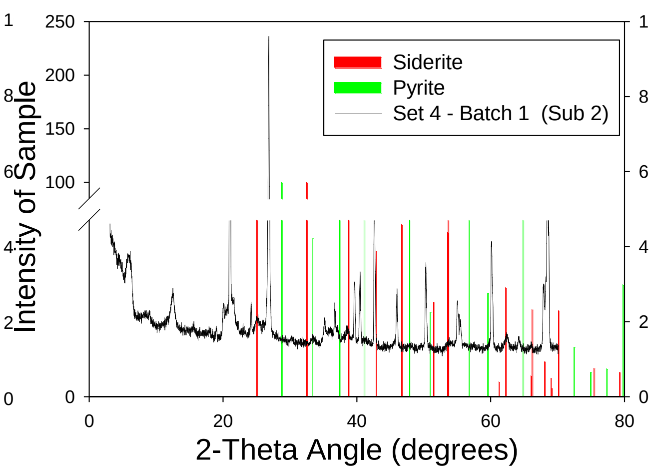


Figure 2-28. Set 4 vs. siderite and pyrite.

Sub-samples were collected from Batch 2 in late-January and left to dry in the anaerobic chamber. Upon drying, the samples were pulverized using a mortar and pestle before being taken for XRD analysis. XRD analyses were conducted on all four sets of the Batch 2 samples. The experimental patterns were then compared against the patterns for siderite and pyrite (Figures 2-29 through 2-32). The set 3 sample which is composed of 12 mL of basal solution, 0.75 grams of molasses (5-10% by weight), and 12 mL of SRS F-Area sediments, was found to have a matching peak with pyrite at the 2-theta value of 28.74. This match corresponded with the maximum intensity peak for pyrite.

Batch 2/ Sub-Sampling 1

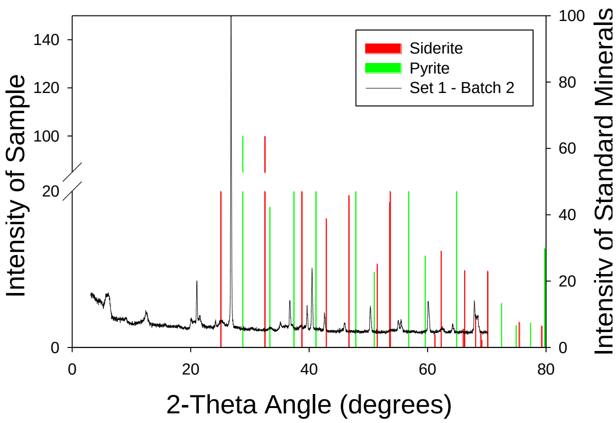


Figure 2-29. Set 1vs. siderite and pyrite.

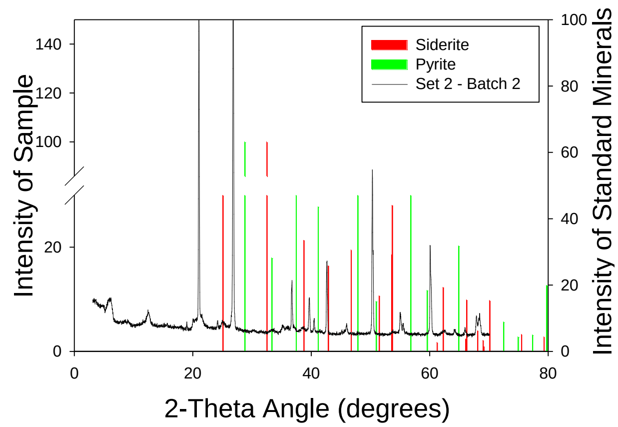


Figure 2-30. Set 2 vs. siderite and pyrite.

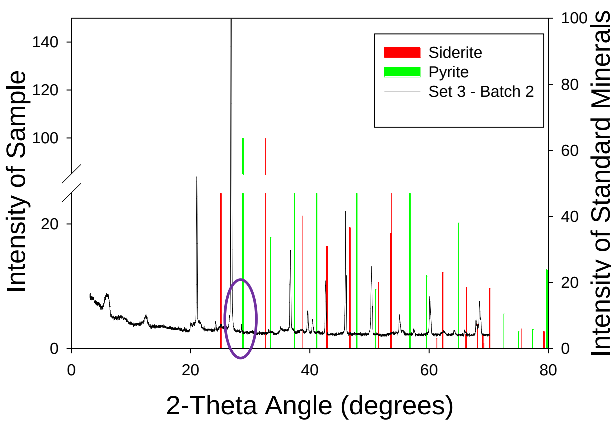


Figure 2-31. Set 3 vs. siderite and pyrite.

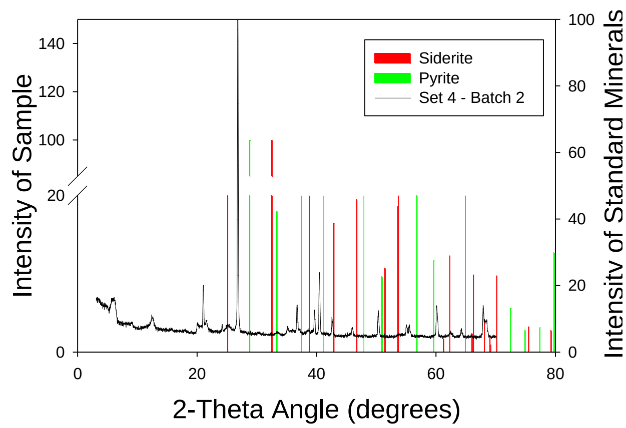


Figure 2-32. Set 3 vs. siderite and pyrite.

On January 30, a deliverable pertaining to Project 2 Subtask 2.2 was completed. This deliverable documented the effectiveness of sulfate and molasses substrate addition to SRS soil to produce anaerobic conditions conducive to uranium reduction and then precipitation as uranium (IV). This was completed by the conducting a microcosm experiments using sediments collected from SRS. The objective of these microcosm experiments was to replicate the anaerobic conditions created as a result of molasses injection performed by ARCADIS at SRS and investigate if any mineralogical changes could occur in the soil. Currently, no ferrous iron solid phases such as pyrite or siderite have been found in the samples. In the coming month, ICP – OES will be used to measure soluble iron concentrations that occur within each of the samples.

The analysis conducted during the month of January confirmed that no ferrous iron solid phases were found to have precipitated in any of the samples from the microcosm experiment. It is believed that this is due to the acidic pH values in the samples as this hindered the formation of bicarbonate/carbonate ions used to form the iron precipitates. In the month of February, it was decided that ICP-OES analysis would be conducted to find the ferrous iron concentrations. DI water was added to all of the samples in the amount of 5 mL and the samples were centrifuged in tubes at 2700 rpm for 20 minutes. The supernatant was collected from each sample and filtered through a 45 µm syringe filter. Standards were prepared for iron analysis with a calibration curve between 1 to 100 ppb. The supernatant was collected and diluted by a factor of 200 in nitric acid (HNO3) 1%. Next, 3 mL of each of the diluted samples were placed into ICP tubes and ICP-OES analysis was conducted. The data obtained from ICP-OES can be found in Table 2-8. The samples varied significantly in iron concentrations, with the greatest amount reaching 13312.80 ppb in Batch 1/Sets 1-2, and the lowest amounts in Batch 2/Sets 2 through 4, where the iron concentration was low enough to be outside of the calibration curve. It was found that the Batch 1 samples which contained sulfate (Sets 1 and 2) did not display a significant difference in average iron concentration in comparison to the samples which contained no sulfate. It also was noted that the Batch 1 samples containing the anaerobic bacteria (Sets 1 and 4) had the highest average iron concentrations in comparison to those which were not inoculated. It is believed that iron-reducing bacteria may have biodegraded molasses using ferric iron as a terminal electron acceptor which would explain the higher soluble ferrous iron concentrations in these samples. Further ICP analysis will have to be conducted on those samples whose iron concentrations were not detected. It is likely that these samples will need a lower dilution factor than the factor of 200 used for the other samples.

Table 2-8. ICP data for Fe concentrations from Batches 1 and 2

Description	Fe Concentration (ppb)	
Batch 1 (Set 1-1)	1650.87	
Batch 1 (Set 1-2)	13312.80	**Set 1 Average**
Batch 1 (Set1-3)	8462.03	7808.57
Batch 1 (Set 2-1)	4705.95	
Batch 1 (Set 2-2)	4757.76	**Set 2 Average**
Batch 1 (Set 2-3)	5815.26	5092.99
Batch 1 (Set 3-1)	5730.32	
Batch 1 (Set 3-2)	4343.13	**Set 3 Average**
Batch 1 (Set 3-3)	5349.70	5141.05
Batch 1 (Set 4-1)	5494.83	
Batch 1 (Set 4-2)	6118.96	**Set 4 Average**
Batch 1 (Set4-3)	7596.79	6403.53
Batch 2 (Set 1)	8651.30	
Batch 2 (Set 2)	Not detected	
Batch 2 (Set 3)	Not detected	**Batch 2 Average**
Batch 2 (Set 4)	Not detected	Need to redo samples with lower dilution factor

In the month of March, a poster titled, "Monitoring of U(VI) Bioreduction After ARCADIS Demonstration at Savannah River Site F-Area," for Subtask 2.2 was completed in preparation for the 2015 Waste Management Symposium in Phoenix, Arizona (Figure 2-33). DOE Fellow Aref Shehadeh presented this poster at the symposium in the student poster competition session, "The Next Generation — Industry Leaders of Tomorrow" alongside the other 19 DOE Fellows and FIU students. Discussions with DOE scientists and researchers gave insight into the next possible steps to take for the microcosm study, such as the use of scanning probe microscopy (SPM) to observe the coatings of the particles in the microcosm sediments. It was suggested with the presumption that the iron compounds which have not been observed might not have a regular structure for the XRD instrument to pick up and that they may exist as coatings on larger particles.

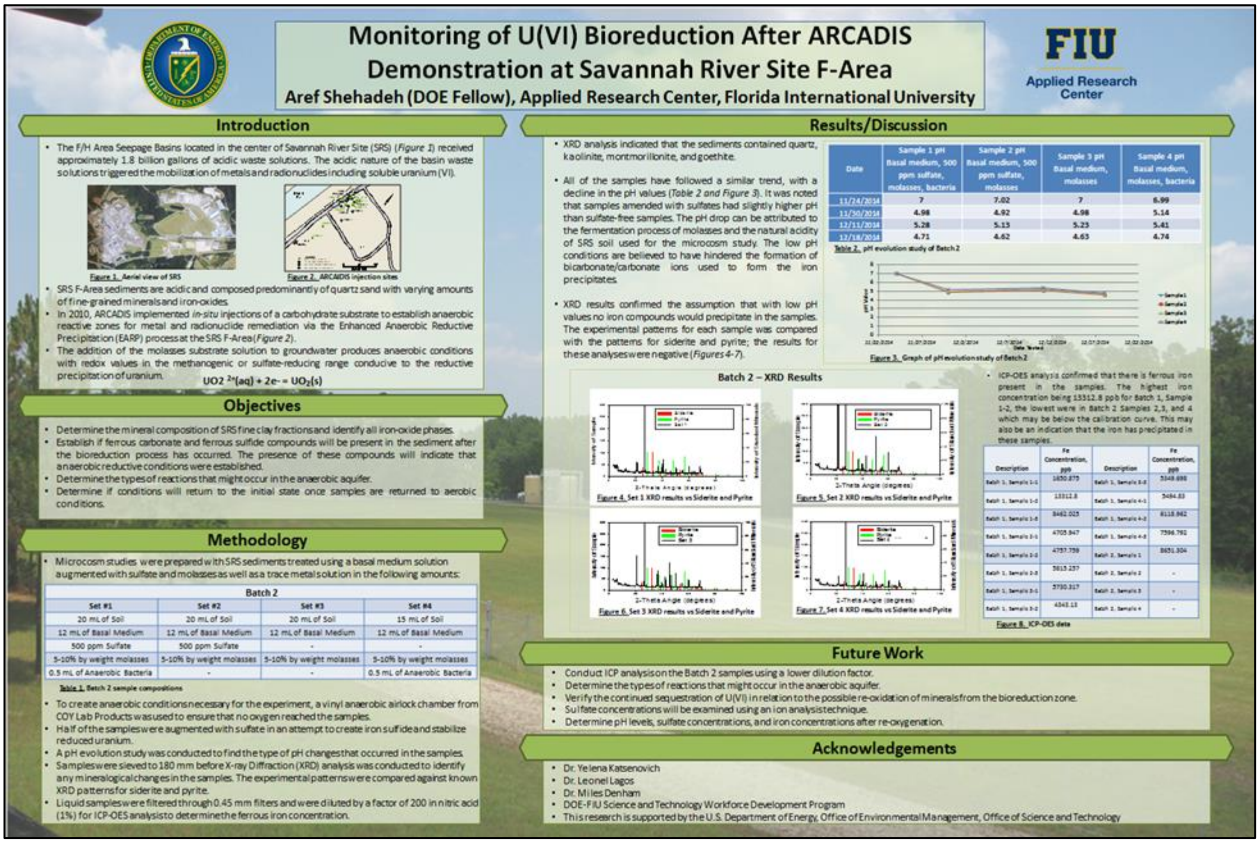


Figure 2-33. DOE Fellow Aref Shehadeh's research poster for WM15.

A presentation pertaining to Subtask 2.2 was also completed for the DOE EM research review for the FIU cooperative agreement, which took place on March 31. An overview of this task was presented to DOE and field site contacts at PNNL, SRNL, and the Germantown and Washington DC headquarters via videoconferencing. Dr. Miles Denham of SRNL suggested using XRD to test for the ferrous iron carbonate ankerite; previous XRD analyses were focused primarily on siderite and pyrite. This will be considered and the XRD data will be analyzed for ankerite in the month of April.

DOE Fellow Aref Shehadeh is also preparing a poster presentation for the 2015 STEM Undergraduate Research Symposium, which will take place at Indian River State College in Port St. Lucie, Florida. The Fellows will be presenting the research they showcased at WM 2015 and will be judged for best poster among 43 other students.

Subtask 2.3: Sorption properties of humate injected into the subsurface system

During January, FIU performed a literature review on experimental approaches to determine the point of zero charge (PZC) of SRS sediments. The PZC value is necessary information that will be used to understand and better explain the soil behavior to adsorb Huma-K and uranium at different pH values. If the pH of a soil is above its PZC, the soil surface will have a net negative charge. If the pH is below PZC, the soil surface will have a net positive charge.The literature review suggested two experimental approaches to determine the PZC. Below is a brief description of both methods.

> *Potentiometric Mass Titrations:* PMTs are performed under a nitrogen atmosphere. A blank solution and suspensions of three different masses of the immersed oxide at constant ionic strength (0.03 M) and temperature (25.0 ± 0.1 °C) are used for the experiments. The titration curves are strongly affected by the mass of the hydroxide at all pH values except that corresponding to the PZC.
>
> *Potentiometric Titrations:* PTs are performed under a nitrogen atmosphere and constant temperature (25.0 ±0.1^{o}C) for three suspensions having the same amount of the immersed oxide but different ionic strengths (0.001, 0.01, and 0.1 M).

In both methodologies, the aqueous suspension containing a given amount of the immersed oxide is equilibrated for 20 h to reach an equilibrium pH value. A small amount of base, 1 M KOH, is added to deprotonate a significant part of the surface sites, rendering the surface negative, and then the suspension is titrated by adding small volumes of a 0.1 or 0.5 M aqueous HNO_3 solution. The pH value is recorded after each addition of the acidic solution as a function of its volume. A similar titrating procedure is followed for the blank solution. The number of hydrogen ions consumed on the surface of the oxide, H+ c (íeq m-2), at each pH value can be determined by subtracting the titration curve of the blank solution from the titration curve of the suspension.

A presentation titled, "The Influence of Humic Acid and Colloidal Silica on the Sorption of U(VI) onto SRS Sediments Collected from the F/H Area," was completed and presented in the oral session 107 "Deep vadose zone characterization and remediation technologies" during the Waste Management Symposia by DOE Fellow and PhD student Hansell Gonzalez (Figure 2-34).

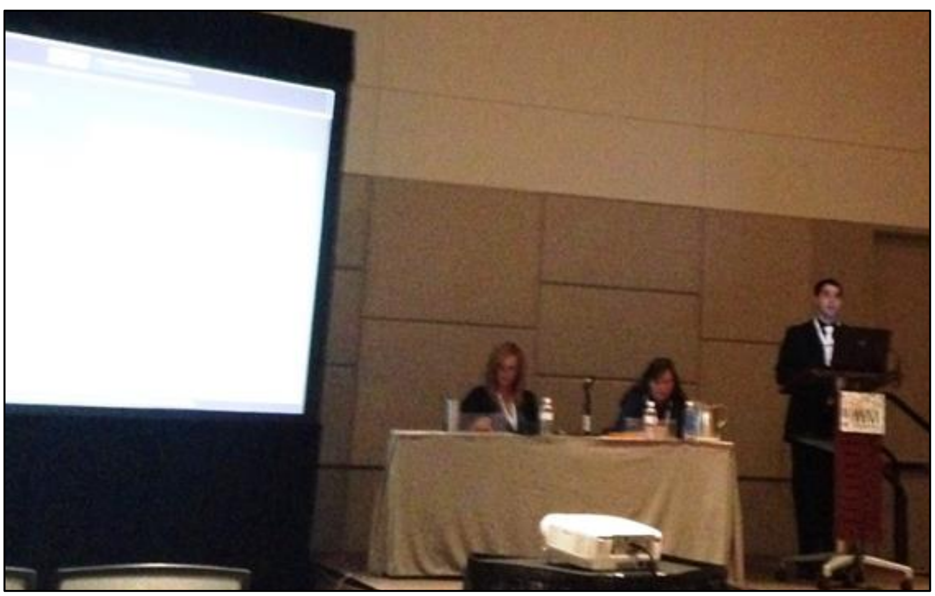


Figure 2-34. DOE Fellow Hansell Gonzalez, a PhD student, presenting a research paper at WM15.

In addition, a poster titled, "Study of an Unrefined Humate Solution as a Possible Remediation Method for Groundwater Contamination," was presented in the Student Poster Competition session by DOE Fellow Hansell Gonzalez. An image of this poster is provided in the Workforce Development section of this report (Project 5).

A technical progress report for the Task 2.3 titled, "The sorption properties of the humate injected into the subsurface system," was prepared and submitted to DOE as a deliverable. Also, the accomplishments for the Task 2.3 were summarized and presented in the DOE EM research review for the FIU cooperative agreement during presentations for FIU Project 2 and FIU Project 5.

Task 3: Evaluation of Ammonia Fate and Biological Contributions during and after Ammonia Injection for Uranium Treatment

Task 3 Overview

The newly created Task 3 relates to the Hanford Site and aims to evaluate the potential biological and physical mechanisms associated with the fate of ammonia after injection into the unsaturated subsurface. These tests will identify and quantify factors controlling the relative rate of these processes. Expected processes include biological transformation, partitioning and geochemical reactions. Tests will examine the mechanisms of potential importance using controlled laboratory systems to complement efforts underway at PNNL.

Task 3 Quarterly Progress

FIU tested and calibrated the Kloehn V6 pumps (using 10 mL syringes) that can inject NH_3 gas with high precision instead of performing manual injection using gas-tight syringes. The Kloehn V6 pump can be controlled using a computer connected via USB cable; the V6 pump can be programmed to pump gas at a specific flow rate and at specific volumes based on the requirements. A temperature controlled bath was installed and tested to maintain uniform temperature during ammonia gas injection since temperature can affect the pH of the solutions.

FIU began using a Kloehn V6 pump with a 10-mL syringe to inject NH_3 gas into DI water and recorded the change in pH. 5% of NH_3 was injected in increments (5 ml, 10 ml) into 50 ml of DI water and the pH was measured and recorded without stirring until the pH reached 11.

Table 2-9 and Figure 2-35 shows the change in pH with the addition of ammonia; pH increased rapidly at the beginning of the experiment, from pH 7.433 to pH 9.225 with the addition of 5 mL of ammonia and reached pH 10.041 with the addition of a total of 15 mL of ammonia. The change in pH with the addition of ammonia was substantially slower after pH 10; a total of 230 mL of ammonia was needed to change the pH from 10 to 11.

Table 2-9. Change in pH with Addition of NH_3

NH_3 mL	Total NH_3	pH
0	0	7.433
5	5	9.225
5	10	9.875
5	15	10.041
5	20	10.138
5	25	10.219

5	30	10.283
5	40	10.378
5	50	10.452
5	60	10.519
5	70	10.589
5	80	10.637
5	90	10.692
5	100	10.725
5	110	10.763
5	120	10.789
5	130	10.817
5	140	10.837
5	150	10.855
5	160	10.872
5	170	10.889
5	180	10.908
5	190	10.924
5	200	10.941
5	210	10.956
5	215	10.96
5	220	10.97
5	225	10.977
5	230	10.982
5	235	10.991
5	240	10.996
5	245	11.002
5	250	11.011

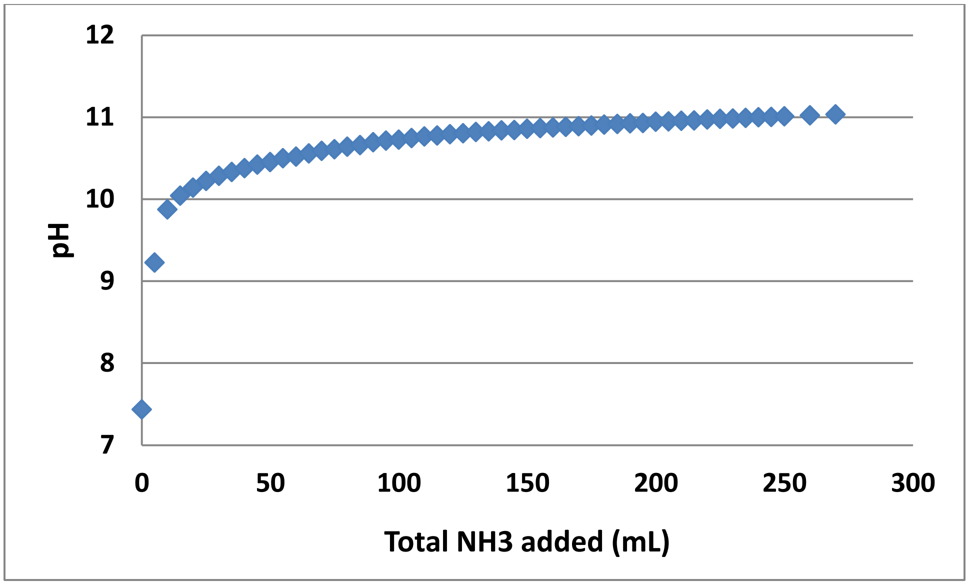


Figure 2-35. Change in the pH with the addition of ammonia gas.

