QUARTERLY PROGRESS REPORT

October 1 to December 31, 2014

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

Principal Investigator:

Leonel E. Lagos, Ph.D., PMP®

Prepared for:

U.S. Department of Energy
Office of Environmental Management
Under Cooperative Agreement No. DE-EM0000598

FIU | 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 October 1 to December 31, 2014. Highlights during this reporting period include:

Program-wide:

- During this quarter, FIU completed the development of the Renewal Application for the new Cooperative Agreement that would begin in May 2015 at the conclusion of the current FIU Year 5. The renewal package was submitted to DOE on November 7, 2014.

Project 1:

- Milestone 2014-P1-19.2.1 and the associated deliverable titled, "Nonmetallic Materials Test Plan for Hanford's HLW Transfer System," was completed and sent to DOE and Hanford site contacts on November 14, 2014, for review and input.
- Milestone 2014-P1-18.2.1 titled, "Complete development of the first prototype of the inspection tool," was completed on December 19, 2014.

Project 2:

- Milestone 2014-P2-M5 titled, "Obtain anaerobic facultative microorganisms, Shewanella sp., from PNNL and complete preparations to set up autunite leaching experiments," was completed on October 3, 2015. Milestone 2014-P2-M2 titled, "Completion of literature review on physical mechanisms associated with the fate of ammonia after injections into subsurface," was completed on October 31, 2015.
- Milestone (2014-P2-M3) for the completion of sample preparation using a reduced amount of silica (50 mM), for Task 1 under Project 2, was completed on November 7, 2014.
- Milestone 2014-P2-M4 for the completion of a draft manuscript on the removal of uranium via ammonia gas injection method was completed on December 15, 2014.

Project 3:

- Milestone 2014-P3-M2, the completion of the literature review for Subtask 2.2, Milestone 2014-P3-M3, the development of a preliminary site conceptual model of Tims Branch for Subtask 2.2, and a related deliverable (literature review summary) were originally due 12/30/14. However, after discussion with SRNL site contacts and notification of DOE HQ, these have been reforecast to March 31, 2015 due to the departure of Dr. Tachiev and Amy Cook, which has delayed the initiation and progress on some of the Project 3 tasks. Dr. Mehrnoosh Mahmoudi (Noosha), ARC's newly hired post-doctoral staff member, and FIU faculty member, Dr. Omar Abdul-Aziz, joined the ARC Project 3 team in December and were introduced during the DOE-ARC Project 3 bi-weekly conference call. They will be supporting the surface/sub-surface hydrological

modeling research and with their assistance it is expected that FIU will be able to meet the new milestone dates.

Project 4:

- Draft papers for the Waste Information Management System (milestone 2014-P4-1.2) and D&D Knowledge Management Information Tool (milestone 2014-P4-3.1) were completed and submitted to the Waste Management Symposium 2015. In addition, the lessons learned lite mobile application for D&D KM-IT (milestone 2014-P4-3.3) was completed and sent to DOE for review/testing on November 7, 2014.

Project 5:

- The DOE Fellows summer internship technical reports were drafted (milestone 2014-P5-M1) and the final reports were submitted to DOE on October 17, 2014.
- DOE Fellows for the Class of 2014 were selected (milestone 2014-P5-M2) and submitted to DOE on October 31, 2014.
- FIU conducted an Induction Ceremony for the new DOE Fellows (Class of 2014) on November 13, 2014 (milestone 2014-P5-M3).

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:

Task	Milestone/ Deliverable	Description	Due Date	Status	OSTI
Program-wide (All Projects)	Deliverable	Draft Project Technical Plan	06/18/14	Completed	
	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*	Will be scheduled based on availability of DOE HQ officials	
	Deliverable	Presentation overview to DOE HQ/Site POCs of the project progress and accomplishments (Year End Review)	06/30/15*	On Target	

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

Project 1
Chemical Process Alternatives for Radioactive Waste

Project Manager: Dr. Dwayne McDaniel

Project Description

Florida International University has been conducting research on several promising alternative processes and technologies that can be applied to address several technology gaps in the current high-level waste processing retrieval and conditioning strategy. The implementation of advanced technologies to address challenges faced with baseline methods is of great interest to the Hanford Site and can be applied to other sites with similar challenges, such as the Savannah River Site. Specifically, FIU has been involved in: 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

Work for the asynchronous pulsing system (APS) subtask was focused on the manufacturing of plugs. After weeks of trials, we have been unable to obtain results that consistently meet the minimum pressure criteria. Several plug making parameters were varied, including mixing speeds, compacting approaches, curing time and curing methods, with no evident pattern for the inconsistencies. In the past, we have run into similar problems and found that sometimes it could be the binding material used (fast set versus slow set). We then noted that our current vendor had changed the type of material to a fast set plaster. We contacted the manufacturer and ordered 2 bags of the slow set material which arrived at the end of October. FIU repeated the trials using the slow setting material to manufacture the plugs. The slow setting material did not provide any improvements; in fact, the blowout pressure was even worse than the fast set material at only 55 psi.

Another possible reason for the low blowout pressure could be that due to the repeated cleaning of the inside of the test section pipe with a wire brush, the inside surface of the test section pipe has become very smooth. This could result in a reduced coefficient of friction between the pipe and the plug material that results in a low blowout pressure. In order to determine if the inside surface roughness of the plug shell had an impact on the blowout strength of the plug, FIU purchased a new plug shell and repeated the tests with the new shell and an old shell using the fast setting material. The new shell unplugged at 50 psi while the old shell held 200 psi before unplugging. Upon closer investigation, it was discovered that the new shell had a protective coating on the inside of the pipe applied during manufacturing. In either case, the 200 psi the old plug held is well below the desired 300 psi pressure.

After consulting with the individual who developed the plug recipe, we were advised that the problem with the plugs lacking the proper strength could be due to excessive mixing time of the

material which results in the material hardening prematurely before it adheres to the shell wall. Since mixing the material with water results in an exothermal reaction, another possible solution is to use colder water during the mixing process to reduce the curing rate of the material. In order to determine if the plug strength issue was due to variations in the plug manufacturing process, we manufactured four batches of plugs while varying different manufacturing parameters. They included: one batch utilized 40^{o} cold water instead of room temperature water to delay the curing process as per the plaster of Paris manufacturer's instructions on the bag, one batch involved pre-mixing the dry components (kaolin and plaster of Paris) before adding the water, and for the last two batches, the mixing time for the plaster was reduced. The blowout test results of the cold water batch was that after a 24 hour curing time, the plugs were not fully cured and the plugs blew out at minimum pressures. We speculate that the temperature may have been too cold to fully activate the plaster. Pre-mixing the dry components did not result in any improvement on the blowout pressure. For the last two batches, we tried to avoid excessive agitation after the addition of the plaster by reducing the mix time from 5 min. to 3 min. After 24 hours, the plugs were fully cured and the outcome of the blowout tests was increased but not to the range we need.

Due to changes in staff, the peristaltic crawler subtask has been placed on hold. FIU has recently interviewed potential replacement engineers and once the hiring process is completed, the task will resume.

FIU Year 4 Carryover Work Scope

Subtask 2.2: Computational Simulation and Evolution of HLW Pipeline Plugs

During October, a mesh assessment was performed to determine the optimal mesh type for the 3D numerical models simulating settling conditions in a horizontal pipe. 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 mixture model is a macroscopic two phase model that is able to compute the flow for a mixture of a solid and liquid. It tracks the average phase concentration, or volume fraction, and solves for one velocity field for each phase. The two phases consisted of one dispersed phase (solid particles) and one continuous phase (liquid). The model combined the k-epsilon turbulence model for the main flow with equations for the transport of the dispersed phase and the relative velocity of both phases. Some of the assumptions made while using the mixture model were that the density of each phase was constant; that the pressure field was the same and the velocity between the two phases could be ascertained from a balance of pressure, gravity, and viscous drag.

The model geometry for the simulations 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 solids were modeled as spherical solid particles of equal size with the particle size set at 45 μm. The solid volume fraction was set at 2.9%. The solid and liquid densities were set at 3147 and 1000 kg/m^3, respectively. 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. For the mesh analysis, two types of mesh were evaluated: (a) tetrahedral mesh and (b) swept mesh as shown in Figure 1-1. The mesh size of the elements was evaluated for three sizes: extremely coarse, coarse and normal.

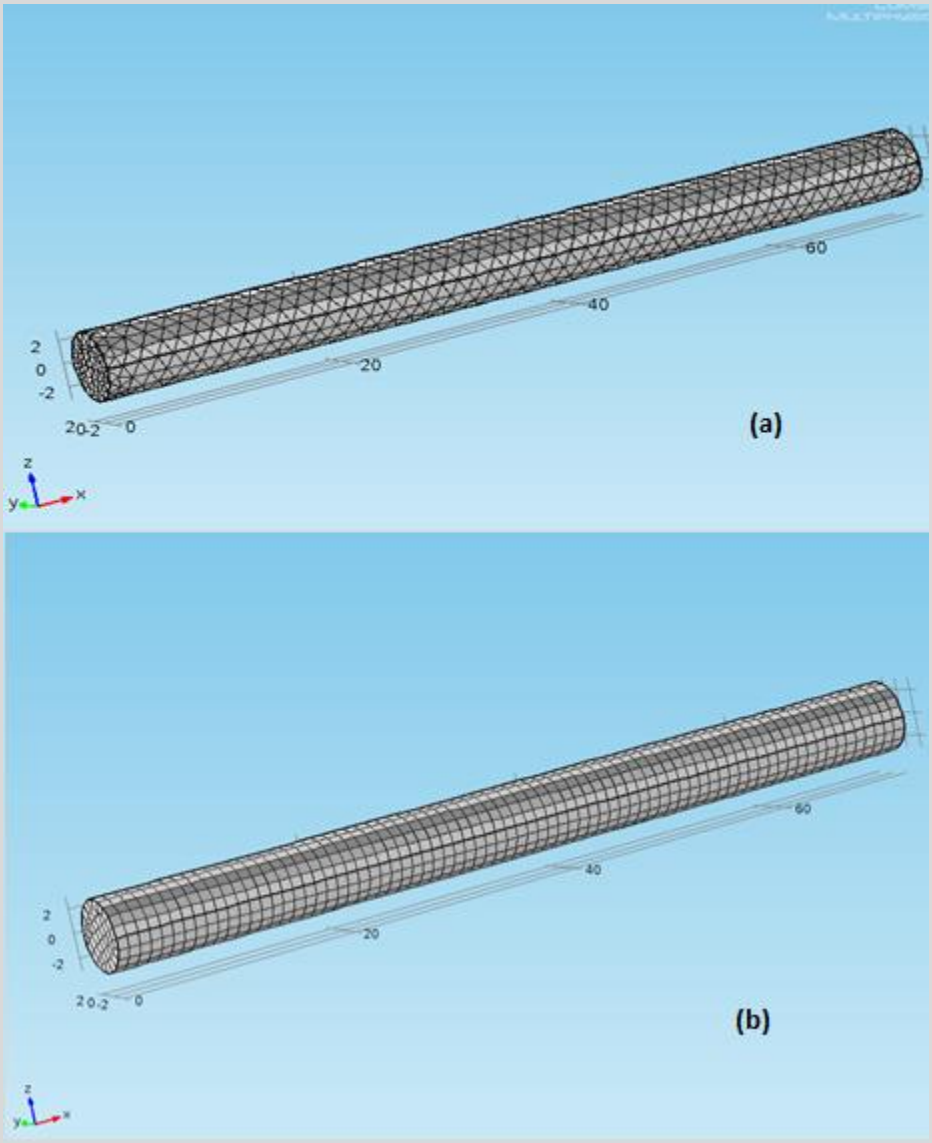


Figure 1-1. Meshed geometry-3D numerical model: (a) tetrahedral mesh and (b) swept mesh

The dispersed phase volume fractions for each of the mesh type and mesh size were computed as shown in Table 1-1.

Table 1-1. Dispersed Phase Volume Fractions by Mesh Type and Mesh Size

Mesh Size	Tetrahedral Mesh (dispersed volume fraction)	Swept Mesh (dispersed volume fraction)
Extremely Coarse	0.034	0.0353
Coarse	0.038	0.039
Normal	0.041	0.042

Both the mesh types produced comparable results; however, there was a high variance in the computational time that each of the mesh types took to converge. For instance, for the coarse mesh size, the tetrahedral mesh model took 66 minutes as compared to the 206 minutes it took for the swept mesh model to complete for comparable dispersed volume fraction computations. Hence, it was concluded that for future virtual models, mesh elements of coarse size and tetrahedral mesh type will be the optimal solution for simulations.

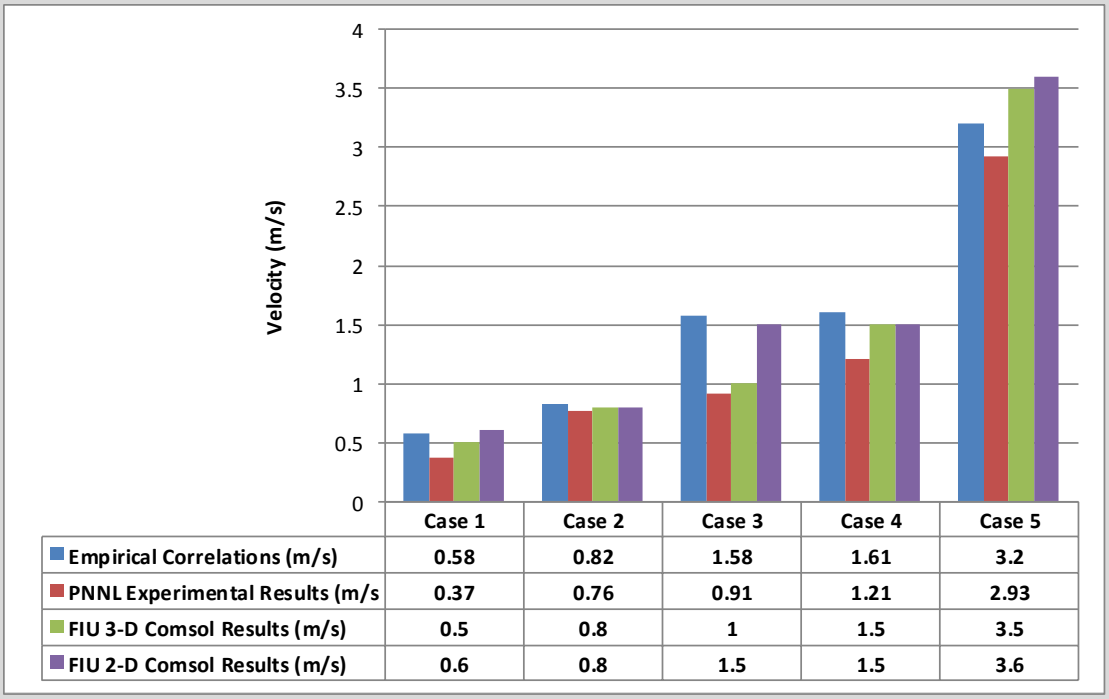
During the month of November, efforts were focused on creating virtual scenarios representing PNNL's experimental studies. The 3-D mixture models to simulate settling of solids were solved via a transient simulation. The behavior of settling was investigated as a function of flow velocity, particle size, solids density and solids volume fraction. Table 1-2 below lists the material properties used for the numerical simulations. The material properties were obtained from the experimental tests done by Pacific Northwest National Laboratory (PNNL) to determine the critical velocity for Newtonian slurries.

Table 1-2. Numerical Simulations Matrix

Test Configuration	1	2	3	4	5
Particle diameter (μm)	14.4	37.7	129.5	182.3	203.9
Solids Density (kg/m^3)	2500	7950	3770	2500	7950
Solids volume fraction (%)	9.8	9.3	8.7	7.4	3
Liquid density (kg/m^3)	1146	1647	1151	999	1026
Liquid viscosity (cP)	10.2	9.3	4.5	1.5	1.6

During the month of December, the critical velocity results obtained by the numerical simulations were compared with the experimental results of PNNL and with the empirical based critical velocity correlations. The 3-D numerical results were also compared with the previous 2-D numerical studies to understand the trade-off between the two studies in terms of computing speed and numerical accuracy.

The numerical results were a good match with the experimental results and demonstrated the use of COMSOL Multiphysics 4.3b to accurately simulate the settling physics as shown in Figure 1-2. Moreover, there was little variance observed between the computed 2-D critical velocity results to those compared with the 3-D results. The 3-D models had relatively longer computing time (> 24 hr) compared to the couple of hours it took for the 2-D models to solve. Hence it was concluded that the 2-D models were a good enough representation and highly accurate of the settling behaviors simulated with the given material properties and future studies would not require 3-D representation.



	Case 1	Case 2	Case 3	Case 4	Case 5
Empirical Correlations (m/s)	0.58	0.82	1.58	1.61	3.2
PNNL Experimental Results (m/s	0.37	0.76	0.91	1.21	2.93
FIU 3-D Comsol Results (m/s)	0.5	0.8	1	1.5	3.5
FIU 2-D Comsol Results (m/s)	0.6	0.8	1.5	1.5	3.6

Figure 1-2. Comparison of numerical results to experimental and empirical results.

During the next reporting period, virtual scenarios will be created simulating settling behavior as a function of particle size, solids density and solids volume fraction.

Task 17: Advanced Topics for HLW Mixing and Processing

Task 17 Overview

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

This task focuses on using the lattice Boltzmann model (LBM) for multiphase flow modeling to improve the capabilities of the multi-phase LBM multiple-relaxation-time (MRT) computer program developed at FIU in order to obtain simulations at the engineering-scale with appropriate physics captured for the fluid-structure interactions.

Due to changes in personnel, the efforts for this subtask have been suspended and we will discuss with DOE and site engineers the future of the subtask.

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

Dr. Seckin Gokaltun attended a 3-day online training on the Star-CCM+ software on October 7-9, 2014 which provided an introduction to the meshing and geometry handling features of the software. One new undergraduate student was hired and he reviewed the literature from past FIU work to get acclimated with the project. The student also completed the necessary lab safety training. The Cd-Adapco company sent FIU a quote for the software and necessary documentation for license agreements which is currently being reviewed by the FIU legal department. The computer hardware requirements necessary to produce simulation results in a reasonable amount of time has been discussed with the FIU IT team and a small scale cluster is going to be built at FIU for this purpose. FIU has received quotes on the computer hardware.

FIU initiated the purchase order for the software license for the Star-CCM+ software FIU for 4 serial seats for serial computing and 90 HPC seats for parallel computing. The software will be installed at FIU's Panther cluster that serves the whole university for high performance computing needs. ARC will invest in the FIU Panther cluster instead of purchasing a small scale computer cluster in order to get access to a larger number of cores. In addition to this, a literature review has been initiated in order to understand the pros and cons of direct numerical simulations (DNS) for turbulent flows of single phase and multiphase fluids. It was observed that the main purpose of DNS is to solve for the turbulent velocity field without the use of turbulent modeling. DNS is used to compute fully nonlinear solutions of the Navier-stoke equations. It can be used to create simplified situations that are not possible in an experimental facility, and can be used to isolate specific phenomena in the transition process. Current computations typically use finite-difference schemes, or a combination of spectral and finite-difference schemes, although finite element approaches using unstructured grids are also being explored. The spectral method is typically preferred unless complex geometries are involved, then finite difference techniques, especially high-order accurate upwind-biased methods, are good candidates. The range of scales in turbulent flows increases rapidly with the Reynolds number and hence most practical engineering problems (e.g. flow around a car) have too wide a range of scales to be directly computed using DNS. Turbulence contains a wide spectrum of vortices with equal physical importance. With an increase of the Reynolds number, the size ratio of the largest to the smallest vortices increases. This makes it difficult to perform the DNS of turbulence with a higher Reynolds number.

After communications with the Cd-Adapco company, it was found that Star-CCM+ utilizes a 2nd order central-differencing scheme with boundedness along with 2nd order implicit temporal discretization which is claimed to be "reasonable" for accuracy as compared to the DNS method that use a high order spatial discretization (≥ 4th) scheme and explicit temporal integration. Therefore, this approach is called a quasi-direct numerical simulation (qDNS) in literature. FIU is currently investigating the literature on qDNS to further understand its advantages and disadvantages for CFD simulations of waste mixing scenarios.

During this period, research papers concerning turbulent Bingham fluids were investigated. Specifically, solutions of Bingham fluids using the Herschel–Bulkley fluid method were studied. A handful of published works were found in which pseudo plastics were the fluid of consideration, most of which included turbulence. A few of these were found that could prove to be good benchmark exercises to be used in Star CCM+ in order to validate our knowledge of the software. "Turbulent Flow of Non-Newtonian Systems" by DW Dodge et al. (1959) investigated fluids traveling through pipes with flow-behavior indexes between 0.3 and 1.0 where Reynolds numbers were as high as 36,000. The relationship between pressure loss and a mean flow rate were established in this work. A second paper titled, "Flow of Non-Newtonian Fluids-Correlation of the Laminar, Transition, and Turbulent-flow Regions," by AB Metzner et al. (1955) established a friction factor vs. Reynolds table for several types of fluids traveling through pipes, including that of Bingham behavior. Finally, a paper by AD Thomas et al. (1987) titled, "Analysis of non-Newtonian turbulent flow- Yield-power-law Fluids," incorporated a new analysis for solving fluid flow through a pipe and extended its use to incorporate the Herschel–Bulkley method for Bingham fluids.

Two of the published works found have been cited by over 500 other works while the last one was found to have been referenced in about 30 different studies. The amount of information given by these articles in regards to the flow conditions was partially achieved. This will continue to be carried out in order to see which work can be replicated in Star CCM+ most easily and accurately in terms of how it was done in the published works.

Task 18: Technology Development and Instrumentation Evaluation

Task 18 Overview

The objective of this task is to assist site engineers in developing tools and evaluating existing technologies that can solve challenges associated with the high level waste tanks and transfer systems. Specifically, 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.

FIU Year 4 Carryover Work Scope

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

During the month of October, the focus for this task was upon completing the experimental setup and experimental plan. The goal of the experiment is to measure the sonar's ability to see and measure the volume of solids on the floor of the mixing tank while solids are being mixing in the tank water. There will be a critical % solids entrained in the water during mixing that will completely obscure the sonar imaging. We will determine that % solids for a sonar positioned 1, 2 and 3 feet above the tank floor. Sonar measurements will be taken during mixing as well as 0, 30, 45, and 60 seconds after the mixing pump is turned off. Hanford engineers have requested tests to image immediately after the pump mixer is stopped and while the micron-sized kaolin particles settle to the floor.

A structure with unistrut components has been designed and is under assembly across the top of the tank to hold the sonar in place and perpendicular to the tank floor even during mixing operations. The unistrut design will hold the SLIM sonar within 3 degrees of the perpendicular in order to reduce errors due to an offset angle. Extra effort has been focused this month on the forces and possible deflections of the sonar during the vigorous mixing motion of the water and entrained kaolin inside the tank. The unistrut design has been reinforced across the tank top to ensure that the sonar remains rigid with respect to its orientation to the tank.

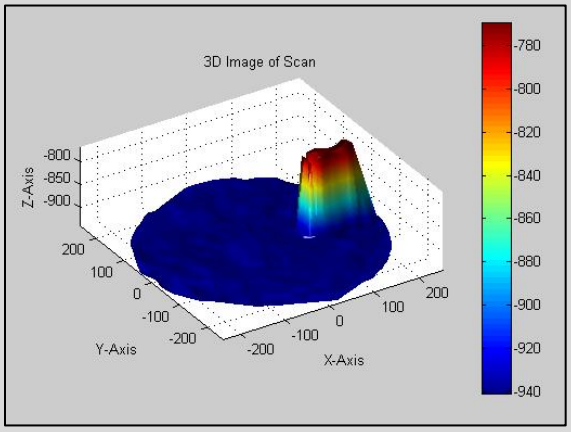
A poster was developed by the DOE Fellow student working on this task and entered into a poster competition at FIU. DOE Fellow Dayron Chigin did an excellent job designing the poster as well as in engaging with competition judges and others interested in his research. He won first prize in the DOE Fellow student poster competition and was awarded in November.

Experimental testing of the SLIM sonar's ability to image through HLW with suspended particles began in November. FIU will determine the % solids at which the sonar can no longer image the tank floor for the sonar positioned 1 meter above the floor, then lower the sonar to 2/3 m above the floor and add kaolin until the imaging of solids or objects on the floor is again lost. Finally, testing at 1/3 m above the tank floor will be done. Sonar measurements will be taken during mixing as well as 0, 30, 45, and 60 seconds after the mixing pump is turned off. Hanford engineers have requested tests to image immediately after the pump mixer is stopped and while the micron-sized kaolin particles settle to the floor.

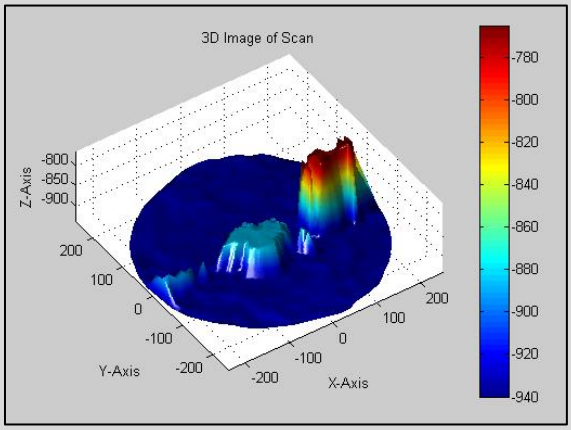
A section of unistrut will be used as the object to be imaged during these initial experiments. The weight of the steel unistrut will keep it from moving during mixing. Also, the unistrut was placed on the tank floor directly in the line of flow of the nozzle to the tank outlet to the pump so that no solids material will accumulate around it as happened around the solid brick used in earlier testing. The test tank is 1 meter in diameter and the sonar is positioned exactly 1 meter above the tank floor for initial tests.

Figure 1-3. Object to be imaged (a section of unistrut or U-channel) (left). Test tank from above showing 3 inlet nozzles and the outlet return (right).

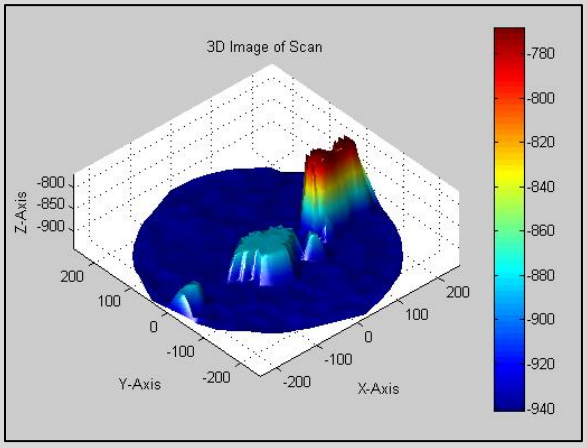
The first sonar scan shown in Figure 1-4 is of the empty tank and the object being imaged is the nozzle directed into the tank. The second and third sonar images show results of imaging for 30 seconds with no kaolin added (0% vol. kaolin) and for imaging 30 seconds with 1% vol. kaolin. Note the sonar images of the nozzle and unistrut on the tank floor are identical in these last two sonar images. These images were created with software developed by FIU that includes MATLAB modules. The object on the left side of sonar scans 2 and 3 is the plastic coupling for the tank outlet that leads to the hose and pump inlet.



Sonar Scan 1



Sonar Scan 2



Sonar Scan 3

Figure 1-4. Sonar Scan 1 (upper left): empty tank with nozzle protruding from the right; Sonar Scan 2 (upper right): same tank with a section of U channel (unistrut) aligned linearly with the nozzle; Sonar Scan 3 (lower left): tank with U channel as well as 1% kaolin added Note – there is no effect of entrained kaolin on the image quality.

This is preliminary data and imaging and the final images are expected to be much sharper in resolution as earlier sonars scans have been.

FIU initiated experimental tests in December of the ability of the 3-D sonar 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.

The calculation for the mass of kaolin clay needed to be added to our tank water to vary the volume % of Kaolin from 1% to 20% is shown in Table 1-3.

Table 1-3. Mass of Kaolin for 1-20 Volume Percent of Kaolin in FIU's Test Tank

Volume Percentages	% Volume (meters cubed)	Mass of Kaolin Required (kg)	Mass of Kaolin (lbs.)
1%	0.006207	16.1382	35.57859848
2%	0.012414	32.2764	71.15719697
3%	0.018621	48.4146	106.7357955
4%	0.024828	64.5528	142.3143939
5%	0.031035	80.691	177.8929924
6%	0.037242	96.8292	213.4715909
7%	0.043449	112.9674	249.0501894
8%	0.049656	129.1056	284.6287879
9%	0.055863	145.2438	320.2073864
10%	0.06207	161.382	355.7859848
11%	0.068277	177.5202	391.3645833
12%	0.074484	193.6584	426.9431818
13%	0.080691	209.7966	462.5217803
14%	0.086898	225.9348	498.1003788
15%	0.093105	242.073	533.6789773
16%	0.099312	258.2112	569.2575757
17%	0.105519	274.3494	604.8361742
18%	0.111726	290.4876	640.4147727
19%	0.117933	306.6258	675.9933712
20%	0.12414	322.764	711.5719697

These masses and volume percentages were calculated for the right cylinder tank with the following parameters:

H, Height of water in the tank H = 1 meter
ID, Inner diameter of the tank ID = 0.889 meters
R, Radius of the tank R = 0.4445 meters
V_f, Volume of a right cylinder of fluid $V_f = \pi \times R^2 \times H$
ρ, density of Kaolin (intrinsic) $\rho = 2600$ kg/m^3

In December, 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. The unfiltered images for both the 30 and 60 degree arc scans are shown in Figures 1-1 through 1-3 for 3% Kaolin by volume.

The sonar image in Figure 1-5 is for the 30 degree swath arc. It is a scan that focuses upon the center of the tank. The dark blue shows the tank floor, the light blue is the top of the piece of unistrut and the orange/red/yellow layer is the kaolin that was not lifted by the mixing in the tank from the nozzle. It is important to note that the pump inlet and outlet were on opposite sides of

the tank at the bottom and the direct fluid flow was in direct alignment with the unistrut and this is why there is no settled Kaolin in this blue flow field.

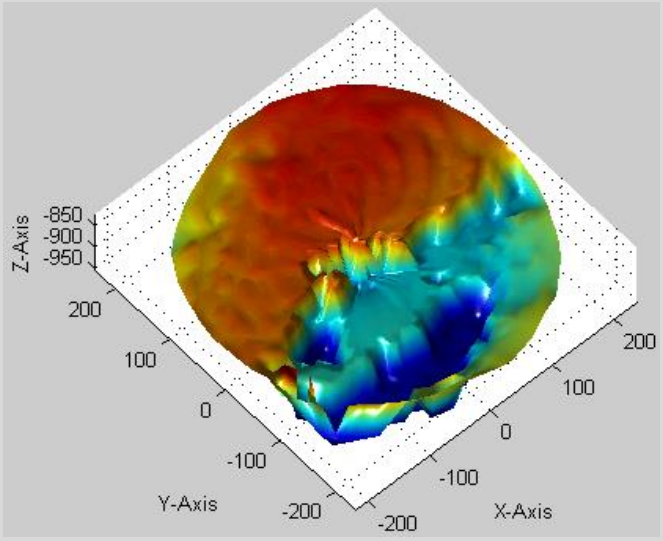


Figure 1-5. 3-D sonar scan for: 30 degree swath arc; 29 seconds; and 3% vol. Kaolin.

The sonar image in Figure 1-6 is of the entire bottom of the tank with the 60 degree swath arc. While the color scale has changed, one can see the above sonar scan between -200 and the 200 range along the X-axis and the -200 and the 250 range along the Y-axis. This image contains no filters. The peaks around the outer circumference of the tank are the tank walls as well as the inlet and outlet pipe fittings for the fluid being pumped.

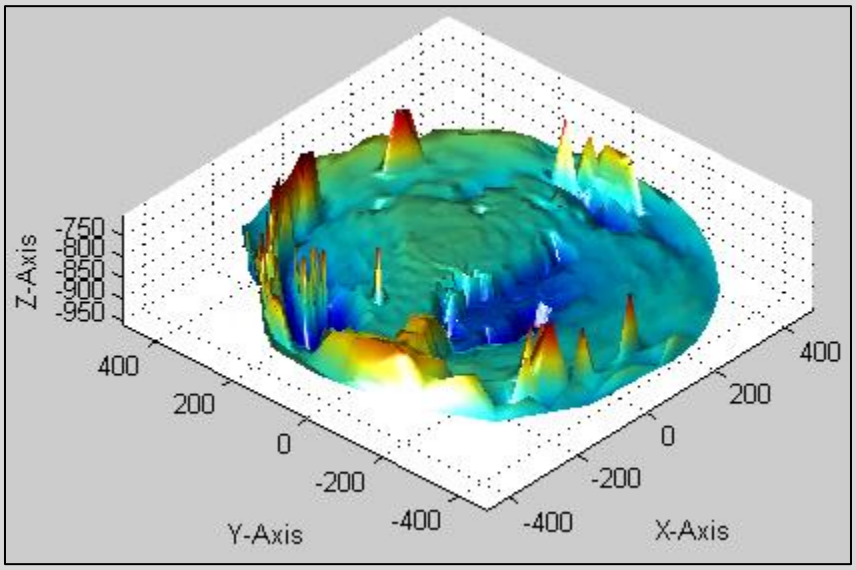


Figure 1-6. 3-D sonar scan for: 60 degree swath arc; 42 seconds; and 3% vol. Kaolin.