Injection of 5% NH_3 gas in 50 mL of DI water was performed using a stirrer, in increments of 5, 10, 20, 30 and 50 mL and the pH was recorded. The speed of the syringe used was 5000 steps/sec. Figure 2-36 and Table 2-10 show the results. The same experiment was previously performed, excluding the stirrer. The purpose of using it this time was to observe any differences in the distribution of ammonia. We noticed that it would take a large amount of NH_3 before the pH could reach 11, requiring more than 1.7 L NH_3; whereas, with the stirrer off, pH reached 11 with 245 mL of NH_3.

A presentation for the DOE EM research review for the FIU cooperative agreement was prepared and given during the videoconferences. It was noted in this discussion that pH should be able to go higher when using more highly concentrated ammonia. For field scale, 5-15% ammonia would be used. FIU will continue adjusting the volume of DI water and ammonia concentrations, and also observe how the speed of the syringe pump may affect ammonia distribution.

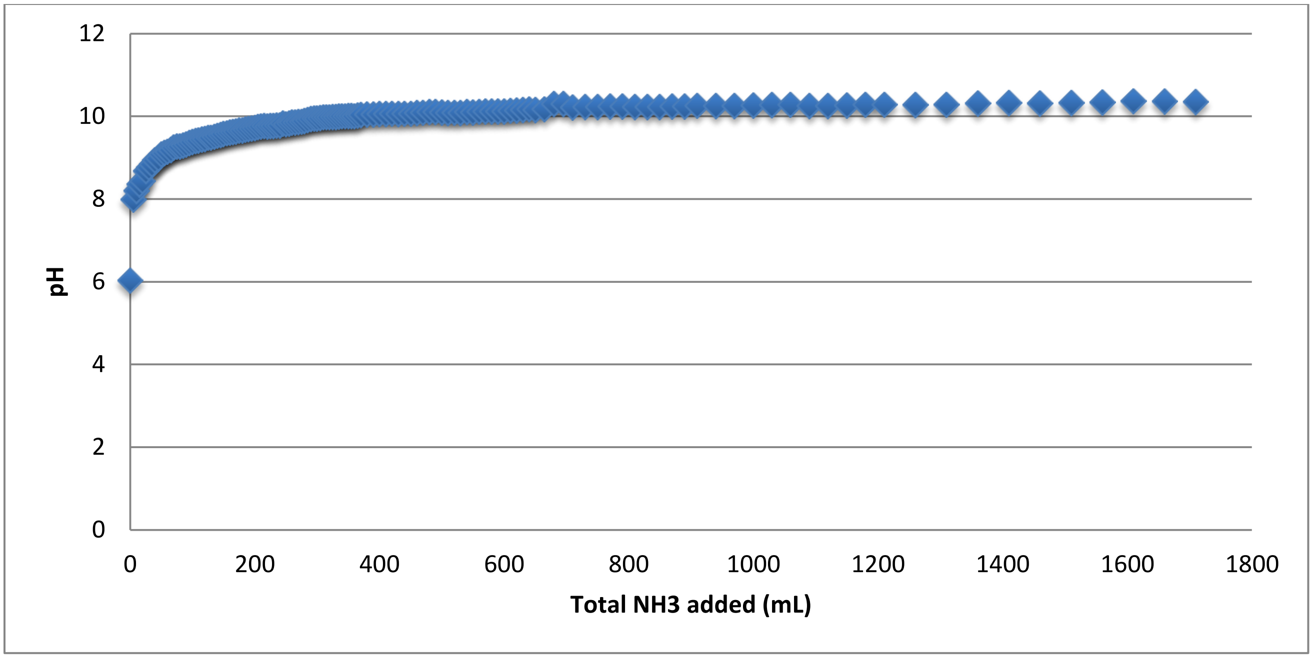


Figure 2-36. Solution changes in pH with the addition of ammonia gas.

Table 2-10. Changes in Solution pH with the Addition of Ammonia Gas

NH3 added (mL)	ΣNH3	pH						
0	0	6.03	5	115	9.439	5	245	9.83
5	5	7.991	5	120	9.457	5	250	9.814
5	10	8.199	5	125	9.485	5	255	9.831
5	15	8.359	5	130	9.49	5	260	9.847
5	20	8.435	5	135	9.512	5	265	9.85
5	25	8.678	5	140	9.534	5	270	9.868
5	30	8.76	5	145	9.547	5	275	9.872
5	35	8.84	5	150	9.575	5	280	9.887
5	40	8.941	5	155	9.592	5	285	9.911
5	45	8.982	5	160	9.609	5	290	9.937
5	50	9.082	5	165	9.625	5	295	9.949
5	55	9.113	5	170	9.637	5	300	9.95
5	60	9.144	5	175	9.656	5	305	9.968
5	65	9.188	5	180	9.666	5	310	9.979
5	70	9.247	5	185	9.692	5	315	9.981
5	75	9.269	5	190	9.694	5	320	9.983
5	80	9.28	5	195	9.71	5	325	9.991
5	85	9.3	5	200	9.719	5	330	9.992
5	90	9.324	5	205	9.744	5	335	9.998
5	95	9.353	5	210	9.757	5	340	10.003
5	100	9.379	5	215	9.768	5	345	10.007
5	105	9.407	5	220	9.761	5	350	10.01
5	110	9.415	5	225	9.77	5	355	10.014
			5	230	9.775	5	360	10.006
			5	235	9.784	5	365	10.024
			5	240	9.779	5	370	10.033

10	380	10.052	50	1260	10.276
10	390	10.053	50	1310	10.287
10	400	10.056	50	1360	10.312
10	410	10.057	50	1410	10.322
10	420	10.068	50	1460	10.316
10	430	10.06	50	1510	10.325
10	440	10.065	50	1560	10.34
10	450	10.071	50	1610	10.365
10	460	10.08	50	1660	10.362
10	470	10.09	50	1710	10.354
10	480	10.106			
10	490	10.102			
10	500	10.097			
10	510	10.084			
10	520	10.092			
10	530	10.084			
10	540	10.103			
10	550	10.099			
10	560	10.111			
10	570	10.118			
10	580	10.119			
10	590	10.123			
10	600	10.124			
10	610	10.137			
10	620	10.141			
10	630	10.152			
10	640	10.176			
10	650	10.153			
15	665	10.173			
15	680	10.297			
15	695	10.3			
15	710	10.213			
20	730	10.226			
20	750	10.229			
20	770	10.236			
20	790	10.236			
20	810	10.231			
20	830	10.226			
20	850	10.229			
20	870	10.237			
20	890	10.246			
20	910	10.26			
30	940	10.251			
30	970	10.251			
30	1000	10.265			
30	1030	10.279			
30	1060	10.282			
30	1090	10.252			
30	1120	10.256			
30	1150	10.272			
30	1180	10.286			
30	1210	10.283			

Milestones and Deliverables

The milestones and deliverables for Project 2 for FIU Year 5 are shown on the following table. Milestone 2014-P2-M1, "Completion of solubility measurements of U(VI)-free samples (FIU Year 5 scope)" and "Completion of solubility measurements using standards such as calcium chloride and lithium chloride to get better deliquescence predictions at low water activities values (carryover scope)," was completed on January 30, 2015. In addition, a deliverable, due January 30, 2015, "Progress report on microcosm studies prepared with SRS sediments augmented with molasses and sulfate for subtask 2.2," was completed and sent to DOE HQ and the SRS site contacts. A deliverable, "A progress report on the solubility measurements via isopiestic method (subtask 1.1) using standards such as calcium chloride and lithium chloride to get better deliquescence predictions at low water activities values (carryover scope)," was completed on February 16, 2015. A deliverable, "FIU's Support for Groundwater Remediation at SRS F/H Area (subtask 2.1)," was completed and sent to DOE HQ and the SRNL site contacts on March 31, 2015.

FIU Year 5 Milestones and Deliverables for Project 2

Task	Milestone/ Deliverable	Description	Due Date	Status	OSTI
Task 1: Sequestering uranium at Hanford	2014-P2-M5	Obtain anaerobic facultative microorganisms, Shewanella sp., from PNNL and complete preparations to set up autunite leaching experiments.	10/03/14	Complete	
	2014-P2-M3	Completion of sample preparation using a reduced amount of silica (50 mM)	11/07/14	Complete	
	2014-P2-M4	Complete preparation of a draft manuscript on the removal of uranium via ammonia gas injection method	12/15/14	Complete	
	2014-P2-M1	Completion of solubility measurements of U(VI)-free samples (FIU Year 5 scope) **and** Completion of solubility measurements using standards such as calcium chloride and lithium chloride to get better deliquescence predictions at low water activities values (carryover scope).	01/30/15	Complete	
	Deliverable	Prepare a progress report on the solubility measurements via isopiestic method (subtask 1.1)	02/16/15	Complete	OSTI
Task 2: Groundwater remediation at SRS	2014-P2-M6	Complete preparations for the microcosm experiments prepared with SRS sediments using sulfate additions.	09/12/14 Re-forecasted to 10/13/14	Complete	

	Deliverable	Progress report on microcosm studies prepared with SRS sediments augmented with molasses and sulfate (subtask 2.2)	01/30/15	Complete	OSTI
	Deliverable	Progress report on batch experiments prepared with SRS sediments, colloidal Si and higher HA concentration up to 50ppm (carryover scope under subtask 2.1).	03/30/15	Complete	OSTI
	Deliverable	Prepare a progress report on sorption properties of the humate injected into the subsurface system (subtask 2.3)	04/03/15	On Target	OSTI
Task 3: Evaluation of ammonia for uranium treatment	2014-P2-M2	Completion of literature review on physical mechanisms associated with the fate of ammonia after injections into subsurface	10/31/14	Complete	

Work Plan for Next Quarter

- Draft the Year End Report for FIU Year 5 (May 2014 to May 2015).
- Subtask 1.2 Prepare uranium-bearing samples and initiate a new round of isopiestic measurements. First check deliquescence of standards, $CaCl_2$ and NaCL, to make sure isopiestic chamber works properly.
- Subtask 1.2: Complete proofs of “imaging” manuscript after acceptance. Learn procedures for the protein analysis, develop a calibration curve and conduct experiments to find a correlation between protein and Shewanella cell concentrations. Initiate preparation of samples for the autunite dissolution experiment.
- Subtask 2.1: Initiate experiments for the optimization of conditions for uranium removal through the addition of sodium silicate (evaluation of sodium silicate concentrations for a longer period of time), as well as monitoring of silicate and iron concentration in the aqueous phase. Start preparations for SEM-EDS of the 0.45 μm filters that were used for sample filtration.
- Subtask 2.2: Conduct sulfate and iron analysis to find mass balance of elements in the samples before and after treatment with molasses.
- Subtask 2.3: Initiate the potentiometric titration of SRS sediment to investigate for the point of zero charge and conduct the titration of Huma-K to determine pKa values of different functional groups.
- Task 3: Continue testing of ammonia injection at 0, 3, 10 mM bicarbonate concentrations.
- Subtask 2.1: Initiate samples preparation to explore the effect of the humic acid concentration up to 30 ppm, which is an average value between 10 ppm and 50ppm. The experimental matrix will be the same as for the study conducted last year using 10 ppm and 50 ppm of HA.

Project 3
Environmental Remediation Technologies (EM-12)

Project Description

For FIU Year 5, FIU will utilize and build upon the capabilities developed under Project 3 in the area of soil and groundwater remediation and treatment technology. FIU will coordinate closely with the Savannah River Site during FIU Year 5 in the execution of the work scope. Tasks will be synergistic with the work SRNL is performing and will involve (1) Modeling of the migration and distribution of natural organic matter injected into subsurface systems; (2) Fate and transport modeling of Hg, Sn and sediments in surface water of Tims Branch; and (3) Analysis of baseline, optimization studies and development of a system improvement plan for the A/M Area groundwater remediation system.

FIU Year 4 Carryover Work Scope

The FIU Year 4 carryover work scope for Project 3 has been completed. The carryover tasks and their completion dates are as follows:

- Final Technical Report for Task 1: EFPC Model Update, Calibration, and Uncertainty Analysis – complete and submitted on July 31, 2014.
- Final Technical Report for Task 2: Simulation of NPDES- and TMDL-Regulated Discharges from Non-Point Sources for the EFPC and Y-12 NSC – complete and submitted on July 31, 2014.
- Final Technical Report for Task 3: Sustainable Remediation and Optimization: Cost Savings, Footprint Reductions, and Sustainability Benchmarked at EM Sites – complete and submitted on September 26, 2014.
- Final Technical Report for Task 4: Geodatabase Development for Hydrological Modeling Support – complete and submitted on June 30, 2014.

Task 1: Modeling of the migration and distribution of natural organic matter injected into subsurface systems

Task 1 Overview

Task 1 aims to assemble, integrate and develop a practical and implementable approach to quantify and model potential natural organic matter (NOM, such as humic and fulvic acids, humate, etc.) deployment scenarios for the range of conditions at DOE sites. Initial laboratory experiments and an initial set of simplified models have been developed at SRNL. Under this task, additional batch and column studies and testing will be conducted at FIU to provide the transport parameters for an extension of the current model scenarios.

Task 1 Quarterly Progress

Subtask 1.2: Column testing of the migration and distribution of humate injected into subsurface systems

- A second batch of soil was received from SRS (FAW-1: 60'-70') and soil characterization studies were completed. This batch of SRS soil was taken from a different depth than the previous samples received. Soil characterization data was similar to the previous batch (FAW-1: 70'-90') except for pH. Although parameters of the two soil samples were comparable, there were some differences noted. After consultation with SRNL's task lead, Miles Denham, a decision was made to use homogeneous soil by combining the soil from the first and second batches in the column studies to ensure consistency in all the columns.
- The bromide sensor was calibrated using various standards and tested for reproducibility.
- The new experimental columns were received. A schematic column set-up was developed and discussed with Jairo Crespo (machine shop/engineering support specialist). A mock up column test will be performed and will be expanded to 4 columns as per the test plan.
- FIU completed testing and calibration of the pumps to be used in the column experiments.
- Miles Denham and Brian Looney (SRNL) provided positive feedback on the task progress during the regular project teleconferences. Brian suggested the use of an inline bromide measurement setup and promised to show a variety of modules that Ralph Nichols (SRNL) has to obtain and record continuous sensor data logging.
- Discussions held with ARC's mechanical engineering team regarding the experimental procedures led to the identification of the tubing and adapters required to complete the column setup that would withstand the maximum pressure that the pump will apply. The initial tubing tested only achieved a 1.74 ml/min flow rate. New tubing was purchased that was expected to achieve flow rates greater than 4.0 ml/min. Pressure tests were carried out with new tubing at maximum speed (4.0 ml/min) to ensure the tubing could withstand the pressure to be applied.
- Finalized the column set-up drawings and configuration with ARC's mechanical engineering team (Amer Awwad & Jairo Crespo) and assembled the columns as per the recommended specifications (Figure 3-1).
- The humate injection scenarios were updated based on new data obtained during the sorption batch experiments and soil characterization studies.
- Kiara Pazan, the DOE Fellow supporting this task, tested a meter procured under Project 2 to determine whether it can be used to measure the concentration values in the column studies. A new meter was also tested to measure the concentration of bromide from the tracer test.
- Kiara Pazan (DOE Fellow) prepared and presented a student poster entitled, "Column Testing of the Migration and Distribution of Humate Injected into Subsurface Systems at Savannah River Site's F/H Area" that was related to this research at the Waste Management Symposium 2015 held in Phoenix, AZ in March (Figure 3-2).

- A presentation of the research conducted under this task was prepared for a research review as a part of the DOE-FIU Cooperative Agreement.

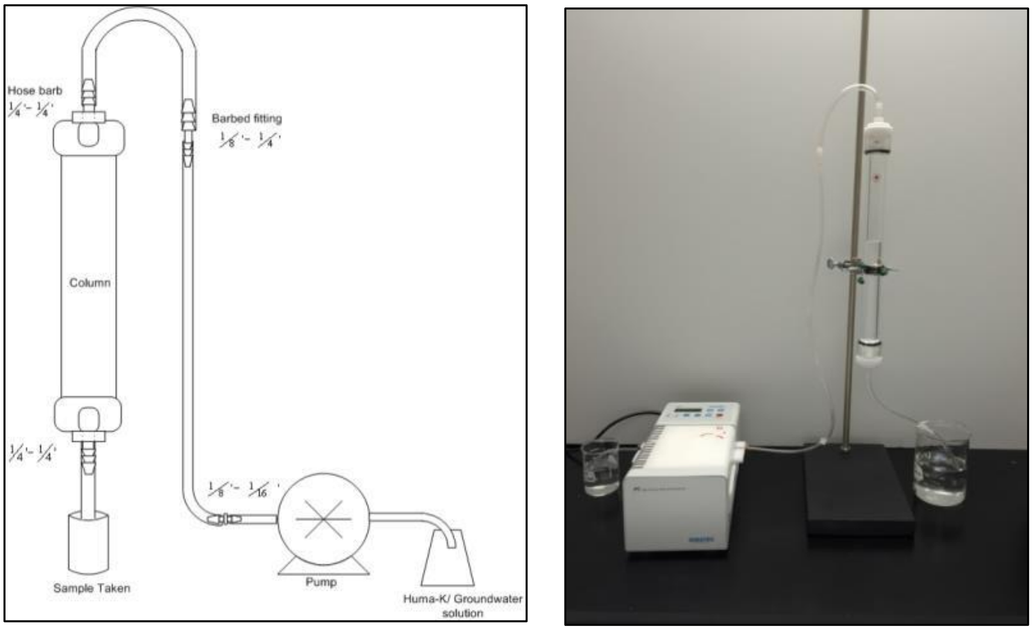


Figure 3-1. Preliminary experimental column design and set-up.

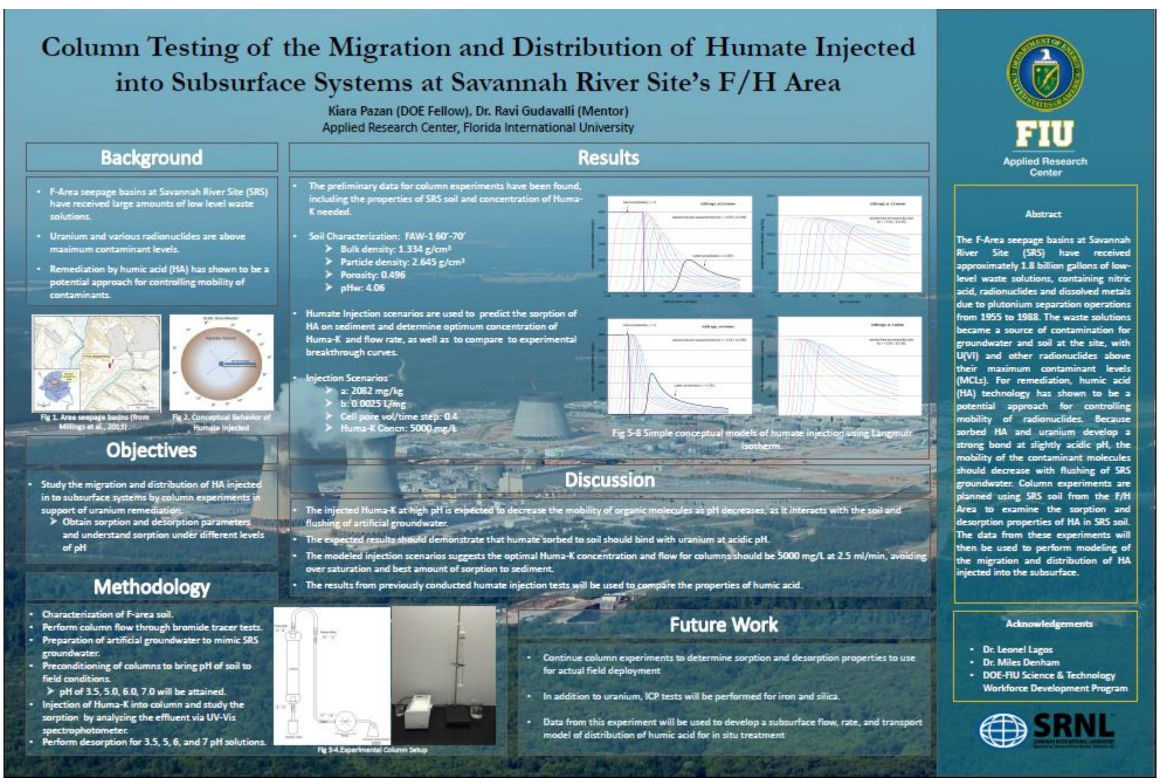


Figure 3-2. DOE Fellow Kiara Pazan student poster presented at Waste Management Symposium 2015.

Subtask 1.3: Development a subsurface flow, fate and transport model of humic acid

This task includes modeling of the migration and distribution of humate injected into subsurface systems during deployment for in situ treatment of radionuclides, metals and organics. Relevant data derived from the column studies will be used for development of a flow and transport model.

Task 2: Surface Water Modeling of Tims Branch

Task 2 Overview

This task will perform modeling of water, sediment, 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.