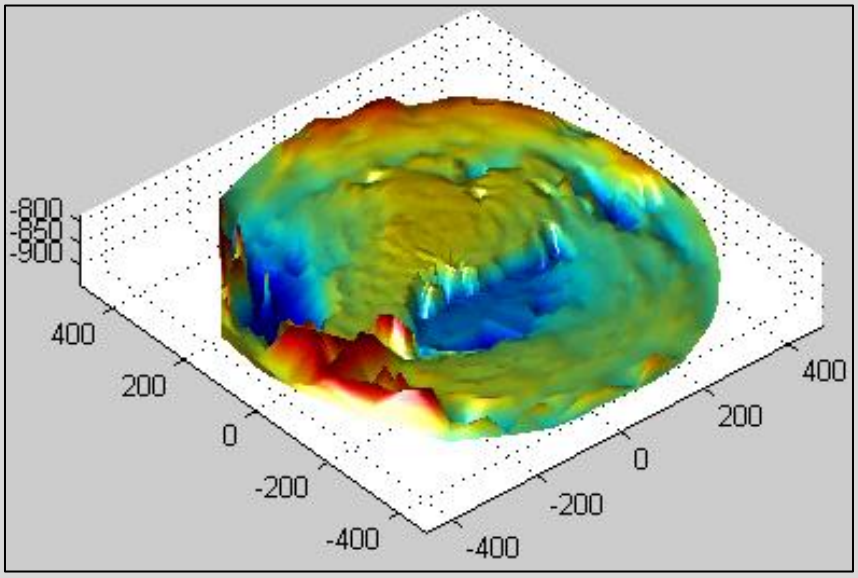


Figure 1-7. 3-D sonar scan for: 60 degree swath arc; 42 seconds; and 3% vol. Kaolin with a simple filter applied to data to remove wall and pipe fittings.

A simple data filter was applied to remove the spikes seen arising from the walls and pipe fittings (tank inlet and outlet fittings) as shown in Figure 1-7. The direct flow of fluid across the bottom of the tank sweeps away all Kaolin but immediately outside of the direct flow, Kaolin is settled on the floor.

The pump and the flow design for the experimental setup will be modified in January to assure that solids at 1-20% vol. of Kaolin will remain suspended and not settle on the floor. Calculations and empirical tests will be used to confirm that the pump flow field is over designed for the mixing and suspension.

FIU Year 4 Carryover Work Scope

Subtask 18.2: Development of Inspection Tools for DST Primary Tanks

The objective of this task is to develop an inspection tool that can provide visual feedback of DST bottoms from within the insulation refractory pads. FIU engineers work directly with site engineers to develop alternative designs based on specified performance criteria. Specific subtasks include: 1) developing design concepts that will allow for the navigation of a remotely controlled device through the refractory pad channels and provide visual feedback. Based on site feedback, an initial prototype will be manufactured and 2) investigating the use of a crawler device similar to the technology developed in Task 2.1 that can navigate through a 4-in air supply pipe that leads to the central plenum.

Experimental testing was conducted to determine a range of expected loads on the inspection tool caused by the tether. At this point in the design process, the values obtained are simply estimates, as we do not have a final configuration for the tether. The experimental set-up includes creating a channel that emulates the first 17 feet of the refractory pad. Two channels were manufactured, measuring 7.85 feet in length, and had a cross section of 1.5 in x 1.5 in. Per

recommendations from WRPS engineers, Kaolin 2200 was used to emulate the surface of the channel and provide a similar coefficient of friction as the refractory pad. The two channels can be spliced together to create a total path length of 15.8 feet.

The tether was comprised of the power cables and camera line. In order to determine the amount of force the device needs to pull, a digital scale was attached to the tether and was pulled over the Kaolin surface inside the channel (Figure 1-8).

Figure 1-8. Pull force tests in the mock-up of the channel.

Six trials were conducted for each of the following configurations:

1) 15.7 feet (Channel 1 and 2, combined)
2) 7.85 feet (Channel 1)
3) 7.85 feet (Channel 2)

Results from the testing are shown in Table 1-4. As expected, the forces were similar for Channel 1 and 2 and adding the individual channel forces were similar to the results obtained from the combined channel.

Table 1-4. Pull Force Trials

	Pull Force (oz)							
	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	Mean Ave	Standard Deviation
(A) 15.7 ft Length Channel 1 and 2 Together	3.1	3.1	4.7	2.7	3.9	3.9	3.57	0.67
(B) 7.85 ft Length Channel 1	2	1.7	2.1	2.8	1.9	2	2.08	0.34
(C) 7.85 ft Length Channel 2	1.6	1.6	2.7	1.5	1.5	1.6	1.75	0.43
(B)+(C)	3.6	3.3	4.8	4.3	3.4	3.6	3.83	0.54

Testing of the initial prototype of the inspection tool was completed in December. A report is scheduled to be provided to DOE and Hanford site engineers at the end of January. Figure 1-9 shows an up-close image of the tool with a small camera installed on the top. Figure 1-10 provides a snapshot of the inspection tool as it travels upside down (via a magnet) through a channel constructed using the Kaolin. The device was able to travel 17 feet, which is the distance

from the insertion point of the refractory pad to the first 90 degree turn. The inspection tool is able to provide visual feedback of the channel as shown in Figure 1-11.

Figure 1-9. Prototype with a small camera attached to the top.

Figure 1-10. Testing of the prototype through a channel manufactured from kaolin to emulate the refractory pad and its coefficient of friction.

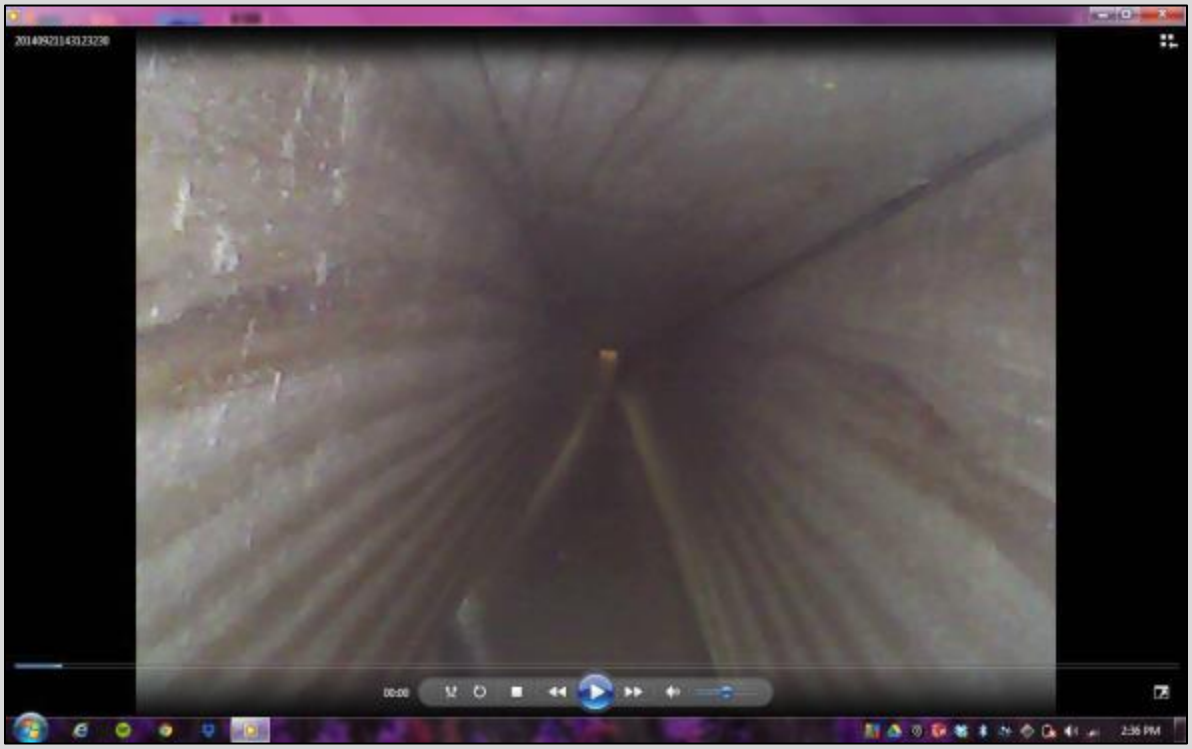


Figure 1-11. Screen capture of the video feed from testing in a mock up channel.

Task 19: Pipeline Integrity and Analysis

Task 19 Overview

The objective of this task is to support the DOE and site contractors at Hanford in their effort to evaluate the integrity of waste transfer system components. 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

FIU Year 4 Carryover Work Scope

Subtask 19.1: Pipeline Corrosion and Erosion Evaluation

Engineers at Hanford provided FIU with additional thickness measurements taken from four nozzles in the POR 104 Valve Pit. All nozzles contained a straight section and a 90° long radius elbow made from Schedule 40, 304L stainless steel pipe. Two of the nozzles have transported approximately 7.27 million gallons of supernatant and the other two transported 7.83 million

gallons of slurry waste. Nozzles labeled C and F transported the supernatant and the nozzles labeled B and E transported the slurry. The steel pipes and elbows were joined with Chem-Joints and a Purex nozzle was also welded to the top side of the elbows.

Previous efforts focused on evaluating the thickness measurements and analyzing the data as a function of radial and longitudinal position. Recent efforts have focused on inserting a compensation curve for the plots associated with the elbows. The compensation curves seek to remove variations of thickness in the elbows that have been caused by manufacturing processes. Literature suggest that there is an expected 10% thinning at the extrados and 10% thickening at the intrados when the elbow is manufactured by bending a straight pipe over a die. Therefore, 10% of the thickness is added at the extrados and 10% is removed at the intrados with proportional thickness values being added at all other locations. This results in no change of the thickness at the top and bottom of the pipeline. Figures 1-12 through 1-15 show the longitudinal average thicknesses grouped by radial position for each elbow in the four nozzles evaluated. Average, maximum manufacturing and minimum manufacturing thicknesses are also plotted for comparison. To differentiate the variations due to erosion and the manufacturing processes, a 10% compensation curve is also provided.

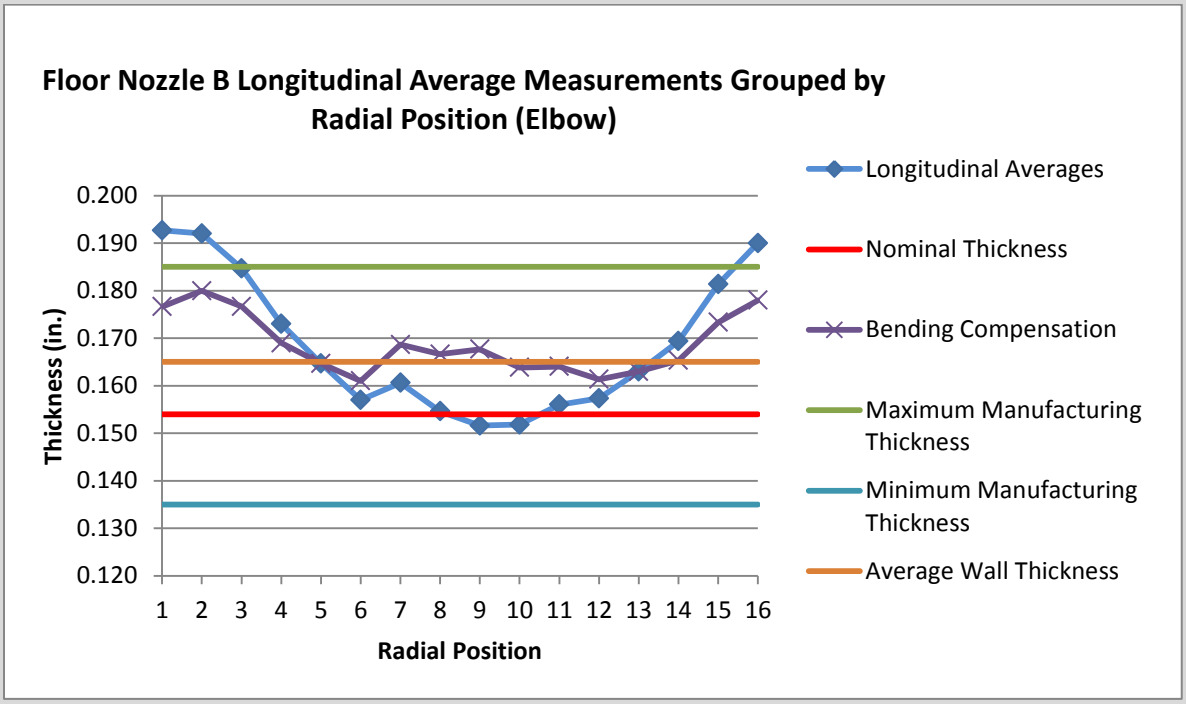


Figure 1-12. Longitudinal average thicknesses for Nozzle B.

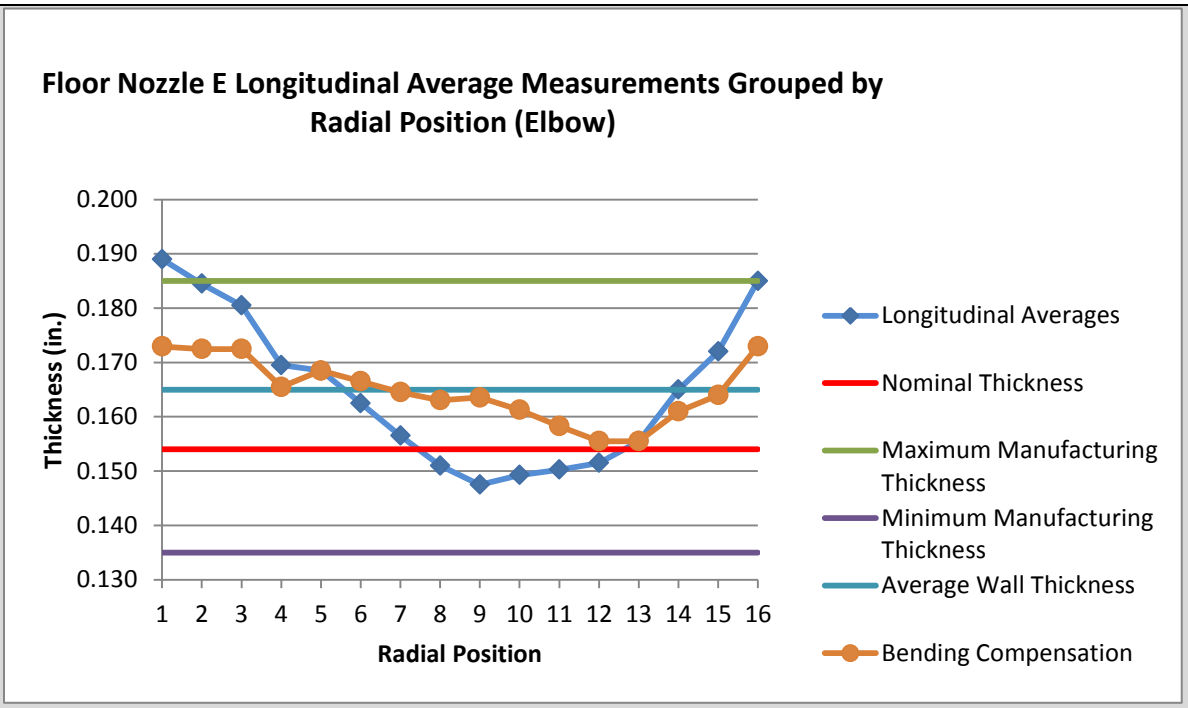


Figure 1-13. Longitudinal average thicknesses for Nozzle E.

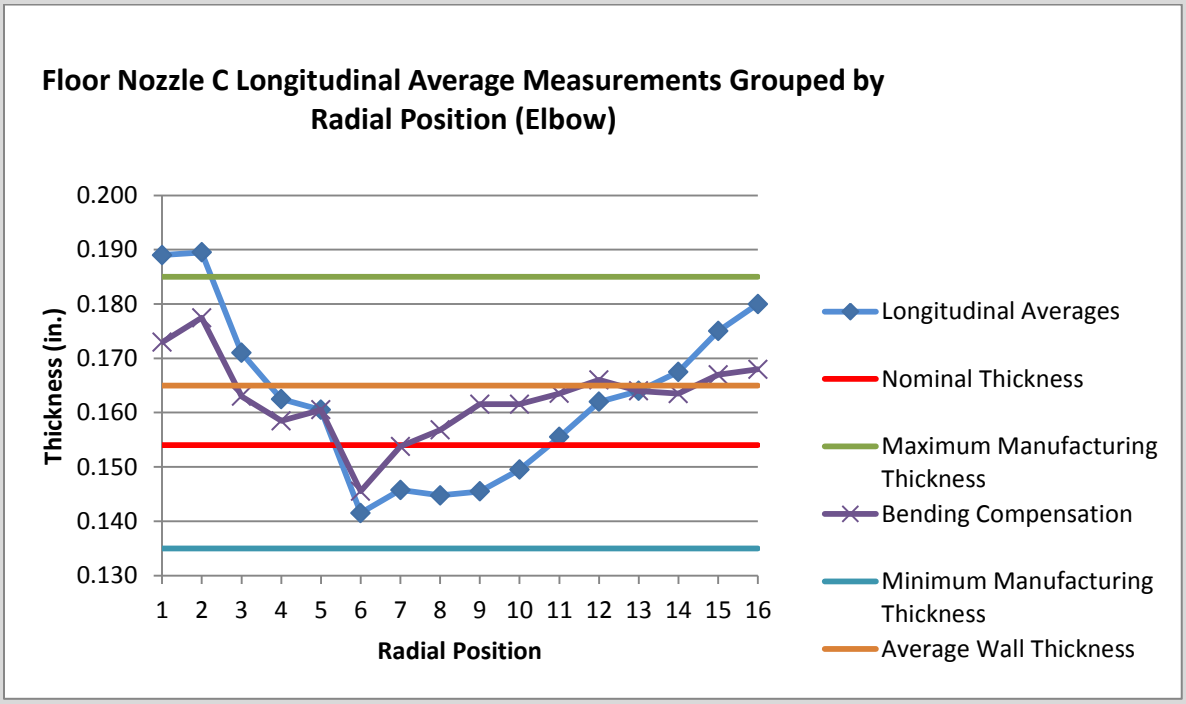


Figure 1-14. Longitudinal average thicknesses for Nozzle C.

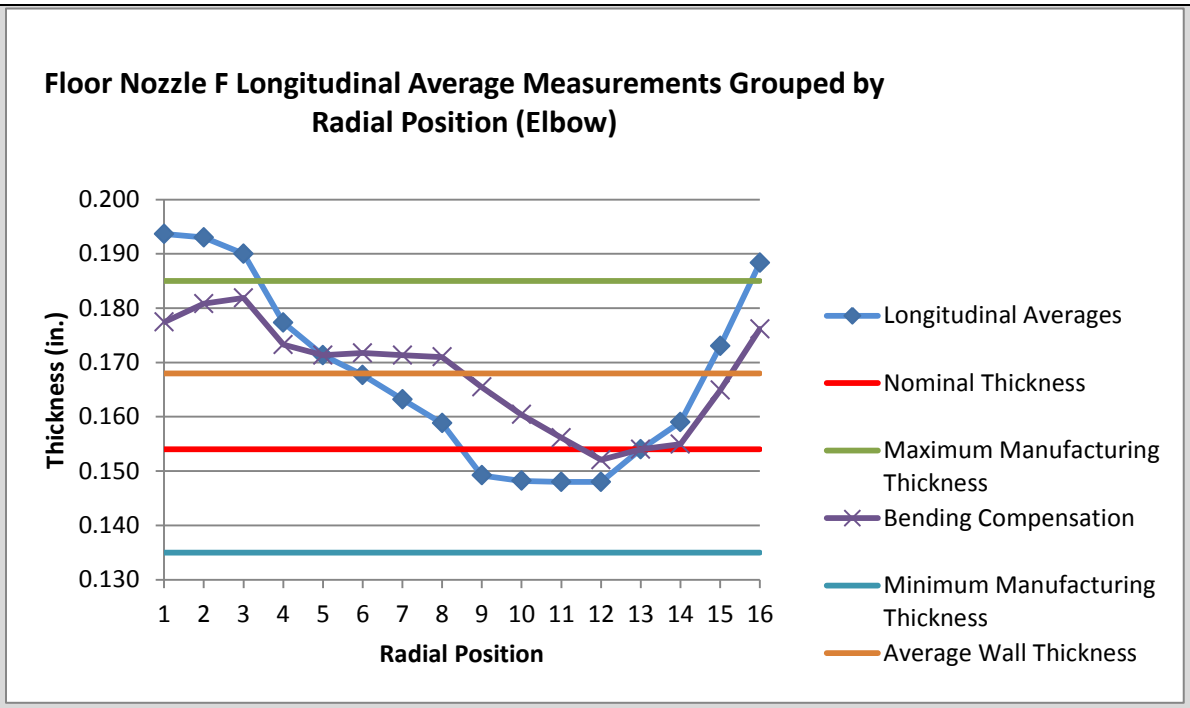


Figure 1-15. Longitudinal average thicknesses for Nozzle F.

For all four elbows, the average wall thickness is above nominal, suggesting that no appreciable wear has occurred. The longitudinal averages have an expected trend for all four, with the thickest measurements at the intrados and the thinnest at the extrados. The compensation curve does reduce the variations observed but no general trends are observed. Location 5 represents the top of the pipe and location 13 represents the bottom. Nozzles F and E do show trends with the top having thicker measurements than the bottom, but this is not true for the elbows in Nozzles B and C.

FIU prepared a report for the analysis associated with the four floor nozzles in the POR 104 Valve Pit. A first draft has been completed and is currently under review at FIU. The write up includes line descriptions in terms of component geometry, material type, flow volume and flow type. Special attention has been paid to the elbows, which can be long radius, short radius and 5D bend elbows. Each elbow can be manufactured differently and therefore have different variation patterns in the nominal thickness. A report from Hanford engineers was provided and reviewed, describing the effects of elbow manufacturing on the resulting thickness at the extrados and intrados of the elbows. This information will be used to discern wear patterns in the thickness from variations due to manufacturing. Table 1-5 shows the average thickness measurements for each component of the nozzles and the corresponding nominal thickness. Only the Purex nozzle had averages slightly below the nominal indicating that little to no wear has occurred on these components.

Table 1-5. Nozzle Thickness Averages

Average Wall Thicknesses (in)					
	Nominal	Nozzle B	Nozzle C	Nozzle E	Nozzle F
Elbow	0.154	0.169	0.163	0.165	0.168
Straight	0.154	0.156	0.157	0.159	0.16
Purex (Below)	0.263	0.26	0.261	0.262	0.259
Purex (Above)	0.28	0.275	0.271	0.278	0.277

Below is a typical write up from the drafted report that precedes the analysis section for Elbow-B from Nozzle B.

Nozzle B of the POR104 valve box was fabricated with a 2" schedule 40 pipe made of ASTM A312 TP 304L stainless steel. It was installed in 2004 and transferred approximately 7.83 million gallons of slurry waste. The nozzles served as connection points between the C-Tank Farm hose-in-hose transfer lines and the valve manifolds which allowed the routing of single-shell tank (SST) waste to the recipient double-shell tank (DST) 241-AN-106. A CAD illustration of the jumper is provided in Figure 1-16.

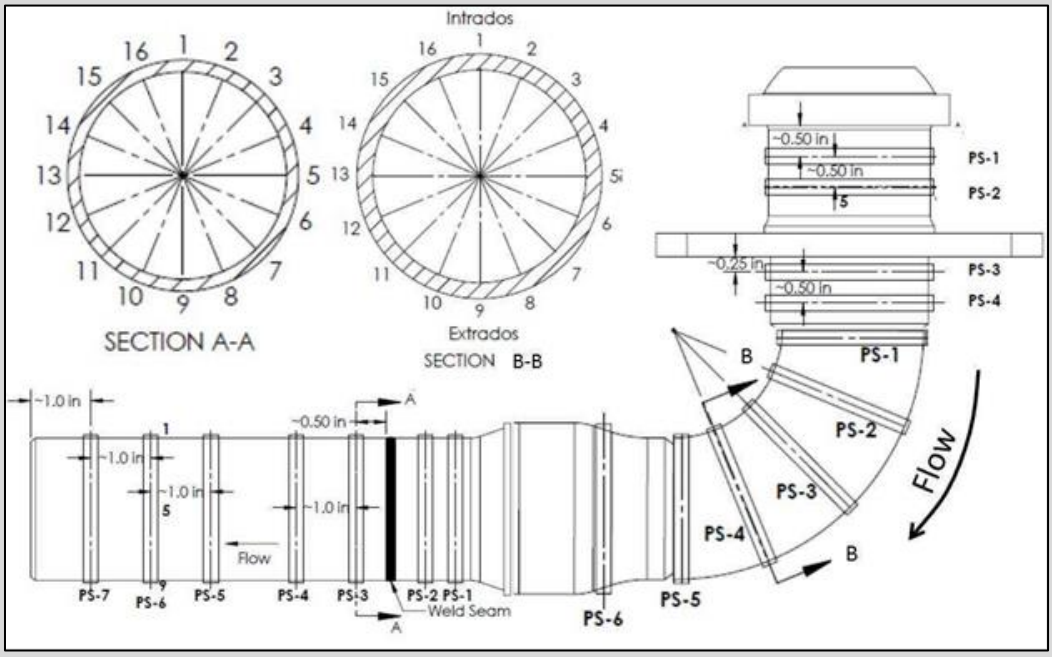


Figure 1-16. POR104 Nozzle B CAD drawing.

Thickness measurements for each nozzle were taken with an Ultrasonic Transducer (Manufacturer: Krautkramer, Model: USN-52L) around the outside diameter of the pipe at the straight sections, elbows, and Purex nozzles. The ultrasonic transducer thickness measurements are plotted and trends are assessed based on the volume of fluid transferred.

Elbow-B (90 degree long radius bend)

A 3D CAD drawing of the floor nozzle with Elbow-B circled is provided in Figure 1-17. The figure also provides the positions at which measurements were taken. The grid was labeled 1 through 16 around the outer diameter of the pipe and PS-1 to PS-6 running horizontally along the

length of the pipe. The sixteen measurements along the outer diameter were taken every 22.5° as shown in Section A-A of the figure. The results of the thickness measurements are shown in Table 1-6.

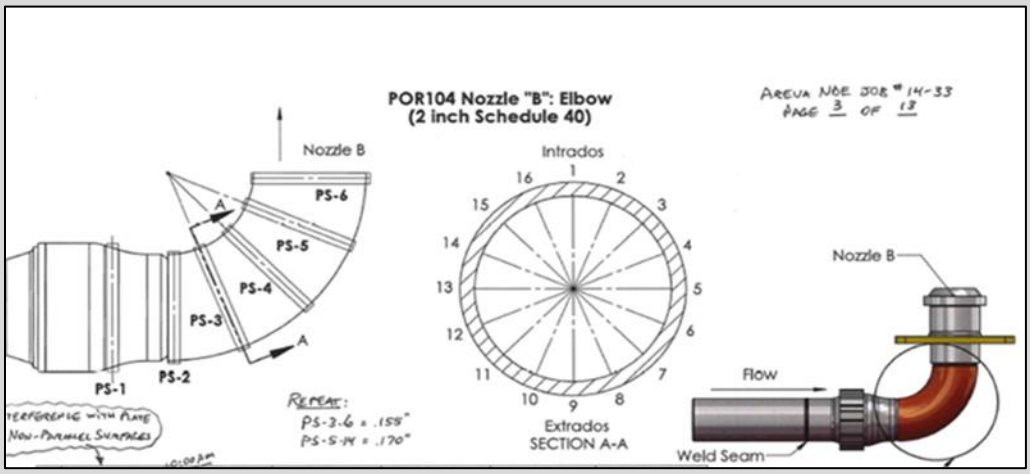


Figure 1-17. Position of UT Measurements around Elbow-B of POR104.

Table 1-6. UT Measurements for Elbow-B of POR104 (in)

Location	PS-1	PS-2	PS-3	PS-4	PS-5	PS-6
1	NR	NR	0.177	0.2	0.201	NR
2	NR	NR	0.181	0.199	0.196	NR
3	NR	NR	0.18	0.189	0.185	NR
4	NR	NR	0.177	0.173	0.169	NR
5	NR	NR	0.168	0.163	0.163	NR
6	NR	NR	0.155	0.156	0.16	NR
7	NR	0.163	0.153	0.153	0.159	0.175
8	NR	0.157	0.146	0.145	0.155	0.17
9	NR	0.154	0.142	0.139	0.151	0.172
10	NR	0.156	0.144	0.141	0.149	0.169
11	NR	0.16	0.148	0.147	0.157	0.168
12	NR	NR	0.155	0.157	0.16	NR
13	NR	NR	0.165	0.162	0.162	NR
14	NR	NR	0.17	0.168	0.17	NR
15	NR	NR	0.18	0.182	0.182	NR
16	NR	NR	0.178	0.193	0.199	NR

A summary of the wall thickness measurements and calculations for Elbow-B is shown in Table 1-7 which includes the average thickness and standard deviations. Nominal, maximum and minimum manufacturing thicknesses are not provided for elbows in current standards so the thicknesses for straight pipe sections are provided for comparison. These manufacturing thicknesses were obtained using information for 2-in Stainless Steel Schedule 40 pipes. Nominal and minimum thicknesses for stainless steel pipe sections were obtained from ASTM A312/A312M-12 Table X1.1. The maximum manufacturing thickness for straight sections, however, was not provided in the tables and was determined following the guidelines from

ASTM A53-1972a Paragraph 14.2. This paragraph states that the outside diameter should not vary more than 1% from the standard specified.

Table 1-7. Summary of Elbow for Nozzle B Thickness Measurements

Overall Average Wall Thickness Measurements	0.169
Overall Standard Deviation	0.016
Average -2 Standard Deviation	0.137
Average +2 Standard Deviation	0.201
Manufacturer Nominal Thickness	0.154
Minimum Manufacturing Thickness	0.135
Maximum Manufacturing Thickness	0.185
Amount of Slurry Transferred	7.83M gal
Note: Nominal thickness based on Stainless Steel, 2" Diameter, Schedule 40	

Additionally a Waste Management Symposia paper was submitted to the conference in November. This paper highlighted the results from the analysis for the 242-A evaporator pit jumpers and the AW-02E feed pit jumpers. This analysis also showed that for the jumpers evaluated, little to no erosion had occurred within the jumpers. FIU is currently awaiting feedback on the paper and will implement revisions once the comments are received.

FIU also began discussions with Hanford engineers to assist on the evaluation of the installation procedures for the real-time ultrasonic thickness sensors for the POR-104 valve box. Data from these sensors have been inconsistent and it was suggested that the installation of the sensors on the pipe has created hindrances for the sensors to produce reliable data. In the near future, FIU will set up a small test bed to evaluate alternative procedures for installing the sensors.

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

The objective of this subtask 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. These nonmetallic materials are exposed to β and γ irradiation, caustic solutions, as well as high temperatures and pressure stressors. How the nonmetallic components react to each of these stressors individually has been well established. However, simultaneous exposure has not been evaluated and is of great concern to Hanford Site engineers.

During this performance period, FIU worked with engineers from WRPS to define the scope of work for the test plan. One of the biggest issues associated with the nonmetallic materials in the HLW lines is the effect of caustic solutions on the hose-in-hose transfer lines (HIHTLs). That said, it was suggested that FIU focus this first phase of testing on only EPDM materials, including the internal tubing of the HIHTLs and O-rings. Additionally it was suggested that we only look at exposure to caustic solutions as a preliminary stressor. After review of the material supplied by the manufacturers, it was clear that reactions with the caustic material are temperature dependent. Thus, it was decided to proceed with the use of EPDM materials with

one caustic solution (one concentration level) with variations in temperature and exposure time. The idea is to evaluate the effect of a caustic solution (i.e. NaOH) at possibly 3 temperatures with various times of exposure (i.e., 1 month, 6 months and 1 year).

Additionally, we will look at evaluating both EPDM components as well as sample coupons. EPDM is used to manufacture the internal tubing of the HIHTLs and O-rings so components of each will be aged in a system configuration setting. Coupons will also be generated from EPDM and aged via caustic/elevated temperature. Quantification of the strength degradation will include standard material tests on the coupons as well as configuration specific aging with the components. Leak and burst tests will be conducted on both aged and baseline material to understand the effect of the caustic material.

Future tests will include adding pressure as a stressor and possibly evaluating additional caustic solutions with Teflon and Tefzel components. Efforts will also focus on understanding how radiation effects may be incorporated into the evaluation in terms of the synergistic effects by reviewing available literature.

After the scope of work for the testing was approved, an initial test plan was developed. The following text provides a brief overview of the test plan.

The experimental approach is to evaluate materials prior to aging by determining baseline properties and mechanical performance. Materials will also be aged via exposure to a chemical simulant at ambient (70^{o}F), operating (130^{o}F) and design temperatures (180^{o}F) for durations of 30, 60 and 180 days. Comparison of the baseline data and the data obtained from the aged specimens will be evaluated to determine the overall synergistic effects of the three stressors. These tests will be conducted on both material coupons as well as in-service configuration assemblies.

To age the in-service configuration specimens, FIU will assemble an experimental setup that includes 3 independent pumping loops with three manifold sections on each loop. Each of the 3 loops will be run at a different temperature (70^{o}F, 130^{o}F and 180^{o}F). Each manifold section can hold up to three test samples and be used for a corresponding exposure time of 30, 60 and 180 days. Three samples of the EPDM inner hose and three samples of the O-rings will be placed in a parallel manifold configuration. A schematic of the setup is shown in the figure below.

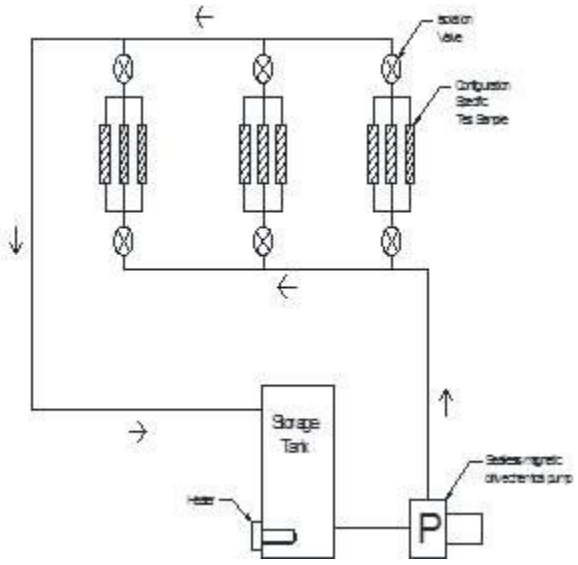


Figure 1-18. Schematic of experimental test loop.

Isolation valves on each manifold will allow removal of samples without affecting the main loop and the rest of the samples. This configuration requires 9 test samples (for both the inner hose and O-rings) for each of the three test loops, requiring a minimum of 27 test samples of each (inner hose and O-rings). Finally, a 25% sodium hydroxide solution will be used as a chemical stressor that will circulate in each of the loops.

The experimental test bed for the coupons will consist of 3 temperature controlled circulating fluid baths of the 25% sodium hydroxide solution – each maintained at a different temperature (70^{o}F, 130^{o}F and 180^{o}F). The coupons will be removed after 30, 60 and 180 days of exposure.

To quantify the degradation in strength of the aged specimen, hose burst and O-ring leak tests will be conducted on both the aged and baseline specimens as per ASTM D380-94 and ASTM F237-05. The tests will be conducted on the 27 aged test samples (9 from each test temperature with 3 at each exposure time).

Testing of aged and baseline coupons will include material property testing. Coupon properties to be evaluated include specific gravity, dimensions, mass, hardness, compression set, and tensile properties (tensile strength, ultimate elongation yield, and tensile stress). Comparisons of test results from aged and baseline material will be conducted to quantify the material degradation.

Once FIU received feedback from Hanford engineers on the first draft of the test plan, we incorporated the comments into the plan. In general, the procedure for aging and testing as well as the number of specimens to be tested were approved. Comments were focused on including text regarding quality control of the specimens and testing. In addition, a point was noted that an acceptable threshold in terms of the degradation of the material should be determined. After the test plan was approved, FIU initiated the process of designing the test set up and acquiring the required equipment and materials.

Milestones and Deliverables

The milestones and deliverables for Project 1 for FIU Year 5 are shown on the following table with status through December 31, 2014. Milestone 2014-P1-19.2.1 and the associated deliverable

titled, "Nonmetallic Materials Test Plan for Hanford's HLW Transfer System," was completed and sent to DOE and Hanford site contacts on November 14, 2014, for review and input. Milestone 2014-P1-18.2.1 titled, "Complete development of the first prototype of the inspection tool," was completed on December 19, 2014.

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	On target	
	Deliverable	Draft summary report for subtask 2.2.1	04/01/15	On target	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	Completed	
	Deliverable	Draft summary report for first prototype (subtask 18.2.1)	01/30/15	On target	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	On target	
	Deliverable	Draft summary report of pilot scale testing of SLIM (subtask 18.1.1)	03/13/15	On target	OSTI
	2014-P1-M18.2.2	Complete analysis design and modifications to the peristaltic crawler	03/20/15	On target	
	Deliverable	Final Deployment Test Plan and Functional Requirements for SLIM (subtask 18.1.2)	05/15/15	On target	
Task 19: Pipeline Integrity and Analysis	2014-P1-M19.2.1	Complete test plan for the evaluation of nonmetallic components	11/14/14	Completed	
	Deliverable	Draft experimental test plan for subtask 19.2.1	11/14/14	Completed	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

- Task 2:
  - For the APS, we will continue with some preliminary tests now that the plug consistency issue has been resolved. The preliminary tests will recreate baseline data with the new plugs and evaluate how air entrainment effects the capabilities of the APS.

- For the peristaltic crawler, an engineer will be hired to replace the previous task manager. Efforts will focus on training the engineer on the scope of work and understanding the technical issues related to the crawler. The engineer will then assist in evaluating approaches to reduce the stress risers induced by the clamps.
- For the computational simulation of plug formation subtask, we will evaluate system configurations provided by site engineers and use one to determine the accuracy of the Comsol modeling. Simulation data will be compared with experimental data and then will be used to assess the effects of pipeline configurations.

- Task 17:
  - FIU will continue the process of acquiring Star-CCM+ as well as acquiring access to FIU's high performance computing system. Single-phase flow tutorials will be run with various rheology models to replicate the Bingham plastic behavior. The flow regime will be laminar flow initially and the Reynolds number will be increased gradually to approach turbulent conditions based on the performance of the software in the HPC set-up at FIU.
  - FIU will also conduct simulations using the 3D MRT LBM code with non-Newtonian gas-liquid systems. Simulation cases will be compared with the 2D simulations.

- Task 18:
  - For the SLIM subtask, the pump and the flow design for the experimental setup will be modified in January to assure that solids at 1-20% vol. of Kaolin will remain suspended and not settle on the floor. Calculations and empirical tests will be used to confirm that the pump flow field is over designed for the mixing and suspension. In addition, the image quality of the sonar data has degraded and FIU has contacted the vendor to attempt diagnostics remotely by allowing their engineers direct access to the sonar system via the internet. If this does not resolve the sonar problem, then the unit will be sent back to the manufacturer and the tests on this task could be delayed 4-6 weeks.
  - For the inspection tool task, FIU will make modifications to the design to improve its ability to navigate through debris/obstacles, by incorporating additional wheels. This will provide similar motion dynamics provided by a tread/wheel system. The unit will be redesigned and tested in a similar manner that was conducted previously.
  - FIU will also begin investigating the modifications necessary for the crawler to navigate through the AY-102 4-inch drain system. Modifications will include alternative approaches to inflating the front and rear cavities. The pressure nozzle will be removed and the tether will be simplified.

Task 19:

  - Efforts for the evaluation of the POR 104 Valve Pit will be completed and a report will be provided to the site. Some of this information will also be represented at the Waste Management Conference. Additionally, FIU will begin

looking at ways to improve the installation procedures for the real time sensors used to measure the pipe wall thickness.

- For the non-metallic materials task, FIU will begin the process of acquiring necessary equipment and facilities to conduct the testing. A test bed will be designed and assembly of the test set up will begin.

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

Subtask 1.1 Overview

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.

FIU Year 4 Carryover Work Scope

During October, several new isopiestic measurements of water activities and osmotic coefficients for the multicomponent mixture samples were obtained using $CaCl_2$ and $LiCl_2$ as standards. We still haven't observed significant changes of the osmotic coefficient to conclude on precipitate deliquescence. The measurements of water activities and osmotic coefficients for the $CaCl_2$ standard were observed between 0.755 and 0.808 and between 1.755 and 1.575, respectively. For the $LiCl_2$, water activity values were between 0.735 and 0.799 and the osmotic coefficient between 1.695 and 1.502. Tables 2-1 and 2-2 display the calculated water activities and osmotic coefficients values. The experiments will be continued with an increased amount of water, up to 40 uL added to each crucible containing standards to speed up the process.

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

a_w $CaCl_2$	Na_2SiO_3+ $Al(NO_3)_3$+ KHCO3 (3mM)	Na_2SiO_3+ $Al(NO_3)_3$+ $KHCO_3$ (50mM)	Na_2SiO_3+ $Al(NO_3)_3$+ $KHCO_3$*(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	2.470	2.754	2.958	1.648
0.786	1.485	1.820	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
0.800	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	1.300	1.814	2.470	2.229	2.489	2.881	1.575

Table 2-2. Values for Water activities, a_w, and Osmotic Coefficients, Ø, for $LiCl_2$ and Multicomponent

a_w $CaCl_2$	Na_2SiO_3+ $Al(NO_3)_3$+ KHCO3 (3mM)	Na_2SiO_3+ $Al(NO_3)_3$+ $KHCO_3$ (50mM)	Na_2SiO_3+ $Al(NO_3)_3$+ $KHCO_3$*(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 $CaCl_2$
0.735	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	3.820	2.688	3.060	3.233	1.601
0.795	1.466	1.901	3.497	2.478	2.786	2.991	1.465
0.795	1.330	1.792	3.408	2.381	2.700	2.964	1.470
0.798	1.347	1.841	3.268	2.392	2.640	3.015	1.493
0.799	1.328	1.853	2.523	2.277	2.542	2.943	1.502

FIU initiated XRD analysis of the multicomponent samples prepared with reduced concentration of Si to 50 mM. The idenfication of uranium minerals is in progress. As found previously, the best match was obtained for nitritine and cejkate solid phases.

During the month of November, new measurements from the isopiestic chamber were obtained after the addition of 20µl and 40µl of pure DIW water to each sample containing standards. Two new water activities and osmotic coefficients values were calculated for the experimental multicomponent and standard samples.

The values of water activities and osmotic coefficients still remain similar to the previous values, 0.811 and 1.563 for the $CaCl_2$ and 0.790 and 1.593 for LiCl. However, after the last addition of 40 uL of pure DIW water to each crucible containing standards, the values of osmotic coefficients started to decrease for both standards. However, the osmotic coefficient for LiCl

decreased approximately 21%. The calculation of the water activities showed an incremental increase for both standards and multicomponent samples. Table 2-3 and Table 2-4 display the last two newly obtained values for water activities and osmotic coefficients for $CaCl_2$ and LiCl, respectively. These results suggest that a larger addition of water in the crucibles containing standards accelerated the increase in water activities. Therefore, an amount of 50 ul of pure water was added to each standard with the total amount of 200 uL for both $CaCl_2$ and LiCl standards.

Table 2-3. Values for Water Activities (a_w) and Osmotic Coefficients (Ø) for $CaCl_2$ and Multicomponent

a_w $CaCl_2$	Na_2SiO_3+ $Al(NO_3)_3$+ KHCO3 (3mM)	Na_2SiO_3+ $Al(NO_3)_3$+ $KHCO_3$ (50mM)	Na2SiO_3+ $Al(NO_3)_3$+ $KHCO_3$* (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 $CaCl_2$
0.7558	1.874	2.187	3.774	2.621	2.961	3.068	1.754
0.7557	1.665	2.048	3.742	2.585	2.916	3.058	1.755
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	1.563
0.825	1.38	2.05	1.953	2.407	2.592	3.141	1.511

Table 2-4. Values for Water Activities (a_w) and Osmotic Coefficients (Ø) for $LiCl_2$ and Multicomponent

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)$CaCl_2$	Na2SiO_3+ $Al(NO_3)_3$+ (50mM) $KHCO_3$+ (5mM)$CaCl_2$	Na2SiO_3+ $Al(NO_3)_3$+ (3mM) $KHCO_3$+ (10mM)$CaCl_2$	Na2SiO_3+ $Al(NO_3)_3$+ (50mM) $KHCO_3$+ (10mM)$CaCl_2$	Ø LiCl
0.734	2.067	2.414	4.164	2.892	3.267	3.385	1.69
0.743	1.762	2.168	3.961	2.737	3.087	3.238	1.625
0.735	1.668	1.972	4.048	2.768	3.146	3.301	1.695
0.762	1.694	2.099	3.923	2.793	3.115	3.345	1.638
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
0.79	1.286	1.85	1.892	2.282	2.48	2.973	1.593
0.824	1.409	2.094	1.995	2.459	2.648	3.209	1.379

A PhD student, Claudia Cardona, completed the X-ray diffraction (XRD) training during the month of November to continue with the analysis of the multicomponent samples. Three samples have already been analyzed out of the six previously prepared samples; two of these samples have been plotted and compared with the patterns looking for possible solid phase matches. The following samples have been analyzed (plotted and compared with possible patterns):

Sample 1: 50 mM of $Na_2SiO_3 \cdot 9H_2O$, 5 mM of $Al(NO_3)_3 \cdot 9H_2O$, 15 mM of $CaCl_2$ and 3 mM of $KHCO_3$

Sample 2: 50 mM of $Na_2SiO_3 \cdot 9H_2O$, 5 mM of $Al(NO_3)_3.9H_2O$, 15 mM of $CaCl_2$ and 50 mM of $KHCO_3$

The experimental XRD data were compared to the American Mineralogist Crystal Database for nitratine, cejkaite, liebigite, rutherfordine, soddyite, agricolaite, and calcite (http://rruff.geo.arizona.edu/AMS/amcsd.php). The experimental XRD intensity peaks compared against the database minerals showed that the major peaks are compatible with nitratine, calcite, cejkaite and possibly agricolaite minerals for both samples analyzed. There were no clear signs of the formation of liebigite. Therefore, additional analyses and literature review have to be conducted to look for these minerals. Figure 2-1 and Figure 2-2 display the XRD patterns for the 50 mM of $Na_2SiO_3.9H_2O$, 5 mM of $Al(NO_3)_3.9H_2O$, 15 mM of $CaCl_2$ and 3 mM and 50 mM of $KHCO_3$.

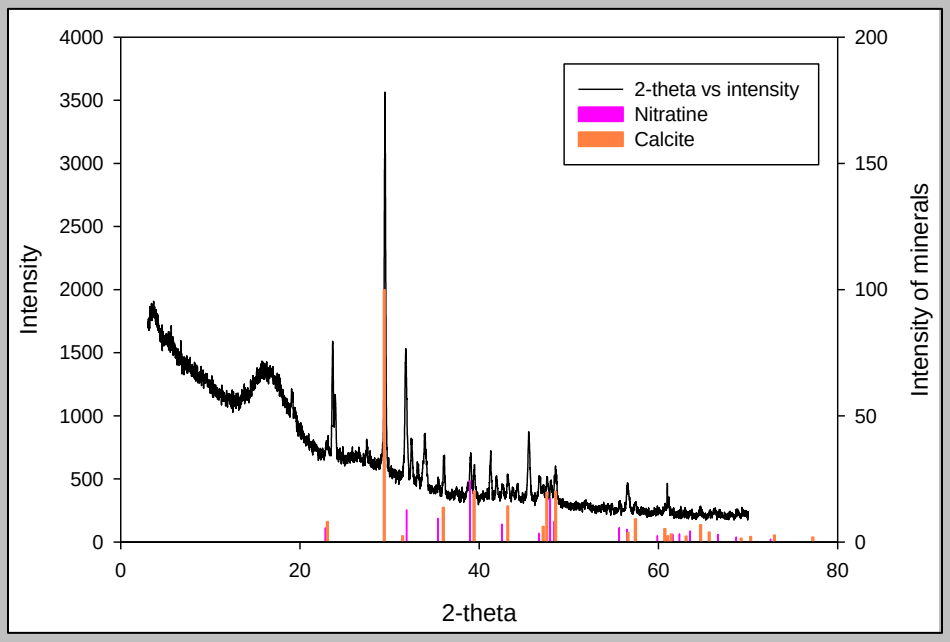


Figure 2-1. XRD results for a sample composed of 50 mM of $Na_2SiO_3.9H_2O$, 15 mM of $CaCl_2$ and 3 mM of $KHCO_3$.

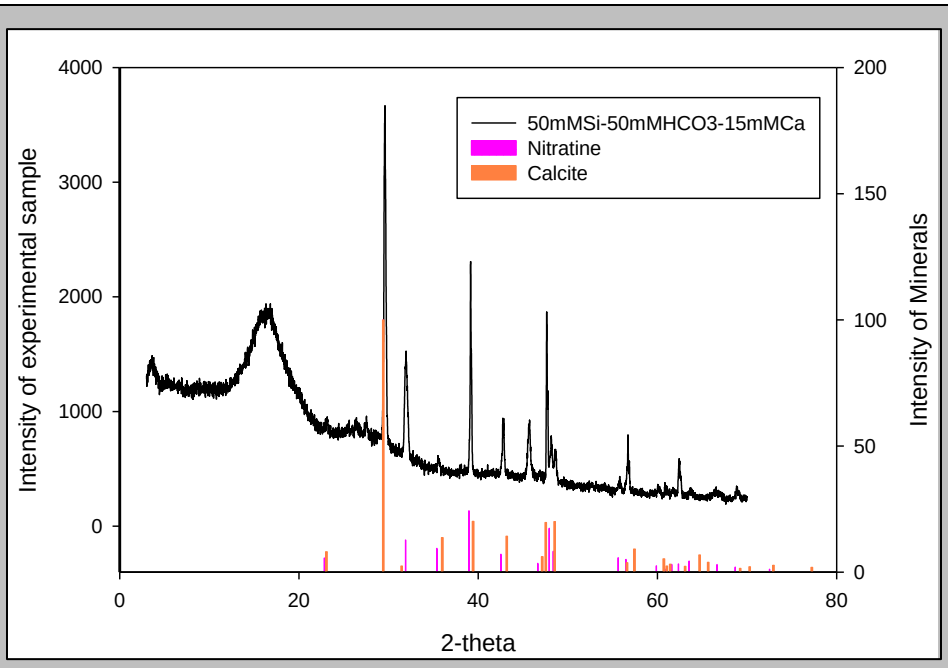


Figure 2-2. XRD results for a sample composed of 50 mM of $Na_2SiO_3.9H_2O$, 15 mM of $CaCl_2$ and 50 mM of $KHCO_3$

During the month of December, two new measurements from the isopiestic chamber were obtained after the addition of 50 uL of pure DI water to the standard samples ($CaCl_2$ and LiCl). Water activities and osmotic coefficients measurements were calculated for the multicomponent and standard samples using previously reported equations.

It was noted that the $CaCl_2$ standard resulted in similar values as were obtained in a previous month, showing only a slight increase in the water activities, from 0.825 to 0.840. The osmotic coefficient values for the same measurements decreased from 1.515 to 1.458. The water activity measurements for the LiCl standard showed a similar trend, a slight increase from 0.824 to 0.832. However, the LiCl osmotic coefficient values increased from 1.379 to 1.430. The osmotic coefficients of the multicomponent samples showed an incremental increase for both standards. Table 2-1 and Table 2-2 display obtained values for water activities and osmotic coefficients for $CaCl_2$ and LiCl. Obtained data is also presented in Figure 2-5 and Figure 2-6.

These results suggested that water addition in the standard samples accelerated the solubility process of the multicomponent samples those deliquescence points were already obtained at water activities 0.81-0.82 (81-82% humidity). The results presented in Table 2-5 and Table 2-6 as well as Figure 2-3 and Figure 2-4 complete the carryover scope of work to investigate the deliquescence behavior of uranium-free multicomponent samples.

FIU initiated preparations of new multicomponent samples that will include 2 ppm of uranium in the solution.

Table 2-5. 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)	Na2SiO_3+ $Al(NO_3)_3$+ $KHCO_3$* (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

Table 2-6. 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)$CaCl_2$	Na2SiO_3+ $Al(NO_3)_3$+ (50mM) $KHCO_3$+ (5mM)$CaCl_2$	Na2SiO_3+ $Al(NO_3)_3$+ (3mM) $KHCO_3$+ (10mM)$CaCl_2$	Na2SiO_3+ $Al(NO_3)_3$+ (50mM) $KHCO_3$+ (10mM)$CaCl_2$	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

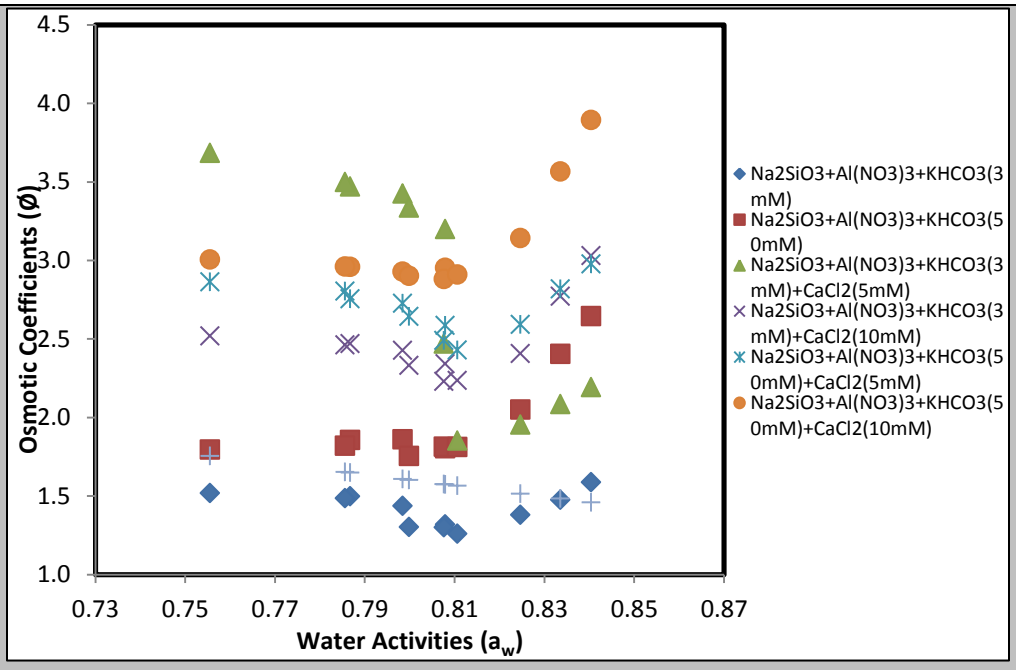


Figure 2-3. Osmotic coefficient for multicomponent samples as a function of water activities, a_w, using $CaCl_2$ as a standard.

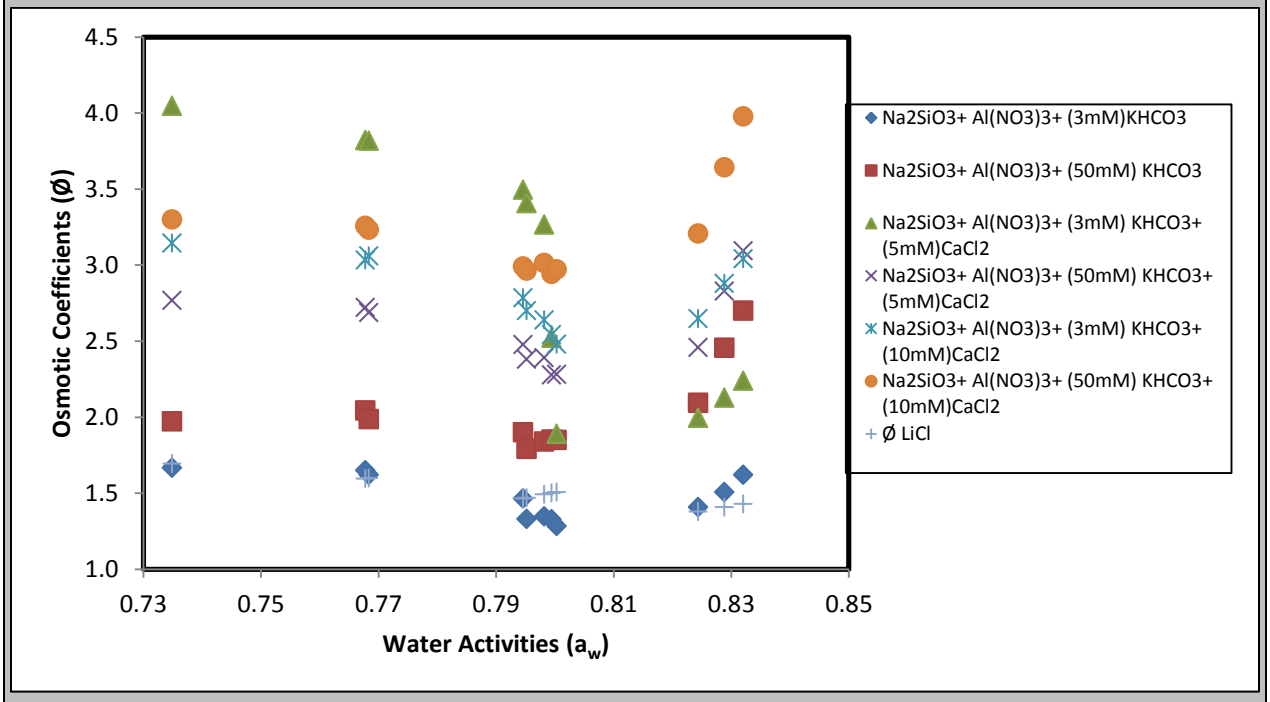


Figure 2-4. Osmotic coefficient for multicomponent samples as a function of water activities, a_w, using LiCl as a standard.

The X-ray diffraction (XRD) analysis for the three remaining samples continued during December; results will be presented in the next report.

In the effort to characterize the solid uranium-phases formed with the application of NH_3 gas to a synthetic pore water solution, transmission electron microscopy (TEM) was looked into as an alternative to bulk powder X-ray diffraction (XRD). This technique offers similar diffraction capabilities while allowing the user to analyze a selected area rather than the bulk sample. It was predicted that this would enable the discernment of the structures of the crystalline uranium phases spotted in scanning electron micrographs. In order to mount the samples onto the TEM grid for analysis, a suspension of the uranium-bearing solids is required. This required the selection of a solution to serve as the suspending agent to our sample that would not dissolve the solid uranium phases we were interested in. In order to determine which solution would work best in our suspension, a limited, qualitative test procedure was drawn up and completed. A series of alcohols (methanol, ethanol, and isopropanol) were used, with water as a control group, to perform 2 minute extractions on a pulverized sample shown to contain solid uranium phases by SEM w/ EDS. The X step procedure included:

1. Approximately 20 mg of crushed sample precipitate was added to a 5-mL vial
2. For every mg of sample, 100 uL of suspending solution was added (e.g.: 23 mg of sample to 2.3 mL of water)
3. Extraction solutions were vortexed for 2 minutes
4. Samples were centrifuged for 2 minutes at 2500 rpm to separate the solid and liquid phases
5. The supernatant was removed by 45-micron filtered syringe
6. Samples were wet ashed and re-suspended in nitric acid for KPA analysis

The extraction products were diluted by 100 and 1000 times for sample analysis. As expected, kinetic phosphorescence analyzer (KPA) data for the water extraction control sample showed significantly higher uranium concentration. Alternatively, the uranium concentration in the ethanol extraction was consistently below the system detection limit. Based on this simple study, ethanol was selected for initial TEM suspension samples; this work is ongoing. SEM w/ EDS analysis is planned for the solid precipitates left behind from the extractions to determine if there was significant change to the morphology compared to the pre-extraction analyses. This study will be repeated with replicate sampling to bolster support for this decision.

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

Subtask 1.2 Overview

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

The revision of two manuscripts conducted in collaboration with PNNL researchers was finalized and the manuscripts were submitted for the peer-review. Sandra Herrera, a new graduate student from the FIU Environmental Engineering Department, completed set up of 16 bottles prepared to study the effect of facultative microorganisms (e.g., Shewanella) on the dissolution of autunite mineral in the presence of the bicarbonate ions. Each sample was prepared aseptically in triplicate and contained Ca-autunite (4.4 mmole of U(VI)) and 50 mL of sterile media solution amended with 0 mM, 3 mM, 5 mM, and 10 mM of bicarbonate. A control bottle was prepared for each bicarbonate concentration, which will be kept bacteria-free. All experimental and control bottles were crimp-sealed and kept in the incubator-shaker at 70 rpm.

Figure 2-5. Control and experimental bottles prepared for the bioleaching experiment.

Sampling was initiated to examine when autunite equilibrates with the media solution before the addition of bacteria. FIU sampled the supernatant solutions of the experimental and control bottles. Aliquots were isolated using 1-ml sterile syringes and they were filtered through 0.45 μm PTFE filters. Thereafter, wet digestion was performed by adding 500 μl of concentrated HNO_3 and 500 μl of concentrated H_2O_2 to each sample on a heating plate until full evaporation was achieved and a white solid residue was acquired. The dry samples were placed in a furnace for 15 min at 450^{o}C and then allowed to cool at room temperature. Finally, the solid samples were dissolved in nitric acid and analyzed via KPA to determine the uranium concentration.

The results of U(VI) concentration in the supernatant as a function of time for each condition studied (0, 3, 5 and 10 mM HCO_3) are compiled in Table 2-7.

Table 2-7. U(VI) Concentration Followed by Standard Deviation in the Aqueous Phase Under All Conditions Studied

HCO_3	Time (days)	U(VI) concentrations (ppb)
	5	26.5 ± 2
	8	84.2 ± 31
0 mM HCO_3	12	6.88 ± 9
	15	63.19 ± 18
	23	60.48 ± 6
	27	63.49 ± 36
	5	723 ± 70
	8	2428 ± 800
3 mM HCO_3	12	1791 ± 200
	15	2400 ± 705
	23	1432 ± 300
	27	1242 ± 300
	5	2441 ± 400
	8	4771 ± 200
5 mM HCO_3	12	4241 ± 700
	15	4429 ± 600
	23	4047 ± 300
	27	2995 ± 100
	5	9238 ± 1300
	8	11089 ± 300
10 mM HCO_3	12	10617 ± 1200
	15	10242 ± 1300
	23	11688 ± 400
	27	7080 ± 700

FIU next conducted uranium analysis on the collected samples. Triplicate results for U(VI) concentrations in the collected supernatant solutions of the bacteria-free samples are presented in Figure 2-6. The results suggested that the increase in bicarbonate concentrations increased U (VI) release from Ca-autunite; however, the effect of anaerobic bacteria on the biodissolution of autunite mineral needs to be evaluated.

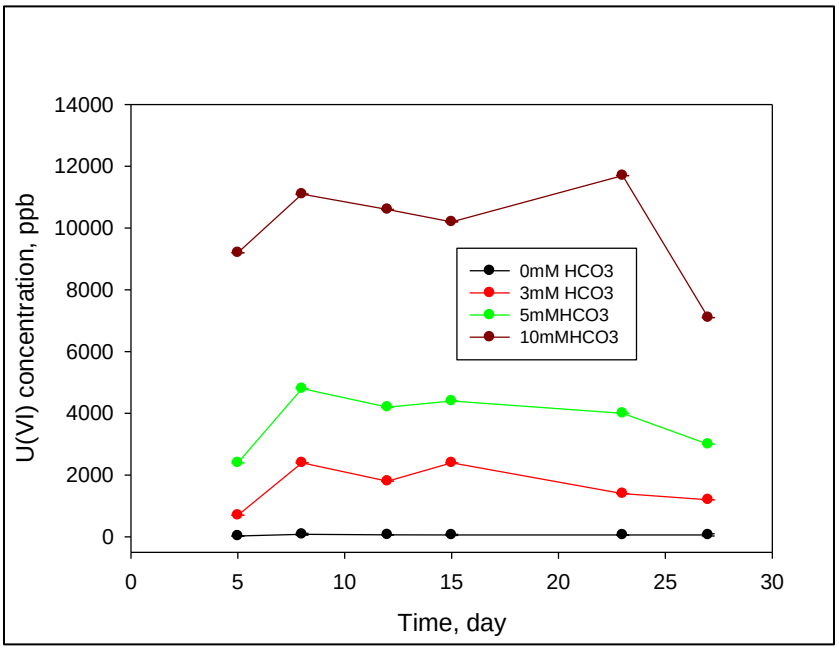


Figure 2-6. Uranium release from Ca-autunite before bacteria inoculation.

For that purpose, *Shewanella Oneidensis MR1* was injected in the experiment bottles; all control bottles were kept bacteria- free.

Shewanella Oneidensis MR1 is a facultative bacterium known as dissimilatory metal-reducing bacteria (DMRB) due to its ability to couple metal reduction, including U(VI), with their metabolism. The U-impacted zone features oxic-anoxic conditions due to the Colombia River near-shore water table fluctuations and this experiment is trying to mimic soil conditions where fluctuations can cause changes in aerobic or anaerobic conditions and investigate the effect of anaerobic bacteria on the dissolution of autunite mineral in the presence of the bicarbonate ions.

The *Shewanella Oneidensis MR1* was obtained from the Pacific North National Lab (PNNL). The bacterium was cultured using the LB medium recipe: 10.0 g of tryptone, 5.0 g of yeast extract, 10.0 g of sodium chloride, with a final pH of 7.0. Hard media was prepared with the addition of 15 g of agar. Bacterial samples were preserved in 25% glycerol and frozen at -80^0C.

The cell density in the culture stock solutions was obtained by means of a hemocytometer. Each bottle was inoculated to have a cell density of 10^6 cells/mL. Experimental bottles were crimp-sealed to maintain anaerobic conditions. All sample collection was performed in the anaerobic glove box via 1 ml syringe. The sampling procedures were similar to those described in previous monthly reports. Samples collected after bacteria inoculation were analyzed for U(VI) via the KPA instrument and data analysis is in progress; results will be presented in the January report.

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

Task 2 Overview

The objectives of the proposed experimental work for subtask 2.1 are: (i) to evaluate whether a base solution of dissolved silica prepared below the equilibrium solubility of amorphous silica, which is usually assumed to be about 100-150 ppm at circumneutral pH conditions, have enough alkalinity to restore the pH of the treatment zone; (ii) to investigate the hypothesis that some

uranium in the current treatment zone is bound to silica; and (iii) to study if any synergy between humic acid (HA) and silica will influence the behavior of uranium.

The objective of subtask 2.2 is to replicate the treatment performed by ARCADIS at SRS and investigate the mineralogical changes that occur in the soil due to the addition of molasses. Specifically, 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 can occur in sediments during the re-oxidation period. These experiments will also explain the types of reactions that might occur in the anaerobic aquifer. An understanding of the technology will be useful to determining if it is a viable option for remediation. The study will evaluate the addition of sulfate in the solution mixture for the formation of iron-bound pyrite phases. The objectives for this study include analysis of groundwater from the contaminated area if samples became available and evaluate the diffusion trap sediment samples via XRD and SEM-EDS methods to greater supplement the on-going microcosm studies on processes occurring in a bioreduction zone.