Task 2 Quarterly Progress

Subtask 2.1: Development of a detailed GIS-based representation of the Tims Branch ecosystem

- Support for the development of the MIKE SHE models is being provided through the preprocessing of the GIS data provided by SRNL. Two process-flow models using ArcGIS ModelBuilder were developed for clipping all the shapefiles within the two experimental domains.
- Various model-specific grid files such as Manning's roughness coefficients, paved runoff coefficients, land cover/land use, topography, etc. were also generated from GIS shapefiles (Figure 3-3).
- 2D and 3D georeferenced maps of Tims Branch and the nearby A/M Area were generated to show the relevant features that will contribute to the contaminant fate and transport modeling (Figures 3-4 and 3-5).

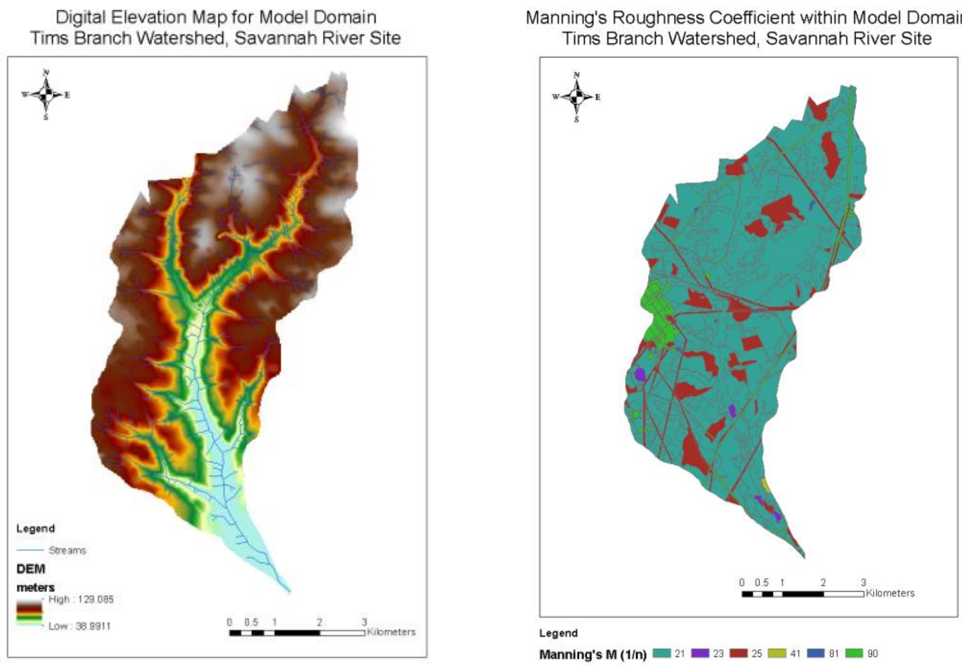


Figure 3-3. Digital elevation model and Manning's roughness coefficient grid files generated and clipped to the model domain to be added to the MIKE SHE model.

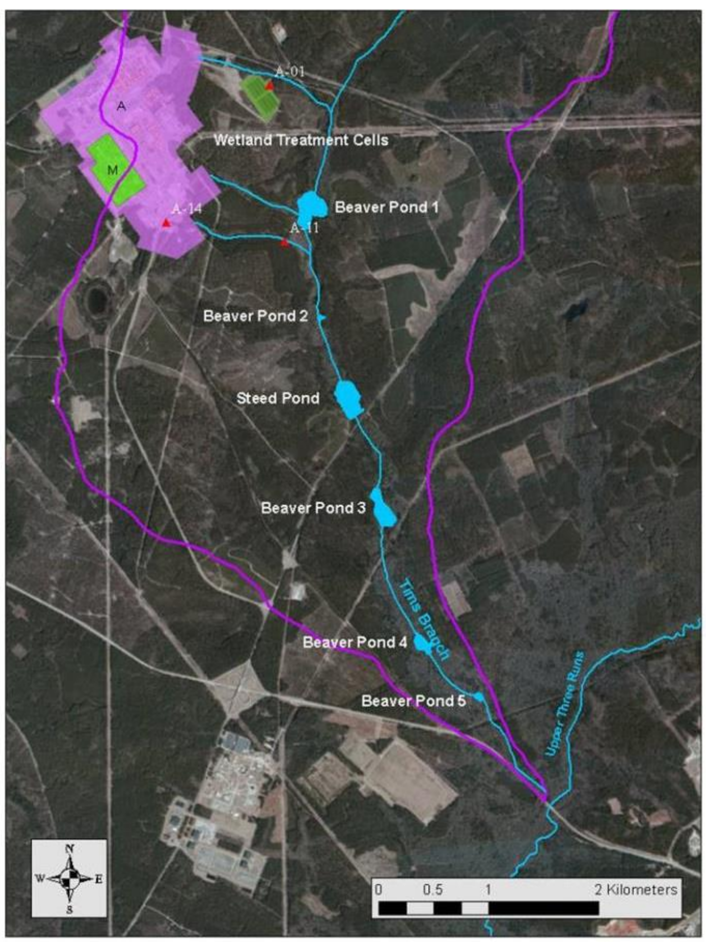


Figure 3-4. 2D Map of SRS A/M Area and Tims Branch.

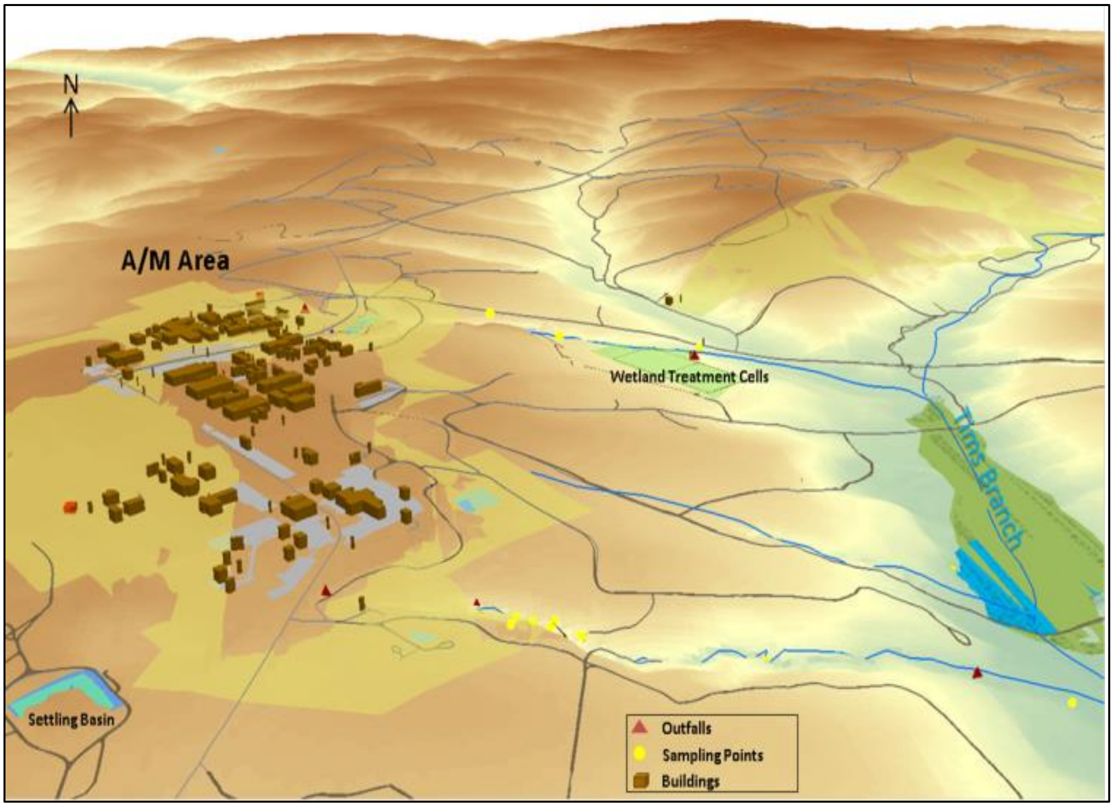


Figure 3-5. 3D Map of SRS A/M Area and Tims Branch.

Subtask 2.2: Modeling of surface water and sediment transport in the Tims Branch system.

- FIU worked on developing a preliminary hydrological model using MIKE SHE/11. Precipitation data and other relevant data parameters have already been added to the MIKE SHE model.
- Approximately 50% of the preliminary input parameters for the MIKE SHE component of the hydrological model were successfully added in February. This included GIS data that has been preprocessed to generate model-specific file types such as topography, landcover/landuse, Manning's coefficient and paved run-off coefficient DFS2 grid files. Other parameters such as precipitation data which was also provided by SRNL for approximately a 50-yr period were added.
- Review of the leaf area index and evapotranspiration rates, soil profile data and other significant parameters was performed. These additional inputs are currently being added.
- A draft process-based conceptual model was submitted to Brian Looney (SRNL). Revisions to the conceptual model were recommended to provide more detail with respect to the contamination source zones and transport mechanisms. Brian noted that the conceptual model should reflect the energy dynamics of the water/sediment transport of tin associated with the mercury treatment. It is important to focus on the surface water compartment, particularly during storm events. It is safe to assume the landcover/landuse and the vegetation to be constant (as opposed to time-varying) as there has not been significant change over the past 20-30 years that should impact the simulations, particularly if the simulations are being run for shorter-term storm events. Noosha will have support from Natalia Duque (DOE Fellow) and Angelique Lawrence in the

development of a second draft based on Brian’s feedback. Guidance has also been provided by Shimelis Setegn as to the relevant components that should be included in the second draft.

- Dr. Mahmoudi completed a literature review (Milestone 2014-P3-M2 – Literature review for the surface water modeling of Tims Branch) to support the hydrological modeling framework for Tims Branch. A literature review summary report entitled “Literature Review for Surface Water Contaminant Fate and Transport Modeling of Tims Branch” was submitted to DOE and SRS on March 31, 2015. The objective of this report was to summarize the literature that has been reviewed and that will be significant in development of the conceptual model of the Tims Branch watershed, as well as the hydrological modeling work to simulate the fate and transport of mercury and tin in Tims Branch. More than 30 SRS-DOE reports and 100 published journals were reviewed. A total of 10 reports were found to be significant to this study and are included in this summary report. Specific reports by Looney (2010, 2012) and Betancourt (2011) were among the most addressed in this literature review and a total of 40 journal articles were found relevant to the study. An additional literature review was performed to explicitly address previous hydrological modeling efforts conducted for Tims Branch; however, it was determined that there were very few studies involving hydrological model development in this watershed.
- The literature review was used to develop a data-driven conceptual model (Figure 3-6) specific to the Tims Branch watershed at Savannah River Site (Milestone 2014-P3-M3 - Development of preliminary site conceptual model of Tims Branch), as well as a generalized process-based conceptual model (Figure 3-7) which depicts the various hydrological components being incorporated in the model development. This report will also be utilized as a foundation for surface water modeling in Tims Branch and other areas at SRS.

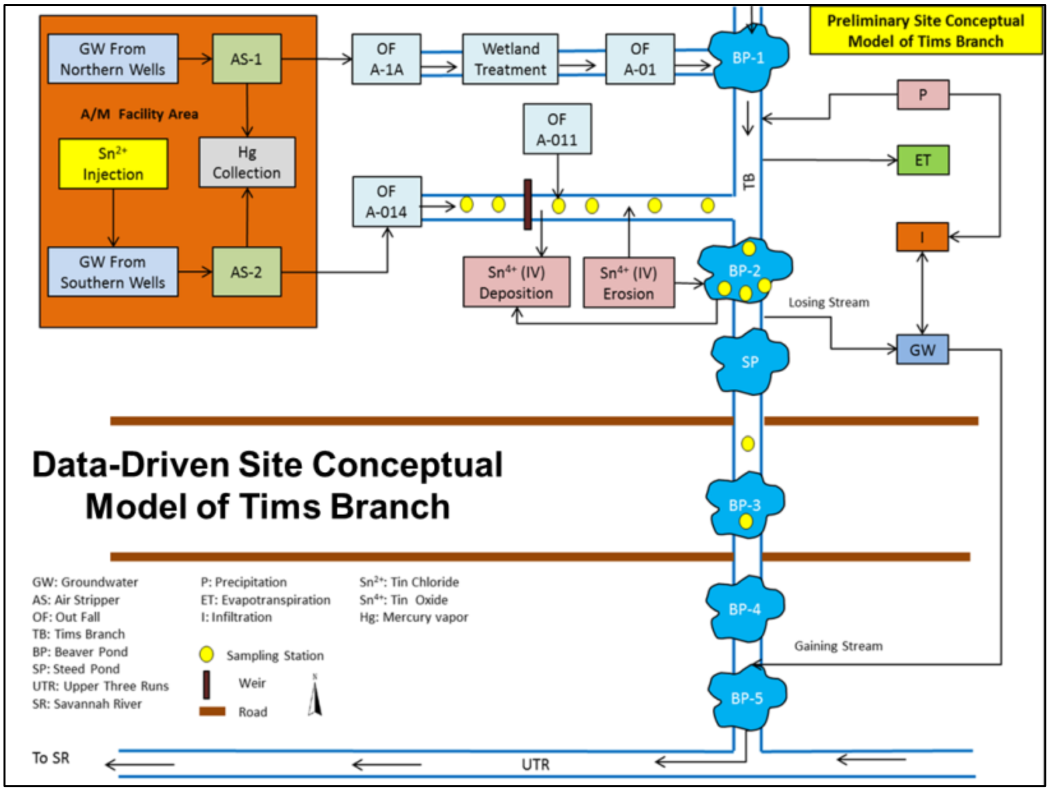


Figure 3-6. Data-driven site conceptual model of Tims Branch.

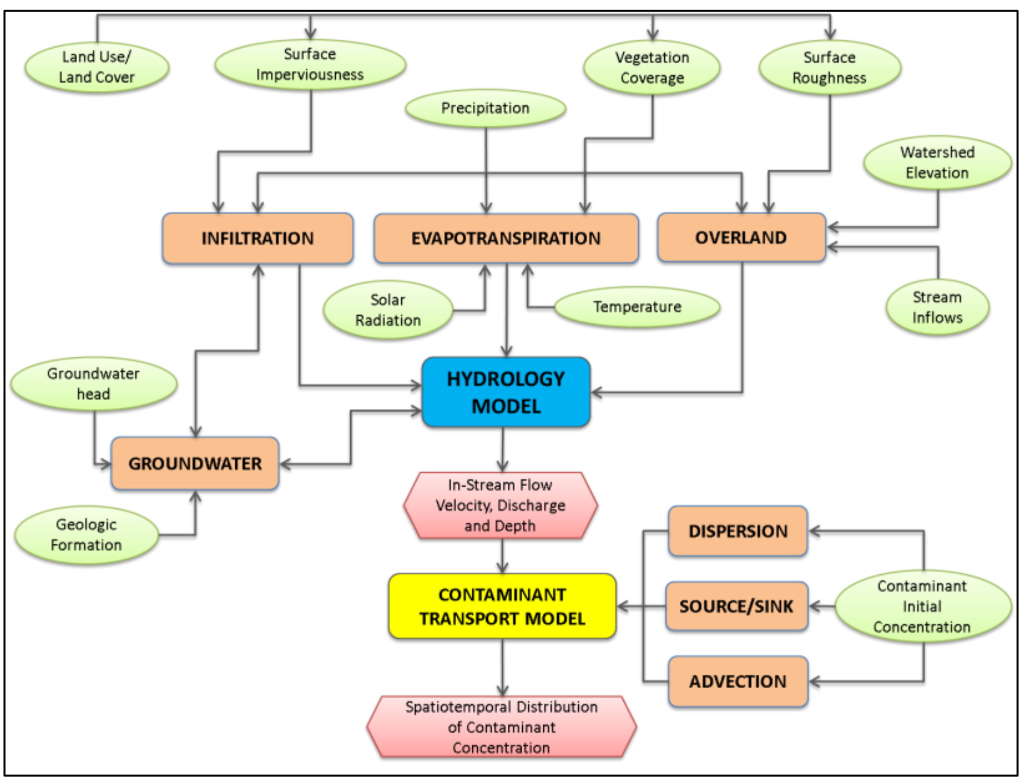


Figure 3-7. Process-based conceptual model for hydrological modeling of Tims Branch watershed.

Task 3: Sustainability Plan for the A/M Area Groundwater Remediation System

Task 3 Overview

This research is conducted in support of EM-13 (Office of D&D and Facilities Engineering) under the direction of Mr. Albes Gaona. FIU will develop a set of proposed actions for the existing infrastructure of the groundwater remediation system that will reduce the environmental burden of the A/M Area groundwater remediation system. Reducing the duration of operation for the treatment system as well as replacing old, inefficient components are preliminary recommendations of these studies. The A/M Area groundwater remediation system has operated continuously for 27 years and is expected to operate continuously for the foreseeable future. Improvements in system performance, increased contaminant recovery, or decreased energy consumption, will have positive enduring benefits due to the long time frame over which the benefits will accrue. This work will directly support the EM-12/EM-13 Sustainable Remediation (SR) program and will be executed in coordination with the SR program lead. The effort is also referred to as "Green and Sustainable Remediation (GSR)" or "Green Remediation" in the literature and in various implemented programs.

Task 3 Quarterly Progress

Subtask 3.1: Analyze Baseline.

The following work was completed during this reporting period:

- Conducted analyses of the pump efficiencies as well as the electrical power used by all pumps and the stripper. Per well analyses of recovery efficiencies and electrical power usage will follow in the next quarter.
- Dr. Roelant and DOE Fellow Yoel Rotterman requested engineering drawings and all possible data on the air stripper at SRS in order to analyze for design modifications. Ralph Nichols committed working to have over 100 identified documents released and to to making inquiries to locate additional reports and drawings. Review of generic air stripper designs continued.
- Piping and Instrumentation Diagrams for the M1 stripper were received and reviewed. Engineering design and As-Built drawings are still at SRNL awaiting release.
- Completed the "Baseline Summary Report for Sustainable Remediation Options for the M1 Air Stripper at DOE SRS" and submitted the report to DOE and SRNL by its due date of February 27, 2015. The location of many months of missing data for contaminant removal per well was put into a database and included in this report.
- Analyzed remediation systems from commercial vendors, especially packed bed material that allows for maximum effectiveness in a counterflow system (downward water flow and upward air flow). Completed a review of state-of-the-art designs for air strippers and awaiting documents from SRS to propose modifications for optimization of the M1 stripper.
- Initiated analysis of monthly electrical energy (kW-hr) used per well on recovery wells 1-12 from Jan. 1987 – Dec. 2012.
- Held discussions with site contacts regarding the possibility of DOE Fellow Yoel Rotterman working at SRS during a 10 week summer internship.

- A Waste Management 2015 paper on the TCE and PCE removal from 12 recovery wells from 1987 to 2012 was written and submitted with Ralph Nichols (SRNL) and DOE Fellow Natalia Duque as coauthors. An oral presentation related to this research was presented by Dr. David Roelant at Waste Management 2015 entitled, "Modeling and Quantitative Assessment of Green and Sustainable Remediation Options for the M1 Air Stripper System at DOE SRS" (Figure 3-8).

Figure 3-8. Dr. David Roelant presenting a paper at the Waste Management 2015 Symposium.

- A student poster related to this task was presented by Natalia Duque (DOE Fellow) at Waste Management 2015 entitled, "Quantitative Assessment of Sustainable Remediation Options for the M-1 Air Stripper System at SRS" (Figure 3-9).

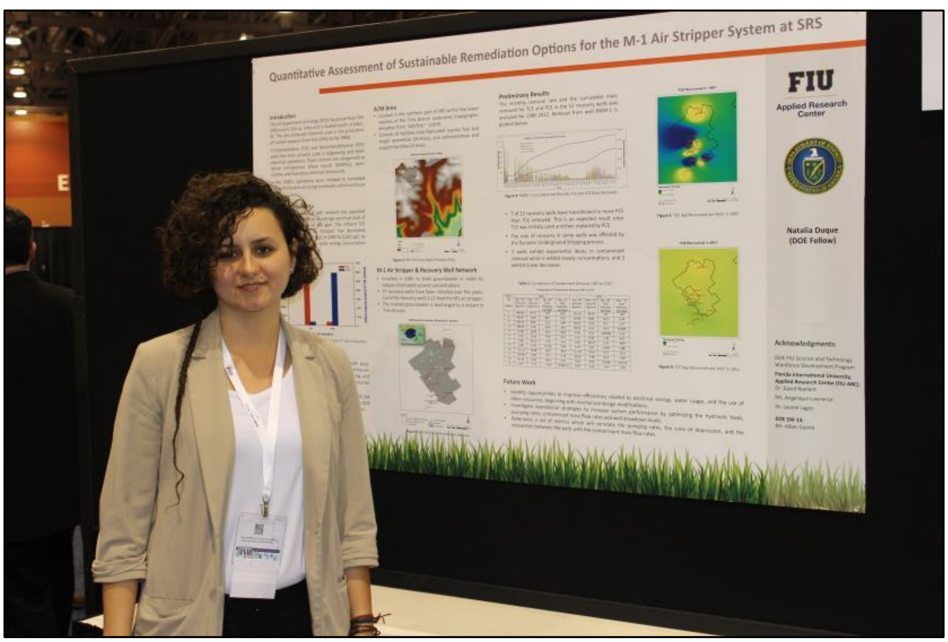


Figure 3-9. DOE Fellow Natalia Duque presenting a poster at the Waste Management 2015 Symposium.

Milestones and Deliverables

The milestones and deliverables for Project 3 for FIU Year 4 are shown on the following table. Milestone 2014-P3-M4, "Completion of Baseline Analysis (Subtask 3.1)" and its associated deliverable "Baseline analysis summary (Subtask 3.1)" for subtask "Sustainability Plan for the A/M Area Groundwater Remediation System" were completed and submitted to DOE HQ and SRS site contacts on the due date, February 27, 2015. Milestone 2014-P3-M2, literature review for the surface water modeling of Tims Branch (Subtask 2.2), and the associated summary report deliverable which is entitled "Literature Review for Surface Water Contaminant Fate and Transport Modeling of Tims Branch" were completed and submitted to DOE and SRS on March 31, 2015. Milestone 2014-P3-M3 – Development of preliminary site conceptual model of Tims Branch (Subtask 2.2) was also completed and submitted on March 31, 2015. Milestone 2014-P3-M6 – Meeting and presentation of project progress at SRS which was due March 18, 2015, has been reforecast to April 13, 2015 due to schedule conflicts of both SRNL and FIU personnel.