The newly created subtask 2.3 relates to the subtask 2.1 and will focus on the humic acid sorption experiments helping to evaluate the distribution of humate injected into the subsurface during deployment for in situ treatment of radionuclides.

Task 2 Quarterly Progress

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

FIU developed an experimental plan outline to prepare for the experiments investigating the effect of alkaline sodium silicate solutions as base additions to increase groundwater pH. Preliminary experiments will be initiated by the equilibration of soil samples and DIW water for a period of 48h (or more if necessary) and pH will be monitored in order to note the soil's capacity to alter the supernatant's pH values.

The next step will be the addition of different concentrations of silicates to the system (up to concentrations slightly lower than silicate solubility in water) in order to: i) assess the potential of silicates to maintain pH values of the system close to neutral, and ii) determine the optimum silicate concentration in order to achieve the desired pH value.

Then soil samples will be equilibrated with the optimum silicate concentration and uranium. The scope of this experiment will be to investigate the removal of uranium from the aqueous phase through precipitation, due to pH elevation, as a result of the presence of silicate. Successful precipitation of uranium can lead to an investigation of the mineralogical changes and microstructure of these precipitates by means of XRD and SEM/EDS.

Finally, it would be of interest to investigate the potential re-solubilization of uranium from precipitates. Analysis of the precipitate through a sequential extraction protocol would provide some basic information about the percentage of uranium in the sediment that is water soluble, exchangeable, acid soluble, etc. It is also of interest to investigate the role of the pH of the aquatic stream that comes in contact with uranium precipitates. pH stat test (CEN/TS 14429) can provide information about the degree of metal leaching as a function of pH.

FIU completed an experiment to determine the effect of silicates on the pH of a soil-deionized water system. A pH reading of solely deionized water was measured at 5.65 at the beginning of the experiment. Afterwards, five individual samples were prepared, each containing 200 mg of

Savanna River Site soil (coarse fraction, 0.18<d<2 mm) and 10 mL of deionized water. The soil water samples were mixed by hand for approximately 20 seconds and the initial pH of the samples was collected prior to any silicate addition, giving a reading of 5.52.

A stock silicate solution was prepared by dissolving 61.6 mg of sodium metasilicate in 100 mL of DI water, yielding a final concentration of 616 ppm.

Each sample was spiked with the appropriate volume from the silicate stock solution in order to achieve a final silicate concentration of 10, 20, 40 and 80 ppm (162, 325, 650 and 1,300 µL/L, respectively). The first sample was the control with no silicates added. The solutions were mixed by hand for 30 seconds and a pH reading for each sample was taken. The samples were covered with caps and placed on a platform shaker at 111 rpm for 24 hours. The pH measurements for each sample were noted at 24 hrs, 48 hrs, and 168 hrs. The experimental results are shown in Table 2-8.

Table 2-8. Effect of Sodium Silicate Additions on the pH Changes of Soil-Water Mixtures

Test Tube Sample Number	Silicate Concentration (ppm)	Initial pH Values	24 Hr pH Values	48 Hr pH Values	168 Hr (7-day) pH Values
1	0	5.52	5.63	5.72	5.65
2	10	7.01	6.60	6.55	6.70
3	20	7.50	6.70	6.70	6.97
4	40	8.93	7.46	7.14	7.31
5	80	9.37	7.87	7.60	7.70

According to Table 2-8, it is clear that pH increased significantly in all of the samples right after the silicate addition; correlating a higher pH increase to a higher added concentration of sodium silicate. There does not appear to be any significant decrease in pH values between 24 hrs and 168 hrs (7 days). The next step of the experiment will be to investigate the optimum silicate concentration in order to raise the pH in samples of SRS soil and SRS synthetic ground water.

FIU also initiated experiments to determine the effect of silicates on the pH of a solution using SRS soil and synthetic groundwater replicated after the site's natural groundwater composition. In order to create the SRS synthetic groundwater, a working solution was first prepared using the chemical concentrations below:

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

After creating a well-mixed stock solution, 1 mL was then diluted into 1 L of slightly acidified (pH 3.6) deionized water to create the working solution. Hydrochloric acid was used to acidify the DI water in order to reflect the natural acidity of the groundwater at the site. Eight samples were prepared, each containing accurately weighed 200 mg of SRS soil (coarse fraction, 0.18<d<2 mm) and 10 mL of the working solution. Each sample was spiked with the appropriate volume from the sodium silicate stock solution in order to achieve the final desired sodium silicate concentrations of 10, 20, 40, 50, 60, 70, and 80 ppm. As in the previous experiment, the first sample was the control with no silicates added.

The solutions were mixed by hand for 30 seconds and an initial pH reading for each sample was taken. The samples were then placed on a platform shaker at 111 rpm for 24 hours. Following an increment of 24, 48, and 72 hours, the pH measurement for each sample was collected. The experimental results are compiled in Table 2-9.

Table 2-9. pH Measurements for Each Sample after the Addition of Sodium Silicate Solutions

Silicate Concentration (ppm)	Amount of Silicate Added	Working Solution Added (mL)	Initial pH Values	24 hr pH Values	48 hr pH Values	72 hr pH Values
0	0 µL	10 mL	3.67	3.72	3.79	3.73
10	162 µL	10 mL	3.82	3.89	4.04	3.90
20	325 µL	10 mL	4.15	4.14	4.24	4.21
40	650 µL	10 mL	4.65	4.74	4.88	4.86
50	811 µL	10 mL	8.00	6.70	6.67	7.00
60	974 µL	10 mL	8.55	7.00	7.00	7.12
70	1.14 mL	10 mL	8.92	7.78	7.22	7.33
80	1.30 mL	10 mL	9.01	8.31	7.43	7.51

The results of the experiment conclude that increasing the amount of silicates added increased the pH of the solution. Additionally, each sample demonstrated a pH increase after initially adding the basic sodium silicate solution and gradually settled to a relatively steady pH after 48 hours. To maintain a stable pH close to neutral, between 50 and 60 ppm appears to be the optimal sodium silicate concentration as seen from the chart below (Figure 2-7).

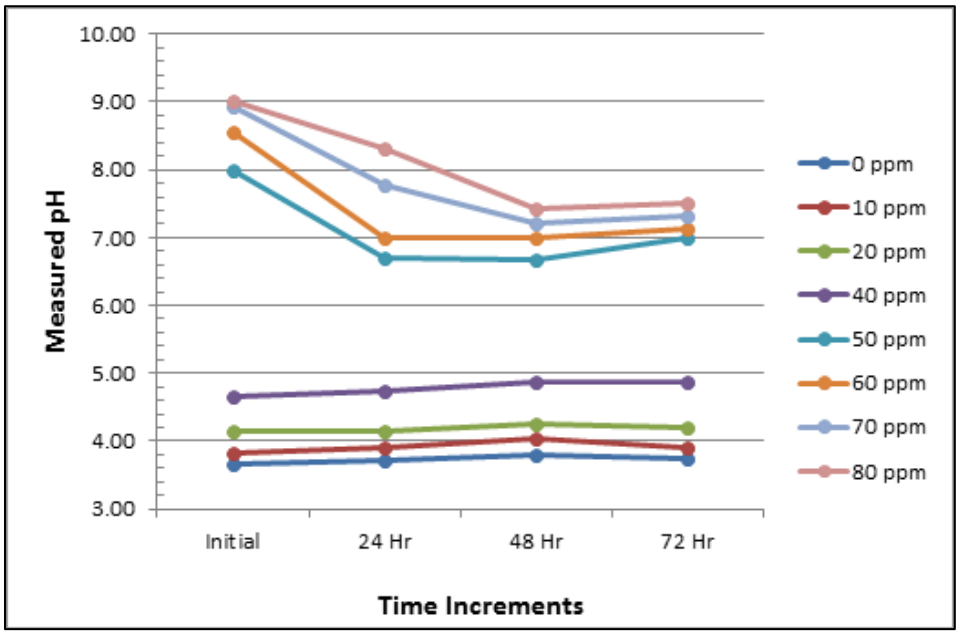


Figure 2-7. Monitored pH over time after the addition of sodium silicate solutions.

FIU Year 4 Carryover Work Scope

During the reporting period, FIU repeated the U(VI) adsorption experiments with 50 ppm HA and 3.5 mM colloidal silica solutions in the pH range of 3-8. A fresh batch of stock solutions were prepared prior to sample preparation; 100 ppm of humic acid (HA) was prepared by mixing 173.9 mg of HA powder in 1L DIW; 2000 ppm of 1L colloidal silica solution was prepared by mixing 2 grams of colloidal silica in 1L of DIW. Triplicate samples of Batches 2 (silica, HA and U) and 3 (HA, U) were prepared by mixing humic acid and colloidal silica oxide as per Table 2-3 and uranium was added prior to the pH measurement. After adding the uranium to the sample, initial pH was measured and recorded. Depending on the desired pH, 0.01M HCl or 0.1M NaOH was added in small increments until the desired pH was achieved; the total amount of acid or base needed to adjust the pH was recorded (Table 2-10). Once all batches were prepared, the samples were placed on a shaker for two days.

Table 2-10. Experimental Batch Composition and Initial Average pH Values

Batch #	*Constituents*							
	SiO_2	Humic Acid	Uranium U(VI)	Average Vol of Acid*	Average Vol of Base*	Water H_2O	Average Initial pH*	Total Volume
	mL	mL	mL	mL	mL	mL	Log(H)	mL
pH 3								
Batch No. 2	2.1	10	0.01	0.2	0	7.89	5.4	20
Batch No. 3	0	10	0.01	0.2	0	9.99	6.13	20
pH 4								
Batch No. 2	2.1	10	0.01	0.038	0	7.89	5.63	20
Batch No. 3	0	10	0.01	0.038	0	9.99	5.9	20
pH 5								
Batch No. 2	2.1	10	0.01	0.021	0	7.89	6.13	20
Batch No. 3	0	10	0.01	0.017	0.01	9.99	6.08	20
pH 6								
Batch No. 2	2.1	10	0.01	0.005	0	7.89	6.23	20
Batch No. 3	0	10	0.01	0	0	9.99	5.99	20
pH 7								
Batch No. 2	2.1	10	0.01	0	0.177	7.89	5.89	20
Batch No. 3	0	10	0.01	0	0.197	9.99	5.79	20
pH 8								
Batch No. 2	2.1	10	0.01	0	0.72	7.89	5.92	20
Batch No. 3	0	10	0.01	0	0.658	9.99	5.96	20

Samples from batches 2 (silica and humic acid) and 3 (humic acid) ranging from pH 3 to 8 were analyzed via kinetic phosphorescence analyzer (KPA). Prior to analysis, samples were centrifuged, followed by filtering through a 0.45 µm porosity filter and diluting 10 fold with a 1% nitric acid solution. Table 2-11 shows the percent removal of uranium (VI) for each condition for batches 2 and 3.

Table 2-11. Percent of Uranium Removal from Batches 2 and 3 in the Presence of 50 ppm HA

pH	Batch	Filtered samples uranium removal (%)	Unfiltered samples uranium removal (%)
3	2	55.17	36.39
	3	49.22	46.3
4	2	53.2	37.1
	3	40.52	38.76
5	2	38.25	43.97
	3	32.98	11.16
6	2	30.87	12.88
	3	32.98	9.11
7	2	19.51	22.7
	3	20.89	16.93
8	2	46.14	30.25
	3	34.17	21.99

The filtered samples reveal a higher level of removal when compared to the unfiltered samples (Figure 2-8). Filtration of samples removes colloidal silica particles in solution as well as humic acid molecules bonded to uranium suspended in solution that cannot pass through the filter; which indicates why a higher percent removal is seen in the filtered samples. At low pH, colloidal silica particles and humic acid molecules will have little surface charge. This allows silica and humic acid to aggregate and precipitate from the solution, especially if uranium binds with silica and HA to neutralize the surface charge. As pH of the solution increases, the percent removal of uranium seems to decrease, which may be due to the high negative charge present on the silica and humic acid molecules, not allowing the uranium to neutralize all these charges and causing repulsion between the silica and humic molecules. With increased pH, the dominant uranium species is now a uranyl carbonate that also has a negative charge; this will further hinder bonding to silica and humic acid due to the electrostatic repulsion that will be induced.

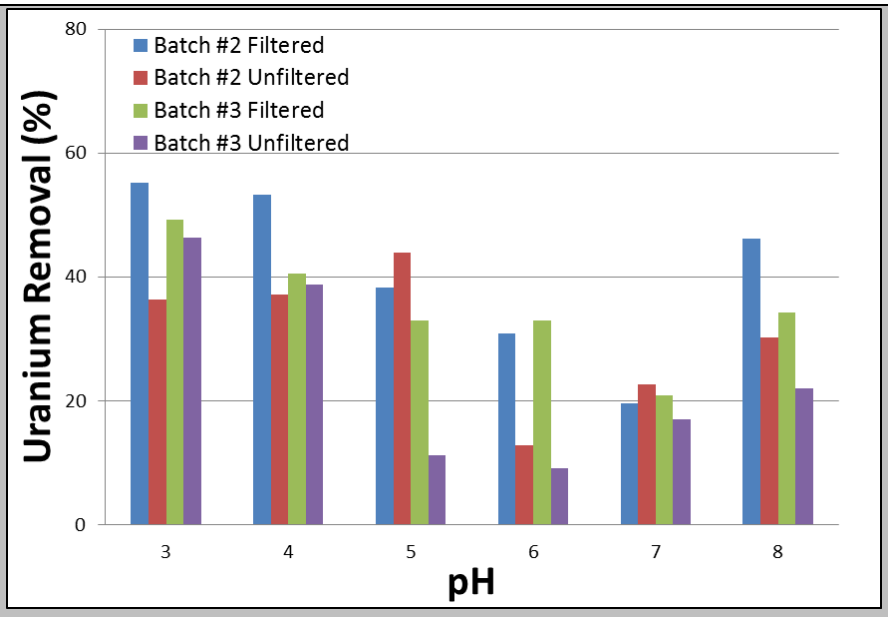


Figure 2-8. Change in uranium removal with pH for batches 2 and 3 at 50 ppm HA.

Samples from 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 prepared. The pH of these samples was in the range of 3-8 and was adjusted by adding 0.01M HCl and 0.1M NaOH in small increments as needed (Table 2-12).The sediment was individually pre-weighed and placed into each centrifuge tube, followed by the addition of humic acid, silicon dioxide and DI water. Uranium was injected prior to adjusting the pH; after adding uranium, the sample was mixed thoroughly and the initial pH was measured and recorded. Small intervals of either acid or base was added in order to adjust pH, after each addition the sample was mixed thoroughly and the pH was measured until the target pH was reached.

Table 2-12. Constituents of Experimental Samples

Batch #	*Constituents*								
	SiO_2	Humic Acid (HA)	Sediments	Uranium U(VI)	Acid	Base	Water H_2O	Initial pH	Total Volume
	ml	ml	mg	ml	ml	ml	ml	Log(H)	ml
pH 3									
Batch No. 5	2.1	10	401.4	0.01	.207		7.89	6.42	20
Batch No. 6	0	10	400.9	0.01	.207		9.99	6.20	20
pH 4									
Batch No. 5	2.1	10	401	0.01	.040		7.89	6.08	20
Batch No. 6	0	10	401	0.01	.050		9.99	6.23	20
pH 5									
Batch No. 5	2.1	10	399.7	0.01	.016		7.89	5.98	20
Batch No. 6	0	10	400.3	0.01	.014		9.99	6.11	20
pH 6									
Batch No. 5	2.1	10	399.8	0.01	.005	.005	7.89	6.07	20
Batch No. 6	0	10	400.2	0.01	.005	.020	9.99	5.96	20
pH 7									
Batch No. 5	2.1	10	400.4	0.01		0.203	7.89	5.73	20
Batch No. 6	0	10	399.8	0.01	.005	.163	9.99	6.07	20
pH 8									
Batch No. 5	2.1	10	400.1	0.01		.300	7.89	6.02	20
Batch No. 6	0	10	400.2	0.01		0.31	9.99	6.11	20

Once all the samples were prepared, the samples were placed on a shaker for two days. After the two days, the samples were centrifuged for 30 minutes at 22° C and 2700 RPM. Samples were filtered through 0.45µm porosity filer and were diluted 10x with 1% nitric acid solution for analysis. Uranium concentration will be measured via KPA and Fe and Si will be analyzed via ICP-OES. Sample analysis is in progress; results of the analysis will be reported in the January monthly report.

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

New SRS F-Area sediments were received by ARC on September 29, 2014. These sediments were sieved through a 180 um mesh size after previously determining the 180 um size to be ideal for the microcosm study. These newly sieved F-Area sediments were then combined with previous F-Area sediments of the same grain size to produce a total of approximately 270 grams. XRD analysis was conducted on the combined sieved soil sample and data processing is in progress with matches to quartz, goethite, montmorillonite and kaolinite phases.

For the microcosm experiment, FIU prepared 4 sets of samples in triplicate for a total of 12 samples. These samples were treated using a basal medium solution augmented with sulfate and molasses (Figure 2-9). The basal medium solution (in g L-1 deionized water) consists of 1.5 $NaHCO_3$, 0.2 NH_4Cl, 0.1 K_2HPO_4 $3H_2O$, 0.055 KH_2PO_4, 0.001 resazurin as a redox indicator, 0.039 Na_2S $9H_2O$ as a sulfur source and reductant, and 0.1 $MgCl_2$ $6H_2O$. In addition, 5 mL L-1 trace metal solution was added. The trace metal solution consists of (in g L-1) 0.005 $FeCl_2$ $4H_2O$, 0.005 $MnCl_2$ $4H_2O$, 0.001 $CoCl_2$ $6H_2O$, 0.0006 H_3BO_3, 0.0001 $ZnCl_2$, 0.001 $NiCl_2$ $6H_2O$, 0.001 Na_2MoO_4 $2H_2O$, and 0.002 $CaCl_2$ $2H_2O$. For the augmented samples, magnesium sulfate anhydrous ($MgSO_4$) was used as a source of sulfate in the concentration of 500 ppm in order to have 20 mg in the sample.

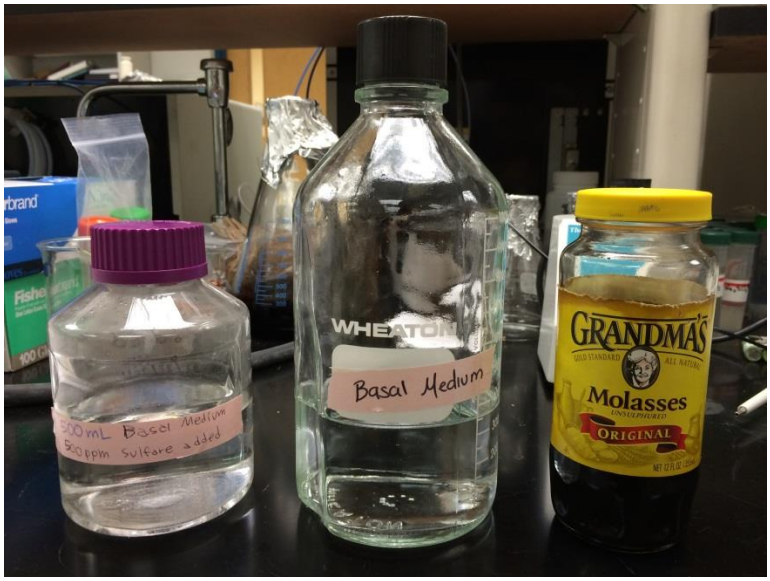


Figure 2-9. Basal medium with 500 ppm sulfate, Basal medium, and Molasses.

Set 1 consisted of 20 mL of soil, 20 mL of basal medium, 500 ppm sulfate, 5-10% by weight molasses, and 5 mL of anaerobic bacteria. Set 2 consisted of 20 mL of soil, 20 mL of basal medium, 500 ppm sulfate, and 5-10% by weight molasses. Set 3 consisted of 20 mL of soil, 20 mL of basal medium, and 5-10% by weight molasses. Set 4 consisted of 15 mL of soil, 15 mL of basal medium, 5-10% by weight molasses, and 5 mL of anaerobic bacteria. Set 4 was decreased to 15 mL of soil instead of 20 mL in order to conserve the SRS F-Area sediments for future use. After purging the anaerobic chamber with nitrogen gas, the samples were placed inside the chamber, where it is expected that they will produce ferrous iron precipitates in the soil (Figures 2-10 and 2-11).

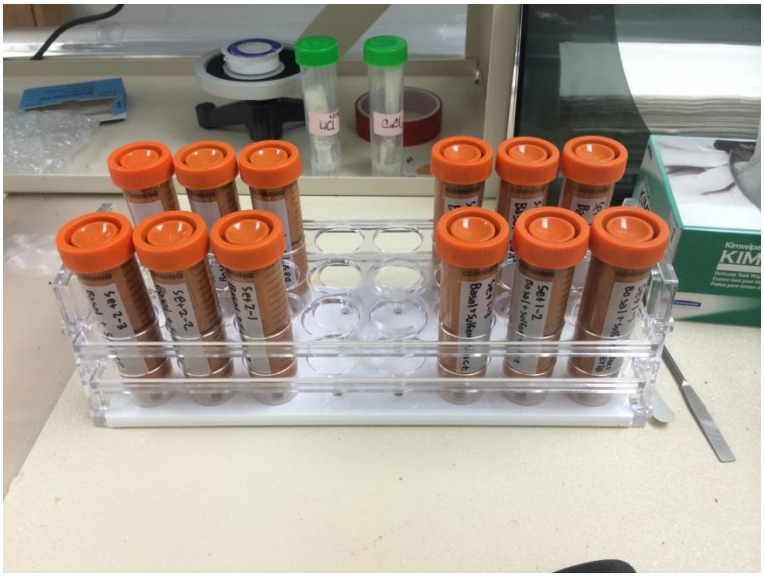


Figure 2-10. Samples prepared for the microcosm experiment

Figure 2-11. Anaerobic chamber used for the microcosm experiment

The pH evolutions of the samples were monitored weekly. We expected to find a more basic pH in Sets 1 and 2 due to the addition of sulfate. Although this was the initial case, there seems to be no significant pH difference from the samples augmented with sulfate to those without sulfate after 2 weeks. The recorded pH values are listed in Table 2-13.

Table 2-13. Microcosm Experiment pH Evolution

	Set 1 (Basal medium, Sulfate, Molass., Bacteria)			Set 2 (Basal medium, Sulfate, Molass.)			Set 3 (Basal Medium, Molass.)			Set 4 (Basal medium, Molass., Bacteria)		
Date	pH (1-1)	pH (1-2)	pH (1-3)	pH (2-1)	pH (2-2)	pH (2-3)	pH (3-1)	pH (3-2)	pH (3-3)	pH (4-1)	pH (4-2)	pH (4-3)
10/13/ 2014	5.95	5.95	5.95	5.95	5.95	5.9	5.55	5.76	5.81	5.95	5.95	5.95
10/21/ 2014	4.81	4.8	4.79	4.91	4.83	4.85	4.77	4.77	4.63	4.86	4.89	4.77
10/30/ 2014	4.82	4.63	4.34	4.85	4.86	4.83	4.86	4.89	4.8	4.93	4.87	4.33

A sharp decrease in pH from week 1 to week 2 was noted and an investigation was conducted to determine the cause. The data from this investigation can be found in Table 2-14. It was concluded through an elimination process that the molasses itself is acidic and had caused the pH drop. Before the molasses addition, the solutions had more basic pH values, which dropped significantly after the addition of molasses.

Table 2-14. pH of Initial Solutions

pH values			
Solution amended with Sulfate, Basal medium and Molasses	Solution amended with Basal medium and Molasses	Basal Medium	Basal Medium amended with 500 ppm of sulfate
4.85	4.57	8.7	8.82

Due to the acidic condition within the samples, we have concluded that a new set of samples would be created using a solution that has been brought to a neutral pH before mixing with soil. It was also determined that a representative sample for each set would be sacrificed and ran through XRD analysis to shed light on the types of reactions that may or may not be presently occurring. XRD analysis would also be conducted on SRS F-Area samples from the previous microcosm experiment to observe if any reactions have taken place in these samples which have been left in the anaerobic chamber for an extended period of time. These samples were taken from depths of 65 feet and 100 feet and were sacrificed in the anaerobic chamber (Figure 2-12). The next step was to sieve the samples through a 180 um mesh prior to XRD.

Figure 2-12. Previous samples sacrificed prior to XRD.

Experiments were continued for 4 sets (in triplicate, for a total of 12 samples) prepared for the microcosm study. These samples were treated using a basal medium solution augmented with sulfate and molasses. The basal medium solution was prepared in DIW according to the same recipe described before.

Early in November, after 3 weeks of keeping the samples in the anaerobic chamber, a representative sub-sample from each set was collected and sacrificed for XRD analysis. It was expected to observe changes in the solid phases composition caused by the addition of molasses. The sub-samples were collected at a fairly low pH between 4.33-4.93. It was observed in the last microcosm study that acidic conditions hinder the formation of carbonate CO_3^{2-}, thus limiting any formation of siderite ($FeCO_3$). All samples displayed nearly identical XRD patterns when compared against the original XRD pattern of the soil before the microcosm experiment began (Figure 2-13 through Figure 2-16). It has been noted that sample 4 (Figure 2-16) has a slight variation in the peak intensities when compared against the other 3 samples. This will be investigated further through XRD data analysis using *MATCH!* Software. According to the XRD analysis, there were no signs of pyrite or siderite formation; results can be observed in Figure 2-17 and Figure 2-18. Results from the next XRD analysis of more recent sub-samples taken at the end of November will also be used to help determine the types of minerals present.

It was observed that some of the original 12 samples, which were placed in the anaerobic chamber in October, were beginning to dry out. It was decided that a small amount of solution would be added to the samples. Two solutions were created for this purpose. Solution 1 consisted of 45 mL of basal medium and 7.1 g molasses (5% by weight). This solution was adjusted to a pH of 7.03 before it was added in the amount of 2 mL per sample to set 3 and set 4 samples. Solution 2 consisted of 45 mL of basal medium augmented with 500 ppm of sulfate, and 7.1 g molasses (5% by weight). This solution was adjusted to a pH of 6.99 before it was added in the amount of 2 mL per sample to set 1 and set 2 samples.

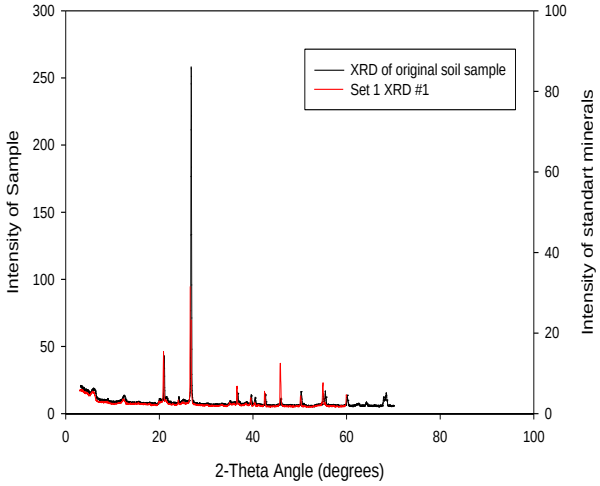


Figure 2-13. XRD of original mixed soil sample vs. set 1 sub-sample.

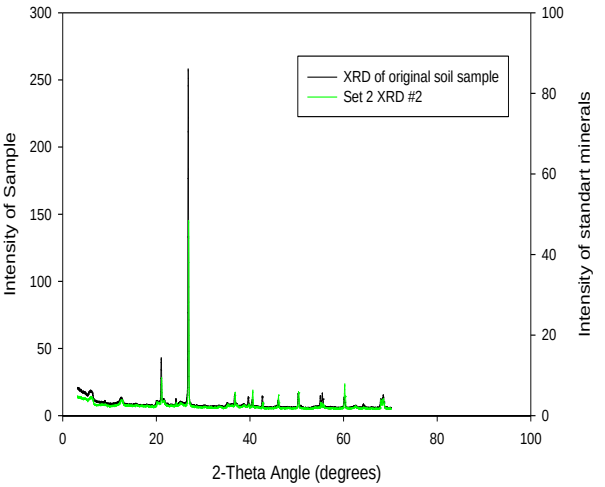


Figure 2-14. XRD of original mixed soil sample vs. set 2 sub-sample.

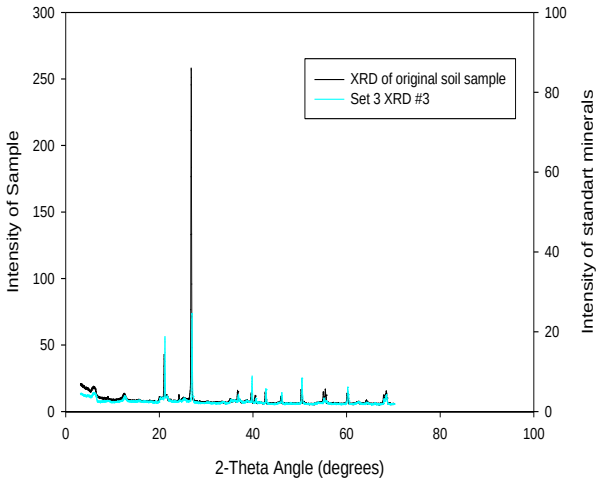


Figure 2-15. XRD of original mixed soil sample vs. set 3 sub-sample.

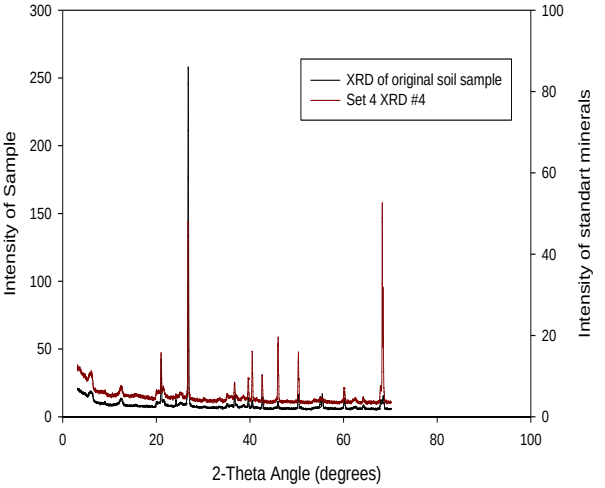


Figure 2-16. XRD of original mixed soil sample vs. set 4 sub-sample.

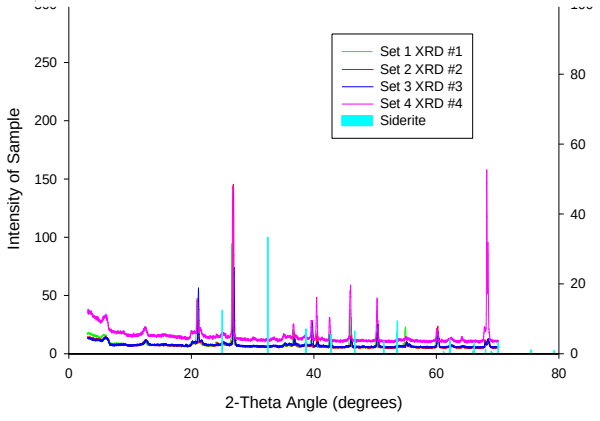


Figure 2-17. XRD of subsample compared to siderite minerals.

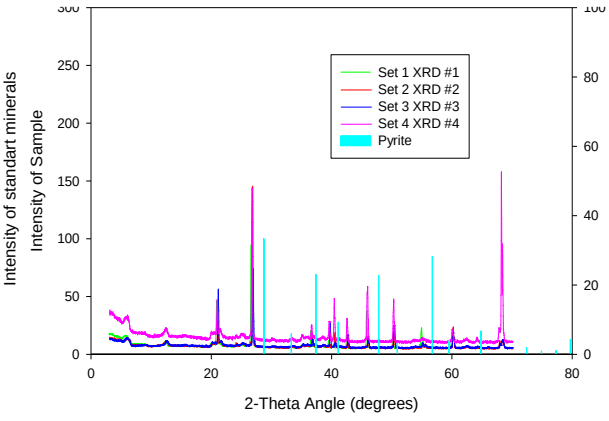


Figure 2-18. XRD of subsample compared to pyrite minerals.

On November 24, 2014, a new set of samples were created for the microcosm study, with a total of 4 samples (Figure 2-19). These samples differed from the previous samples because the new ones were first pH adjusted to 7 before the addition of the SRS F-Area sediments. Sample 1 consisted of 12 mL of basal solution augmented with 500 ppm of sulfate, 0.75 grams of molasses (5-10% by weight concentration), 12 mL of SRS F-Area sediments and 0.5 mL of anaerobic bacteria. Sample 2 consisted of 12 mL of basal solution augmented with 500 ppm of sulfate, 0.75 grams of molasses (5-10% by weight concentration), and 12 mL of SRS F-Area sediments. Sample 3 consisted of 12 mL of basal solution, 0.75 grams of molasses (5-10% by weight concentration), and 12 mL of SRS F-Area sediments. Sample 4 consisted of 12 mL of basal solution, 0.75 grams of molasses (5-10% by weight concentration), 12 mL of SRS F-Area sediments, and 0.5 mL of anaerobic bacteria. The initial pH values of the newly created samples ranged from 6.99 to 7.03.

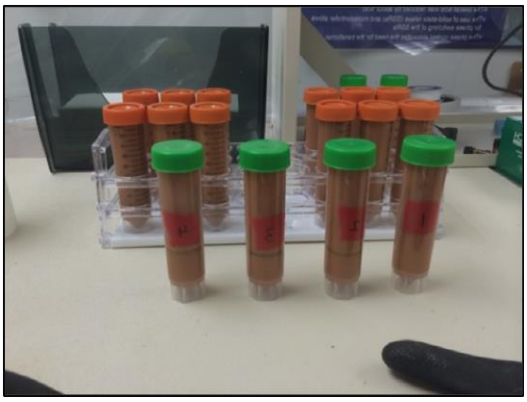


Figure 2-19. Microcosm samples: 4 newly prepared (green caps) and 12 original (orange caps).

In December, another set of sub-samples (Figure 2-20) from the original 12 samples will be taken for XRD analysis to observe if any changes in mineralogical composition have occurred since the first set of sub-samples were analyzed. XRD will also be conducted on representative samples from the previous microcosm study conducted last year by DOE Fellow Valentina Padilla to determine whether there are any long-term effects of molasses on the sediments. These samples were taken from a 65 and 100 foot depth (Figure 2-21). The samples were sacrificed and sieved through a 180 µm mesh size to remove larger sand particles to prevent quartz peaks from dominating any XRD results. Monitoring of the pH evolution of the latest 4 samples will also be conducted as well as XRD analysis of sub-samples to be taken at a future date.

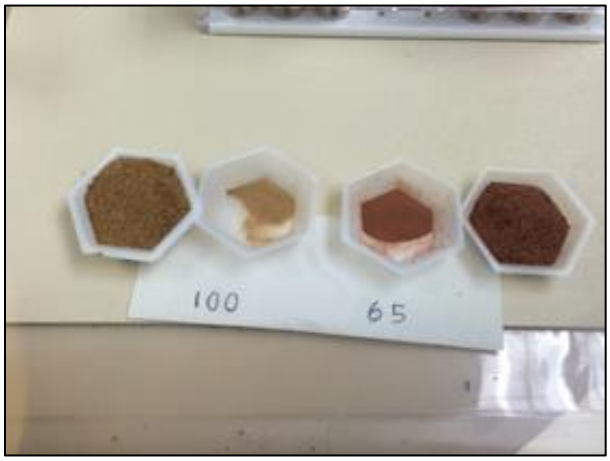


Figure 2-20. Second set of sub-samples from original 12 samples.

Figure 2-21. Sieved and unsieved representative sample from previous microcosm study.

During the month of December, four new representative sub-samples were taken from the microcosm experiment that began in October. This new set of sub-samples was taken two weeks after the first set of sub-samples. XRD analysis was conducted on the samples to determine if any mineralogical changes had occurred in the two-week period. The data obtained via XRD analysis can be observed in Figures 2-22 through 2-25. Further analysis using *MATCH!* Software will be used to determine if there are any matches with siderite or pyrite.

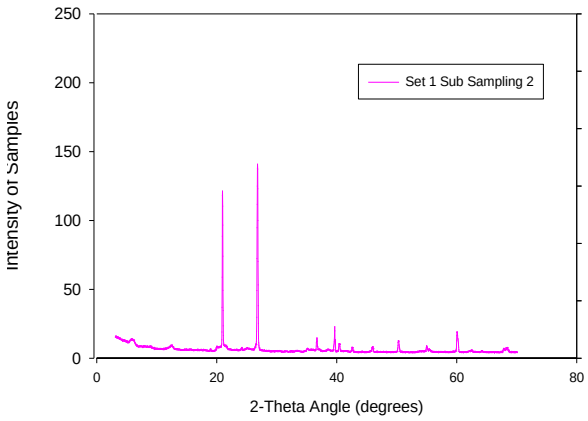


Figure 2-22. Microcosm Sub-Sampling #2, Set 1

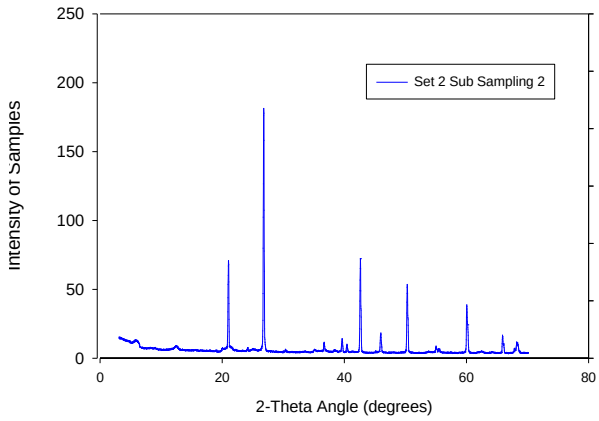


Figure 2-23. Microcosm Sub-Sampling #2, Set 2

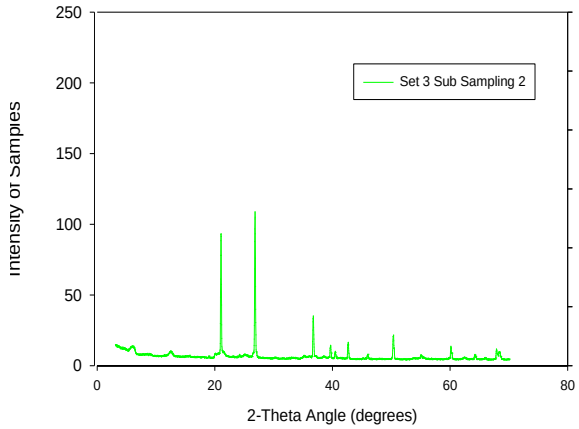


Figure 2-24. Microcosm Sub-Sampling #2, Set 3

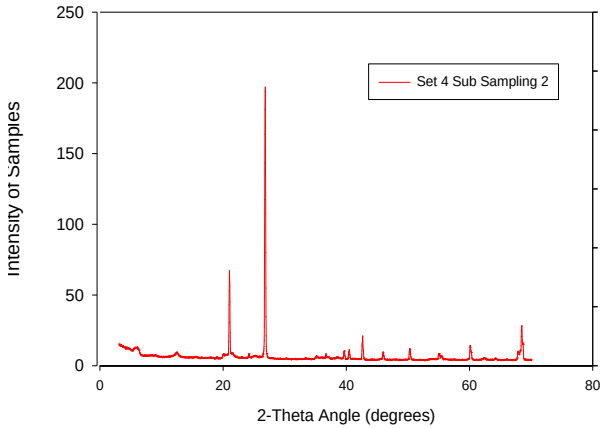


Figure 2-25. Microcosm Sub-Sampling #2, Set 4

As shown in Figure 2-26, all four of the new sub-samples have similar XRD patterns with only slight variations in the intensity of certain peaks.

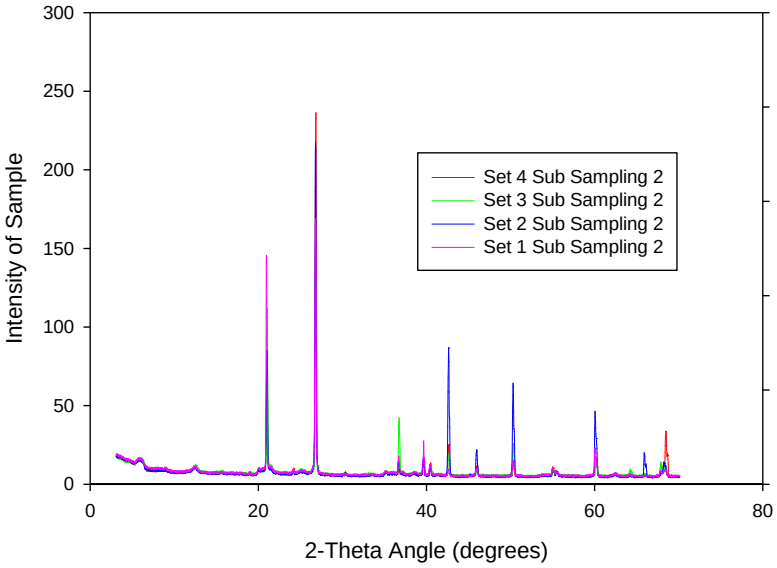


Figure 2-26. Microcosm study- all sets from sub-sampling #2.

The pH evolution of the microcosm samples was also monitored and recorded in Table 2-15 and graphed in Figures 2-27 through 2-30. Almost all of the samples have followed a similar trend, with a decline in the pH value. This can be attributed to the fermentation process of molasses and the natural acidity of SRS soil used for the microcosm study. It was noted that samples amended with sulfates had slightly higher pH than sulfate-free samples. In addition, there was an increase in the pH of some of the samples from 11/30/2014 to 12/11/2014. This increase in the pH was caused by the addition of a pH-neutral solution to each of the samples to prevent the samples from drying out. These solutions were added in the amount of 2 mL per sample with the correct

solution composition corresponding to each sample. By 12/11/2014, it was observed that the pH again dropped in almost all of the samples.

Table 2-15. pH Evolution of the Microcosm Study

	Set 1 *(Basal medium, Sulfate, Molass., Bacteria)*			**Set 2** *(Basal medium, Sulfate, Molass.)*			**Set 3** *(Basal Medium, Molass.)*			**Set 4** *(Basal medium, Molass., Bacteria)*		
Date (2014)	pH (1-1)	pH (1-2)	pH (1-3)	pH (2-1)	pH (2-2)	pH (2-3)	pH (3-1)	pH (3-2)	pH (3-3)	pH (4-1)	pH (4-2)	pH (4-3)
10/13	5.95	5.95	5.95	5.95	5.95	5.9	5.55	5.76	5.81	5.95	5.95	5.95
10/21	4.81	4.8	4.79	4.91	4.83	4.85	4.77	4.77	4.63	4.86	4.89	4.77
10/30	4.82	4.63	4.34	4.85	4.86	4.83	4.86	4.89	4.8	4.93	4.87	4.33
11/30	4.74	3.95	3.91	3.89	3.95	4.22	4.26	3.91	4.96	4.11	4.02	4.12
12/11	4.73	3.94	3.9	4.01	4.04	4.35	4.39	4.22	5.29	4.37	4.31	4.4
12/18	4.87	4.01	3.95	3.87	3.91	4.06	3.91	3.86	4.74	3.94	3.88	3.97

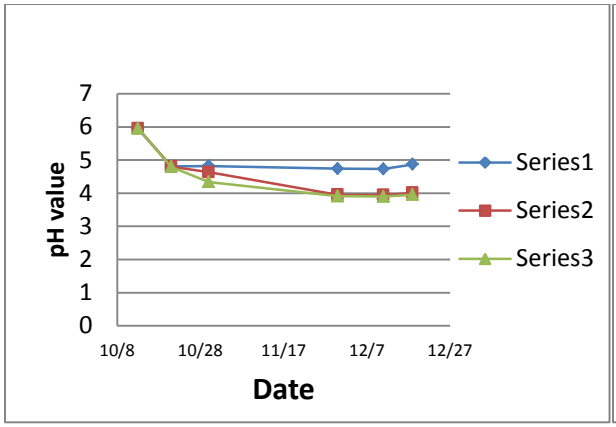


Figure 2-27. Set 1 pH evaluation

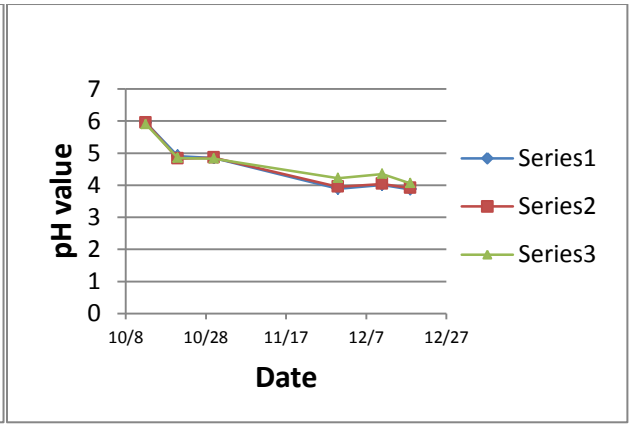


Figure 2-28. Set 2 pH evaluation

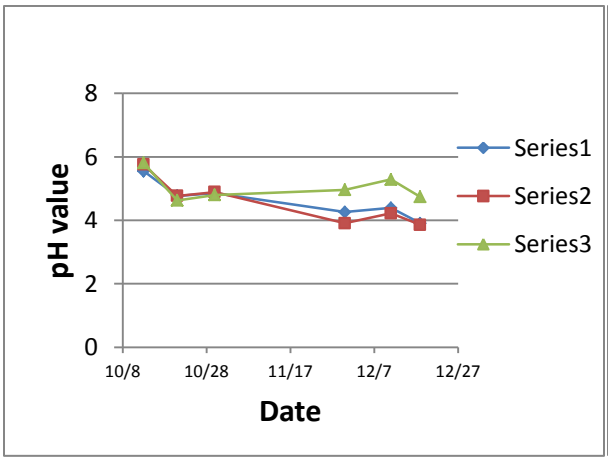


Figure 2-29. Set 3 pH evaluation

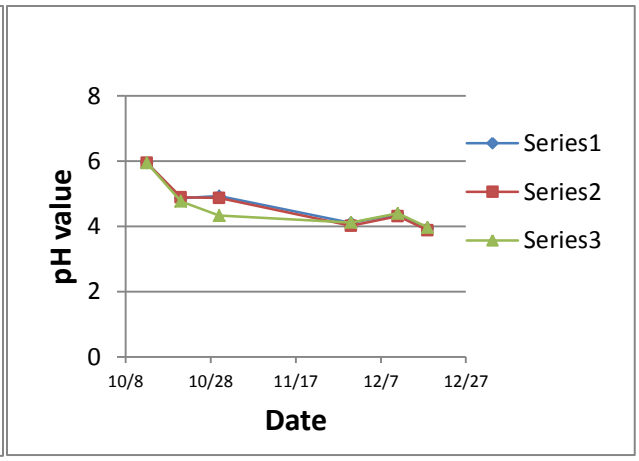


Figure 2-30. Set 4 pH evaluation

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

During the month of October, certain conditions were tested for the measurement of humate concentration via UV-vis spectrophotometer in order to determine chemical interferences that could potentially affect the results of the experiments. In addition, two different wavelengths (254 nm and 450 nm) were compared to find out which wavelength gives better results for the measurements of various humate concentrations.

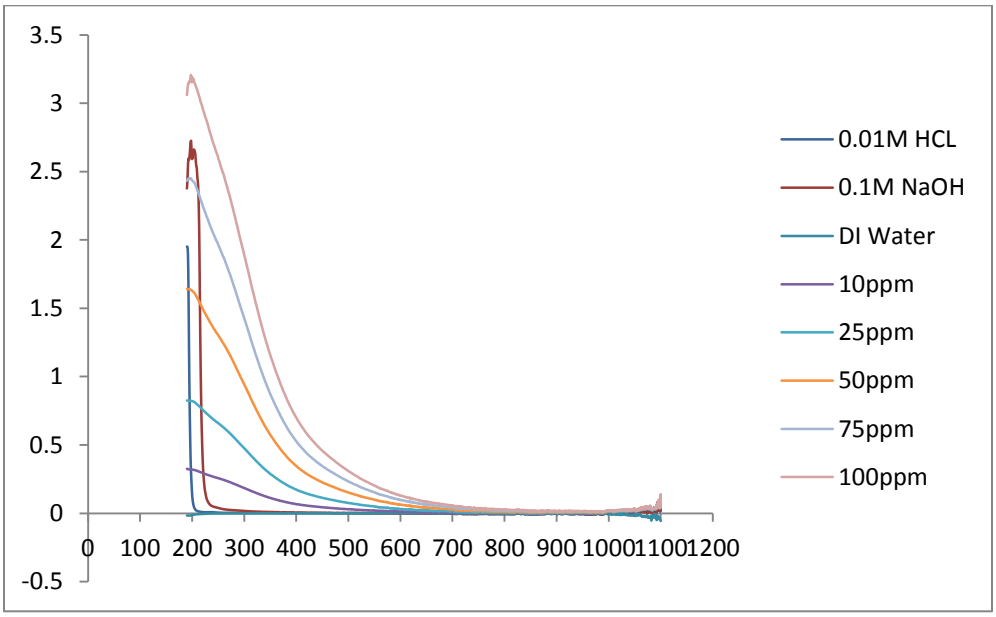


Figure 2-31. Test for NaOH and HCl.

From Figure 2-31, NaOH shows a strong absorption of light at 218 nm. As the wavelength increased, the absorption goes to zero. This suggests that the addition of NaOH would not interfere at any wavelength with the humate reading. Measurements showed that HCl will not interfere as well because it has an absorbance of zero at 225 nm.

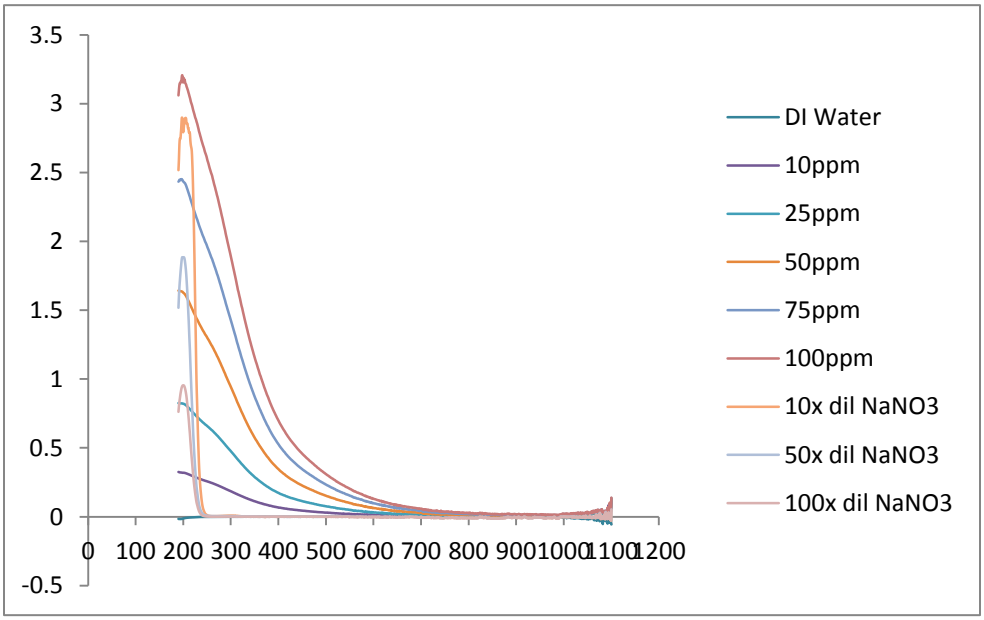


Figure 2-32. Test for $NaNO_3$.

$NaNO_3$ is chemicals specie that could interfere with humate readings. Figure 2-32 shows that nitrate species absorb at 200 nm and, once it is diluted, the absorption of light is decreasing. For the purpose of measuring humate concentration, either the 254 nm or the 450 nm wavelength will not interfere with the absorbance of light for the humate solution in case $NaNO_3$ species are present in the solution.

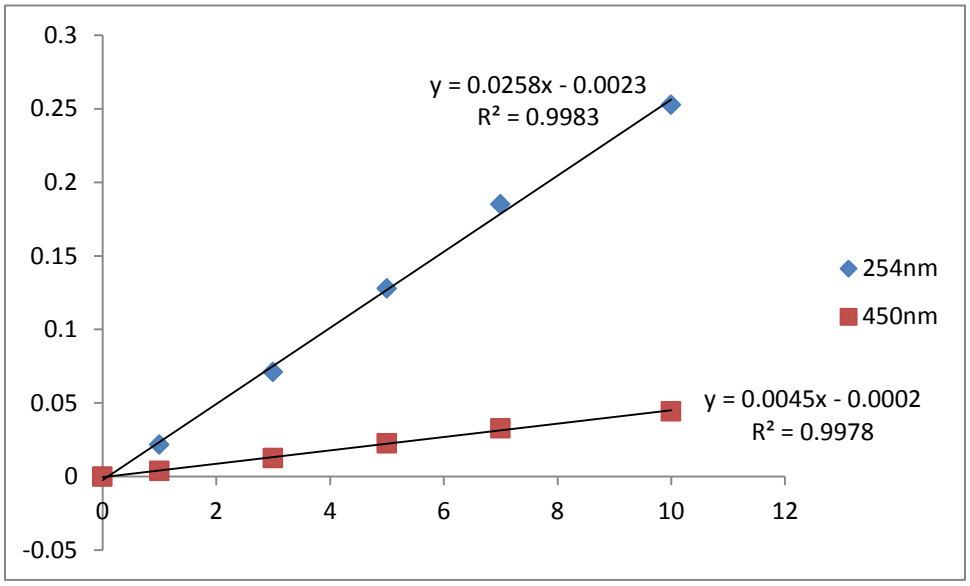


Figure 2-33. Standard Calibration Curve at 254 nm and 450 nm.

Figure 2-33 presents the calibration curve for the humate solution at two different wavelengths. It was concluded that the 254 nm wavelength is more sensitive for the measurement of humate because the slope is higher and it can accurately detect lower concentrations of humate compared to the 450 nm wavelength.

During the month of November, FIU started sorption experiments using humate solutions with pH adjusted to 4 and sediments shipped from the Savannah River Site. The experiment was done at laboratory ambient temperature (between 20 and 23°C) in triplicate. The procedure of the experiment included the following steps:

First, the sediments (FAW1 70'-90') were sieved to a particle size of ≤ 2 mm. Sediments in the amount of 1g were weighed in 36 centrifuge tubes. The following concentrations of humic acid (HA) were used for the sorption experiment: 10, 25, 50, 100, 150, 200, 250, 300, 350, 400, 450, and 500 ppm. The concentrations of HA were pipetted into each centrifuge tube. DI water was added to a volume of 19 mL in order to leave 1 mL of volume for pH adjustment. pH was adjusted to 4 for all the samples by using either 0.01 M HCL or 0.1 M NaOH. DI water was added to reach a final volume of 20 mL in each tube. All samples were vortex mixed and placed on a shaker table at 100 RPM for a period of 24 hours in order to reach adsorption equilibrium. The position of the centrifuge tubes was kept almost horizontal in order to maximize contact area between the liquid and sediment. Once the samples were allowed to equilibrate for 24 hours, they were centrifuged at 2700 RPM to separate the liquid solution from the sediment with the sorbed humate. The supernatant was analyzed using a Thermo Scientific Genesys 10S UV-Vis spectrophotometer in order to determine the concentration remaining in solution. The analysis was done at 254 nm. The results are presented in Figure 2-34.

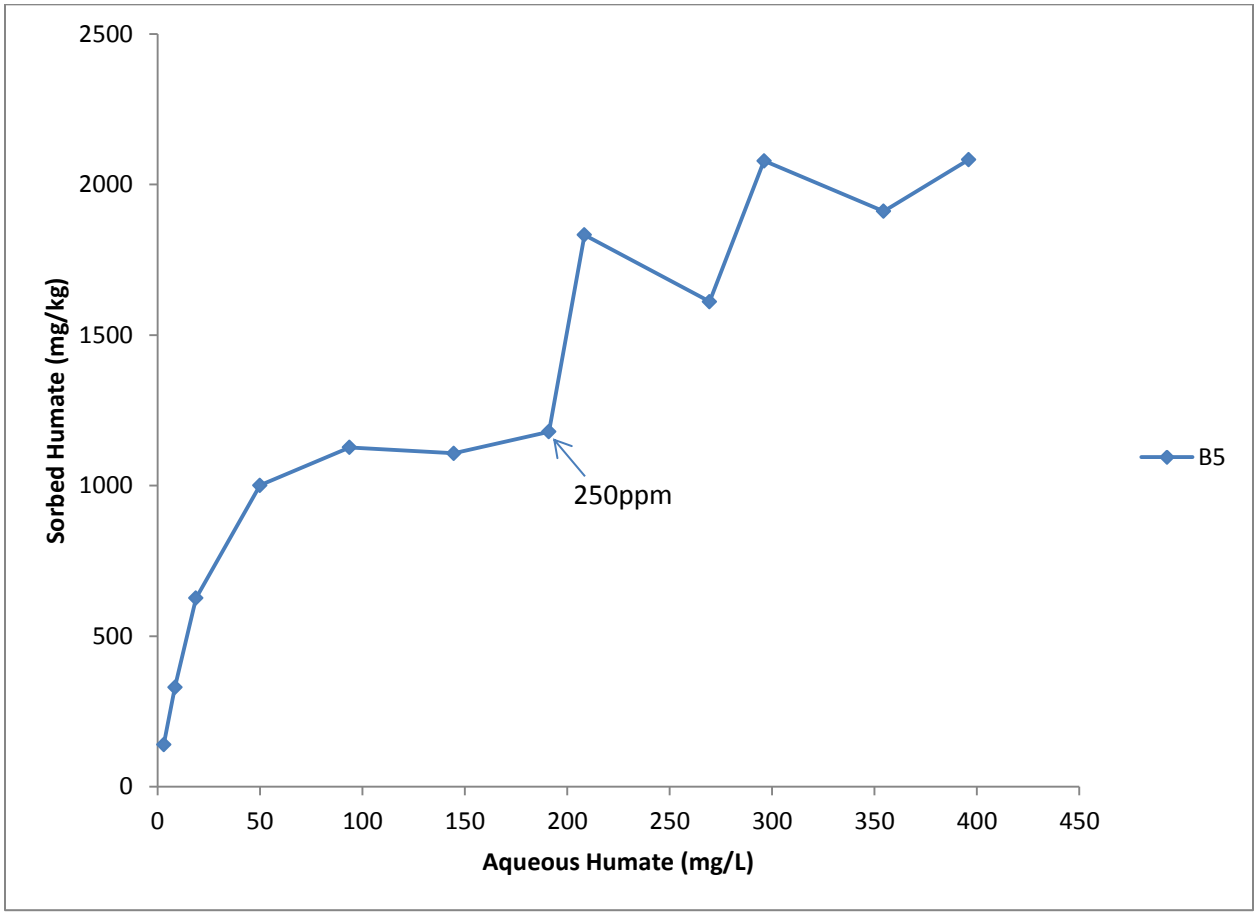


Figure 2-34. HA sorption results at pH 4.

From the results, it can be seen that the sorption of humate to the sediments follows a Langmuir isotherm up to 250 ppm. This means that after a saturation point is reached, no more sorption can occur. It was noticed that beyond 250 ppm (from 300 to 500 ppm), the sorption of the humate to the sediment increased. Probably there is another mechanism of interaction besides sorption between humate and sediments. Since humic molecules have some hydrophobic character, at higher concentrations, they will agglomerate to reduce their contact with water, and when the samples are centrifuged, the agglomerated humic molecules are removed from solution.

In order to test if agglomeration and precipitation of the humic molecules occur, samples containing the same concentrations without sediment at pH 4 and without pH adjustment will be tested. This will help determine other removal processes of humic molecules from solution besides sorption to the sediments. The results will be presented in the next monthly report.

During the month of December, sediment-free samples were prepared using the same concentrations of Huma-K as the ones used for the sorption experiment at pH 4. The purpose of this experiment was to determine if there was another mechanism going on in the removal of humic molecules from solution besides sorption. The following concentrations (in ppm) of Huma-K were used: 10, 25, 50, 100, 150, 200, 250, 300, 350, 400, 450, and 500. The same experimental procedure used in the sorption experiment was performed in this experiment: pipet

the desire concentration, adjust the pH to 4, put samples in the shaker table for 24 hours, and centrifuge samples.

It was noticed that after the samples were centrifuged, a precipitation of Huma-K appeared at the bottom of the centrifuge tubes as shown in Figure 2-14. The two samples in Figure 2-35 have the same concentration (100 ppm) but different pH values. The sample on the left has a pH value of 7.69, and the sample on the right has a pH value of 4. From Figure 2-35, it can be clearly seen that at acidic pH values (in this case pH 4) precipitation of Huma-K is higher than at circumneutral pH values.

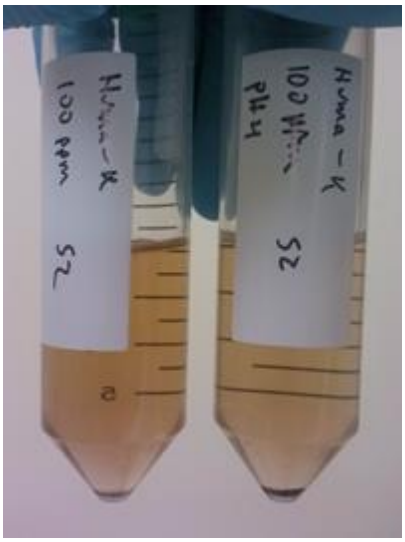


Figure 2-35. Comparison of two Huma-K samples (concentration100ppm) at two different pH values

All the samples were analyzed using the UV-vis spectrophotometer at 254 nm wavelength. Figure 2-36 shows the results from the experiment. At pH 4, precipitation of Huma-K is increased with the increase of concentration. The explanation for this behavior is that at low pH values, humic molecules tend to be less negatively charged, and this allows them to aggregate, forming suspended colloidal particles that precipitate. When the samples are centrifuged, the precipitate settles on the bottom of the centrifuge tube as shown in Figure 2-35. Initial concentration of Huma-K has an effect on the precipitation of Huma-K.

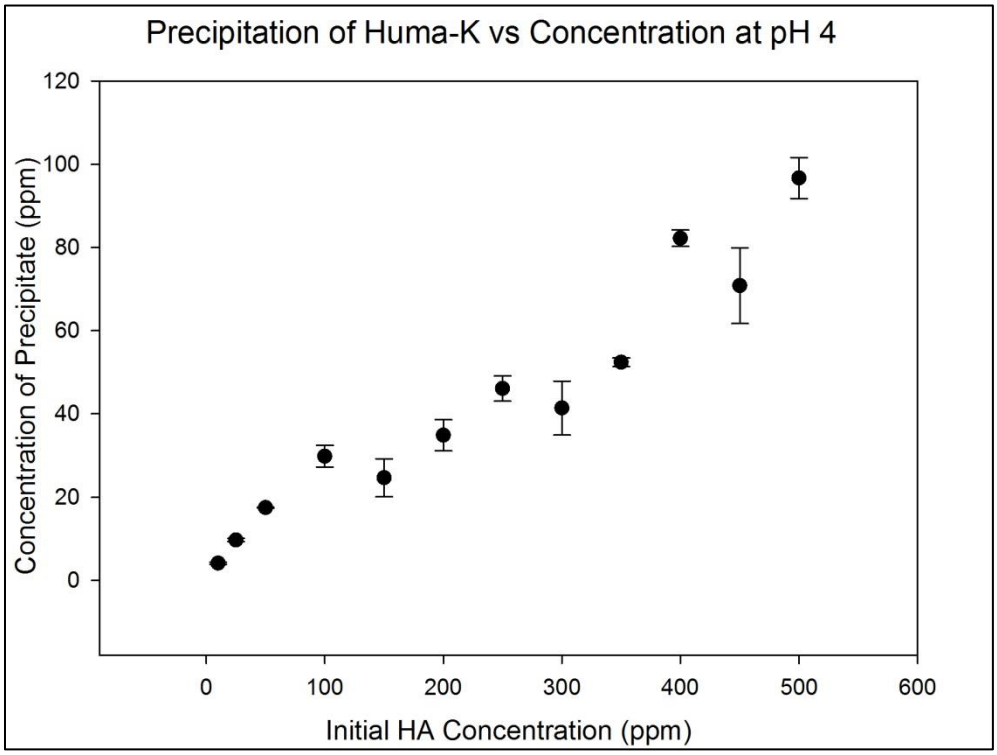


Figure 2-36. Precipitation of Huma-K at pH 4.

Another experiment that was started and completed this month was the removal of Huma-K by SRS sediments at different pH values. The purpose of this experiment was to determine if the removal of Huma–K using the same concentration (50 ppm) would increase or decrease at different pH values. The pH values tested were: 4, 5, 6, 7, 8, and 9 (Figure 2-37). The highest percent of Huma-K removed to the sediments is at pH 4 (62.8%). When the pH is increased, the removal is decreased. At pH 9, only 6% of Huma-K is sorbed to the sediments. A possible explanation is that as the pH is increased, sediments become more negatively charged as well as humic molecules. The Huma-K removal is decreased due to the electrostatic repulsion between humic molecules and sediments. Increase of pH diminishes removal of humic molecules by the sediments.

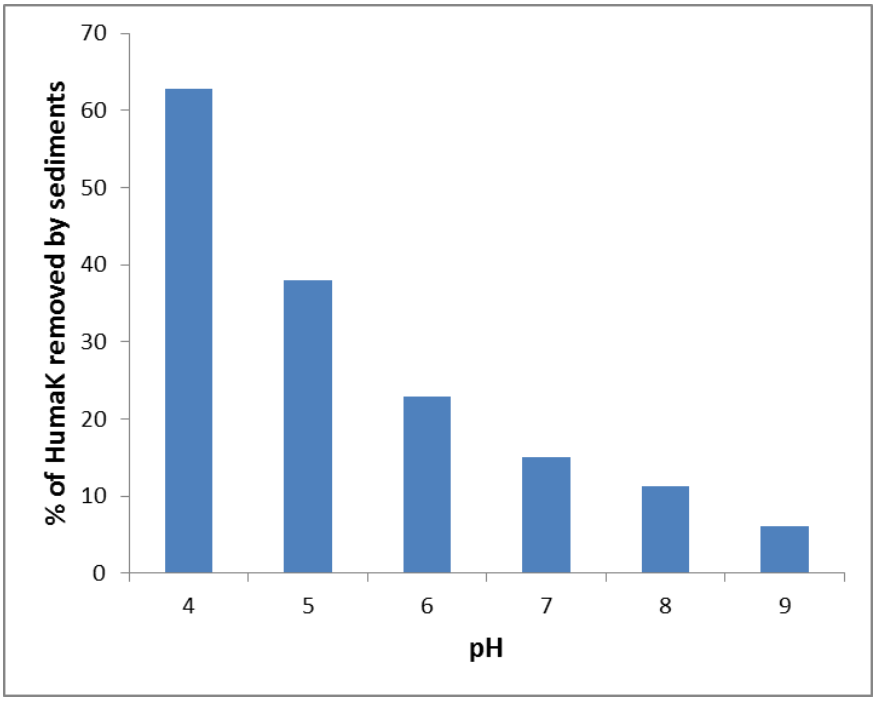


Figure 2-37. Percent of 50 ppm Huma-K removal by sediments.