FIU Year 5 Milestones and Deliverables for Project 3

Task	Milestone/Deliverable	Description	Due Date	Status	OSTI
Task 1: Modeling of the migration and distribution of natural organic matter injected into subsurface systems	2014-P3-M1	Completion of work plan for experimental column studies (Subtask 1.1)	9/30/14	Complete	
	Deliverable	Work plan for experimental column studies (Subtask 1.1)	9/30/14	Complete	
	Deliverable	Technical Report for Task 1	6/3/15	On Target	
Task 2: Surface Water Modeling of Tims Branch	2014-P3-M2	Completion of literature review (Subtask 2.2)	12/30/14 Reforecast to 3/31/15	Complete	
	Deliverable	Literature review summary (Subtask 2.2)	12/30/14 Reforecast to 3/31/15	Complete	
	2014-P3-M3	Development of preliminary site conceptual model of Tims Branch (Subtask 2.2)	12/30/14 Reforecast to 3/31/15	Complete	
	Deliverable	Technical Report for Task 2	6/10/15	On Target	
Task 3: Sustainability Plan for the A/M Area	2014-P3-M4	Completion of Baseline Analysis (Subtask 3.1)	2/27/15	Complete	

Groundwater Remediation System	Deliverable	Baseline analysis summary (Subtask 3.1)	2/27/15	On Target	
	Deliverable	Technical Report for Task 3	6/17/15	On Target	
Project-wide	Deliverable	Draft Project Technical Plan	6/18/14	Complete	
	Deliverable	Two (2) abstract submissions to WM15	8/15/14	Complete	
	2014-P3-M5	SRS site visit and meeting	8/5/14	Complete	
	2014-P3-M6	Meeting and presentation of project progress at SRS	3/18/15 Reforecast to 4/13/15	Reforecast	

**Final documents will be submitted to DOE within 30 days of the receipt of comments on the draft documents.*

Work Plan for Next Quarter

Project-wide

- Draft the Year End Report for FIU Year 5 (May 2014 to May 2015).

Task 1: Modeling of the migration and distribution of natural organic matter injected into subsurface systems

- A single column will be filled with SRS soil and DI water pumped through the columns for a period of 1 week to eliminate air trapped in the column. This will also help to examine the pressure exerted on the tubing and connectors.
- The next step will be to conduct a bromide tracer test, analyze the results and perform the required calculations to determine an optimal flow rate for the column experiments.
- After finishing the bromide tracer test, humate will be injected into the first column and the experiment will be continued with one column at a time. Additional columns will then be added (one at a time) and the aforementioned tests repeated.
- GIS data for the F/H Area (entire GSA) will be requested in order to begin pre-preparation for the modeling work (Subtask 1.3).
- Kiara Pazan (DOE Fellow) supporting this task will present a poster based on this research at the Life Sciences South Florida STEM Undergraduate Research Symposium being hosted at Indian River State College on April 4, 2015.
- Submit technical report due 6/3/15.

Task 2: Surface Water Modeling of Tims Branch

- Noosha Mahmoudi and Angelique Lawrence will visit SRS on 13-14 April, 2015 to tour the A/M Area and Tims Branch to gain a better understanding of the hydrology of the Tims Branch watershed and define future work scope for FIU Year 5 work as well as for the next DOE-FIU 5-yr cycle. This will fulfill Milestone 2014-P3-M6, "Meeting and presentation of project progress at SRS", which had to be reforecast due to schedule conflicts.
- The hydrological model will be completed using MIKE SHE/11 to depict the spatiotemporal distribution of tin in Tims Branch. This includes:
    - Complete input of all hydrogeological parameters.
    - Incorporation of the Tims Branch river network using MIKE 11.
    - Model calibration and sensitivity analysis.
- Simulations will be run to determine the fate and transport of tin in Tims Branch during extreme rainfall events. Consideration will also be given to the possibility of tin methylation under these extreme conditions.
- Additional topographic information will be examined for comparative analysis of change in topography over time that may have an influence on the watershed hydrology.
- Submit technical report due 6/10/15.

Task 3: Sustainability Plan for the A/M Area Groundwater Remediation System

- Analysis of the recovery efficiency (per well, per month, per 1000 gallons pumped) for all recovery wells will be completed and sent to SRNL 4/22 for review and comments.
- Pump efficiencies and electrical power usage by groundwater pumps for all recovery wells delivering water to the two air strippers on site will be analyzed. Final energy efficiency analysis will be completed by May 15th.
- Analyze additional M1 stripper design and operation performance documentation received and initiate a Sustainable Remediation analysis of the M1 air stripper.
- Submit technical report due 6/17/15.

Project 4
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 HQ (EM-13). 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 Year 5:

- Task 1: Waste Information Management System (WIMS)
- Task 2: D&D Support to DOE EM for Technology Innovation, Development, Evaluation and Deployment
- Task 3: D&D Knowledge Management Information Tool (KM-IT)

Task 1: Waste Information Management System (WIMS)

Task 1 Overview

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

During this performance 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 is expecting to receive the new set of waste stream forecast and transportation forecast data from DOE within the next few weeks. The revised waste forecast data will be received as formatted data files and, to incorporate these new files, FIU will build a data interface to allow the files to be received by the WIMS application and import it into SQL Server. SQL server is the database server where the actual WIMS data is maintained. FIU will complete the data import and deploy onto the test server for DOE testing and review. Once FIU has incorporated feedback from the data review, the new data will be deployed on the public server. The 2015 waste data will replace the existing previous waste data and will become fully viewable and operational in WIMS.

WIMS was presented to the Waste Management Symposium 2015 during poster session 49C on March 17, 2015, in Phoenix, AZ. Figure 4-1 shows Dr. Himanshu Upadhyay and Mr. Walter Quintero presenting the WIMS poster at WM15.

Figure 4-1. Mr. Walter Quintero and Dr. Himanshu Upadhyay presenting the WIMS poster at WM15.

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

<u>Task 2 Overview</u>

This task provides direct support to DOE EM for D&D technology innovation, development, evaluation and deployment. For FIU Year 5, FIU will assist DOE EM-13 in meeting the D&D needs and technical challenges around the DOE complex. FIU will concentrate its efforts this year on working with the Savannah River Site to identify and evaluate innovative technologies in support of the SRS 235-F project. In addition, FIU will continue to support DOE EM-13 in their interactions with EFCOG via the development of lessons learned and best practices from across the DOE Complex. FIU will further support the EM-1 International Program and the EM-13 D&D program by participating in D&D workshops, conferences, and serving as subject matter experts.

<u>Task 2 Quarterly Progress</u>

DOE Fellows supporting this task include Jesse Viera (undergraduate, mechanical engineering), Janesler Gonzalez (undergraduate, mechanical engineering), and Meilyn Planas (undergraduate, electrical engineering). DOE Fellows Jesse Viera and Janesler are primarily supporting the organic semiconductor thin film research, the noncombustible fixatives research, and the fogging research and evaluation. DOE Fellow Meilyn Planas is supporting the development of a decision model for contamination control products.

Subtask 2.1.1: Development of a Decision Model for Contamination Control Products

In support of the development of a decision model for contamination control products, FIU is interacting with SRS to identify the product search parameters based on project-specific needs and site applications. FIU conducted bi-monthly phone calls with Michael Serrato (SRNL) during March to discuss task progress. The contamination control product list is continuously being updated by contacting new potential vendors and requesting the required information about their decontamination products.

The design and development the web-based fixative model application is in progress. Design of the web-based database has been initiated and is ongoing. The group (Criteria), category (sub-criteria) and products are taken as main credentials and other requirements are linked for decision making. SQL statements for the database have been created and will be tested for normalization. The database will be implemented in SQL server. Once the web-based application is complete, it will be made available through the D&D Knowledge Management Information Tool portal for beta testing and input from field site users.

DOE Fellow Meilyn Planas prepared and presented a student poster entitled, “D&D Decision Model and Mobile Application for Selection of Fixative, Strippable Coating, and Decontamination Gel Products” that was related to this research at the Waste Management Symposium 2015 held in Phoenix, AZ in March (Figure 4-2).

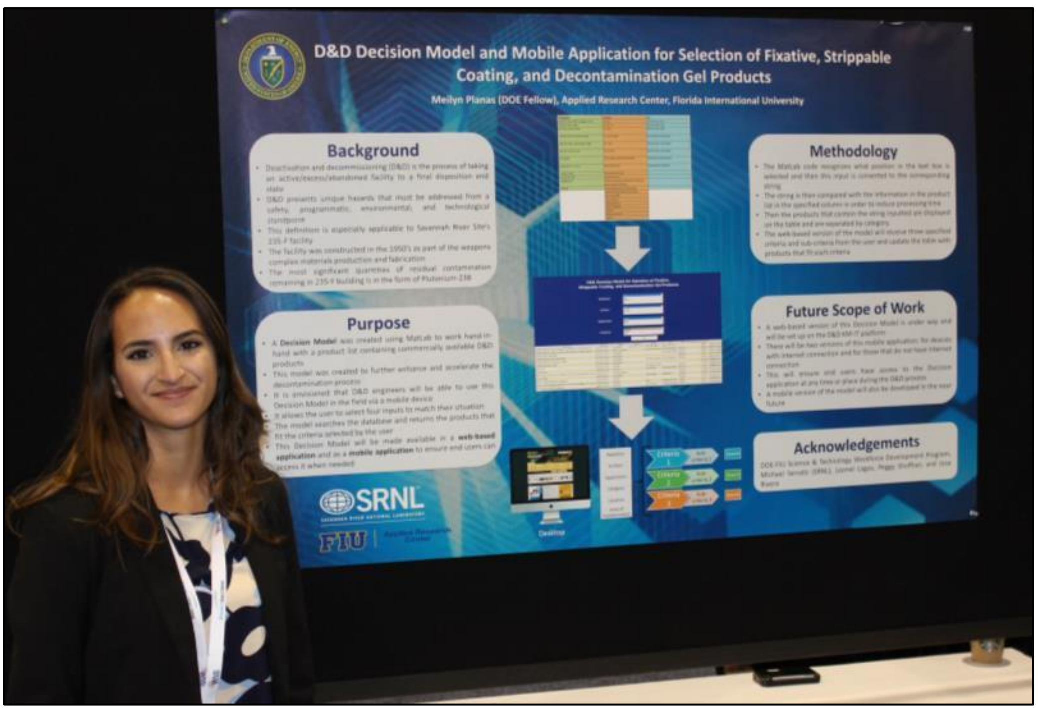


Figure 4-2. DOE Fellow Meilyn Planas presenting her research poster at WM15.

Subtask 2.1.2: Organic Semiconductor Thin Films for Polymer Interface and Electrostatic Applications

FIU conducted bimonthly phone calls with Michael Serrato (SRNL) to continue discussions on this subtask.

Subtask 2.2 Support to DOE EM-13 and Interface with EFCOG

FIU was providing support to the EFCOG DD/FE Working Group in the development of lessons learned and best practices for deactivation and decommissioning (D&D) throughout the DOE complex. The objective of these efforts is to capture previous work performed by the D&D community and facilitate the transfer of knowledge and lessons learned. DOE requested that EFCOG restructure the organization and the DD/FE WG was sunsetted as part of this restructuring. FIU staff and DOE Fellows supporting this work will continue to work closely with DOE and members of the D&D community of practice in the collection of information and the development of relevant lessons learned and best practices. Once approved, these documents will be made available via D&D KM-IT.

FIU Year 4 Carryover Work Scope

Subtask 2.1.2: Fogging research and evaluation

FIU conducted teleconference calls during this reporting period with Michael Serrato at SRNL as well as with Steve Reese at INL to discuss the collaboration to perform a technology demonstration to test and evaluate the FX2 Advanced Fogging Technology, developed at INL, for potential implementation at the SRNL 235-F facility.

Development of the FX2 Advanced Fogging Test Plan was completed and reviewed by the primary stakeholders (FIU ARC, INL, and SRNL), receiving concurrence and final approval by all signatories (see Figure 4-3) in January 2015. All test objectives, testing methods, roles and responsibilities, and a detailed timeline / program of action and milestones (POAM) were agreed upon.

FX2 ADVANCED FOGGING TECHNOLOGY:
TECHNOLOGY DEMONSTRATION TEST PLAN

Approval Page

FLORIDA INTERNATIONAL UNIVERSITY – APPLIED RESEARCH CENTER
(FIU – ARC)

Test Engineer (Prepared by) Date 1/15/2015

Project Manager Date 1/23/2015

IDAHO NATIONAL LABORATORY

Date 1/15/2015

SAVANNAH RIVER NATIONAL LABORATORY

M.G. Serrato
Environmental Stewardship Directorate
Date 1/29/2015

Figure 4-3. Signed approval page for the FX2 Advanced Fogging Test Plan.

ARC prepared the Radioactive Materials Handling Request Form required by the FIU Radiation Safety Officer (RSO) as outlined in the FX2 Test Plan. The final request form was forwarded to the FIU RSO who approved the purchase order (PO) for four (4) Po-210 sealed point sources. FIU ARC engaged vendors and received quotes for

Po-210 single source alpha emitters. During March, final approval from the FIU Radiation Safety Officer and committee was received for the use of Po-210 sealed point sources during the testing and the PO was subsequently forwarded to the vendor. FIU received shipment of the Po-210 sealed point sources from the selected vendor.

FIU prepared a PO and purchased a commercial airborne particle counter (HandiLaz Mini from Particle Measuring Systems, Figure 4-4). The HandiLaz Mini airborne particle counter supported a portion of Test Objective 3.1 outlined in the FX2 Test Plan to evaluate the fogging agent in its ability to control potential airborne particulates.

Figure 4-4. HandiLaz Mini from Particle Measuring Systems

FIU ARC also engaged potential vendors for quotes associated with outsourcing the ASTM standardized tests designed to characterize the FX2 Fogging Agent, specifically in the areas of burn rate, viscosity, density, and surface tension. Once a vendor was selected, FIU completed preparing a purchase order for outsourcing ASTM standardized tests to an analytical laboratory.

FIU completed the design phase of the hot cell mockup modifications required to support the execution of the FX2 Test Plan and purchased all necessary materials needed to complete the proposed modifications. The facilities were inspected by the FIU RSO and determined to be satisfactory to support test objective for determining the shielding properties against an alpha emitter. During March, FIU finalized the modifications to the hot cell mock-up facility.

FIU acquired the ImageJ software necessary to support portions of the test plan objectives. Familiarization and training with the software was conducted in order to ensure a high level of proficiency with the software prior to actual execution.

FIU received two (2) commercial foggers and associated equipment from INL to support the FX2 Test Plan in February and received the FX2 fogging agent from INL in early March. FIU performed functional testing of the equipment received from INL to ensure that everything was in working condition. These tests were all favorable.

The technology demonstration was performed from March 30 to April 3, 2015 at the ARC Technology Testing & Demonstration Facility in Miami where an existing hot cell mockup facility was modified to meet the objectives of the demonstration (Figure 4-5). Steve Reese from INL participated in the demonstration.

Figure 4-5. Hot cell mockup facility (left), DOE Fellows with FX2 fogging agent (right).

The technology demonstration of the FX2 Advance Fogging Technology at FIU included tests to evaluate the following:

- Ability to fix loose contamination to different types of surfaces (glass, concrete, steel, and plastic) and adhesiveness to the surface.
- Ability to cover locations outside of the direct line-of-sight of the fogger.
- Capacity to knockdown airborne particulates.
- Characteristic properties of the product:
    - Burn rate (ASTM D84)
    - Flammability (ASTM D3065)
    - Viscosity (ASTM D2196)
    - Surface Tension (ASTM D1331)
    - Density (ASTM D792)
- Reactivity to flame and heat sources.
- Ability to shield against an alpha emitting point source.
- Coverage of surface area, as quantified via use of ImageJ software analysis.
    - Uses contrast analysis to determine coverage of the product.
    - Correlates radiation shielding to the coverage results.

Preliminary results from the testing and evaluation indicate that the technology was capable of successfully achieving the objectives of this demonstration. The FX2 advanced fogging agent, dispersed via commercial off-the-shelf foggers (Cyclone Ultra-Flex Fogger by Curtis Dyna-Fog), had a clear qualitative ability to cover horizontal surfaces within the hot cell mock-up facility both within the direct line-of-sight of the fogger and outside of the direct line-of-sight of the fogger.

Figure 4-6. Mixing FX2 (left), filling fogger (middle), photographing sample for ImageJ (right).

The results of the flammability tests performed by FIU indicated that the fogging agent is not flammable, with the exposed flame extinguishing within seconds of being exposed to the dispersed fog. Preliminary results also showed the ability of the fogging agent to provide significant shielding against an alpha emitting point source.

Quantitative analyses and out-sourced laboratory analysis of the fogging agent are still in progress. The final results of the testing and evaluation, including the technology demonstration report and additional photographs and videos taken during the demonstration will be made available to the general D&D community through the D&D Knowledge Management Information Tool located on the web at www.dndkm.org.

DOE Fellow Jesse Viera prepared and presented a student poster entitled, “FX2 Advanced Fogging Technology” that was related to this research at the Waste Management Symposium 2015 held in Phoenix, AZ in March (Figure 4-7).

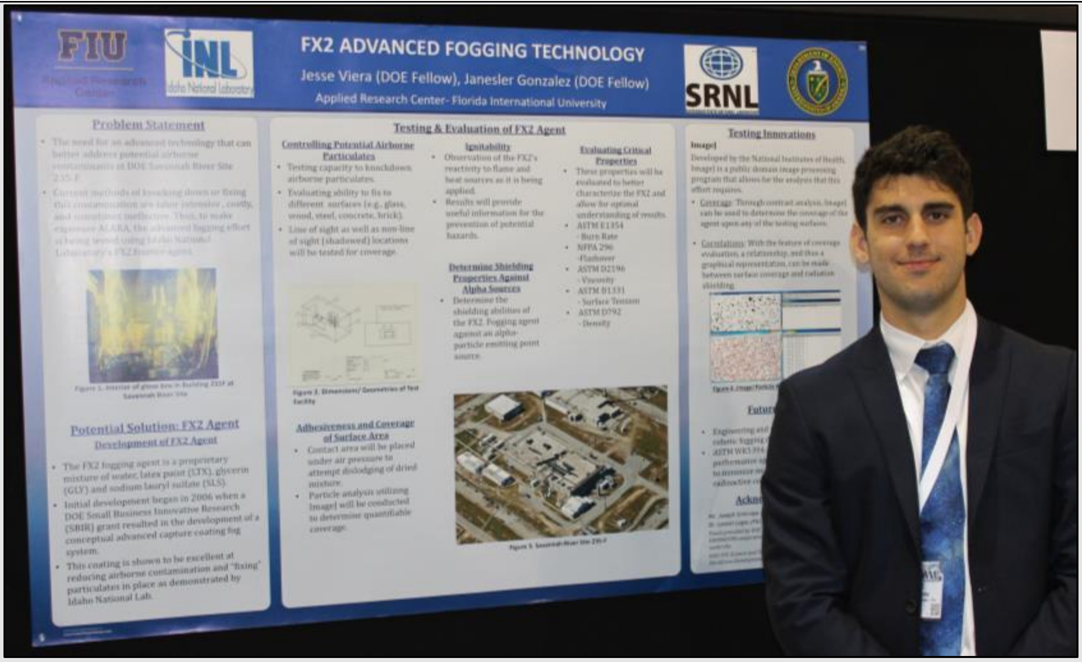


Figure 4-7. DOE Fellow Jesse Viera presenting his research poster at WM15.

Subtask 2.1.3: Incombustible fixatives

A literature search continued to identify the best fixatives in the areas of flash point and burn rate that could potentially be combined / layered to achieve an optimization in resiliency against fire hazards. The desired objective for the literature search is to identify the top 2-3 fixatives that are industry leaders in trapping radionuclides, and see if they can be combined / layered with the industry leaders in fire protection (flash point / burn rate) to produce a synergistic effect that enhances overall resiliency.

FIU continued discussions with Mike Serrato at SRNL on the research for this task. Mike sent FIU a list of fixatives that SRNL is considering for evaluation as meeting their needs for an incombustible fixative which primarily consisted of various formulations of DeconGel as well as dicalcium silicate. Based on discussion with DOE during the FIU Research Review presentations, FIU will work with SRNL to expand on the list of potential fixatives. FIU will next develop a test plan to test these fixatives, first focusing on baseline testing for each fixative product used in isolation. Future work will consider the best fixatives in the areas of flash point and burn rate that could potentially be combined/layered to achieve an optimization in resiliency against fire hazards.

FIU also reached out to several campus laboratories (within the Engineering Center and at other University departments) to find out if the equipment needed for the flash point and burn rate tests were available at the university. The equipment available did not meet ARC's requirements for the flash point and the burn rate test planned. FIU subsequently obtained two (2) quotes for flashpoint testing equipment to support the Incombustible Fixatives subtask and completed development of a purchase order.

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-13 & EM-72), 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 completed the development of a Google Web Analytic report for D&D KM-IT for the third quarter of 2014 (July to September) and submitted it to DOE on January 8, 2015. FIU also completed the development of a Google Web Analytic report for D&D KM-IT for the fourth quarter of 2014 (October to December) and submitted it to DOE on March 4, 2015. These reports included information from Google Analytics and Google Web Master tools and a narrative to explain the results. The results for the fourth quarter reflect that the D&D KM-IT website is recovering from a third quarter traffic drop. All of the major metrics showed improvement with the exception of Bounce Rate and Percentage of New Sessions. The largest improvements were in Pageviews with an increase of 21% closely followed by Pages per Session with a 19% increase. Figure 4-8 shows an infographic of the web analytics for the fourth quarter of 2014.

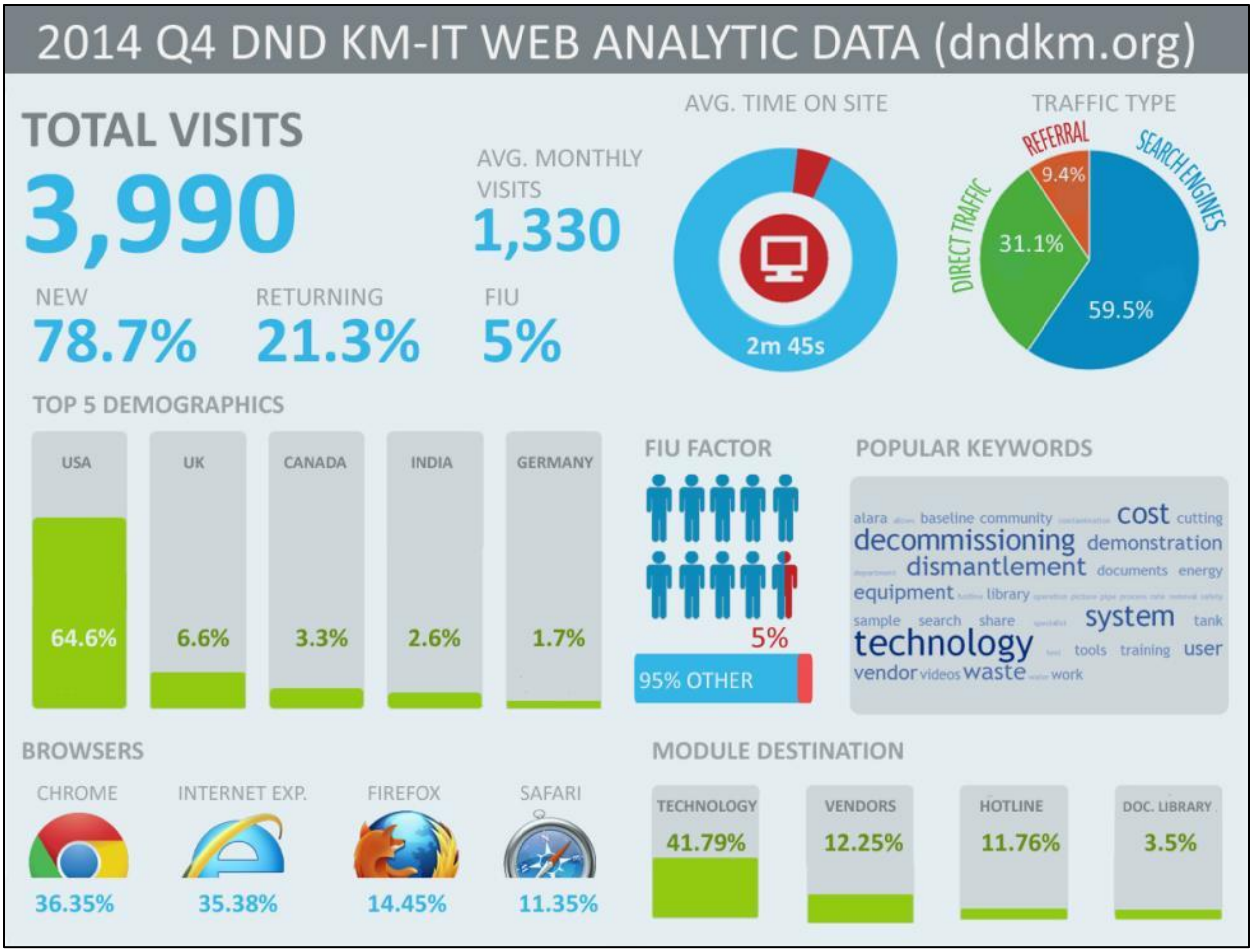


Figure 4-8: Infographic for 2014 Q4 Based on Web Analytic Data for D&D KM-IT.

FIU also completed the design and development of the best practices lite mobile application and submitted it to DOE for review/testing on January 16, 2015 (milestone 2014-P4-M3.4). The mobile system component provides access to important D&D KM-IT features through wireless devices, including iPhone (3.1 and above), iPad, Blackberry (6.0 and above), Android (2.1 and above), and Windows (7 and above) smart devices.

DOE Fellows and other FIU students are supporting D&D KM-IT by reviewing the information in the vendor and technology modules, updating contact information, and researching additional relevant D&D technologies offered by existing vendors. As of March 27, the system included a total of 1186 technologies (+465 from December) and 898 vendors (+225 from December). This large increase is primarily due to the integration of the robotics database from Congentus/NuVision, which is discussed below.

FIU received information from DOE on the modified protective suits at Richland with a request to make the information available to the D&D community through D&D KM-IT. FIU added the provided "good practice" document to the D&D KM-IT Best Practices module. FIU added a second document describing the innovative PPE technologies and methodologies to the D&D KM-IT Document Library. The vendors and technologies for the PPE components were added to the Vendor module and the Technology module, as appropriate. A newsletter based on this information was also prepared and distributed to the D&D community via the registered users of D&D KM-IT.

In preparation for holding D&D KM-IT workshops to DOE HQ audiences, FIU developed an overview presentation in Powerpoint. This presentation was sent to DOE for review on January 9, 2015.

FIU developed and sent out two newsletters from D&D KM-IT. The first was based on best practice for the modified protective suits (i.e., PPE) developed at Richland (Figure 4-9) which was sent to the registered users of D&D KM-IT. The second was announcing the events for D&D KM-IT at WM15 (Figure 4-10) and was sent to the conference attendees.

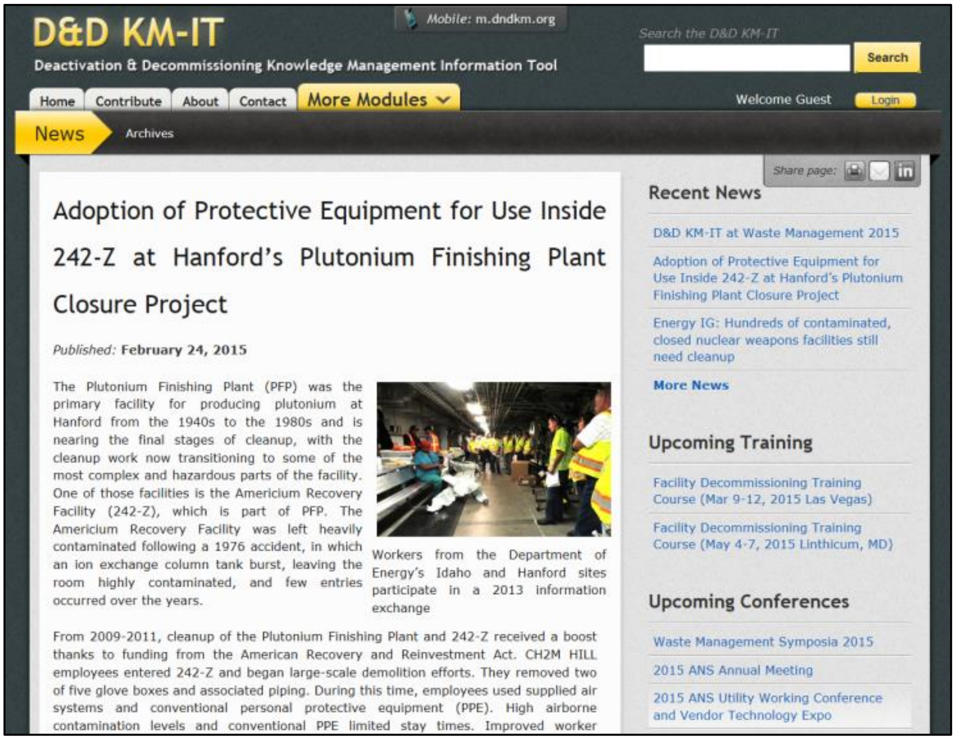


Figure 4-9. Newsletter on Hanford PPE best practice.

D&D KM-IT at Waste Management 2015

Published: **March 04, 2015**

D&D KM-IT

Visit Us @ WM15
Booth #733

Applied Research Center
Florida International University

Come learn about new developments and capabilities integrated into the D&D Knowledge Management Information Tool (http://www.dndkm.org) at our booth #733 in the exhibitor hall at Waste Management Conference 2015 in Phoenix, AZ from March 15-19, 2015. We also have a formal presentation in Session 067 on Tuesday, March 17, during the 1:30-5:00 pm session in Room #106B.

Plan to attend a workshop on D&D KM-IT at our booth **#733** on Monday, March 16, at 2:00, where we will conduct a demonstration of the D&D Knowledge Management Information Tool (D&D KM-IT), the web-based knowledge management information tool custom built for the D&D user community.

Waste Management 2014 Exhibit Hall Reception

Come to our "one-on-one" demonstrations of D&D KM-IT being offered at our booth during exhibitor hall hours. The capabilities of the system will be demonstrated, showing the available features and newly added content of the D&D KM-IT, including over 350 newly added robotic technologies. The D&D KM-IT system was developed by Florida International University - Applied Research Center (FIU-ARC) in collaboration with the Department of Energy (DOE HQ).

Figure 4-10. Newsletter to announce D&D KM-IT presence at WM15.

A database of robotic technologies, originally developed by NuVision/Cogentus, was sent to FIU from DOE, with a request to evaluate the potential for integrating the data into the D&D KM-IT framework for ongoing hosting/maintenance of the information. FIU was able to extract the database from the file received and determined that it was a MYSQL database file format. A MYSQL server database was installed to match the file and then FIU imported that file into the new FIU MYSQL server database.

FIU then created a script and exported the information and documents successfully from the file. FIU developed the data interface and mapping file for the import process since the two data structures (robotics database and D&D KM-IT framework) are different. FIU developed the data structure that can import the technology titles and description mapping to KM-IT as well as combined the technology notes and operational experience data sections and mapped it to a new comments section within KM-IT. In addition, FIU created a new Group within the D&D KM-IT Technology module for "Robotics" and subsequently updated the categories and subcategories within this group based on the main_function and robotics_category information included in the original robotics database.

D&D KM-IT links each technology entry to a specific vendor. Within the original robotics database, the vendor information is buried in a column titled manufacturer_developer with no easy way to extract that information because of the lack of structure. Identifying and extracting the vendor information had to be a manual process which was assigned to six (6) DOE Fellows and FIU Graduate Research Assistants.

During February, the six (6) DOE Fellows and other FIU Graduate Research Assistants assisted in manually extracting the vendor information from the original database, creating vendor entries in D&D KM-IT for each, and assigning the technologies to the correct vendor. After performing QA/QC on the new robotics entries, 376 were made live on the production server by February 18. During March, FIU continued to research and update the robotic entries that had missing data. An additional 68 robotic technologies, for a current total of 444, were made live on the production server. All of the data and accompanying information (photos, documents, etc.) within the robotics database from NuVision/Cogentus were integrated into the technology datasheets on D&D KM-IT. Figure 4-11 shows the Technology module homepage with the showing the robotic technology database; Figure 4-12 shows a few of the robotic technologies now available on the system.

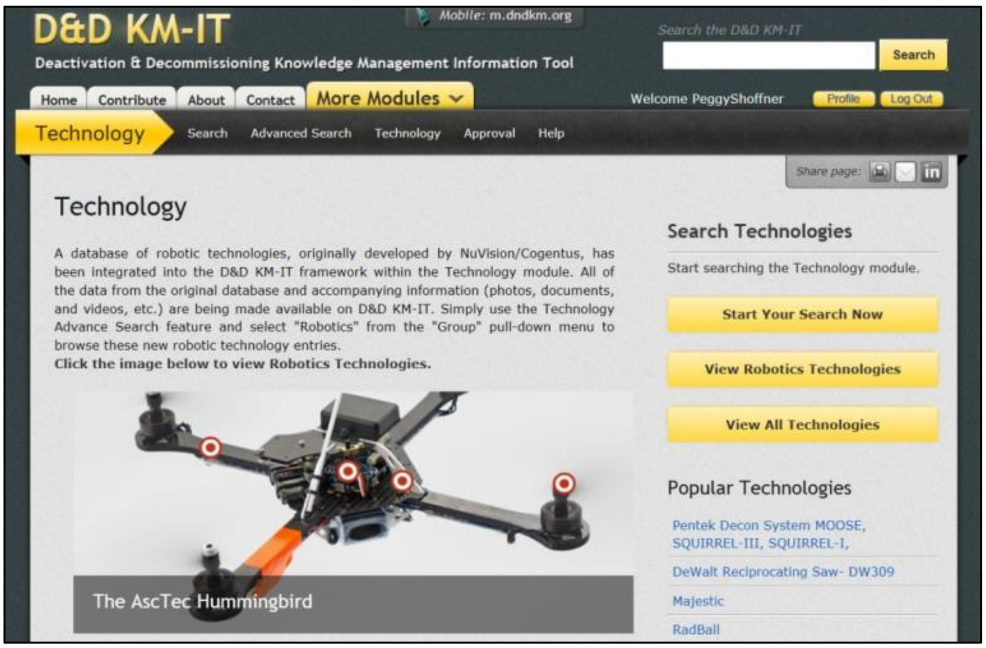


Figure 4-11. Technology module homepage showing robotics technologies.

Figure 4-12. Robotic technologies newly integrated into D&D KM-IT Technology module. From left: Mighty Mouse by Sandia National Lab, Big Dog by Boston Dynamics, and HRP-3 Promet MK-II by Kawada Industries.

FIU presented D&D KM-IT during an oral presentation for Session 067 of the Waste Management Symposium 2015 on March 17, 2015 (Figure 4-13). FIU also hosted a booth (#733) in the exhibitor hall during the conference (Figure 4-14). FIU hosted a workshop on D&D KM-IT on Monday, March 16, to provide live demonstrations of the system and to show the available features and the newly added content, including over 400 newly added robotic technologies from the robotics database developed by Cogentus/NuVision. During the operation of the exhibitor booth and oral presentation of D&D KM-IT, FIU encouraged conference attendees to become active users of the system as well as to register as subject matter specialists. Significant interest was shown in the knowledge management of D&D as reflected by the increase in user registrations (65) during the conference, increasing the total number of registered users from 660 to 725. In addition, the number of subject matter specialists increased by 14, from 69 to 83.

Figure 4-13. Dr. Hiimanshu Upadhyay presenting D&D KM-IT during WM15.

Figure 4-14. DOE Fellows and ARC staff at FIU booth during WM15 Exhibit Hall.

Additional DOE Fellows and FIU graduate students also presented research posters related to this project during the WM15 student poster competition are included in this report under Project 5, including: Andrew De La Rosa (DOE Fellow) - Malware Forensics on Mobile Devices for DOE-EM Applications; Steve Noel (DOE Fellow) - D&D Knowledge Management Information Tool Feasibility Study for Cross-Platform Mobile Applications; Santosh Joshi (Graduate Research Assistant) - Deactivation and Decommissioning Web Log Analysis Using Big Data Technology; Jorge Deshon (DOE Fellow) - Best Practices Mobile Application for D&D KM-IT; and Kavitha Megalageri (Graduate Student Assistant) - Knowledge Management Information Tool Analytics with Distributed Database Engine.

FIU developed a brief “Thank you” notice and sent it out to the new users who registered on D&D KM-IT during the Waste Management 2015 conference (Figure 4-15) to thank them for their interest and encourage them to continue using and contributing to the system.

Figure 4-15. Thank you notice to new D&D KM-IT users.

Milestones and Deliverables

The milestones and deliverables for Project 4 for FIU Year 5 are shown on the following table. Milestone 2014-P4-M3.4, the deployment of the best practices mobile application to DOE for review/testing, was completed on January 16, 2015. In addition, a deliverable on the preliminary metrics progress for outreach and training activities for D&D KM-IT was submitted to DOE on January 16, 2015. One deliverable, to host a D&D workshop with the D&D community was completed on March 16, 2015 during the Waste Management conference. Milestone 2014-P4-M3.5, originally due in March, has been reforecast to 5/15/15 due to additional work scope (integration of the Cogentus/NuVision robotics database into D&D KM-IT). This milestone includes the addition/editing of four Wikipedia articles. Finally, a milestone for a D&D subtask has been re-defined after discussions with Mike Serrato at SRNL to better meet the research needs of the site. Milestone 2014-P4-M2.2 was re-defined from a draft summary report for SRS 235-F facility on organic semiconductor thin films (subtask 2.1.2) to a draft test plan for incombustible fixatives (subtask 2.1.3) with a due date of 5/15/15.

FIU Year 5 Milestones and Deliverables for Project 4

Task	Milestone/ Deliverable	Description	Due Date	Status	OSTI
Task 1: Waste Information Management System (WIMS)	2014-P4-M1.1	Import 2015 data set for waste forecast and transportation data	Within 60 days after data received from DOE	On Target	
	2014-P4-M1.2	Submit draft paper on WIMS to Waste Management Symposium 2015	11/07/14	Complete	
Task 2: D&D Support to DOE EM for Technology Innovation, Development, Evaluation, and Deployment	2014-P4-M2.1	Preliminary decision model for contamination control products (subtask 2.1.1)	03/06/15	Complete	
	2014-P4-M2.2	Draft test plan for incombustible fixatives (subtask 2.1.3)	04/10/15	Re-Defined	OSTI
	Deliverable	Lessons Learned and Best Practices	30 days after approval from DOE & EFCOG	On Target	
	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 Knowledge Management Information Tool (KM-IT)	Deliverable	First D&D KM-IT Workshop to DOE EM staff at HQ	08/29/14**	To be scheduled based on availability of DOE HQ officials	
	2014-P4-M3.2	Deployment of popular display on homepage of KM-IT to DOE for review/testing	09/05/14	Complete	
	Deliverable	Metrics Definition Report on Outreach and Training Activities	09/30/14	Complete	
	Deliverable	Second D&D KM-IT Workshop to DOE EM staff at HQ	09/30/14**	To be scheduled based on availability of DOE HQ officials	
	2014-P4-M3.1	Submit draft paper on D&D KM-IT to Waste Management Symposium 2015	11/07/14	Complete	
	2014-P4-M3.3	Deployment of lessons learned lite mobile application to DOE for review/testing	11/07/14	Complete	
	Deliverable	Preliminary Metrics Progress Report on Outreach and Training Activities	01/16/15	Complete	
	2014-P4-M3.4	Deployment of best practices mobile application to DOE for review/testing	01/16/15	Complete	
	2014-P4-M3.5	Four Wikipedia edits/articles	03/20/15 Reforecast to 5/15/15	Reforecast	
	Deliverable	First D&D KM-IT Workshop to D&D community	03/31/15	Complete	
	Deliverable	Second D&D KM-IT Workshop to D&D community	04/30/15	To be scheduled based on availability of DOE HQ officials	
	Deliverable	Metrics report on outreach and training activities	05/09/15	On Target	
	Deliverable	Draft Security Audit Report	30-days after completion of audit	On Target	
	Deliverable	D&D KM-IT Performance Analysis Report	Quarterly	On Target	
	Deliverable	Draft Tech Fact Sheet for new modules or	30-days after	On Target	

		capabilities of D&D KM-IT	deployment of new module or capability		

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

Work Plan for Next Quarter

- Draft the Year End Report for FIU Year 5 (May 2014 to May 2015).
- Task 1: Perform database management, application maintenance, and performance tuning to WIMS.
- Task 1: Receive from DOE and complete importation of new dataset into WIMS and deploy for DOE review and testing. To incorporate these new files, FIU will build a data interface to allow the files to be received by the WIMS application and import it into SQL Server. SQL server is the database server where the actual WIMS data is maintained. FIU will incorporate the revised waste forecast and transportation data files. The 2015 waste data will replace the existing previous waste data and will become fully viewable and operational in WIMS.
- Task 2: Complete web-based preliminary decision model for the selection of contamination control products.
- Task 2: Develop a phase I test plan for evaluating a set of incombustible fixatives, selected by FIU and SRS.
- Task 2: FIU will collaborate with INL and SRS on the fogging research and evaluation task by completing the implementation of the FX2 advanced fogging technology demonstration test plan at FIU and developing the technology demonstration report and DOE Tech Fact Sheet.
- Task 3: Complete draft of D&D KM-IT website analytics report for the calendar year January to December 2014 time period and submit to DOE for review.
- Task 3: Complete 4 edits/articles related to D&D topics on Wikipedia.
- Task 3: 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 5
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

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 program director coordinated with DOE-HQ, DOE sites, DOE national laboratories, and DOE contractors for placement of DOE Fellows for summer 2015 internships. The DOE Fellows revised their resumes to send to potential placements.

Brady Lee and Sabrina Saurey from PNNL visited FIU-ARC in January. DOE Fellows supporting the PNNL research work under Project 2 participated and presented during their visit. In addition, the DOE Fellows showcased the laboratories and the current research they are conducting to support DOE-EM’s mission.

FIU hosted Mr. Jim Voss, managing director of the Waste Management Symposium, during the DOE Fellows lecture series on Tuesday January 27, 2015 at FIU (Figure 5-1 to Figure 5-3). Mr. Voss gave a lecture titled, “Magnetic Separation of Uranium and Plutonium.” After the lecture, Mr. Voss toured ARC’s research laboratories and interacted with the DOE Fellows.

Figure 5-1. Mr. Jim Voss presenting at the DOE Fellows lecture series.

Figure 5-2. DOE Fellows lecture series.

Figure 5-3. Mr. Jim Voss with DOE Fellows Program Director Leonel Lagos and DOE Fellows.

The DOE Fellows Class of 2014 participated in two DOE Fellows 101 training sessions. Dr. Lagos discussed about DOE Fellows program components and provided them with a document detailing the expectations of the program, summer internship opportunities, and hands-on research at ARC.