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

Following the scope of the investigation for Subtask 3.1, involving the analysis of NH_3 partitioning in the bicarbonate-amended solutions under the influence of different temperature conditions, the continuous literature reviews have led to the selection of a preliminary method of analysis of ammonia gas by using ion-selective electrode to ultimately determine the equilibrium concentrations between ammonia gas and the aqueous media.

After determining the experimental method, the set up was designed. The set up consists of a pH/temperature module, a conductivity/temperature module, an ammonia ion-selective electrode and a magnetic stirrer (probe and paddle) attached to the VERSA STAR benchtop meter. All instruments and modules have been attached and calibrated to standards prior to beginning the testing phase. In addition, it has been determined that, in order to evaluate samples at varying temperatures, a Barnstead Max Q 7000 water bath is needed. Other instruments and components necessary for the experimental phase have also been received and they include Khloen pump syringes in 25 mL. and 50 mL sizes., a 2L PTFE Luer-Lok (TLL) gastight syringe and Cole-

Parmer gas sampling bags, FEP – 5mil thickness/4.7 L. All instruments have been tested and calibrated and placed in the fume hood where all the experiments will take place.

The next step was to set up the Khloen pumps and test them using ammonia or nitrogen gas, depending on the set up allowed by the hardware installation. A computer/laptop to run the Khloen commands was reformatted for use with this task. The code for the Kloehn pump needed to be written to accommodate the different phases for this experiment. It consists of the extraction of solutions with various concentrations of bicarbonate to record dissolved ammonia concentrations vs. injected ammonia. After this step, the experimentation began and, during the first phase, determination of ammonia partitioning within DI water was calculated and compared to literature values. During this phase, the selected method was also assessed in order to determine its effectiveness for further steps of the procedure.

The final configuration of the experimental set-up for this task was finalized. Final calibration and functionality determination testing was also performed. The Barnstead Max Q 7000 was placed with the other components of the set-up and elements of the experiment and calibrated accordingly to determine its effectiveness in temperature control of the solution tested. The Khloen Syringe Pump system was calibrated for the use in the distribution of gas into the solution at specific release rates and amounts. In addition, these pumps will be further used for the injection of bicarbonate solution to the DI water further in the testing process. The computer commands needed for the initial phase of the experiment have been designed to accommodate the ammonia gas flow rates into solution according to the different installed syringes (25 mL and 50 mL) that will be used to extract the ammonia gas from the sampling bags to create varied ammonia gas concentrations.

Following the experimental setup, a test was performed to assess the functionality value of the instruments and the experimental design. Due to this test, it was determined that the bench-top meter experiences difficulty achieving stabilization when placed under the fume hood. Also, it is necessary that the stirrer be in place as the ammonia gas is injected into the solution to maximize mixing rates and to obtain accurate readings while the reaction is occurring. Modification to the set-up has been performed as well as the relocation of sensitive instruments.

Further testing will be performed for a variety of volumes (50 mL, 75 mL, and 100 mL) of 5% ammonia injected in DI water to determine the pH variations and the consistency of the experimental setup. Once the determination of the set-up functionality is achieved, testing using various ammonia gas dilutions from 100% ammonia will begin.

Following the scope of the investigation and using the selected experimental method for this task involving the use of ion selective measurements, several trials have been completed to determine the most efficient measurement and application methods as well as the effectiveness of the calibration and efficiency of the instruments.

Trials for the experimental set up were performed using 250 mL of DI water and injections of 5% ammonia gas by using 50-mL and 2-L air tight syringes. The gas was transferred from the tank into a gas bag to facilitate the use of various syringe volumes and also to maintain the accuracy of the syringe extractions. Measurements of temperature and pH were taken prior to the addition of any gaseous ammonia in order to determine the changes after the injections. The pH of the DI water was recorded at 5.194 and the temperature was measured to be 20.5ºC. Additions of ammonia gas were made at 50 mL, 100 mL and 200 mL until a total volume of 1000 mL of gaseous ammonia had been injected into the DI water in the beaker.

The ammonia gas was injected into the water and mixed into solution by means of a continuous stirring motion provided by the attached stirrer. Measurements of the pH and the temperature were made after each addition as shown in Table 2-16 and the comparison of measurements is shown in the graph in Figure 2-38.

Table 2-16. Changes of DI Water pH and Temperature after 5% Ammonia Gas Addition

Volume of 5% ammonia gas added	*Total volume of 5% ammonia gas added*	*pH*	*Temp C*
0	0	5.194	20.5
50	50	5.039	20.5
50	100	5.028	20.5
100	200	5.333	20.4
200	400	7.969	20.3
200	600	8.672	20.3
200	800	9.049	20.3
200	1000	9.243	20.2

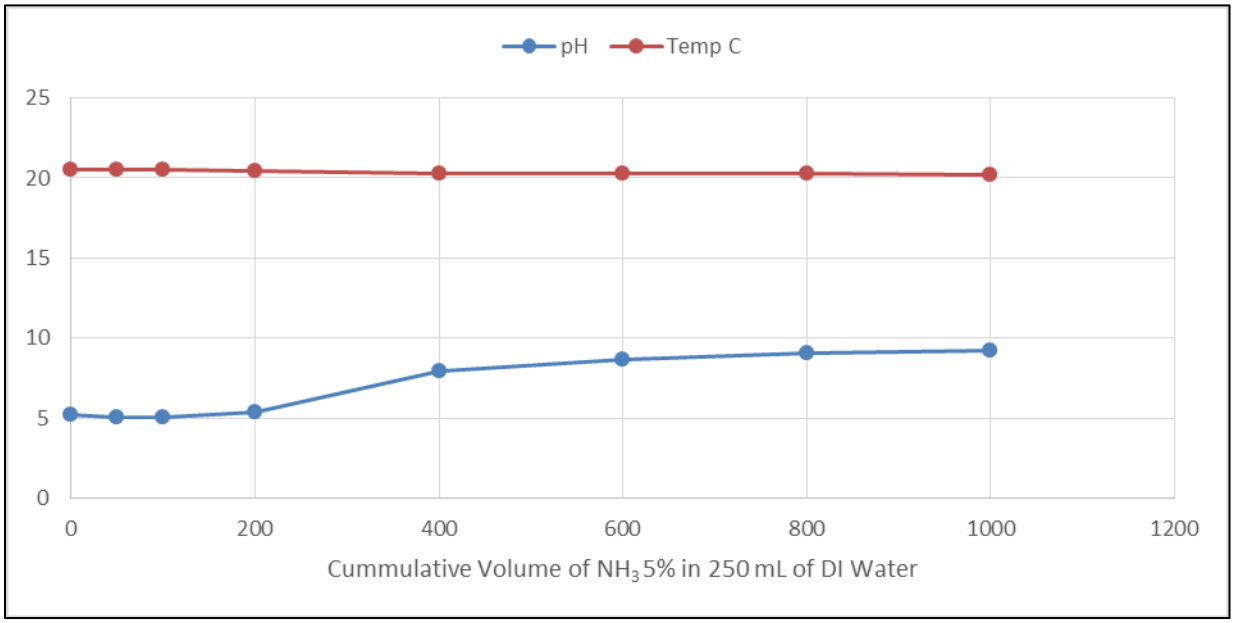


Figure 2-38. Changes of Di water pH and temperature as a result of 5% ammonia gas addition.

Observations of the data showed a pattern of pH decreasing with the first additions of gaseous ammonia; however, pH increased after the solution had been injected with 400 mL of ammonia gas. Also, the temperature began decreasing with each subsequent addition of ammonia; however, the decrease was not significant. Based on the preliminary testing, the results followed the expected behavior of the pH after addition of the gaseous ammonia.

Based on the evaluation of the experimental method and the instrument efficiency, several flaws were found regarding the use of some of the instruments. Injection of gaseous ammonia into the solution was found to be somewhat difficult, especially as the size of the syringe increased up to 2 L. This difficulty in manipulations using a 2-L syringe caused delays within the injection time

and may have altered the obtained results as well as the efficiency of the mixing of the solution. Further experiments will be done using injections into solution by a Khloen pump system. In addition, a larger beaker might be more efficient since it will allow for more space for the electrode holder as well as a larger volume of the initial DI water to create the solution.

Further testing will also be performed using a variety of volumes (50 mL, 75 mL, 100 mL, and 200 mL) of various ammonia gas dilutions from 100% ammonia. This phase of the experiment is set to begin within the first week of January. The addition of bicarbonate to the DI water solution will begin shortly after the ammonia experimental phase has been completed..

Milestones and Deliverables

The milestones and deliverables for Project 2 for FIU Year 5 are shown on the following table with status through December 31, 2014. Milestone (2014-P2-M5), "Obtain anaerobic facultative microorganisms, Shewanella sp., from PNNL and complete preparations to set up autunite leaching experiments," and milestone (2014-P2-M2), "Completion of literature review on physical mechanisms associated with the fate of ammonia after injections into subsurface" were completed on October 3 and October 31, respectively. Milestone (2014-P2-M3), "completion of sample preparation using a reduced amount of silica (50 mM)" was completed on November 7. Milestone (2014-P2-M4), "completion of preparation of a draft manuscript on the removal of uranium via ammonia gas injection method" was completed on December 15.

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	Completed	
	2014-P2-M3	Completion of sample preparation using a reduced amount of silica (50 mM)	11/07/14	Completed	
	2014-P2-M4	Complete preparation of a draft manuscript on the removal of uranium via ammonia gas injection method	12/15/14	Completed	
	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	On Target	
	Deliverable	Prepare a progress report on the solubility measurements via isopiestic method (subtask 1.1)	02/16/15	On Target	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	Completed	
	Deliverable	Progress report on microcosm studies prepared with SRS sediments augmented with molasses and sulfate (subtask 2.2)	01/30/15	On Target	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	On Target	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	Completed	

Work Plan for Next Quarter

- Subtask 1.2 Complete fabrication of a new isopiestic chamber with the lower head space and move all equipment to the radiation lab to start deliquescence experiments with uranium-bearing samples. Continue with multicomponent samples characterization studies to investigate the mineralogical and morphological characteristics of uranium-bearing solid-phases. Complete preparation of U(VI)- bearing samples. Submit a progress report on the task.

- Subtask 1.2: Complete comment resolution of the "imaging" manuscript after peer-review. Complete data analysis of the biodissolution experiments with autunite and initiate preparation of new experimental bottles to repeat some experimental steps.

- Subtask 2.2: Continue monitoring of evolution of samples pH amended with and without sulfate for ARCADIS work and conduct XRD analysis of subsamples. Submit a progress report on the task.

- Subtask 2.3: Continue sorption experiments with HA in the pH range between 4 and 9.

- Task 3: Continue testing of ammonia injection at 0 mM bicarbonate concentrations.

- Subtask 1.1: Submit a progress report on this task.
- Subtask 2.1: As part of the carry over scope, complete sample analysis to explore the effect of the higher humic acid concentrations up to 50 ppm. The experimental matrix is the same as for the study conducted last year using 10 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.

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 1.1: Work plan for experimental column studies

- The work plan for the experimental column studies was completed and submitted to SRS & HQ (EM-12) on 9/30/14. Positive feedback was provided by the SRNL task lead, Miles Denham, and approval given to continue with the progress of setting up the column study as outlined in the work plan.

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

- The first part of test plan involved performing calculations to determine the concentrations of humic acid, flow rates and column dimensions using a spreadsheet provided by SRNL (Brian Looney) to support this phase of the project.
    - Based on information from Brian Looney, the model is based on the Langmuir isotherm and is fully reversible (i.e., humate entering the column will exit without binding to sediment) and assumes that the column reaches equilibrium. Brian also indicated that there will be a deviation in the data that is obtained during the column studies, and the model can be updated based on the findings.
    - Procured sensors, chemicals and equipment needed for the experiments.

- Several scenarios with varying flow rates and concentrations were tested to find the best suitable parameters for the column experiments. Information obtained from these scenarios was discussed with Brian Looney and Miles Denham (SRNL).

- The column test scenarios were revised (Table 3-1) by varying flow rates (0.1 - 4.0 ml/min) and concentrations (5,000 - 20,000 mg/l) to determine the most suitable parameters for loading soil in the columns. Test results showed:
  - For batch #1, parameters 5,000 mg/l at 0.1 ml/min provided the best distribution of humate (Figure 3-1).
  - For batch #2, parameters 10,000 mg/l at 0.1 ml/min provided the best distribution of humate (Figure 3-2).

Table 3-1. Humate injection scenarios, flow rate, concentration and mass of humate required

Parameter	Batch 1	Batch 2
a (mg/kg)	1900	3000
b (l/mg)	0.003	0.004
Porosity	0.4	
Cell pore vol/time step	0.4	
Flow rate (ml/min)	0.1 - 4.0	
Conc (mg/L)	5000, 10000, 15000, 20000	

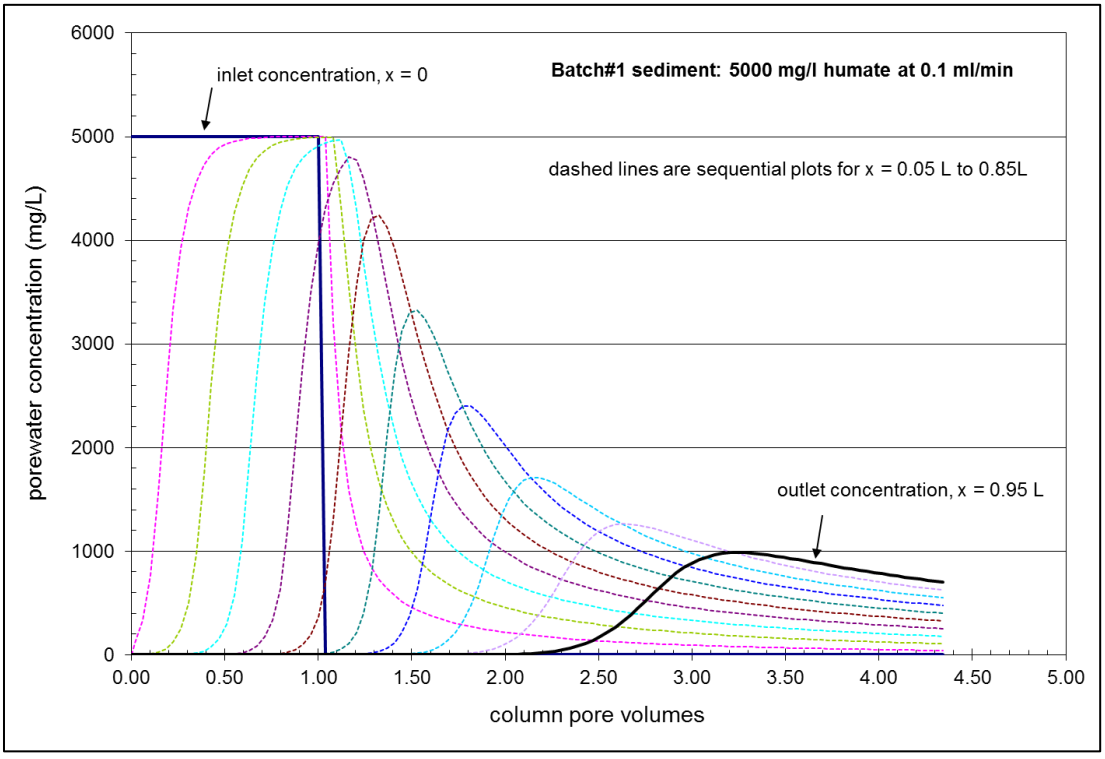


Figure 3-1. Humate injection scenario at 5000 mg/l and 0.1 ml/min for batch #1 sediment.

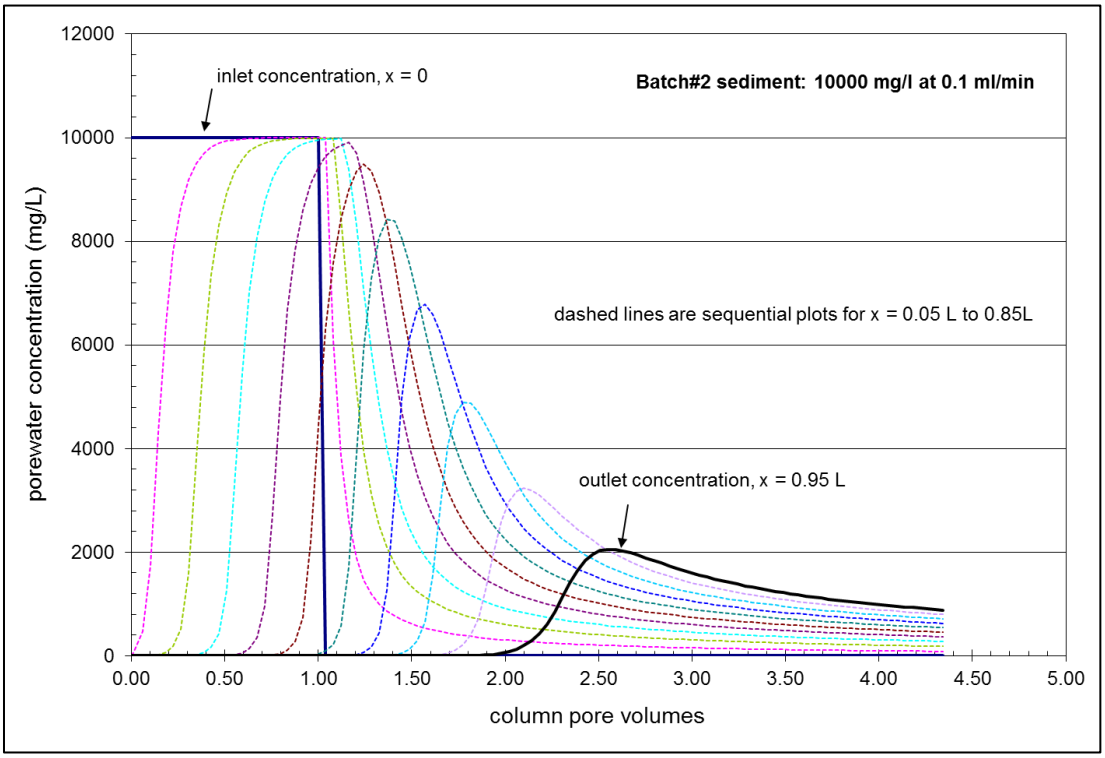


Figure 3-2. Humate injection scenario at 10000 mg/l and 0.1 ml/min for batch #2 sediment.

- Completed characterization of soil sediment (FAW-1: 70'-90') obtained from SRS. Triplicate soil samples sieved through 2-mm sieves were prepared to measure soil bulk density, particle density, porosity and soil pH.
    - The bulk density of soil was gravimetrically determined using an uncompact volume and oven-dried mass. The bulk density was calculated with the following equation:

$$Bulk\ density\ \left(\frac{g}{cm^3}\right) = \frac{Oven\ dry\ soil\ weight}{Volume\ of\ soil}$$

	Samples		
	1	**2**	**3**
Empty beaker weight (g)	29.2168	29.6607	29.8252
Volume of soil (cm^3)	50.0000	51.0000	50.0000
Oven dry soil + beaker weight (g)	100.3792	97.759	97.5736
Oven dry soil weight (g)	71.1624	68.0983	67.7484
Bulk density (g/cm^3)	1.4232	1.3353	1.3550
Average Bulk density (g/cm^3)	1.3712		

    - The particle density, ρ_p, was determined for the soil using the equation:

$$\rho_p = \frac{\rho_w\ (W_s - W_a)}{[(W_s - W_a) - (W_{sw} - W_w)]}$$

where:
ρ_w = Density of water in grams per cubic centimeter at observed temperature
W_s = Weight of volumetric flask plus soil
W_a = Weight of empty flask
W_{sw} = Weight of flask filled with soil and water slurry
W_w = Weight of flask filled with water at observed temperature

	Samples		
	1	**2**	**3**
Weight of empty flask (g)	19.2526	19.1696	19.2292
Weight of air dried soil (g)	12.5016	12.5022	12.5024
Weight of flask+soil (g)	31.7542	31.6718	31.7316
Weight of flask+soil and water slurry (g)	51.9144	51.7707	51.8783
Weight of flask+water (g)	44.1354	44.0885	44.133
Temperature (Celsius)	24.0000	23.5000	24.0000
Density of water (g/cm³)	0.9973	0.9974	0.9973
Particle density (g/cm³)	2.6400	2.5871	2.6211
Average particle density (g/cm³)	2.6161		

- The total porosity, Pt, of the samples was determined using the particle density and dry bulk density previously calculated in the following formula:

$$Pt = 1 - \frac{\rho_b}{\rho_p}$$

	Sample		
	1	**2**	**3**
Total porosity	0.4609	0.4839	0.4830
Average total porosity	0.4759		

- The soil sample pH in a 1:1 soil:water suspension was determined. The pH of the distilled water was 5.48.

	Sample		
	1	**2**	**3**
Weight of soil (g)	10.0083	10.015	10.0227
pH	5.84	5.88	5.88
Average pH	5.87		

- Glass columns from ACE Glass Inc. were considered for the column experiments and multiple size options are available. Consideration was given to the use of 25 mm x 300 mm or 25 mm x 450 mm columns. Alternative column types, such as acrylic columns, that may be more cost effective, were also researched. After discussion with Miles

Denham and Brian Looney from SRNL, it was decided that 1" (internal diameter) x 12" (length) columns will be purchased for the experiments.

- The bromide electrode was received and is being calibrated and preliminary testing will be conducted for reliability of measurement.
- Miles suggested that XRF analysis be conducted on the soil samples after the experiments have been completed for aluminum and iron concentrations.
- 25 x 300 mm glass chromatograph columns with PTFE adapters were ordered and received.
- Approximately 3 kg of soil collected from FAW-1 at a depth of 60'-70' was shipped from SRS to FIU. Characterization of this soil was completed. The objective was to determine the porosity through bulk density and particle density analysis, as well the pHw of the soil. The sediment was sieved prior to experiment to obtain particle sizes less than 2 mm. This information will be used for future calculations in the column experiments that will be performed. The procedures and results of the soil characterization are as follows:

  - **Bulk Density Analysis**

    The bulk density of soil was gravimetrically determined using an uncompact volume and oven dried mass. The bulk density, ρ_b, was calculated with the following equation:

$$\text{Bulk density } \left(\frac{\text{g}}{\text{cm}^3}\right) = \frac{\text{Oven dry soil weight}}{\text{Volume of soil}}$$

	Sample		
	1	**2**	**3**
Empty beaker weight (g)	28.5273	31.9488	29.5372
Soil Volume (cm^3)	50	50	50
Oven dry soil + beaker weight (g)	95.9204	99.7194	94.5193
Oven dry soil weight (g)	67.3931	67.7706	64.9821
Bulk density (g/cm^3)	1.3479	1.3554	1.2996
Average Bulk density (g/cm^3)		1.3343	

  - **Particle Density Analysis**

    The particle density, ρ_p, was determined for the soil using the equation:

$$\rho_p = \frac{\rho_w\,(W_s - W_a)}{[(W_s - W_a) - (W_{sw} - W_w)]}$$

    where:

    ρ_w = Density of water in grams per cubic centimeter at observed temperature
    W_s = Weight of volumetric flask plus soil

W_a = Weight of empty flask
W_{sw} = Weight of flask filled with soil and water slurry
W_w = Weight of flask filled with water at observed temperature

	Sample		
	1	**2**	**3**
Weight of empty flask (g)	19.2513	19.1701	19.2293
Weight of flask+soil	31.7364	31.6689	31.7292
Weight of flask+soil and water slurry	51.9231	51.8301	51.9312
Weight of flask+water	44.1457	44.0478	44.1403
Temperature (Celsius)	24	24	24
Density of water (g/cm³)	0.9973	0.9973	0.9973
Particle density (g/cm³)	2.6449	2.6429	2.6473
Average particle density (g/cm³)		2.6450	

- **Porosity**

The total porosity, Pt, of the samples was determined using the particle density and dry bulk density in the following formula:

$$Pt = 1 - \frac{\rho_b}{\rho_p}$$

	Sample		
	1	**2**	**3**
Total porosity	0.4904	0.4871	0.5091
Average total porosity		0.4955	

- **Soil pHw**

The soil sample pH in a 1:1 soil: water suspension was determined.

	Sample		
	1	**2**	**3**
Weight of soil (g)	10.0325	10.0269	10.0044
pH	4.09	4.06	4.04
Average pH		4.06	

- **Comparing Previous Results**

Soil characterization was previously completed for FAW-1 70'-90' soil using the same procedure and equipment, noting there was a slight difference in color. At this

depth, the average bulk density and particle density were 1.3712 and 2.6161, respectively. The average total porosity was determined to be 0.4759. Comparing this value and the 0.4955 porosity of FAW-1 60'-70' soil, the results are similar. A difference that was evident between the depth levels was the measured pH. For the 70'-90' soil, the average pH was 5.87, whereas the 60'-70' soil had an average pH of 4.06.

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

- The GIS data provided by SRNL has been imported into ArcGIS and reviewed to become familiar with the layout of the Savannah River Site and the logistics with respect to where Tims Branch flows relative to the A/M area (Figure 3-3).

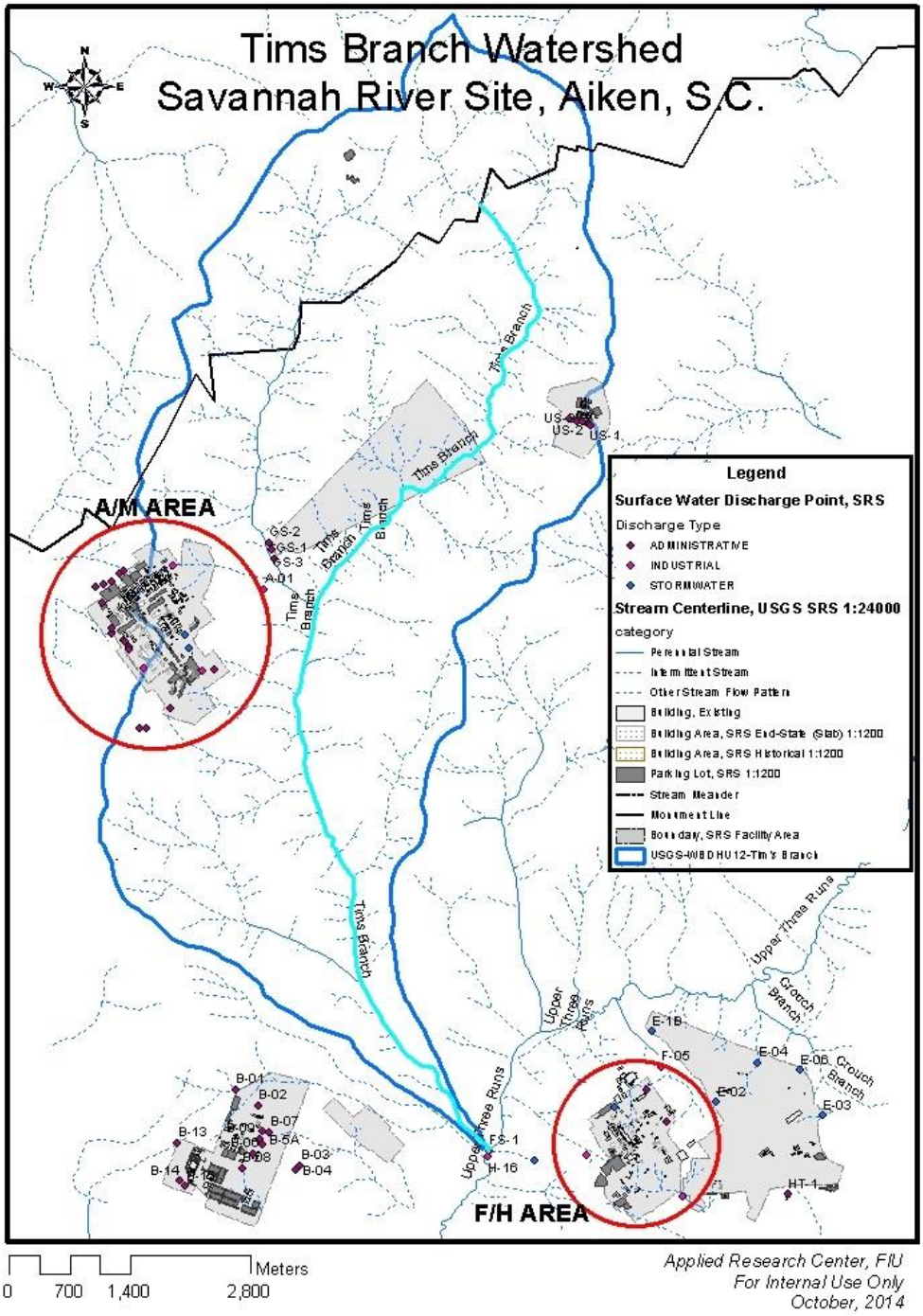


Figure 3-3. Map of Tims Branch Watershed created during preliminary GIS data review.

- After consultation with the SRNL lead for this task regarding the model domain, which may result in exclusion of a part of Tims Branch that runs offsite SRS, it was left to FIU to determine the best approach, however suggestions were made to:
    - Determine a method of approximating the contributions made by the tributaries offsite with respect to flow and transport, or
    - Ensure that it is taken into account in the study that these tributaries have been excluded.

- ArcGIS geoprocessing tools were therefore used on the GIS data provided by SRNL to create two model domains. One set would encompass any relevant data within the entire Tims Branch watershed (including the portion off-site SRS) and the other set would only contain data in the Tims Branch watershed that falls within the SRS boundary. This will provide the option of using either domain for the hydrological model or perhaps running the model with both domains to see if there is any significant difference in results.
- Below is a snapshot of the model domain that comprises the portion of the Tims Branch watershed that falls within the SRS boundary (essentially a subset of the data provided). The model domain created is the green shaded area in Figure 3-4.

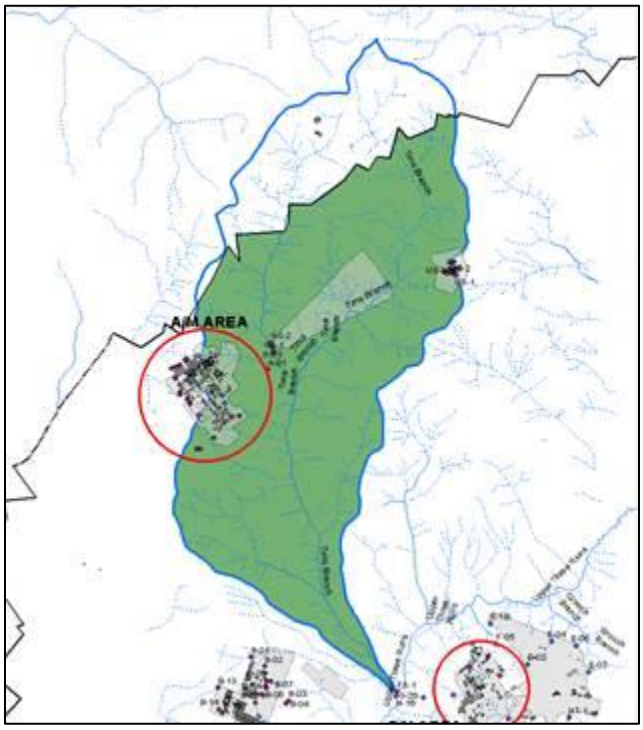


Figure 3-4. Model domain.

- A process flow model was developed by Natalia Duque (DOE Fellow) to document the process of how this was done for reporting purposes (Figure 3-5).

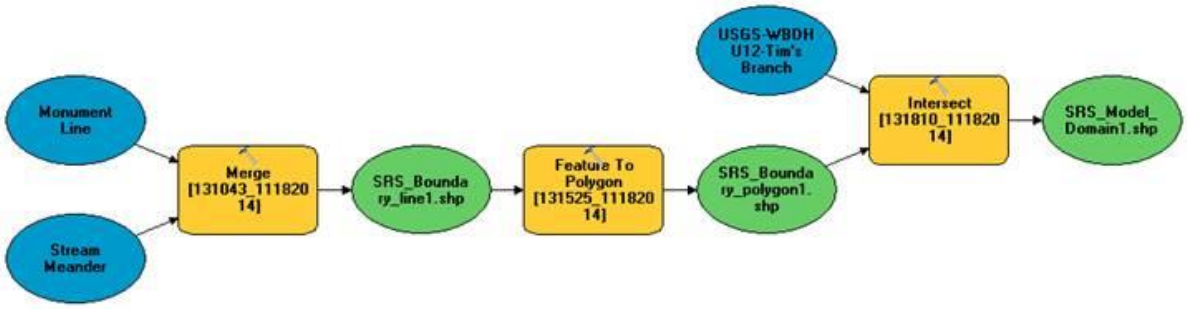


Figure 3-5. ArcGIS ModelBuilder process flow diagram.

- Another process flow model was also created to automate the process of clipping the relevant GIS files to be used in the hydrological model to the specified model domains so that the data can be input into the MIKE SHE/11 model.
- Some of the clipped data has been added to MIKE SHE to begin preliminary development of the hydrological model. Two separate models are being developed, one for each model domain previously described.
- A 3D representation of the SRS A/M area and the underlying VOC contaminant plume within the Tims Branch watershed was also created using the ArcGIS ArcScene interface.