DOE Fellows Aref Shehadeh (undergraduate in environmental engineering), Christian Pino (undergraduate in chemistry), Christine Wipfli (undergraduate in environmental engineering), and Kiara Pazan (undergraduate in environmental engineering) submitted research abstracts and completed preparations to participcate in the Life Science South Florida - 2015 STEM Undergraduate Research Symposia to be held on Saturday, April 4, 2015 at Indian River State College Pruitt Campus.

In addition, DOE Fellows Ryan Sheffield, Max Edrei and Janesler Gonzalez prepared posters for the ANS conference to be held at Texas A&M University College Station on April 9 – 11, 2015.

DOE Fellows participated in the Engineering Expo held by FIU on Friday, February 27. This event is organized by FIU's College of Engineering and opens the doors for elementary, middle school and high school students. DOE Fellows actively participated in the event and showcased their hands-on research related to DOE EM.

During the March 31 to April 3 program review conducted between DOE EM and FIU ARC as part of the DOE Cooperative Agreement, twelve (12) DOE Fellows presented during the technical (projects 1-4) and workforce development presentations to highlight the applied research they are performing for DOE EM as part of this Cooperative Agreement.

DOE Fellows completed preparation and participated in the Waste Management 2015 Symposia (WM15) in Phoenix, AZ, from March 15-19, 2015. Among the many distinguished industry leaders that the FIU students met during the conference, they had the chance to take photos with Mr. Mark Whitney, Principal Deputy Assistant Secretary for Environmental Management (Figure 5-4) and Dr. Monica Regalbuto, Associate Principal Deputy Assistant Secretary for Environmental Management (Figure 5-5).

Figure 5-4. DOE Fellows, Dr. Lagos and DOE-EM's Mr. Mark Whitney.

Figure 5-5. DOE Fellows with Dr. Triay, Dr. Lagos and DOE-EM's Dr. Monica Regalbuto & Ms. Ana Han.

A total of twenty (20) DOE Fellows and other FIU students attended WM15 and presented technical posters during Session 33 (Student Poster Competition: The Next Generation – Industry Leaders of Tomorrow). The Fellows presented the hands-on DOE-EM research that they have actively participated in at FIU's ARC and during their summer internships at DOE sites, national laboratories, and site contractors. DOE Fellow Christine Wipfli won the student poster competition for her research on *Sodium Silicate Treatment for Uranium Bearing Groundwater Systems at the F/H Area of the Savannah River Site* (Figure 5-6), marking the fifth time a DOE Fellow has won the Waste Management Student Poster Competition.

Figure 5-6. WM15 Student Poster Winner – Christine Wipfli (DOE Fellow).

In addition, 1 Ph.D. level DOE Fellow, Hansell Gonzalez, presented his research during the professional oral session 107 (Deep Vadose Zone Characterization and Remediation Technologies) on Wednesday, March 18, 2015:

- The Influence of Humic Acid and Colloidal Silica on the Sorption of U(VI) onto SRS Sediments Collected from the F/H Area (15499), Yelena Katsenovich, Hansell Gonzalez (DOE Fellow), Miles Denham (SRNL), Ravi Gudavalli, Leo Lagos. **Presenter: Hansell Gonzalez (DOE Fellow)**

DOE Fellow Robert Lapierre was awarded a graduate level 2015 Roy G. Post Foundation Scholarship. Also during the conference, DOE Fellow Robert Lapierre participated in a panel during Session 38 titled “Graduating Students and New Engineers - Wants and Needs.” During this panel session, students and industry and government representatives shared their perspectives of the newer generation entering a workforce primarily occupied by workers nearing retirement age (Figure 5-7).

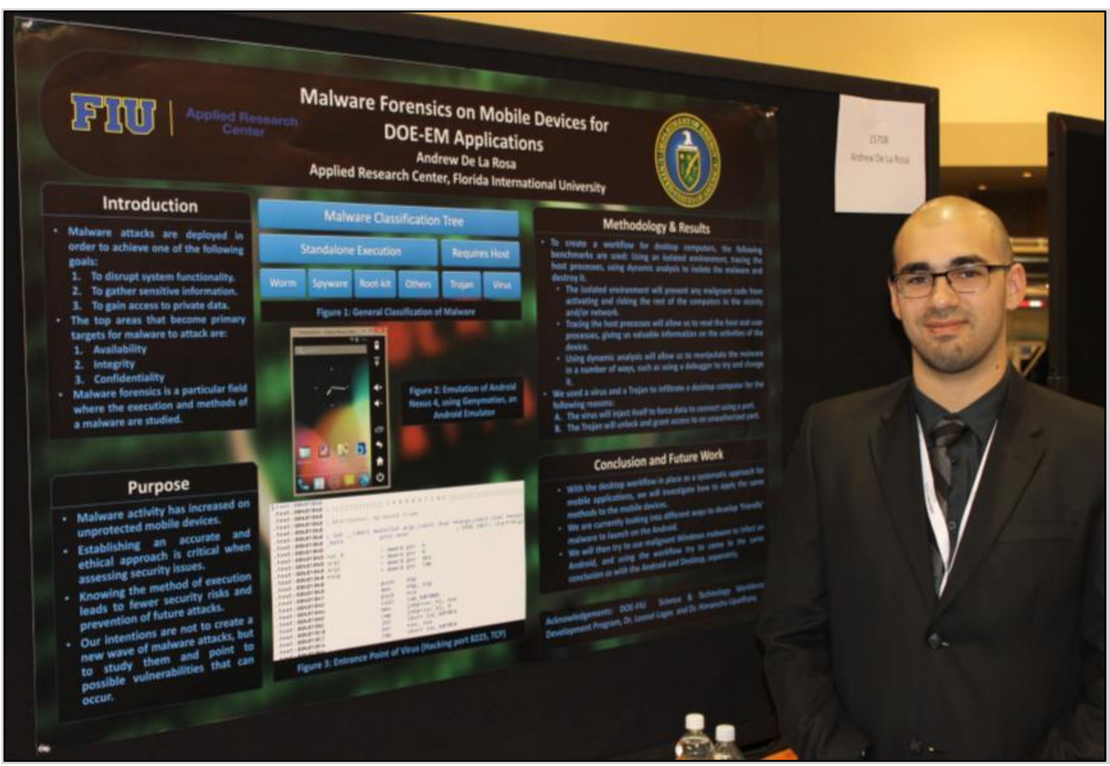
Figure 5-7. DOE Fellow Robert Lapierre in Graduating STEM Students Entering the Workforce Panel

Photos of the DOE Fellows and other FIU students presenting their research posters during the Student Poster Competition at WM15 are presented below along with their research abstract.

Malware Forensics on Mobile Devices for DOE-EM Applications

Andrew De La Rosa (DOE Fellow)

The purpose of malware forensics is to apply forensic investigative techniques on malware infections. While the recovery of damaged files caused by malware is important, the analysis of the execution of the malware is now an area of research and of particular interest to the U.S. Department of Energy's Office of Environmental Management (DOE-EM). According to Kaspersky's analysis for 2014, there are over 6 billion attacks launched worldwide which is an increase from the 5.2 billion attacks catalogued in 2013. Malware, by nature, is designed to disrupt and destroy data and many antiviruses simply quarantine and destroy the dangerous file; however in order to recover certain files, it is sometimes necessary to know the method of execution. Furthermore, many users are now transitioning to the use of mobile devices to perform their day-to-day activities. Unfortunately, any device that has internet connectivity is a potential victim to malware threats. Many mobile devices have a mobile version of an antivirus, but this in no way compares to the power of the desktop version; instead, the malware signatures have a similarity to the desktop version of the malware. The environment the malware is developed on is isolated from any internet access and currently has its signatures viewed and analyzed by virustotal.com, and every known major antivirus. Virtual machines have been created (Windows XP and Windows 7) to test the capture rate at which the malware is detected by the system. Several open-source programs are used to analyze the malware such as Resource Hacker and IDA Pro, which show the assembly code on where the objects are moving in the system. The strings in the code, the calling of the objects, and the size of the file will help the analysis especially when using the Process Explorer, to see the flow of memory and what processes are running.



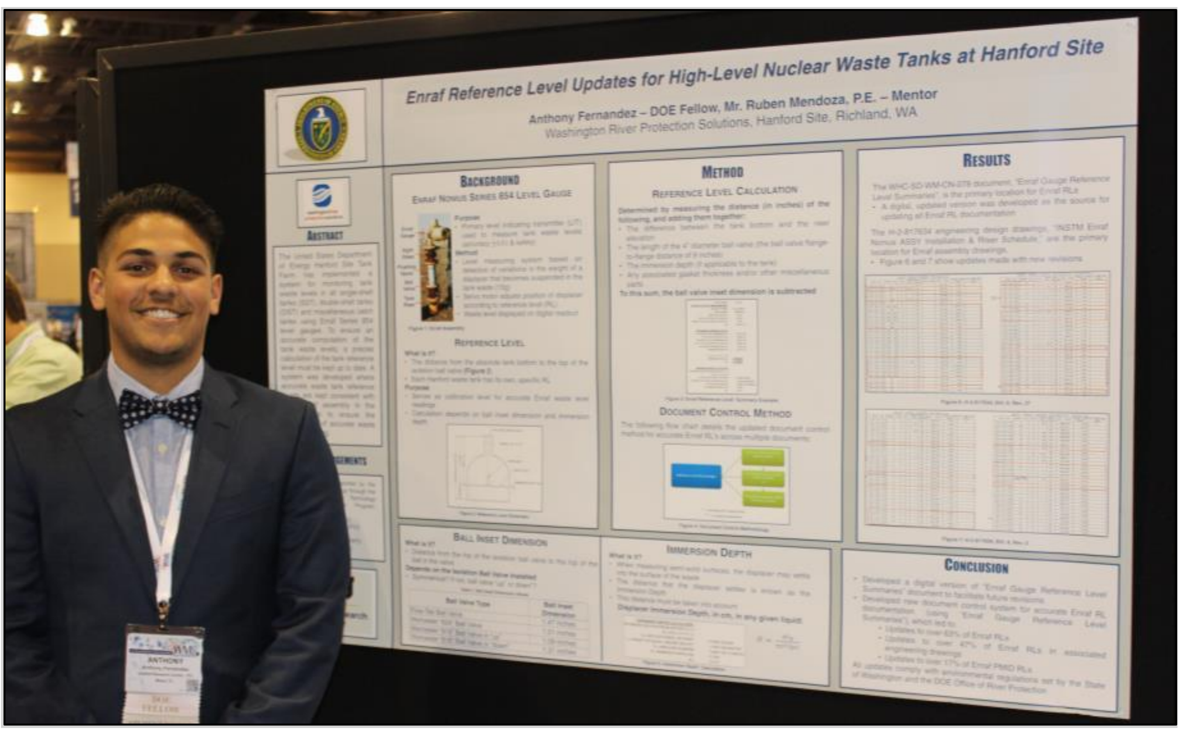
Enraf[(R)] Reference Level Updates for High-Level Nuclear Waste Tanks at Hanford Site

Anthony Fernandez (DOE Fellow)

The U.S. Department of Energy's Hanford Site Tank Farm has implemented a system for monitoring tank waste levels in all single-shell tanks (SST), double-shell tanks (DST) and miscellaneous catch tanks using Enraf Series 854 level gauges and densitometers. To ensure an accurate computation of the tank waste levels, a precise calculation of the tank reference level must be kept up to date.

Due to an outdated document control system for Enraf and densitometer reference levels, inconsistencies were detected between field walk downs of Enraf and densitometer assemblies and the documentation containing reference levels. The development of an updated document control system for Enraf & densitometer reference levels was deemed necessary for the continuation of accurate waste level monitoring in the Hanford Tank Farms. The creation of a digital, easily updatable WHC-SD-WM-CN-078, Revision 1 ("Enraf Gauge Reference Level Summaries") document was the first step in facilitating a method for tank waste reference levels to be kept updated in future revisions.

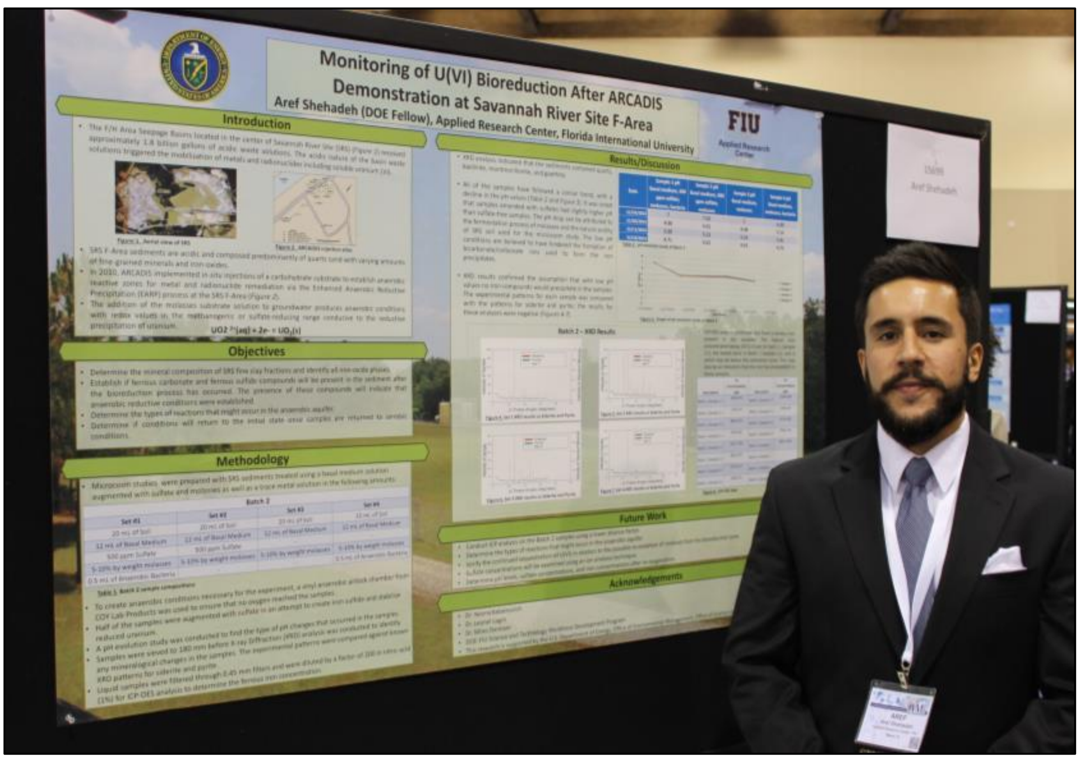
Using WHC-SD-WM-CN-078, Revision 1, The Enraf and densitometer reference levels were updated in their associated documents and in their PMID's to show consistency with WHC-SD-WM-CN-078, Revision 1 document.



Monitoring of U(VI) Bioreduction after ARCADIS Demonstration at Savannah River Site F-Area

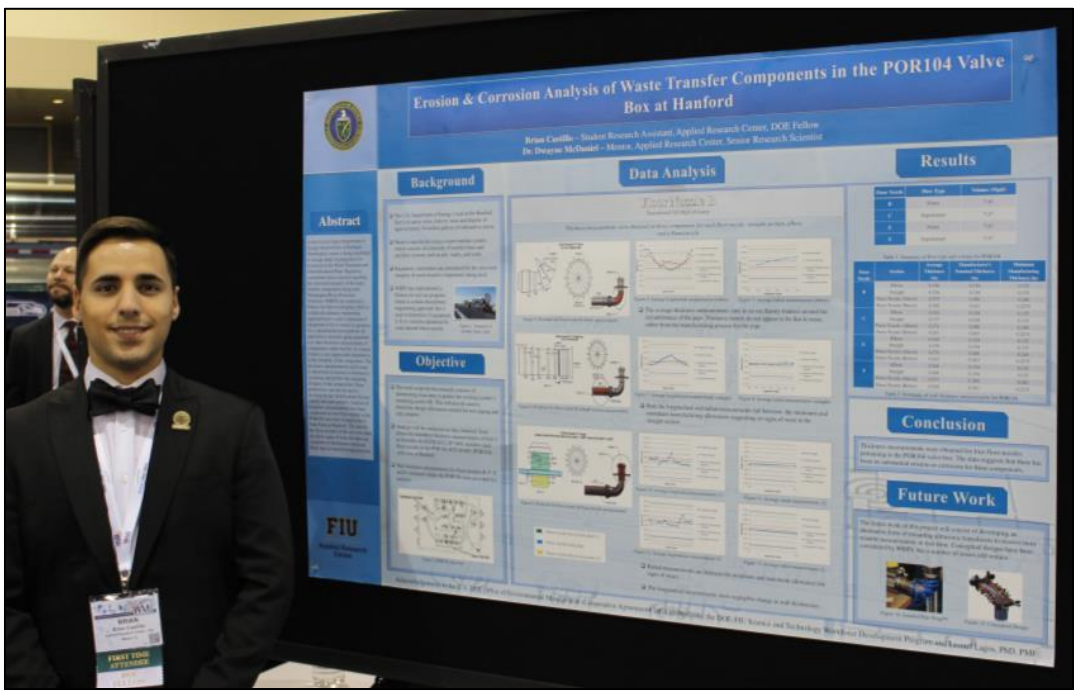
Aref Shehadeh (DOE Fellow)

From 1955 to 1989, unlined basins at the Savannah River Site received approximately 1.8 billion gallons of acidic waste solutions, much of which seeped into the surrounding soil and groundwater. The mobilization of metals and radionuclides included soluble uranium (VI) which is now present in the F-Area sediments. In 2010, ARCADIS implemented in-situ injections of a carbohydrate substrate to establish anaerobic reactive zones for metal and radionuclide remediation via the Enhanced Anaerobic Reductive Precipitation (EARP) process at the SRS F-Area. The addition of a molasses substrate solution to groundwater produces anaerobic conditions with redox values in the methanogenic or sulfate-reducing range conducive to the reductive precipitation of uranium. To determine the effectiveness of this process, a microcosm study will be prepared with SRS sediments, augmenting the solution mixture with molasses and sulfate. The sulfate reduction process will lead to an increased pH of the water, often to a near neutral condition. . The study aims to determine whether forms of reduced iron such as siderite and pyrite would arise in the reducing zone and if any mineralogical changes occurred in the sediments during the re-oxidation period. These experiments will also explain the types of reactions that might occur in the anaerobic aquifer.



Erosion & Corrosion Analysis from POR104 Valve Box at Hanford
Brian Castillo(DOE Fellow)

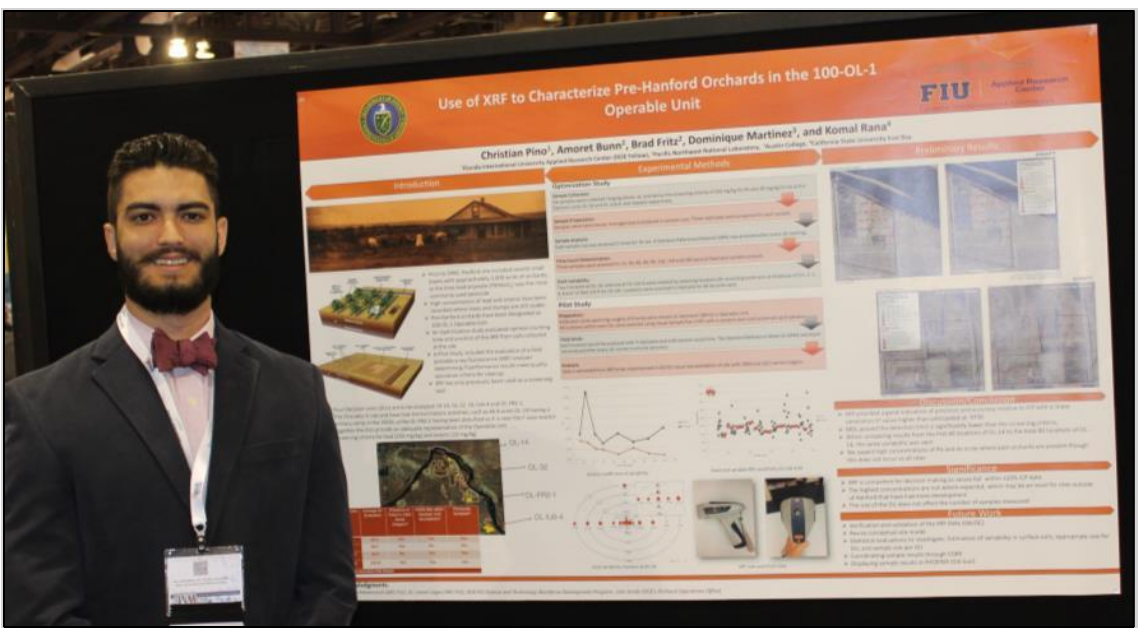
At the United States Department of Energy Hanford Site in Richland, Washington, waste is being transferred to storage tanks in preparation for treatment at the Waste Treatment and Immobilization Plant. Regulatory committees have concerns regarding the structural integrity of the waste transfer components being used. Washington River Protection Solutions (WRPS) has employed a Fitness-for-Service program, which is a multi-disciplinary engineering approach that is used to determine if equipment is fit to remain in operation for a specified projected period. An approach to monitor aging equipment is to take thickness measurements of components when feasible, to evaluate if there is any appreciable degradation in the integrity of the components. The thickness measurements can be used to determine if erosion or corrosion is occurring and predict the remaining lifespan of the components. These predictions can also be used to develop design modifications for new piping and pipe jumpers. Analysis of thickness measurements have been conducted on four floor nozzles in the POR104 valve box located in the C-Tank Farm at Hanford. The data for the floor nozzles of the valve box does not show signs of wear, but there are variations in thicknesses which are likely due to manufacturing processes.