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

- Progress on the modeling component of this task was delayed while a new task lead was being sought. SRNL meanwhile assisted FIU with the acquisition of relevant GIS data to support this task.
- Dr. Mehrnoosh Mahmoudi (Noosha), ARC's newly hired post-doctoral staff member, and FIU faculty member, Dr. Omar Abdul-Aziz, joined the ARC Project 3 team in December and have initiated work on the surface/sub-surface hydrological modeling research, beginning with a review of the literature provided by SRNL as well as available online databases for any other relevant documents that can assist in developing the site conceptual model.
- The literature review has suggested that there are no prior or existing hydrology and transport modeling/simulation efforts for the area of interest within the Tims Branch watershed. No literature pertaining to surface water/groundwater modeling attempts has been found.
- Preliminary development of a conceptual model of the Tims Branch watershed is also underway. The conceptual model of combined processes and input parameters being developed illustrates the systematic sequence of mechanisms and parameters involved in the modeling process.
- The first step toward model development consists of developing the surface water model that includes all the input parameters as shown in the conceptual model. GIS data provided by SRNL for the Tims Branch watershed has been clipped, preprocessed and input into the MIKE SHE hydrological model based on specified boundary conditions determined in coordination with the SRNL task lead.

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:

- FIU provided a 12-page data analysis report of 18 recovery wells that was sent to Ralph Nichols (SRNL) on October 15, 2014. In preparation for this report, FIU's review of the spreadsheets provided by SRNL revealed several data gaps.
- FIU communicated with the SRNL Sustainable Remediation task lead (Ralph Nichols) regarding the per well contaminant recovery and pumping data missing. FIU provided correlation of missing and outlier data from the 18 recovery wells with a goal of identifying the reason for outliers and to suggest corrected data for the Sustainable Remediation analysis.
- Additional reports were provided for FIU to review for the missing recovery well data. (Table D-23 was reviewed for detailed well reports between 1996-1998). Tables of the monthly average precipitation from 1982 through December 2012 were also provided by SRNL.
- FIU was able to locate a significant amount of missing data from the additional reports; however, some data is still missing. An updated document was prepared by FIU for SRNL identifying the still missing and questionable data for their review.
- FIU will focus the GSR or Sustainable Remediation analyses on wells 1-12 that are connected to the M1 air stripper.
    - A pilot air-stripper used onsite in 1985 was moved in 1986 and renamed the A2 air stripper. A2 has been shut down but is likely to restart as concentrations are rebounding since it was shut down. Wells 13-15 are on A2.
    - One year, SRS was negotiating its Part B permit and summary reports were not created that year. Round sheet reports will have the necessary data in them.
    - More analysis is required to determine if air stripping operations for 1982 – 1986 should be included in the analysis. Pumps and operations were on and off during those years but concentrations were very high for those years too. FIU needs to balance a huge effort to get the data with the return on investment or impact of the data on the sustainability analyses. (i.e., FIU needs to determine if the mass of TCE and PCE recovered would make the effort worthwhile.)
- Groundwater pump rates and total volume pumped were plotted along with PCE and TCE recovered/destroyed for each of 18 wells and for all combined (1987-2012).
- FIU initiated analysis of the pump power requirements and electrical energy consumed for 1987-2012. A plot of the monthly electric energy usage for 1987-2012 will be included in a baseline summary report due in February. This report will also include an analysis of pump efficiencies, pump replacements, electrical power used per month, etc.

- Contaminant recovery data provided:
    - Date (month)
    - Monthly average TCE and PCE concentration (µg/L)
    - Monthly pump operation times (hours)
    - Monthly average flowrates (gpm)
- Contaminant recovery calculations:
    - Mass recovery rates for TCE and PCE (g/min)
    - Recovered contaminant per month (kg/month)
    - Cumulative recovered contaminant (kg of contaminant)
- Formulas used in calculations:
    - Mass recovery rate $(\dot{m})$ for each time interval (Δt):

$$\dot{m}_{rw} = \bar{C}_{rw} * \bar{Q}_{rw}$$

Where:

$\bar{C}_{rw}$ = Average contaminant concentration recovery well for time interval

$\bar{Q}_{rw}$ = Average flowrate in recovery well for time interval

- Recovered contaminant per month:

$$Amount\ of\ recovered\ contaminant = \dot{m}\ * minutes\ in\ a\ month$$

- Figures 3-6 and 3-7 show the amount of TCE removed for February 1987 and February 2011, respectively. These show how the contaminant recovery has changed over 25 years.

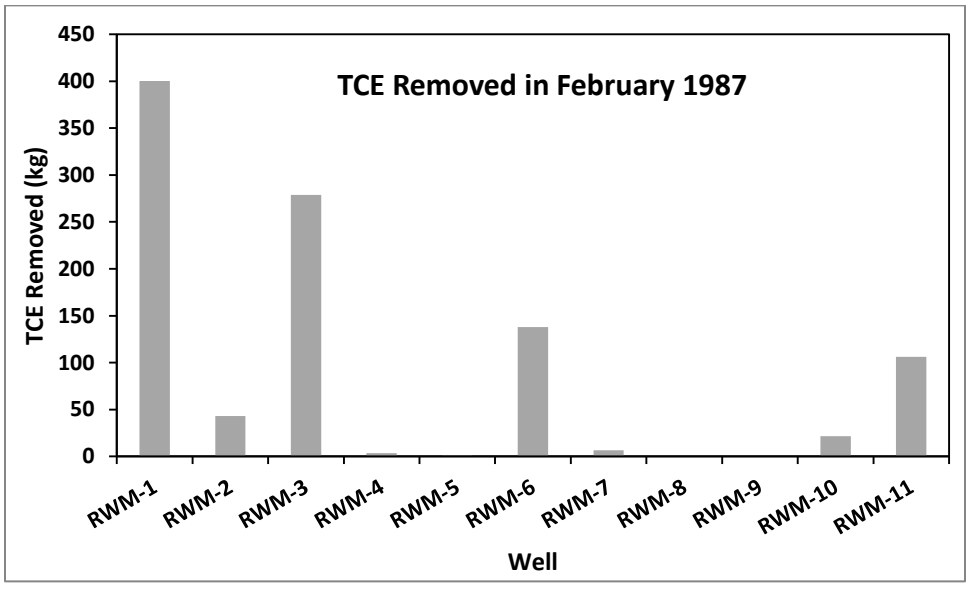


Figure 3-6. TCE removed in February 1987.

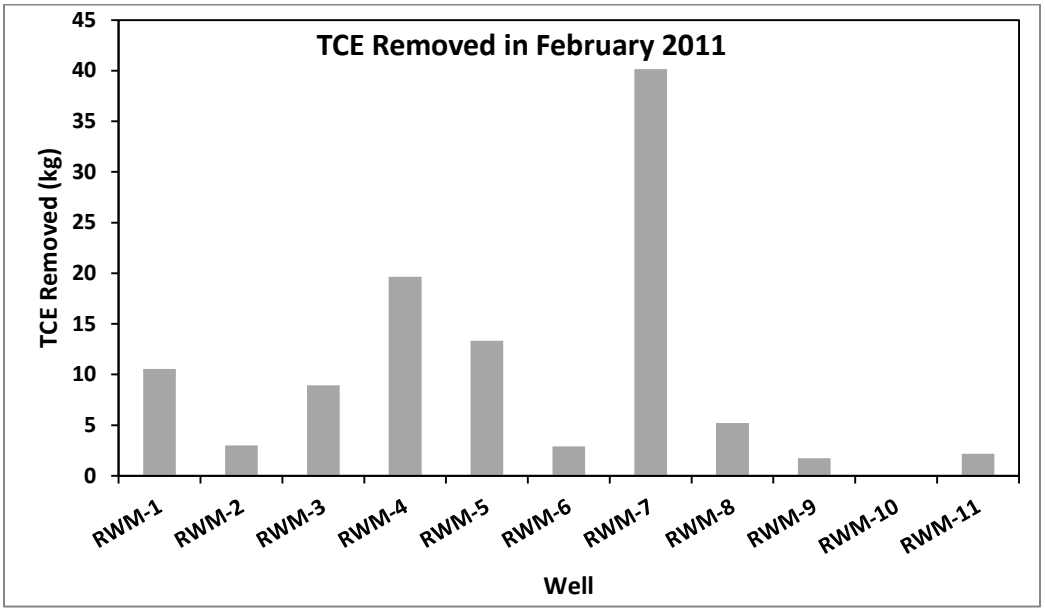


Figure 3-7. TCE removed in February 2011.

- Tables 3-2 and 3-3 provide an excerpt of the data for the sustainability analysis for RWM-1 for years 1987 and 2011, respectively.

Table 3-2. Data for Sustainability Analysis (RWM-1, 1987)

Date	TCE concentration (ug/L)	PCE concentration (ug/L)	Operation (hours)	Flowrate (gpm)	Flowrate (L/min)	TCE Mass Recovery Rate (ug/min)	TCE Mass Recovery Rate (g/min)	PCE Mass Recovery Rate (ug/min)	PCE Mass Recovery Rate (g/min)	TCE (Kg)/mo.	TCE accum (Kg)	PCE (Kg)/mo.	PCE accum (Kg)
Jan-87	62,200	25,800		37	140.098	8.71E+06	8.714	3.61E+06	3.615	388.9984703	388.9984703	161.3530632	161.3530632
Feb-87	77,100	30,000		34	128.739	9.93E+06	9.926	3.86E+06	3.862	400.2076789	789.2061492	155.7228323	317.0758955
Mar-87	75,800	20,300		30	113.593	8.61E+06	8.610	2.31E+06	2.306	384.3671337	1173.573283	102.9373722	420.0132677
Apr-87	70,900	21,200		30	113.593	8.05E+06	8.054	2.41E+06	2.408	347.9227565	1521.496039	104.0333207	524.0465884
May-87	69,000	25,600		27	102.234	7.05E+06	7.054	2.62E+06	2.617	314.8970844	1836.393124	116.8313821	640.8779705
Jun-87	70,300	25,900		27	102.234	7.19E+06	7.187	2.65E+06	2.648	310.4805755	2146.873699	114.3875805	755.2655509
Jul-87	61,800	24,800		21	79.515	4.91E+06	4.914	1.97E+06	1.972	219.3630897	2366.236789	88.02920106	843.294752
Aug-87	55,700	19,500		15	56.797	3.16E+06	3.164	1.11E+06	1.108	141.2219614	2507.45875	49.4403635	892.7351155
Sep-87	66,900	24,100		20	75.729	5.07E+06	5.066	1.83E+06	1.825	218.8625521	2726.321303	78.84286255	971.577978
Oct-87	65,280	22,845		33	124.953	8.16E+06	8.157	2.85E+06	2.855	364.1244741	3090.445777	127.4268323	1099.00481
Nov-87	59,500	20,600		34	128.739	7.66E+06	7.660	2.65E+06	2.652	330.9110186	3421.356795	114.5675123	1213.572323
Dec-87	52,200	19,800		34	128.739	6.72E+06	6.720	2.55E+06	2.549	299.9889133	3721.345708	113.7888981	1327.361221

Table 3-3. Data for Sustainability Analysis (RWM-1, 2011)

Date	TCE concentration (ug/L)	PCE concentration (ug/L)	Operation (hours)	Flowrate (gpm)	Flowrate (L/min)	TCE Mass Recovery Rate (ug/min)	TCE Mass Recovery Rate (g/min)	PCE Mass Recovery Rate (ug/min)	PCE Mass Recovery Rate (g/min)	TCE (Kg)/mo.	TCE accum (Kg)	PCE (Kg)/mo.	PCE accum (Kg)
Jan-11	12,000	27,000	593	9	35.214	4.23E+05	0.423	9.51E+05	0.951	18.86340023	22208.70102	42.44265051	14679.04098
Feb-11	13,000	23,000	667	10	36.350	4.73E+05	0.473	8.36E+05	0.836	19.05314654	22227.75416	33.7094131	14712.7504
Mar-11	10,000	24,000	668	10	37.864	3.79E+05	0.379	9.09E+05	0.909	16.90268838	22244.65685	40.5664521	14753.31685
Apr-11	11,000	27,000	648	11	41.272	4.54E+05	0.454	1.11E+06	1.114	19.612571	22264.26942	48.13994699	14801.4568
May-11	9,300	24,000	740	11	40.515	3.77E+05	0.377	9.72E+05	0.972	16.8198652	22281.08929	43.40610375	14844.8629
Jun-11	10,000	24,000	720	11	42.408	4.24E+05	0.424	1.02E+06	1.018	18.32033321	22299.40962	43.9687997	14888.8317
Jul-11	10,000	24,000	741	9	33.321	3.33E+05	0.333	8.00E+05	0.800	14.87436577	22314.28399	35.69847785	14924.53018
Aug-11	5,200	41,000	694	10	37.864	1.97E+05	0.197	1.55E+06	1.552	8.789397955	22323.07339	69.30102234	14993.8312
Sep-11	10,000	25,000	716	10	39.379	3.94E+05	0.394	9.84E+05	0.984	17.01173798	22340.08512	42.52934495	15036.36055
Oct-11	11,700	27,900	743	10	36.729	4.30E+05	0.430	1.02E+06	1.025	19.18286104	22359.26798	45.74374555	15082.10429
Nov-11	11,600	23,300	720	10	37.864	4.39E+05	0.439	8.82E+05	0.882	18.97463082	22378.24262	38.11283605	15120.21713
Dec-11	12,400	24,400	742	9	35.593	4.41E+05	0.441	8.68E+05	0.868	19.70177357	22397.94439	38.76800606	15158.98513

- FIU completed review of the SRS documents, locating most missing data as well as collecting information on dates when some wells and the air stripper were not operational.
- Using all of the data collected to date, plots were made of the monthly recovery of TCE and PCE in the Recovery Wells RWM 1-12 from 1987 – 2012. In addition, the cumulative recovery in each of these wells from their installation and use was overlaid upon the monthly recovery plots.
- The monthly recovery of TCE and PCE in the Recovery Wells RWM 1-12 was compared against the monthly rainfall to identify how high rain months and low rain months affected recovery.
    - The graphed results were sent to Ralph Nichols, Brian Looney, and Carol Eddy-Dilek for review. Sample graphs for RWM-1 and the monthly rainfall at the site are shown in the following two figures.
    - The results of the analysis of some wells display exponential decrease in kg recovered each month over the years, some wells show linear decreases and still others show the same recovery rate over the past 20-25 years.
    - The effects of *in situ* thermal treatment of the vadose zone greatly increased the soil temperature and increased the recovery rates in nearby wells with significant remaining contamination remaining. The timing of the movement of TCE and PCE plumes across the 12 recovery wells near the heated zone is being analyzed for correlation to spatial location of the wells and the movement of the plumes in the vadose zone.
    - A paper was submitted to Waste Management describing the analysis of contaminant recovery for recovery wells 1-12 for 1987-2012.
    - Finally, the plots allow one to see trends and some additional questionable data. Overall, the remaining missing data and data errors can be seen from the plots to not contribute significantly to the overall recovery per month currently or the accumulated mass over the operational life of the wells.

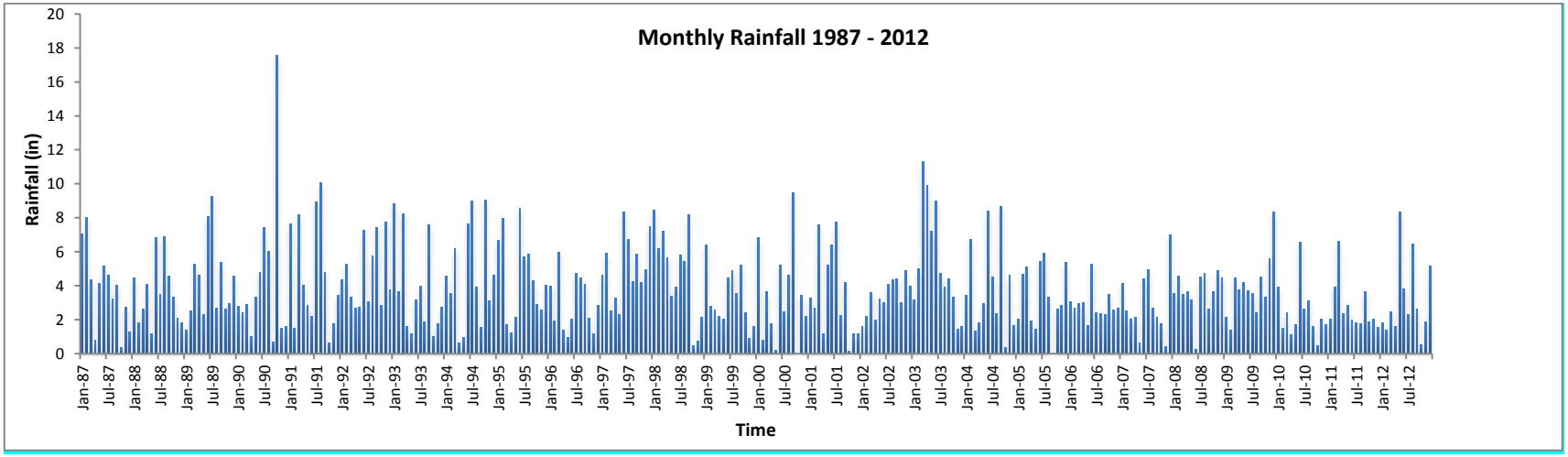


Figure 3-8. Sample monthly rainfall graph for 1987 to 2012.

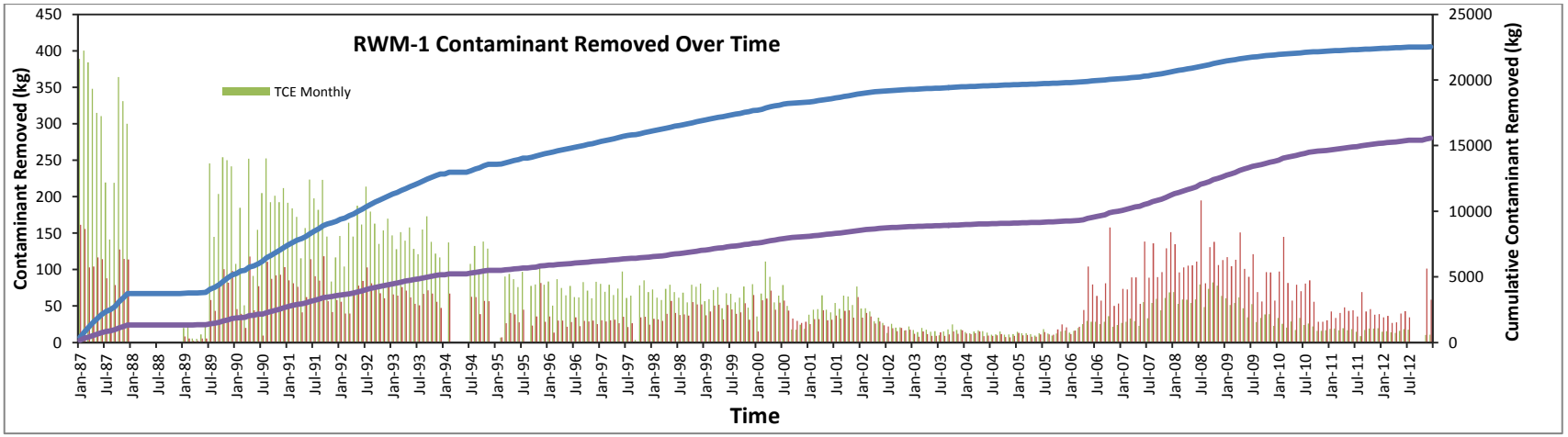


Figure 3-9. Sample graph showing amount of contaminant removed over time for RWM-1.

- FIU has discussed the results of graphs of monthly and cumulative TCE and PCE removal with Ralph Nichols, SRNL, Ralph will:
    - Prioritize remaining missing data blocks and identify any to continue to investigate and will specify how FIU should treat all remaining missing data (e.g., assume pumps and recovery and stripping from these wells were offline for these missing data periods)
    - Send FIU info on which wells are connected to the 2 steam flooding operations carried out
    - Comment on the decrease in TCE and increase in PCE in some of the recovery wells
    - Identify and send any documents specifically focused upon the air stripper design, maintenance, and energy usage
- Yoel Rotterman (DOE Fellow), a mechanical engineering student, has joined this task. He has begun analysis of the air stripper design, pumping and energy usage to:
    - Plot use of energy per kg of contaminant (TCE+PCE) removed from 1987 – 2012.
    - Understand design and operation of SRS's M1 air stripper and provide analysis and optimization of the air stripper design and operation (e.g., cost effectiveness of system upgrades or other modifications compared to system replacement).
- Preparation of a slide presentation for an oral presentation and a poster both for Waste Management 2015 is ongoing and will be completed in January.

Milestones and Deliverables

- The milestones and deliverables for Project 3 for FIU Year 4 are shown on the following table with status through December 31, 2014. Milestone 2014-P3-M2 (completion of literature review for Subtask 2.2), Milestone 2014-P3-M3 (development of a preliminary site conceptual model of Tims Branch for Subtask 2.2), and a related deliverable (literature review summary) were originally due 12/30/14. However, after discussion with SRNL site contacts and notification of DOE HQ, these have been reforecast to March 31, 2015 due to the departure of Dr. Tachiev and Amy Cook which has delayed the initiation and progress on some of the Project 3 tasks. Dr. Mehrnoosh Mahmoudi (Noosha), ARC's newly hired post-doctoral staff member, and FIU faculty member, Dr. Omar Abdul-Aziz, joined the ARC Project 3 team in December and were introduced during the DOE-ARC Project 3 bi-weekly conference call. They will be supporting the surface/sub-surface hydrological modeling research and with their assistance it is expected that FIU will be able to meet the new milestone dates. Two (2) technical papers were submitted to WM15 and will be presented at the conference in March 2015.

FIU Year 5 Milestones and Deliverables for Project 3

Task	Milestone/Deliverable	Description	Due Date	Status	OSTI
Task 1: Modeling of the migration	2014-P3-M1	Completion of work plan for experimental	9/30/14	Completed	

and distribution of natural organic matter injected into subsurface systems		column studies (Subtask 1.1)			
	Deliverable	Work plan for experimental column studies (Subtask 1.1)	9/30/14	Completed	
	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	Reforecasted	
	Deliverable	Literature review summary (Subtask 2.2)	12/30/14 Reforecast to 3/31/15	Reforecasted	
	2014-P3-M3	Development of preliminary site conceptual model of Tims Branch (Subtask 2.2)	12/30/14 Reforecast to 3/31/15	Reforecasted	
	Deliverable	Technical Report for Task 2	6/10/15	On Target	
Task 3: Sustainability Plan for the A/M Area Groundwater Remediation System	2014-P3-M4	Completion of Baseline Analysis (Subtask 3.1)	2/27/15	On Target	
	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	Completed	
	Deliverable	Two (2) abstract submissions to WM15	8/15/14	Completed	
	2014-P3-M5	SRS site visit and meeting	8/5/14	Completed	
	2014-P3-M6	Meeting and presentation of project progress at SRS	3/18/15	On Target	

**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

- Present two (2) technical papers at WM15 in March 2015.
- Prepare a presentation of the project progress and accomplishments for SRS/SRNL and DOE-HQ EM-12/13 (Mid-Year Review) in March 2015 (date subject to change pending availability of SRS/SRNL and DOE-HQ EM-12/13 personnel).

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

- Complete bromide sensor calibration and test the performance (reliability & reproducibility) of the sensor.
- Prepare a mockup column to test the experimental setup. This, once successful, will be eventually expanded to 4 columns for completion of a bromide tracer test, and the humic acid sorption and desorption experiments.

Task 2: Surface Water Modeling of Tims Branch

- Milestone 2014-P3-M2, Completion of literature review (Subtask 2.2) and its associated deliverable, Literature review summary, both originally due on 12/30/14, have been reforecast to 3/31/15.
- Milestone 2014-P3-M3, Development of preliminary site conceptual model of Tims Branch (Subtask 2.2) was also due on 12/30/14 and has been reforecast to 3/31/15.
- The aforementioned milestones and deliverables were reforecast to provide adequate time for the new FIU-ARC task leads replacing Dr. Georgio Tachiev and Amy Cook to complete the tasks.
- The path forward for next quarter will be to complete and summarize the literature review and finalize the Tims Branch conceptual model with input and guidance from the SRNL task lead, Brian Looney, by 3/31/15.
- Primary focus in the coming weeks will be on refinement of the preliminary conceptual model of the Tims Branch watershed and preliminary development of a hydrological model using MIKE SHE/11.
- Conversations were held between FIU and Brian Looney at SRNL to determine a path forward for the modeling component of this task now that Noosha and Omar have joined the Project 3 team. It was suggested by Brian Looney to contact the Savannah River Ecology Laboratory to determine if they have relevant data to assist in this project and to hold discussions with subject matter experts there who may also be able to guide us on Task 2 modeling efforts. FIU is to follow up with Brian for contact information in this regard.

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

- DOE Fellow Yoel Rotterman will continue to study the design of the air stripper technology and the pumping operations to identify design modifications for improvements to energy efficiency and overall effectiveness. FIU will discuss modifications under consideration with SRNL during the month of February 2015.

- A baseline summary report for this task is on schedule for completion by the February 27 due date.
- FIU will identify applied remediation publications to publish a paper on the proposed mechanical designs and projected system improvements.
- FIU will develop both a presentation and a student poster for Waste Management Symposium 2015 for this task. A paper was submitted in December 2014.

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

Mr. Andrew Szilagyi, Director of the Office of D&D and Facility Engineering (DOE EM-13) visited FIU in November to attend the Induction Ceremony for the new DOE Fellows, Class of 2014. During his visit, FIU presented the Project 4 research tasks, progress, and proposed scope for the DOE-FIU Cooperative Agreement renewal.

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 also completed drafting a paper on WIMS and submitted it to the Waste Management 2015 Symposium (milestone 2014-P4-1.2).

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

Task 2 Overview

This task provides direct support to DOE EM for D&D technology innovation, development, evaluation and deployment. For FIU 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.

Task 2 Quarterly Progress

On November 12, FIU provided a presentation brief to Mr. Andrew Szilagyi (DOE EM-13, Office of D&D/Facility Engineering) on the D&D subtasks under this project, including the contamination control decision model, thin films, incombustible fixatives, and advanced fogging. Based on feedback received, all subtasks were aligned with guidance received from DOE-EM, and compliment several strategic initiatives being pursued in other areas. Input was incorporated and the updated brief was forwarded to SRNL and INL lead POCs as well.

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. A selection of these search parameters is being used to develop a preliminary decision model to better guide the product end users in the selection of the appropriate products. FIU will incorporate DOE site feedback and additional search parameters into the decision model to begin development of a more robust decision model.

FIU conducted bi-monthly phone calls with Michael Serrato (SRNL) during this quarter to discuss task progress. FIU worked on developing the web-based fixative model application. A design has been selected for the graphical user interface (GUI) that will be displayed and the functionality of each item has been mapped out. The steps which the user would take to decide on a product to use for the specific D&D application are being taken into consideration in order to facilitate the use of the application. All the products will be categorized by the criteria selected to be displayed on the GUI; additional criteria can be added in the future. The web-based application will be made available through the D&D Knowledge Management Information Tool portal (Figure 1).

The contamination control product list is continuously being updated by contacting new potential vendors and requesting the required information about their decontamination products.

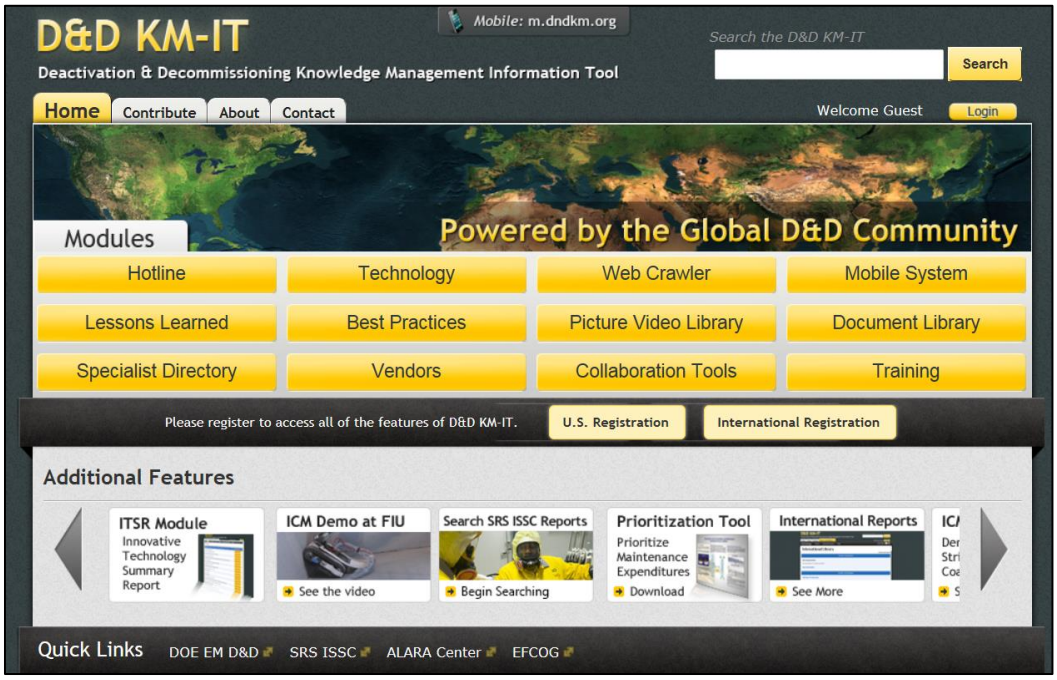
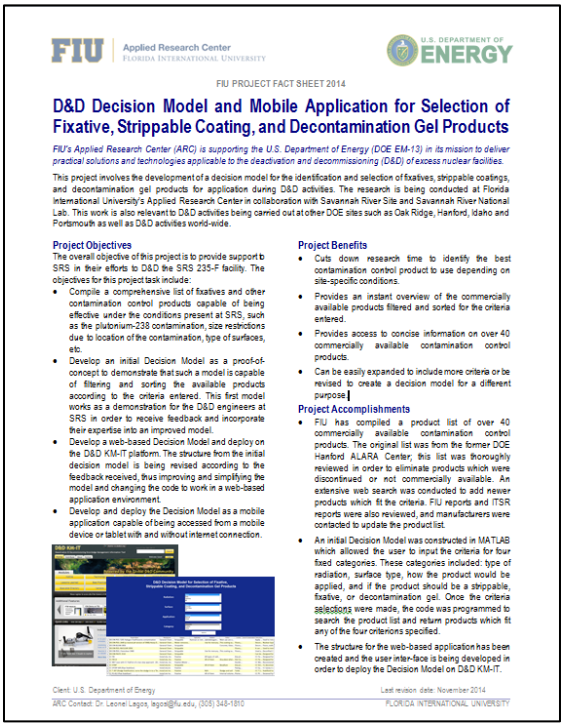


Figure 4-1. D&D KM-IT will host the web-based fixative decision model application.

An ARC Fact Sheet was developed for the Contamination Control Decision Model task and provided to DOE EM-13 in November. This fact sheet is shown in Figure 4-1.



FIU Applied Research Center, Florida International University — U.S. Department of Energy

FIU PROJECT FACT SHEET 2014

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

FIU's Applied Research Center (ARC) is supporting the U.S. Department of Energy (DOE EM-13) in its mission to deliver practical solutions and technologies applicable to the deactivation and decommissioning (D&D) of excess nuclear facilities.

This project involves the development of a decision model for the identification and selection of fixatives, strippable coatings, and decontamination gel products for application during D&D activities. The research is being conducted at Florida International University's Applied Research Center in collaboration with Savannah River Site and Savannah River National Lab. This work is also relevant to D&D activities being carried out at other DOE sites such as Oak Ridge, Hanford, Idaho and Portsmouth as well as D&D activities world-wide.

Project Objectives

The overall objective of this project is to provide support to SRS in their efforts to D&D the SRS 235-F facility. The objectives for this project task include:

- Compile a comprehensive list of fixatives and other contamination control products capable of being effective under the conditions present at SRS, such as the plutonium-238 contamination, size restrictions due to location of the contamination, type of surfaces, etc.
- Develop an initial Decision Model as a proof-of-concept to demonstrate that such a model is capable of filtering and sorting the available products according to the criteria entered. This first model works as a demonstration for the D&D engineers at SRS in order to receive feedback and incorporate their expertise into an improved model.
- Develop a web-based Decision Model and deploy on the D&D KM-IT platform. The structure from the initial decision model is being revised according to the feedback received, thus improving and simplifying the model and changing the code to work in a web-based application environment.
- Develop and deploy the Decision Model as a mobile application capable of being accessed from a mobile device or tablet with and without internet connection.

Project Benefits

- Cuts down research time to identify the best contamination control product to use depending on site-specific conditions.
- Provides an instant overview of the commercially available products filtered and sorted for the criteria entered.
- Provides access to concise information on over 40 commercially available contamination control products.
- Can be easily expanded to include more criteria or be revised to create a decision model for a different purpose.

Project Accomplishments

- FIU has compiled a product list of over 40 commercially available contamination control products. The original list was from the former DOE Hanford ALARA Center; this list was thoroughly reviewed in order to eliminate products which were discontinued or not commercially available. An extensive web search was conducted to add newer products which fit the criteria. FIU reports and ITSR reports were also reviewed, and manufacturers were contacted to update the product list.
- An initial Decision Model was constructed in MATLAB which allowed the user to input the criteria for four fixed categories. These categories included: type of radiation, surface type, how the product would be applied, and if the product should be a strippable, fixative, or decontamination gel. Once the criteria selections were made, the code was programmed to search the product list and return products which fit any of the four criterions specified.
- The structure for the web-based application has been created and the user inter-face is being developed in order to deploy the Decision Model on D&D KM-IT.