Use of X-ray Fluorescence to Characterize Pre-Hanford Orchards in the 100-OL-1 Operable Unit

Christian Pino (DOE Fellow)

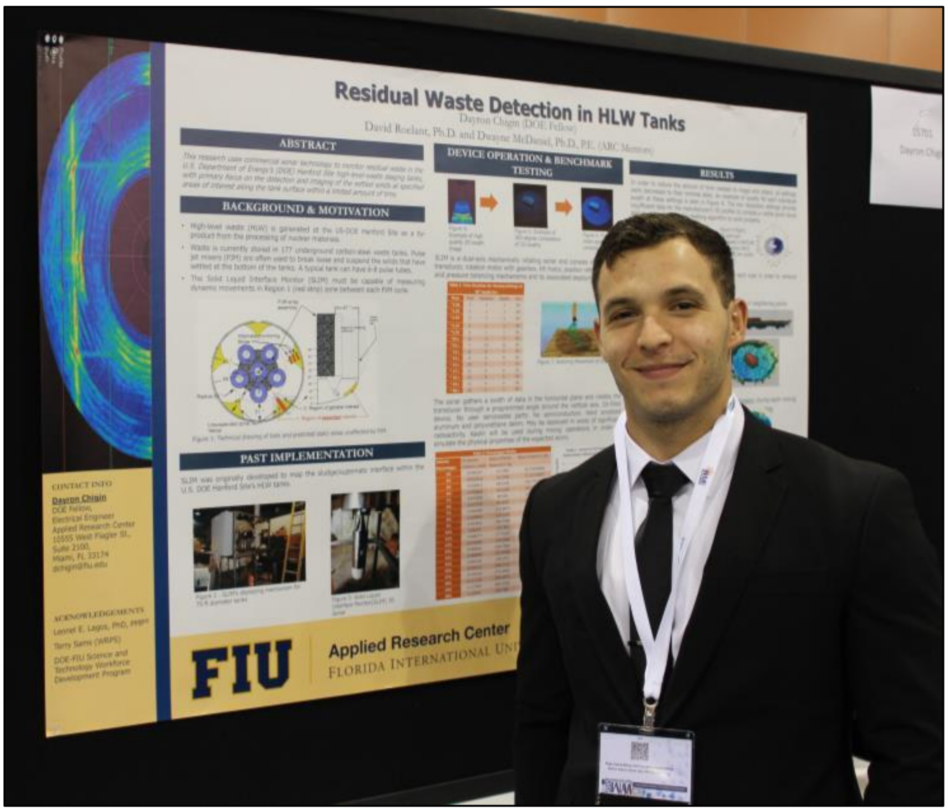
Prior to 1943, the Hanford Site included several small towns with approximately 8,000 acres of agricultural development. About 5,000 of those acres were used for orchards, with lead arsenate (PbHAsO4) being the common pesticide for controlling coddling moths in fruit trees. Higher concentrations of lead and arsenic were recorded in the vicinity of the old orchards at the Hanford Site. In year 1980, U.S. Department of Energy's Richland Operating Office, Environmental Protection Agency, and Washington Department of Ecology investigated the lead arsenate residues under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and designated the pre-Hanford orchards 100-OL-1 Operable Unit. Initial characterization activities included a pilot study to evaluate the use of a field portable x-ray fluorescence (XRF) analyzer and determine if the performance of the instrument provides results that meet quality assurance criteria for cleanup decisions. An optimization study was performed to evaluate the counting times and position of the XRF using soil collected from the orchards on the Hanford Site. The optimization study confirmed that the variability in the field was more significant than operator or instrument variability. The surface soil at four Decision Units (DU) OL-14, OL-32, OL-IU6-4 and OL-FR2-1 was evaluated with the XRF. Due to distinct past activities in each site, orchard activity may or may not have been present in every DU; however, all together they provide an adequate representation of the entire 100-OL-1 Operable Unit. Results indicated that there were areas in each DU with concentrations above the screening criteria for both lead (250 mg/kg) and arsenic (20 mg/kg).



Residual Waste Imaging in High Level Waste Mixing Tanks

Dayron Chigin (DOE Fellow)

This research uses commercial sonar technology to monitor residual waste in the United States Department of Energy's (DOE) Hanford Site high-level-waste (HLW) staging tanks, with primary focus on the detection and imaging of the settled solids at specified areas of interest along the tank surface within a limited amount of time. Pulverized Kaolin will be used in order to simulate the expected behavior of the residual waste within these HLW tanks. The data acquired from the commercial sonar technology will be processed in MatLab through a multiple meshing and filtering algorithm. After the proper algorithms have been applied, the volume of each data set will be derived in order to determine the settling or dynamic movement of the specified areas of interest.



Study of an Unrefined Humate Solution as a Possible Remediation Method for Groundwater Contamination at Savannah River Site's F/H Area

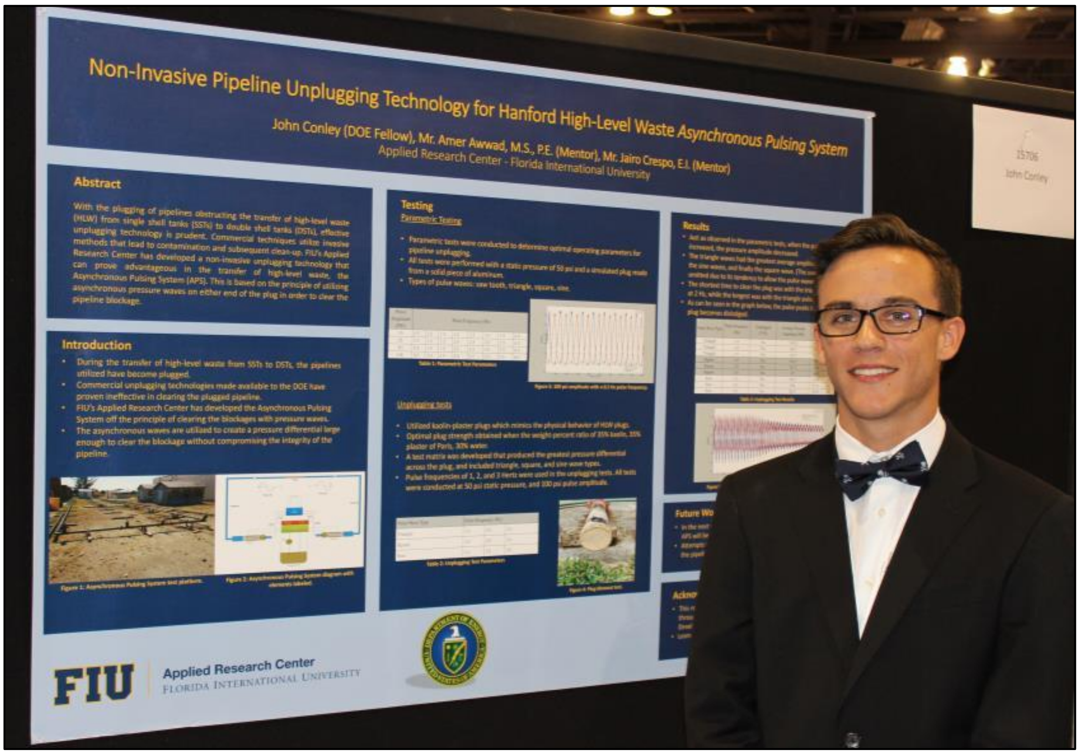
Hansell Gonzalez (DOE Fellow)

Unrefined, low cost humic substances are being tested by Savannah River National Lab as possible amendment for the remediation of groundwater contaminated by an acidic plume. Humic substances can remove contaminants such as Uranium, Sr-90, and I-129 from groundwater. The objective of the ongoing study is to understand the sorption and desorption characteristics of humic substances onto aquifer sediments after injection, the maximum loading capacity of the sediments, and what fraction of humic molecules is retained by the sediments. A UV-vis spectrophotometer was used for the measurement of the concentration. The ratio of absorbances, E4/E6 and EET/EBZ, will provide information about molecular weight and degree of substitution of the humic molecules. This information is useful for planning a strategy for full scale deployment of a groundwater remediation technology at Savannah River Site.

Non-Invasive Pipeline Unplugging Technology for Hanford High-Level Waste Asynchronous Pulsing System

John Conley (DOE Fellow)

With the plugging of pipelines obstructing the transfer of high-level waste (HLW) from single shell tanks to double shell tanks, an effective unplugging technology is prudent. Commercial techniques utilize invasive methods that can lead to contamination and unnecessary clean-up. FIU's Applied Research Center has developed the Asynchronous Pulsing System (APS), a non-invasive unplugging technology that can prove advantageous in the transfer of high-level waste. It is based on the principle of utilizing asynchronous pressure waves on either end of the plug in order to clear the pipeline blockage. This non-invasive technology has proven its ability to clear blockages in previous testing.



D&D Decision Model and Mobile Application for Selection of Fixative, Strippable Coating, and Decontamination Gel Products

Meilyn Planas (DOE Fellow)

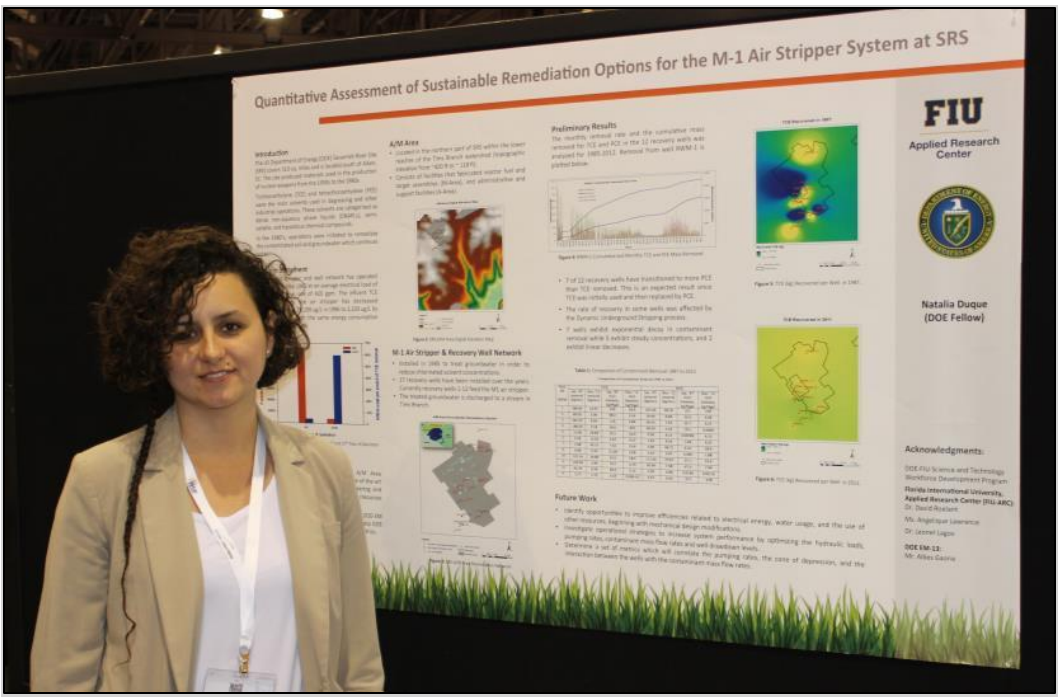
In an effort to contribute and accelerate the D&D of Savannah River Site's 235F facility, Florida International University's Applied Research Center is developing a Decision Model that facilitates rapid selection of fixative, strippable coating, and decontamination gel products. These coatings are used to adhere particles to surfaces or absorb particles to be later stripped off and disposed. The vast variety of available products makes it difficult for end users to be aware of their existence and effectiveness. Therefore, a product list containing the effectiveness of all commercially available products in handling most decontamination situations is very appealing to DOE and DOE contractors. FIU has compiled a comprehensive list of these products and their capabilities, including the surfaces they are capable of decontaminating, the radiation they can handle, application instructions, etc. A Decision Model was created using MATLAB to work hand-in-hand with the product list and further assist in the D&D process. This Decision Model allows users to select inputs relative to their situation, such as radiation, surface, and application. The model then searches the database and returns products that fit the criteria selected. Users will have access to information related to all of the products that can possibly treat the type of contamination specified and thus make more informed decisions when selecting a product that best satisfies their needs. This Decision Model will be deployed as a web-based application on the D&D KM-IT platform and will be made available as a mobile application.

Quantitative Assessment of Sustainable Remediation Options for SRS

Natalia Duque (DOE Fellow)

The Applied Research Center at Florida International University is working on the development of a set of proposed actions that will help reduce the environmental burden of the A/M Area groundwater remediation system at the Savannah River Site. This remediation system has been in continuous operation for 29 years and is expected to remain in operation for several more years. The outcome of this task is expected to convey improvements in system performance, help increase contaminant recovery, and/or decrease energy consumption.

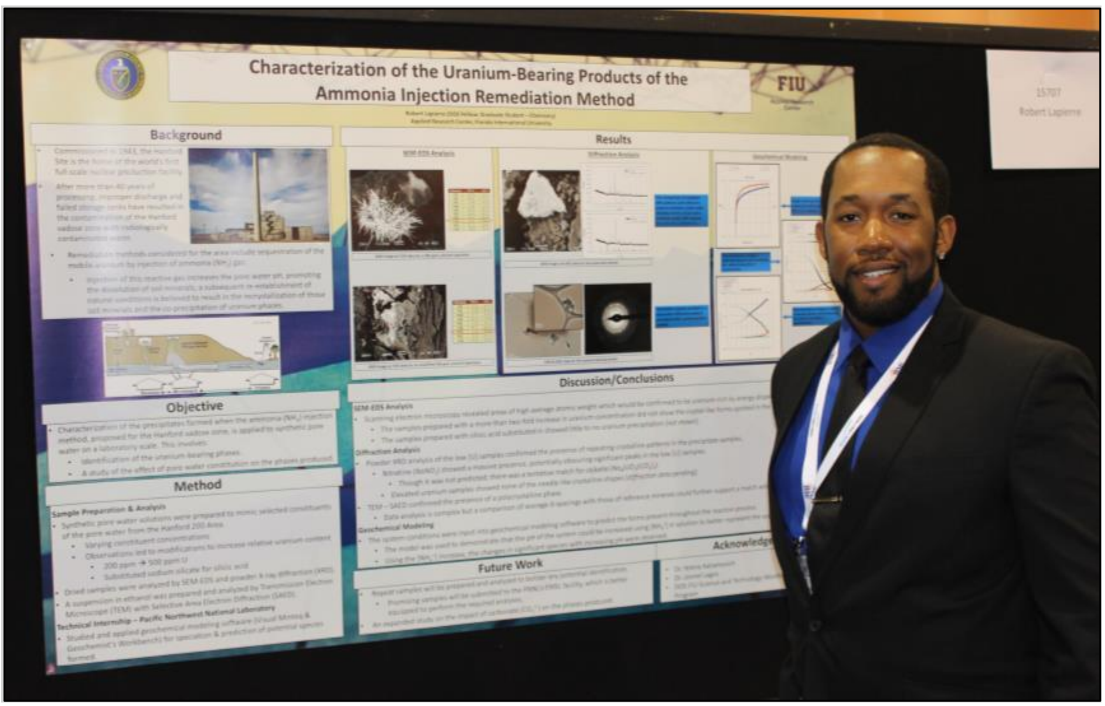
State-of-the-art modeling tools will be used to determine a baseline that will serve as the basis for identifying system optimization opportunities and evaluating options. The overall system efficiency will be provided along with recommendations on how to optimize the hydraulic loads, pumping rates, contaminant mass flow rates, and well drawdown levels.



Studying the Ammonia Gas (NH_3) Injection Methodology Proposed for Remediation of the Hanford Deep Vadose Zone

Robert Lapierre (DOE Fellow)

Contamination in the Hanford vadose zone presents a potential future threat to the ecosystem as the toxins slowly move toward the Columbia River. The injection of reactive gases has been studied by Pacific Northwest National Laboratory as a method of remediation for radionuclide contamination in the Hanford vadose zone. More specifically, the injection of ammonia (NH3) gas has been proposed as a potential method of reducing the mobility of uranium phases in the subsurface of the Hanford 200 Area vadose zone. In support of the ongoing research, a laboratory scale evaluation of the method was performed using the gas injection of a synthetic porewater prepared to represent aqueous phase present in the 200 Area subsurface. In order to develop a careful identification of the uranium-bearing products, a variety of analytical methods were used, including SEM/EDS, X-Ray diffraction, KPA, and TEM analysis. Additionally, geochemical modeling software was utilized to predict the changes in speciation associated with the system.



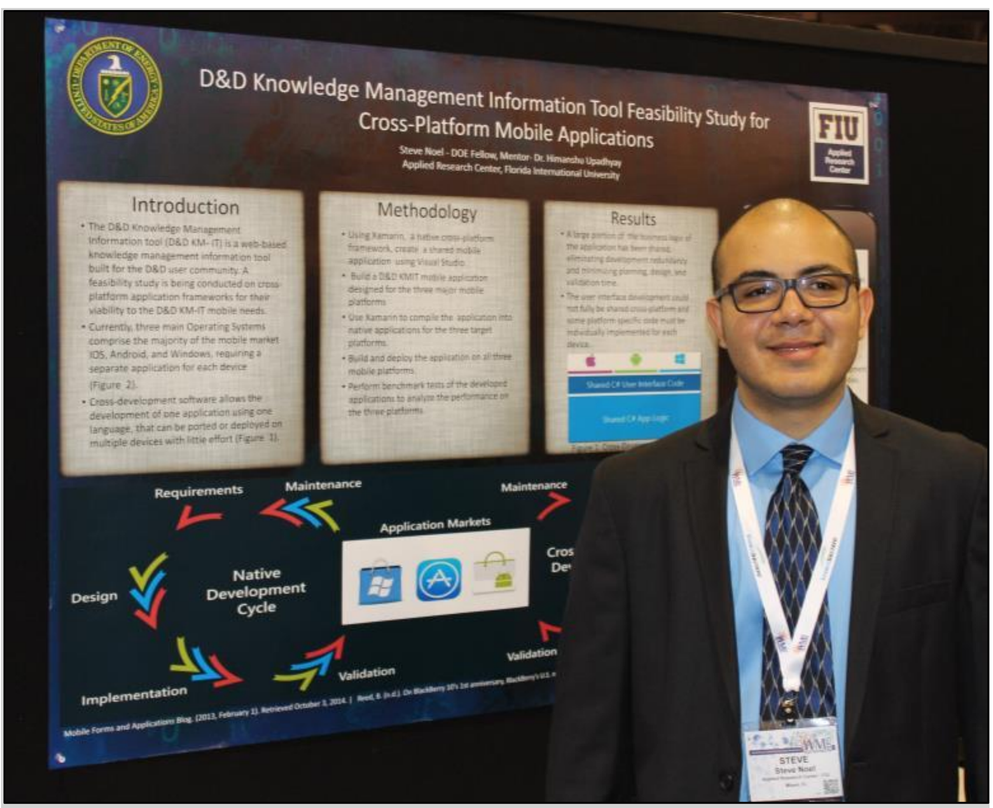
D&D Knowledge Management Information Tool Feasibility Study for Cross-Platform Mobile Applications

Steve Noel (DOE Fellow)

To increase the accessibility of the Department of Energy's (DOE) Deactivation & Decommissioning Knowledge Management Information Tool (D&D KM-IT), a native cross-platform mobile application is needed. A cost/benefit analysis is therefore currently being conducted to determine the feasibility of using cross-platform mobile development software for the D&D KM-IT platform.

Cross-platform development allows developers to code one application and deploy it on multiple devices with little effort. Xamarin is a native cross-platform development framework that allows developers to create native mobile applications.

The feasibility study will test the overhead of a Xamarin application in terms of its memory usage and responsiveness to determine if it is a viable solution for D&D KM-IT needs. Device memory is an important factor in device and application performance. A large application takes time to launch which may affect the device's responsiveness. Another important metric being tested is performance. Can Xamarin be used for quick real-time applications that require intensive computational power from the device, or is it more efficient to create device-specific applications? The study will also test whether the code reusability purported by Xamarin is more time saving than using other frameworks, or if it is similar to individual platform development.



Deactivation and Decommissioning Web Log Analysis Using Big Data Technology

Santosh Joshi (Graduate Research Assistant)

The D&D KM-IT is a web-based knowledge management information tool custom built for the deactivation and decommissioning (D&D) user community. D&D KM-IT allows project managers around the DOE complex to share innovative ideas, lessons learned, past experiences, and practices; and to collaborate virtually on the implementation of proven processes and practices. The system allows interested users to post questions/problems related to specific areas of interest. D&D KM-IT provides secured user registration, role management, custom work flow, basic/advanced search, problem/solution fact sheets, and link/document management.

A feasibility study has been conducted to effectively analyze web-logs generated from D&D KM-IT and to extract useful information such as user behavior, user location, keywords and security breaches using the Apache Hadoop Framework. The Apache Hadoop software library allows distributed processing of large data sets across clusters of computers using a simple programming model called MapReduce. It is designed to scale up from single servers to thousands of machines, each offering local computation and storage. The Hadoop Distributed File System (HDFS) splits files into large blocks and distributes the blocks amongst the nodes in the cluster.

The MapReduce programming framework is used to write programs that process massive amounts of unstructured data in parallel across a distributed cluster of processors to extract the required data.

Best Practices Mobile Application for D&D KM-IT
Jorge Deshon (DOE Fellow)

The Best Practices module for the Deactivation and Decommissioning Knowledge Management Information Tool (D&D KM-IT) shares the knowledge that gave the suitable/appropriate results for past projects through a community-based database. This would help the D&D community with safeguarding success for future projects and preventing previous mistakes. The database includes best practice documents that are contributed by D&D community members while working with DOE fellows at ARC-FIU. There is a formal approval process on KM-IT for publishing the best practices documents. Once approved, the document is accessible in multiple formats and available for download.

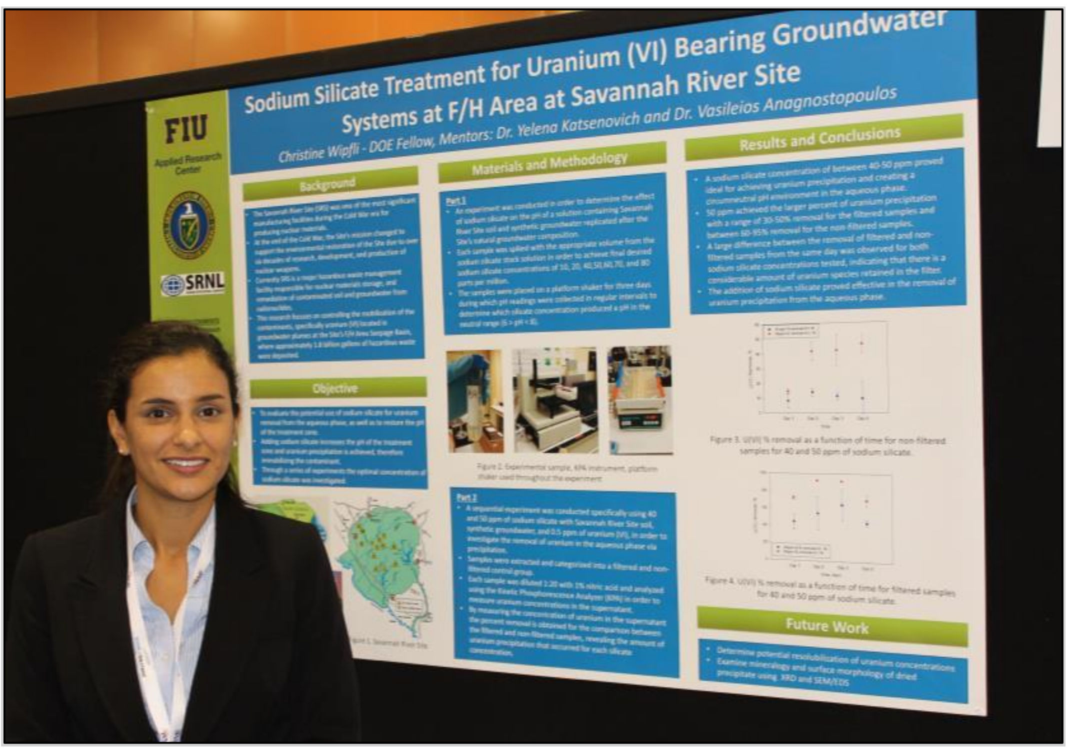
The mobile application for the Best Practices module of the D&D KM-IT uses the jQuery mobile framework which has a "mobile-first" approach in mind based on HTML5 and CSS3. The application is designed to be responsive to fit on any sized screen as well as cross-browser and cross-platform. Using Ajax, the module becomes more bandwidth efficient by refreshing the data in a page instead of reloading the entire page. This function allows multiple parts of a page to have different tasks going on while still running smoothly and efficiently.

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

Christine Wipfli (DOE Fellow)

The Savanah River Site (SRS) was one of the most significant manufacturing facilities during the Cold War era for producing nuclear materials. At the end of the Cold War, the Site's mission changed to support the environmental restoration of the Site due to over six decades of research, development, and production of nuclear weapons. Currently SRS is a major hazardous waste management facility responsible for nuclear materials storage and remediation of contaminated soil and groundwater from radionuclides.

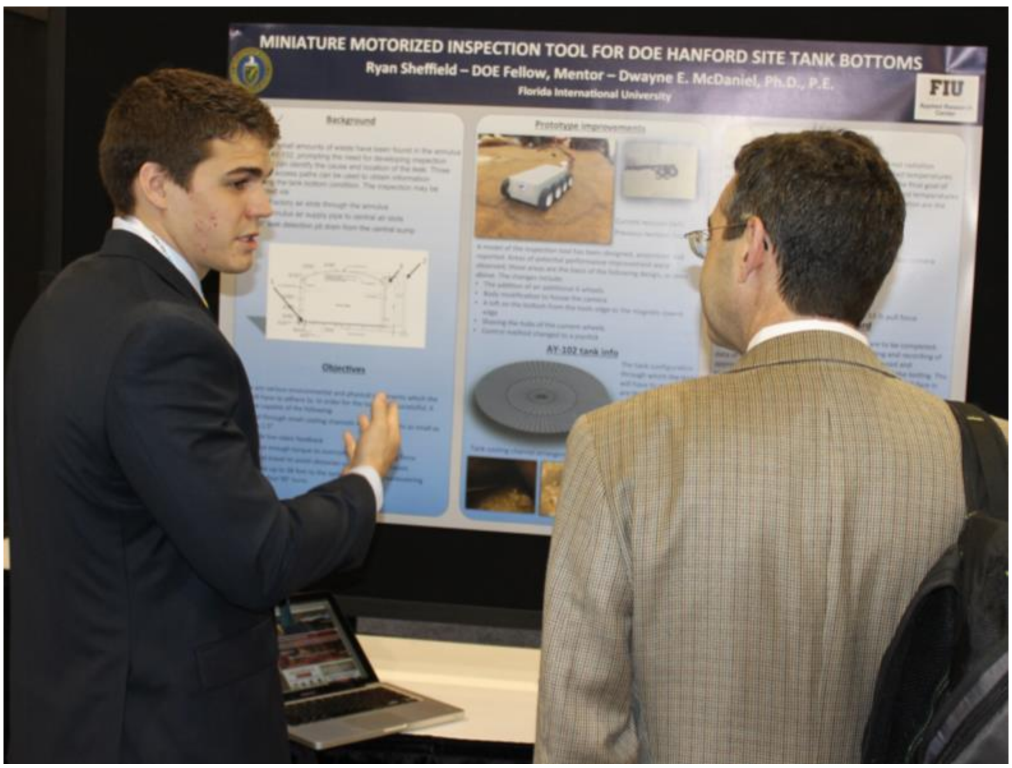
This research focuses on controlling the mobilization of the contaminants, specifically uranium (VI) located in groundwater plumes at the Sites' F/H Area Seepage Basin, where approximately 1.8 billion gallons of hazardous waste were deposited. The objective is to evaluate the potential use of sodium silicate for uranium removal from the aqueous phase, as well as to restore the pH of the treatment zone. Adding silicates increases the pH of the treatment zone and uranium precipitation is achieved, therefore immobilizing the contamination. Through a series of experiments the optimal concentration of silicates was investigated.



Miniature Motorized Inspection Tool for Department of Energy Hanford Site Tank Bottoms

Ryan Sheffield (DOE Fellow)

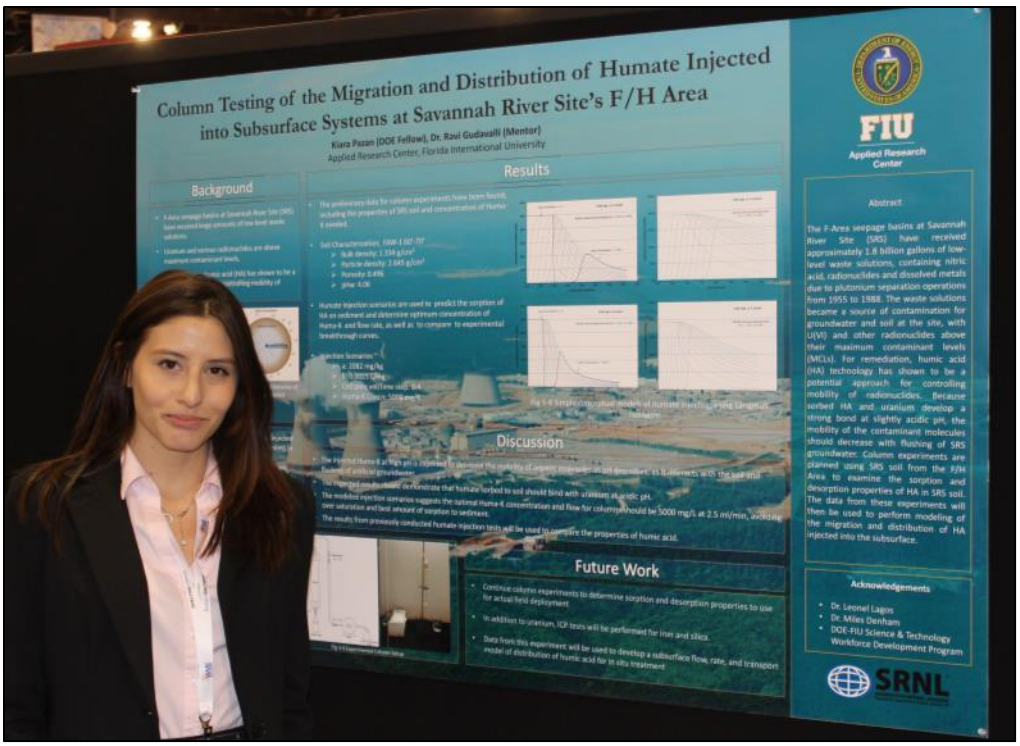
Traces of waste have been discovered in the annulus of tank AY-102 at the Hanford DOE site, prompting a need to investigate the source of leakage via a miniature motorized inspection tool. There are environmental constraints which the tool will have to adhere to, such as being able to withstand elevated temperatures and levels of radiation that are present. The method of entry will be via a 42 inch diameter riser, which will in turn gain the tool access to the refractory slot openings. To accomplish the task delegated, the tool must successfully be able to navigate up to 38 feet to the tank center, maneuver through four 90°-turns, and provide visual feedback, in slots with a width as small as 1.5 inches. This is to be accomplished while inflicting minimal damage to the refractory pad. A small, wheeled, remotely-controlled device is being developed to meet these objectives. The device will utilize a magnet to allow inverted travel along the tank bottom. This presentation describes the development of a prototype of this inspection device.



Column Testing of the Migration and Distribution of Humate Injected into Subsurface Systems at Savannah River Site's F/H Area

Kiara Pazan (DOE Fellow)

The F-Area seepage basins at Savannah River Site (SRS) have received approximately 1.8 billion gallons of low-level waste solutions, containing nitric acid, radionuclides and dissolved metals due to plutonium separation operations from 1955 to 1988. The waste solutions became a source of contamination for groundwater and soil at the site, with U(VI) and other radionuclides above their maximum contaminant levels (MCLs). For remediation, humic acid (HA) technology has shown to be a potential approach for controlling mobility of radionuclides. Because sorbed HA and uranium develop a strong bond at slightly acidic pH, the mobility of the contaminant molecules should decrease with flushing of SRS groundwater. Column experiments are planned using SRS soil from the F/H Area to examine the sorption and desorption properties of HA in SRS soil. The data from these experiments will then be used to perform modeling of the migration and distribution of HA injected into the subsurface.

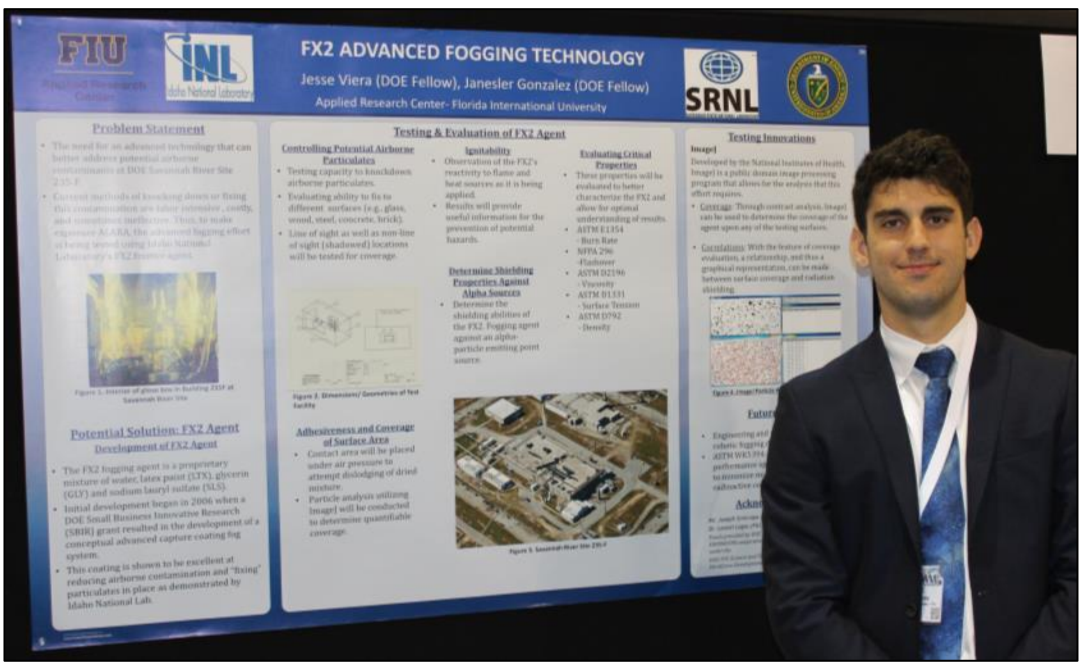


Innovative Applications and Demonstration of Advanced Fogging Technologies to Address Loose Contamination at Savannah River Site's 235F Facility

Jesse Viera (DOE Fellow)

In decommissioned radioactive facilities nationwide, the need for prevention of radioactive contamination is crucial. Currently, workers at the U.S Department of Energy (DOE) are required to enter these facilities and cover the walls with a fixative layering to trap the contamination. In the process, they are exposed to dangerous airborne contamination that could give way to acute and chronic damage.

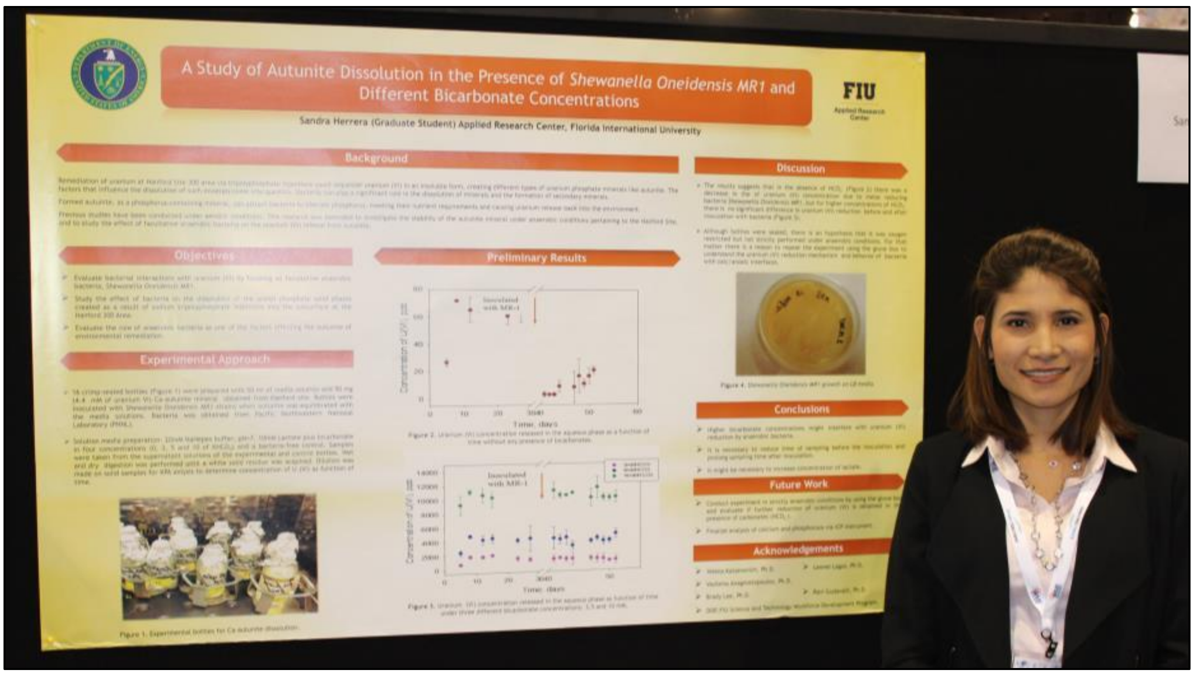
Through an enterprise collaboration between the U.S. DOE, Savannah River Site, Savannah River National Lab, Idaho National Lab, and the Applied Research Center at Florida International University, advanced testing is underway to better trap and fix this airborne contamination through the FX2 advanced fogging technique. This is an integrated method to mitigate the airborne contamination hazards with minimal to no personnel entry. Optimization of the coverage in the facility plays a significant role in this endeavor. This will be done by experimenting with airflow manipulation, multiple nozzle techniques, and robotic devices. In addition, the flammability properties of the FX2 fogging agent will be tested to ensure the safety of the product upon application, as well as its shielding properties against radiation.



A study of Ca-Autunite dissolution in the presence of Shewanella Oneidensis MR1 and different bicarbonate concentrations

Sandra Herrera (Graduate Student Assistant)

The research evaluates bacterial interactions with uranium (VI) by focusing on facultative anaerobic bacteria, Shewanella oneidensis MR1; the goal of the research is to study their effect on the dissolution of the uranyl phosphate solid phases created as a result of sodium tripolyphosphate injections into the subsurface at the Hanford 300 Area. The Columbia River at the site exhibits water table fluctuations, which create an oxic-anoxic interface that in turn, due to activates of facultative anaerobic bacteria, can affect the stability of uranium-bearing soil minerals. Understanding the effect of anaerobic bacteria as a factor affecting the outcome of remedial actions is very important and the protection of water resources from contaminated groundwater is a key role of the overall Hanford cleanup.



Knowledge Management Information Tool Analytics with Distributed Database Engine
Kavitha Megalageri (Graduate Student Assistant)

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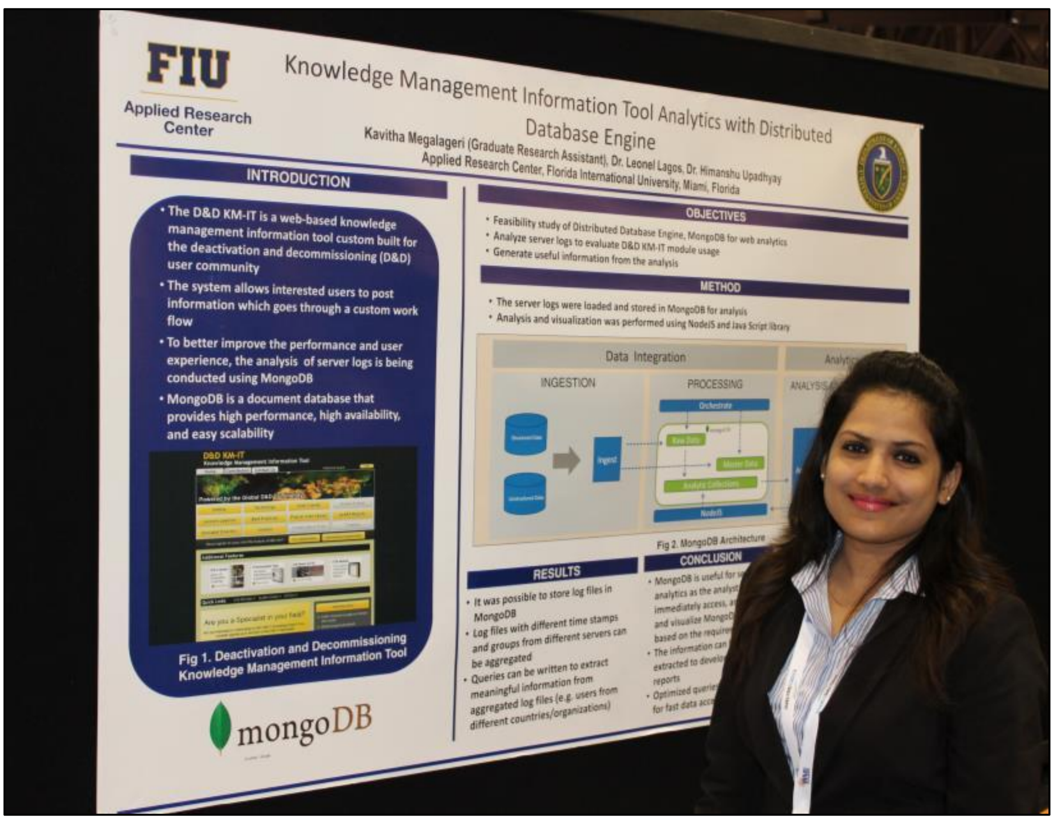
An analysis of D&D KM-IT server logs has been conducted to assess the feasibility of using a distributed database engine, MongoDB, as a viable analytic tool. MongoDB is a document database that provides high performance, high availability, and easy scalability. MongoDB stores data using a flexible document data model. It provides auto-sharding for horizontal scale out, native replication and automatic leader election to support high availability across racks and data centers. Comprehensive secondary indexes, including geospatial and text search, as well as extensive security and aggregation capabilities make it more reliable for analyzing D&D KM-IT server logs



During this month, the Fellows continued their research in the four 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.

Milestones and Deliverables

The milestones and deliverables for Project 5 for FIU Year 5 are shown on the following table. Milestone 2014-P5-M4, submission of the student poster abstracts to Waste Management Symposium 2015 was completed by the due date of January 15, 2015.

FIU Year 5 Milestones and Deliverables for Project 5

Milestone/ Deliverable	Description	Due Date	Status	OSTI
2014-P5-M1	Draft Summer Internships Reports	10/04/14	Complete	
Deliverable	Deliver Summer 2014 interns reports to DOE	10/17/14	Complete	
Deliverable	List of identified/recruited DOE Fellow (Class of 2014)	10/31/14	Complete	
2014-P5-M2	Selection of new DOE Fellows – Fall 2014	10/31/14	Complete	
2014-P5-M3	Conduct Induction Ceremony – Class of 2014	11/13/14	Complete	
2014-P5-M4	Submit student poster abstracts to Waste Management Symposium 2015	01/15/15	Complete	
Deliverable	Update Technical Fact Sheet	30 days after end of project	On Target	

Work Plan for Next Quarter

- Draft the Year End Report for FIU Year 5 (May 2014 to May 2015).
- Continue research by DOE Fellows in the four DOE-EM applied research projects under the cooperative agreement and research topics identified as part of their summer 2014 internships.
- Complete Spring 2014 campaign to recruit new students into the DOE Fellows program.
- Complete coordination of internship placements for summer 2015 at DOE sites, national laboratories, DOE-HQ, and DOE contractors and make arrangements for travel and housing. DOE Fellows will begin summer internships in June 2015.