Client: U.S. Department of Energy — Last revision date: November 2014

ARC Contact: Dr. Leonel Lagos, lagos@fiu.edu, (305) 348-1810 — FLORIDA INTERNATIONAL UNIVERSITY

Figure 4-2. ARC Fact Sheet for D&D Decision Model for selection of fixative, strippable coating, and decontamination gel products

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

FIU conducted bimonthly phone calls with Michael Serrato (SRNL) during this quarter to continue discussions on the refinement of the scope under this subtask, the development of a program of action and associated milestones. According to the site POC, this topic is gaining additional interest at the site. FIU will perform research into organic semiconductor thin films for polymer interface and electrostatic applications to identify suitable carbon-based materials to meet the site needs, including a low temperature technique, high flexibility, and low cost.

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

DOE requested that EFCOG restructure the organization in order to maximize the effectiveness of the Working Groups and promote greater accountability. As part of this restructuring, several Working Groups were sunsetted, including the D&D/FE Working Group. The remaining EFCOG Working Groups are:

- Project Management
- Waste Management
- Safeguards & Security
- Safety

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. 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.

During November, FIU discussed with DOE and provided the three open best practices needing DOE review and approval to finalize and publish

FIU Year 4 Carryover Work Scope

Subtask 2.1.2: Fogging research and evaluation

FIU conducted bimonthly phone calls with Michael Serrato (SRNL) this quarter to continue discussions for both carryover tasks (fogging research and incombustible fixatives). Rick Demmer and Steve Reese at INL were integrated into these teleconferences for the fogging research task.

FIU conducted a teleconference with Rick Demmer at Idaho National Laboratory (INL) concerning the fogging research and evaluation task. INL has received funding to execute a related research task and FIU is collaborating where feasible to optimize the overall impact of the research and minimize any duplication of effort between FIU and INL. FIU coordinated with the SRNL POC (Mike Serrato) and INL POCs (Rick Demmer and Steve Reese) to refine the scope for FIU's advanced fogging technology research and evaluation subtask (see scope of work below). FIU further coordinated

with INL to plan for a site visit in November to finalize a draft test plan for the testing and evaluation of the FX2 Advanced Fogging Delivery System Technology. FIU coordinated to receive all literature to date associated with FX2 Fogging Delivery System from INL for review.

On November 18-20, Mr. Joseph Sinicrope and Mr. Amer Awwad from FIU conducted a site visit to Idaho National Laboratory to be briefed on the FX2 Fogging Agent in support of the Advanced Fogging Research subtask. Participants from INL included Mr. Rick Demmer, Mr. Steve Reese, and Mr. Don Fox. Meetings included a detailed history of the development of the FX2 Fogging Agent to date, a review of the tests and results achieved thus far by INL, a demonstration of the equipment and parameters used during the last test, and development of the test objectives for the next iteration of experiments at FIU. Based on the general concurrence received from all the various stakeholders, FIU started development of the cold demonstration test plan to be conducted at FIU.

During the month of December, FIU completed development of the initial draft for the FX2 Fogging Agent Test Plan. The test plan outlines all components associated with the demonstration, testing, and evaluation of the FX2 fogging agent developed by INL. Based on close coordination with SRNL, INL, and DOE EM, FIU will test and evaluate the FX2 agent on or about 24-28 March 2015. The draft Test Plan has undergone an internal review and will be forwarded to INL and SRNL for their review.

All equipment and materials necessary to support the FX2 fogging agent test plan have been identified and vendor quotes are being obtained for equipment that does not already reside at FIU. It is anticipated that purchases of the necessary equipment and supplies will occur throughout the month of January 2015.

Potential vendors to conduct the flash point and burn rate tests for the FX2 fogging agent have been identified. It is anticipated that formal quotes will be obtained and a vendor selected in January 2015 to conduct these tests.

FIU also conducted several radiation surveys (with alpha and beta emitters) with the objective of finding a material that is permeable to alpha and beta radiation and that such material can also be used in the cold demonstration test planned to be conducted at FIU.

Subtask 2.1.3: Incombustible fixatives

Through regular discussions with Mike Serrato (SRNL), FIU has finalized the refinement of the task scope for the incombustible fixatives research. During October, FIU initiated a literature search for the 2 to 3 top-rated fixatives in ASTM ratings for ignition point and burn rate. FIU also initiated a literature search to identify the laboratory and equipment requirements that are needed to execute the scope of work. FIU contacted vendors to request prices, ordering information and availability for fixatives that could be tested using the combining/layering approach. FIU also collected helpful information by reviewing the procedures and equipment setups used by other laboratories that have done similar testing with fixatives.

During the month of November, FIU continued the literature research to identify the 2

to 3 top-rated fixatives in ASTM ratings. FIU also continued the outreach to the private sector to identify the equipment needed to carry out the ignition point and the burn rate tests.

After an extensive literature search, ten (10) private sector enterprises were engaged to identify costs and benefits associated with conducting ASTM D93 (Flash Point) and ASTM E84 (Burn Rate) standardized testing. Identification of the necessary equipment to conform to the respective ASTM standards was completed, and quotes to ascertain a rough order of magnitude (ROM) for pricing were requested. Several vendors have provided quotes with the prices and details of equipment required to perform the testing at FIU.

Simultaneously, the identification of private sector analytical labs that could conduct the testing via an outsourcing option was also completed, and associated ROM pricing options obtained. FIU is evaluating the two options, in-house versus outsourcing, and analyzing any potential laboratory modifications needed to accommodate the testing equipment for the in-house option.

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. ARC toured one of the laboratories to see their equipment, though additional information is required; the equipment may not meet ARC's requirements for the flash point and the burn rate tests planned.

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 schedules bi-weekly meetings with DOE via teleconference to discuss project task progress and address action items. Meetings were held between FIU and DOE on October 9, October 23, November 6 and November 20, 2014.

FIU worked on the development of a Google Web Analytic report for D&D KM-IT for the third quarter of 2014 (July to September). This report includes information from Google Analytics and Google Web Master tools and a narrative to explain the results.

In addition, during October, FIU finalized a newsletter on fixatives and other contamination control products, based on comments received from DOE. The final newsletter was sent out to all D&D KM-IT registered users on October 17 (Figure 4-3).

FIU completed drafting a paper on D&D KM-IT and submitted it to the Waste Management 2015 Symposium (milestone 2014-P4-M3.1). FIU received comments from DOE on the draft paper and will incorporate the comments and submit the final paper to the conference by the conference deadline of January 16, 2015.

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 December 8, the system included a total of 721 technologies (+14 from September) and 673 vendors.

FIU completed the design and development of the lessons learned lite mobile application and sent the link to DOE for review/testing on November 7, 2014 (milestone 2014-P4-M3.3). 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. Figures 4-4 shows screenshots of the lessons learned mobile application for Android, iPhone, and Windows devices during testing.

FIU also began the design and development of the best practices lite mobile application, due to DOE for review/testing by 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.

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 is currently working on developing 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. Once completed, the data will be imported into KM-IT database. The next step will be to modify the application and user interface layer to display the data on the KM-IT staging server followed by QA/QC before making it live on the production server. All of the data and accompanying information (photos, documents, etc.) within the robotics database from NuVision/Cogentus will be integrated for deployment on 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 is undergoing internal review and revision prior to being sent to DOE for review.

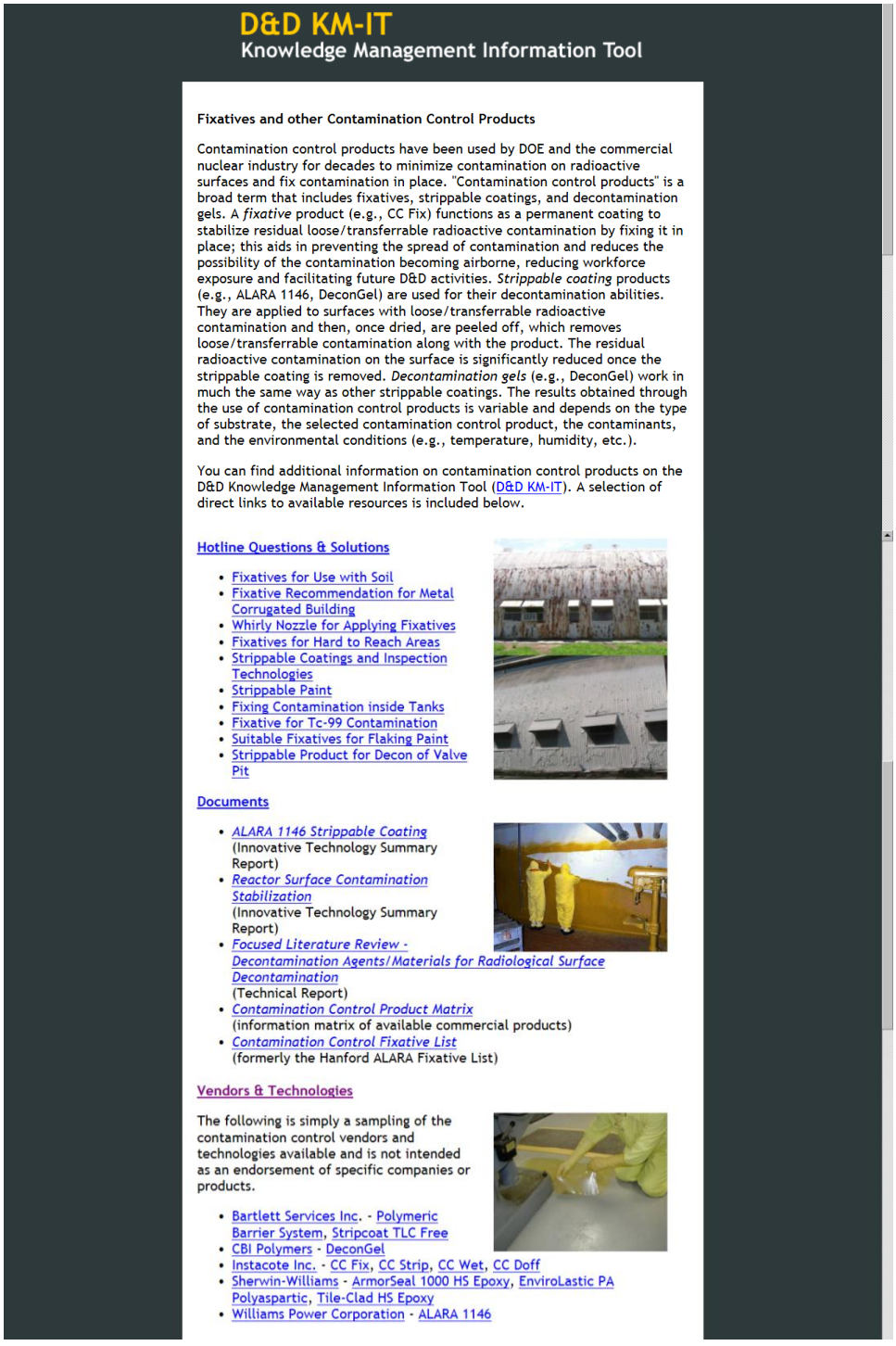


Figure 4-3. Screenshot of final fixatives newsletter for D&D KM-IT user base.

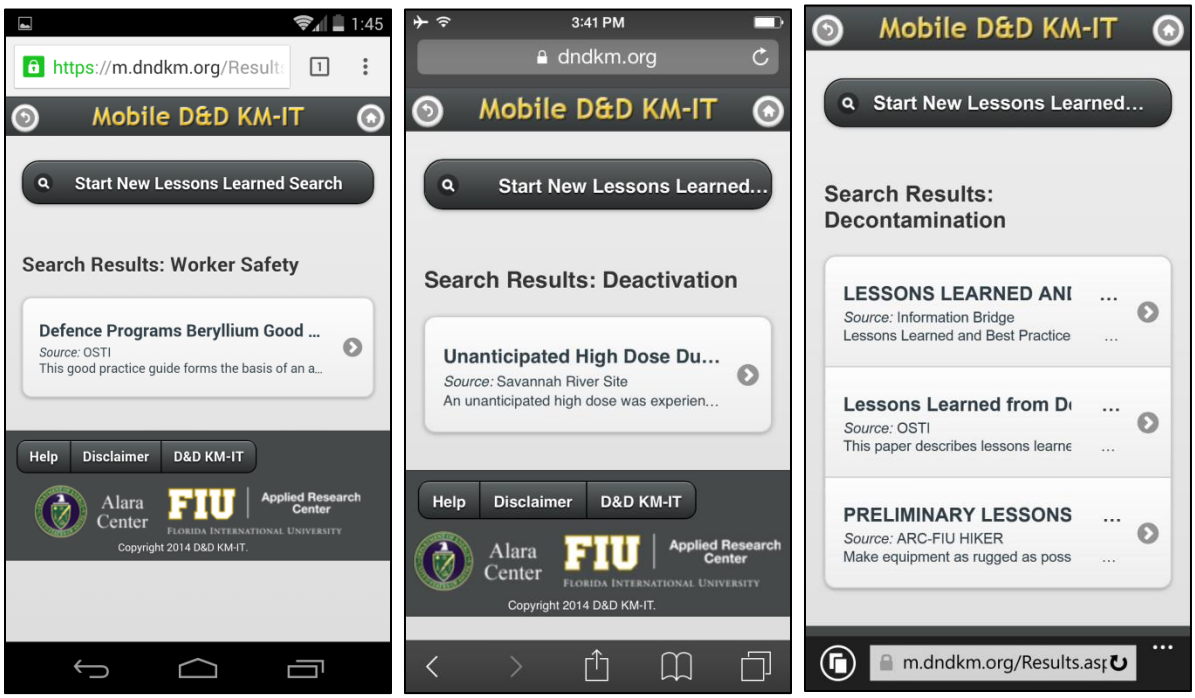


Figure 4-4. Screenshots during testing of D&D KM-IT lessons learned lite application.

Milestones and Deliverables

The milestones and deliverables for Project 4 for FIU Year 5 are shown on the following table with status through December 31, 2014. Draft papers for the Waste Information Management System (milestone 2014-P4-1.2) and D&D Knowledge Management Information Tool (milestone 2014-P4-3.1) were completed and submitted to the Waste Management Symposium 2015. In addition, the lessons learned lite mobile application for D&D KM-IT (milestone 2014-P4-3.3) was completed and sent to DOE for review/testing on November 7, 2014

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 receipt of data from DOE	On Target	
	2014-P4-M1.2	Submit draft paper on WIMS to Waste Management Symposium 2015	11/07/14	Completed	
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	On Target	
	2014-P4-M2.2	Draft summary report for SRS 235-F Facility on organic semiconductor thin films (subtask 2.1.2)	04/10/15	On Target	OSTI
	Deliverable	Lessons Learned and Best Practices	30 days after final 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**	Will 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	Completed	
	Deliverable	Metrics Definition Report on Outreach and Training Activities	09/30/14	Completed	
	Deliverable	Second D&D KM-IT Workshop to DOE EM staff at HQ	09/30/14**	Will 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	Completed	
	2014-P4-M3.3	Deployment of lessons learned lite mobile application to DOE for review/testing	11/07/14	Completed	
	Deliverable	Preliminary Metrics Progress Report on Outreach and Training Activities	01/16/15	On Target	
	2014-P4-M3.4	Deployment of best practices mobile application to DOE for review/testing	01/16/15	On Target	
	2014-P4-M3.5	Four Wikipedia edits/articles	03/20/15	On Target	
	Deliverable	First D&D KM-IT Workshop to D&D community	03/31/15	On Target	
	Deliverable	Second D&D KM-IT Workshop to D&D community	04/30/15	On Target	
	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 capabilities of D&D KM-IT	30-days after deployment of new module or capability	On Target	

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

Work Plan for Next Quarter

- Task 1: Perform database management, application maintenance, and performance tuning to WIMS.
- Task 1: Develop and present technical poster on WIMS to WM15.
- Task 1: FIU will maintain close communication with DOE on the WIMS data import for 2015. DOE will complete the data call, review the data, identify issues/disconnects, and work with the sites to address any concerns/findings. Once all issues are addressed, DOE will lock the data and will provide FIU with the new dataset. Expected timeframe is March/April 2015. 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. Once FIU receives the dataset, 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: FIU will continue a subtask in support of the SRS 235-F facility by conducting a focused literature search to identify suitable organic materials that could be fused using low temperature. Needs for the fused material include high flexibility and low cost.
- Task 2: FIU will continue a subtask in support of the SRS 235-F facility by conducting a focused literature search on incombustible fixatives.
- Task 2: FIU will collaborate with INL and SRS on the fogging research and evaluation task by completing a test plan and making preparations for a cold demonstration/testing at FIU.
- Task 3: Complete draft of D&D KM-IT website analytics report for the October to December time period and submit to DOE for review.
- Task 3: Complete development of the best practices lite mobile application for D&D KM-IT and send to DOE for review and testing.
- 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.
- Task 3: Develop and present oral presentation on D&D KM-IT to WM15.

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 Fall 2014 application process was completed. A total of 41 applications were received, a package containing all the applications were sent to Ms. Melody Bell at DOE-HQ for review and input. FIU students' applications were reviewed, and selected candidates were interviewed by the DOE Fellows selection committee during the month of October. The committee was integrated by FIU's Arts & Science and ARC. The following 15 FIU STEM students were selected as new DOE Fellows; this list was sent to DOE on October 31, 2014 to complete the project milestone 2014-P5-M2 and associated deliverable.

Table 5-1. FIU Minority STEM Students Selected for DOE Fellows Class of 2014

DOE Fellow	Current Academic Status	Major
Andrew De La Rosa	Undergraduate	Computer Engineering
Anthony Fernandez	Undergraduate	Mechanical Engineering
Aref Shehadeh	Undergraduate	Environmental Engineering
Brian Castillo	Undergraduate	Biomedical Engineering
Christine Wipfli	Undergraduate	Environmental Engineering
Janesler Gonzalez	Undergraduate	Mechanical Engineering
Jesse Viera	Undergraduate	Mechanical Engineering
John Conley	Undergraduate	Mechanical Engineering
Jorge Deshon	Undergraduate	Computer Engineering
Kiara Pazan	Undergraduate	Environmental Engineering
Maria Diaz	Undergraduate	Environmental Engineering
Maximiliano Edrei	Undergraduate	Mechanical Engineering
Meilyn Planas	Undergraduate	Electrical Engineering
Ryan Sheffield	Undergraduate	Mechanical Engineering
Yoel Rotterman	Undergraduate	Mechanical Engineering

Seven (7) DOE Fellows participated in the FIU McNair Scholars Research Conference held at the main FIU campus on October 16 - 18, 2014. These Fellows presented posters on the research they perform at ARC or during their summer internships.

FIU conducted the annual DOE Fellows Poster Exhibition and Competition on October 23, 2014. The purpose of this event was to showcase the DOE Fellows' research accomplishments for the past year as a result of their participation in various U.S. Department of Energy - Environmental Management (DOE-EM) related applied research projects. A total of 17 posters were exhibited. Some of the projects showcased by the students were a result of their summer internship assignments at DOE Savannah River Site, Pacific Northwest National Laboratory, DOE Hanford Site, and DOE Headquarters (DOE-HQ) in Washington, DC. Additional posters reflected the DOE Fellows' DOE-EM applied research that they conduct at the Applied Research Center (ARC) as part of the DOE-FIU Cooperative Agreement sponsored research. For some of the graduate students, these projects are also a part of their thesis towards a master's or Ph.D. degree. This year's panel of judges comprised of Dr. Ines Triay (ARC Executive Director), Ms. Connie Young (representing DOE's Savannah River National Laboratory) , Dr. Konstantinos Kavallieratos (Associate Professor, FIU Department of Chemistry), and Dr. David Kadko (ARC Associate Director). This year, the poster exhibition and competition was conducted at FIU's Engineering Center's Panther Pit and was attended by FIU faculty, ARC personnel, and FIU students. The winners of this competition will be announced during the 2014 DOE Fellows Induction Ceremony on November 13, 2014.

The posters presented included:

- **Malware Forensics on Mobile Devices for DOE-EM Applications**
  Andrew De La Rosa (Computer Engineering)
- **Enraf Reference Level Updates for High-Level Nuclear Waste Tanks at Hanford**
  Anthony Fernandez (Mechanical Engineering)

- **Monitoring Mineralogical Changes Occurring in Sediments via the EARP Process**
  Aref Shehadeh (Environmental Engineering)
- **Erosion & Corrosion Analysis from POR104 Valve Box at Hanford**
  Brian Castillo (Mechanical Engineering)
- **Use of XRF to Characterize Pre-Hanford Orchards in the 100-OL-1 Operable Unit**
  Christian Pino (Chemistry)
- **Deliquescence Behavior of Precipitates by the Isopiestic Method**
  Claudia Cardona (Environmental Engineering)
- **Residual Waste Detection in HLW Tanks**
  Dayron Chigin (Mechanical Engineering)
- **Computational Simulation and Evolution of HLW Pipeline Plugs**
  Deanna Moya (Mechanical Engineering)
- **Miniature Motorized Vehicle for Department of Energy Hanford Site Tank Bottoms**
  Gabriela Vazquez (Mechanical Engineering)
- **Study of an Unrefined Humate Solution as a Possible Remediation Method for Groundwater Contamination**
  Hansell Gonzalez (Chemistry)
- **Non-Invasive Pipeline Unplugging Technology for Hanford High-Level Waste Asynchronous Pulsing System**
  John Conley (Mechanical Engineering)
- **Evaluation of Ammonia Gas Partitioning in Aqueous Solutions in the Presence of Bicarbonate Ions**
  Maria Diaz (Environmental Engineering)
- **D&D Decision Model and Mobile Application for Selection of Fixative, Strippable Coating, and Decontamination Gel Products**
  Meilyn Planas (Electrical Engineering)
- **Quantitative Assessment of Sustainable Remediation Options for SRS**
  Natalia Duque (Environmental Engineering)
- **Characterization of the Uranium-Bearing Products of the Ammonia Injection Remediation Method**
  Robert Lapierre (Chemistry)
- **Heating, Ventilation, and Air Conditioning Design Assessments for Hanford Waste Immobilization and Treatment Plant**
  Sasha Philius (Mechanical Engineering)
- **D&D Knowledge Management Information Tool Feasibility Study for Cross-Platform Mobile Applications**
  Steve Noel (Computer Science)

Figure 5-1. DOE Fellows and Panel of Judges at the 2014 DOE Fellows Poster Exhibition and Competition.

Figure 5-2. DOE Fellows presenting their research at the 2014 DOE Fellows Poster Exhibition and Competition.

The DOE Fellows finalized their DOE Fellows Summer Internship Reports. These reports were submitted to DOE on October 17, 2014 and posted on the DOE Fellows website. The DOE Fellows, internship locations, and technical report titles are provided below.

Table 5-2. DOE Fellows and Summer Internship Technical Reports

DOE Fellow		Location	Report Title
1	Deanna Moya	DOE-HQ EM-12, Cloverleaf, MD	*Advanced Simulation Capability for Environmental Management (ASCEM)*
2	Natalia Duque	DOE-HQ EM-13, Forrestal, Washington D.C.	*Sustainable Remediation and Literature Review for Savannah River Site A/M Area Groundwater Remediation System*
3	Carmela Vallalta	WRPS, Hanford, WA	*Analysis of Tank Chemistry Compliance with Chemistry Specification in Double-Shell Tanks*
4	Sasha Philius	WTP (Bechtel), Hanford, WA	*HVAC Design Assessments for the Hanford Waste Treatment and Immobilization Plant*
5	Anthony Fernandez	WRPS, Hanford, WA	*Enraf & Densitometer Reference Level Updates for High-Level Nuclear Waste Tanks at Hanford Site*
6	Christian Pino	PNNL, Richland, WA	*Use of XRF to Characterize Pre-Hanford Orchards in the 100-OL-1 Operable Unit*
7	Robert Lapierre	PNNL, Richland, WA	*Studying the NH3 Injection Methodology Proposed for Remediation of the Hanford Deep Vadose Zone*
8	Hansell Gonzalez	SRNL, Savannah River, SC	*Study of an Unrefined Humate Solution as a Possible Remediation Method for Groundwater Contamination*
9	Steve Noel	SRNL, Savannah River, SC	*Development of Web Applications for Savannah River Site*

On November 13, 2014, FIU conducted the eighth (8^{th}) annual DOE Fellows' Induction Ceremony. This year, fifteen (15) FIU STEM students were inducted as DOE Fellows. Mr. Kenneth Picha (Acting Deputy Assistant Secretary for Tank Waste and Nuclear Materials Management, DOE Office of Environmental Management) was one of the keynote speakers for the ceremony. Mr. Picha remarked on the continuing partnership between DOE and FIU over the last two decades and the DOE EM environmental challenge. He also pointed out that a former DOE Fellow (Mr. Edgard Espinosa - DOE Fellow Class of 2007) currently works in his group at DOE EM-20. Mr. Picha concluded his remarks by welcoming the new class of DOE Fellows.

Other distinguished guests included Mr. Andrew Szilagyi (Director, Office of D&D and Facility Engineering, DOE EM), Mr. Steven Tibrea (Savannah River National Laboratory), Ms. Margie Brown (Minority Serving Institute Outreach Program Manager, Georgia Tech Research Institute), Dr. Elizabeth Fleming and Dr. Carlos Ruiz (Army Corps of Engineers), Mr. Jamey Capers (Indian River State College Regional Center for Nuclear Education and Training), Mr. James Ault (Florida Power & Light), Mr. Lorenzo Cabrera and Chris Wright (Cabrera Services), Dr. Carlos Mallol and former DOE Fellow Lilian Marrero (MWH America Inc.). FIU was represented at the event by Dr. Andrés Gil (Vice President for Research), Dr. Todd Crowl (Director FIU's Southeastern Research Center), Dr. Inés Triay (ARC Executive Director) and Dr.

Leonel E. Lagos (ARC Director of Research/DOE Fellows Program Director), as well as FIU faculty, staff, and students.

Mr. Picha and the other distinguished guests had the opportunity to participate in morning tours of the ARC research laboratories and listen to DOE Fellows presenting their research work. Presentations were given by Dr. Lagos and DOE Fellows Anthony Fernandez, Meilyn Planas, and Christian Pino. Dr. Lagos presented an overview of the DOE Fellows program. DOE Fellow Anthony Fernandez presented his summer internship experience and research on updating Enraf reference levels for high-level nuclear waste tanks at the Hanford Site under the supervision of Mr. Ruben Mendoza. DOE Fellow Meilyn Planas presented her DOE EM research on the D&D decision model for the selection of fixatives, strippable coatings, and decontamination gels. DOE Fellow Christian Pino presented his summer internship experience and research on using an XRF to characterize pre-Hanford orchards under the supervision of Mr. Amoret Bunn.

Tours of the ARC facilities included visits to the environmental technology laboratory, the composites laboratory, the cybersecurity research laboratory, the soil & groundwater laboratory, the high bay facility, the radiological laboratory, and the ARC technology demonstration area. Technologies showcased included the peristaltic crawler and asynchronous pulsing unit for pipeline unplugging, the in situ decommissioning sensor network (ISDSN) test cube, the D&D Knowledge Management Information Tool (D&D KM-IT) cross-platform mobile application development and cybersecurity infrastructure, and the SLIM sonar technology for detecting residual waste in high-level waste (HLW) tanks. Additional applied research presented during the facilities tours included computational fluid dynamics for multiphase flow in Hanford tanks, a study of unrefined humate solution as a possible remediation method for groundwater contamination at SRS, and soil and groundwater research being performed for Hanford's uranium contamination. In addition, 17 DOE Fellows had the opportunity to showcase their research by presenting posters as part of the afternoon events.

During this year's Induction Ceremony, 15 new FIU STEM students were inducted as DOE Fellows:

- Brian Castillo - undergraduate, biomedical engineering
- John Conley - undergraduate, mechanical engineering
- Andrew De La Rosa - undergraduate, computer engineering
- Jorge Deshon - undergraduate, computer engineering
- Maria Eugenia Diaz - undergraduate, environmental engineering
- Maximiliano Edrei - undergraduate, mechanical engineering
- Anthony Fernandez - undergraduate, mechanical engineering
- Janesler Gonzalez - undergraduate, mechanical engineering
- Kiara Pazan - undergraduate, environmental engineering
- Meilyn Planas - undergraduate, electrical engineering
- Yoel Rotterman - undergraduate, mechanical engineering
- Ryan Sheffield - undergraduate, mechanical engineering
- Aref Shehadeh - undergraduate, environmental engineering
- Jesse Viera - undergraduate, mechanical engineering
- Christine Wipfli - undergraduate, environmental engineering

In addition, awards were presented to the DOE Fellows that won the DOE Fellows Poster Exhibition and Competition held on October 23, 2014. First place was awarded to Mr. Dayron Chigin for his poster titled, "Residual Waste Detection in HLW Tanks." Second place went to Ms. Gabriela Vazquez for her poster titled, "Miniature Motorized Vehicle for Department of Energy Hanford Site Tank Bottoms." Third place was awarded to Mr. Anthony Fernandez for his poster titled "Enraf Reference Level Updates for High-Level Nuclear Waste Tanks at Hanford."

For the sixth year, the DOE Fellow of the Year Award and the Mentor of the Year Award were presented in the ceremony. DOE Fellows were requested to nominate their ARC mentors and ARC mentors were requested to nominate the DOE Fellows. An ARC committee was established to review and select the winners from the submitted nominations. The 2014 Mentor of the Year Award went to research analyst Mr. Jairo Crespo and the 2014 DOE Fellow of the Year Award was awarded to Mr. Anthony Fernandez (DOE Fellows Class of 2014) and Mr. Hansell Gonzalez Raymat (DOE Fellows Class of 2013).

The new DOE Fellows also received a congratulatory letter from our Congresswoman Ileana Ros-Lehtinen welcoming them into this Fellowship. Ms. Ros-Lehtinen also highlighted the need for students to pursue STEM careers and the DOE Fellows role as future leaders in the practice of keeping our nation's nuclear weapons facilities in safe condition.

Figures 5-3 and 5-4 show photos from the event and Figure 5-5 shows an invitation to the DOE Fellows Induction Ceremony

Figure 5-3. Newly inducted DOE Fellows, Class of 2014, with representatives from FIU, DOE EM, and other distinguished guests.

Figure 5-4. DOE Fellows presenting their applied research to DOE EM and other visitors.

Figure 5-5. Invitation to the DOE Fellows Induction Ceremony.

Each new DOE Fellow has been assigned to an ARC staff member to act as their mentor and supervise their EM research work. New DOE Fellows completed required FIU environmental health and safety trainings. The new DOE Fellows also began working on their brief bios to include on the DOE Fellows website.

During December, 20 DOE Fellows and other FIU graduate students developed abstracts on their research at ARC or during their summer internship for the Student Poster Competition at the Waste Management 2015 Symposium. The DOE Fellows also began working on short videos

briefly describing their research for submittal to the conference. The student poster titles planned for WM15 and the research abstracts are as follows:

1. **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.

2. **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.

3. **Monitoring Mineralogical Changes Occurring in Savannah River Site F-Area Sediments via Enhanced Anaerobic Reductive Precipitation Process - 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.

4. **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.

5. **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).

6. **Deliquescence Behavior of Synthetic Precipitates Formed during Ammonia Gas (NH3) Injection Applied for Hanford 200 Area via Isopiestic Method - Claudia Cardona(DOE Fellow)**

   Experimental measurements by an isopiestic method were conducted to study the deliquescence behavior of the multicomponent precipitates combined of Na2SiO3, Al (NO3)3, KHCO3, and CaCl2 at 25oC. The studied multicomponent precipitates were prepared synthetically and mimicked possible formed precipitates in the vadose zone of the Hanford Site 200 Area after ammonia gas (NH3) injection. Six multicomponent salt compositions containing 3 mM and 50 mM KHCO3 and 0, 5 and 10 mM of CaCl2 were evaluated for deliquescence in the isopiestic apparatus using LiCl and CaCl2 as standard solutions. The initial molalities ranged from 1.36 and 2.05 mol.Kg-1. Water activities and osmotic coefficients of the multicomponent salts were calculated at each step to observe the changes in slope which mark the phase changes of the multicomponent salt mixtures.

7. **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.

8. **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.

9. **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.

10. **Evaluation of Ammonia Fate During and After Ammonia Gas Injection (NH3) for Uranium Treatment into the Hanford Site Unsaturated Subsurface - Maria Diaz (DOE Fellow)**

    Through the investigation of methods and technologies for the stabilization of uranium within the vadose zone, reactive gas injections such as ammonia gas were found to be effective within the vadose zone under conditions of low soil moisture content. This method allows for the uncontrolled downward migration of contaminants as well as the added water in the vadose zone to be reduced. Preliminary testing of ammonia gas injections have demonstrated the potential ability for the sequestration of radionuclides within the vadose zone, however further research is necessary to determine the mechanisms associated with the fate of ammonia gas during and after the injections. The partitioning and adsorption of the ammonia gas in the presence of bicarbonate ions will be investigated to identify changes in the pH and temperature of the system in order to assess possible changes in the soil conditions specifically relevant to the Department of Energy's Hanford Site. This project has been funded by the United States Department of Energy.

11. **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.

12. **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.

13. **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.

14. **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.

15. 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.

16. 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.

17. 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.

18. 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.

19. 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.

20. **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 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.

DOE Fellows Jorge Deshon, Anthony Fernandez, Janesler Gonzalez, Maximiliano Edrei, Kiara Pazan, Jesse Viera, and Christine Wipfli attended and passed the hands-on radiation safety training provided by FIU's radiation safety officer.

Five of our current DOE Fellows graduated with a bachelor's degree and participated in the FIU graduation ceremony held on December 16, 2014.

- **Gabriela Vazquez** (Mechanical Engineering) – DOE Fellow Class of 2012
- **Dayron Chigin** (Electrical Engineering) – DOE Fellow Class of 2012
- **Sasha Philius** (Mechanical Engineering) – DOE Fellow Class of 2013
- **Andrew de La Rosa** (Computer Engineering) – DOE Fellow Class of 2014
- **Maria E. Diaz** (Environmental Engineering) – DOE Fellow Class of 2014

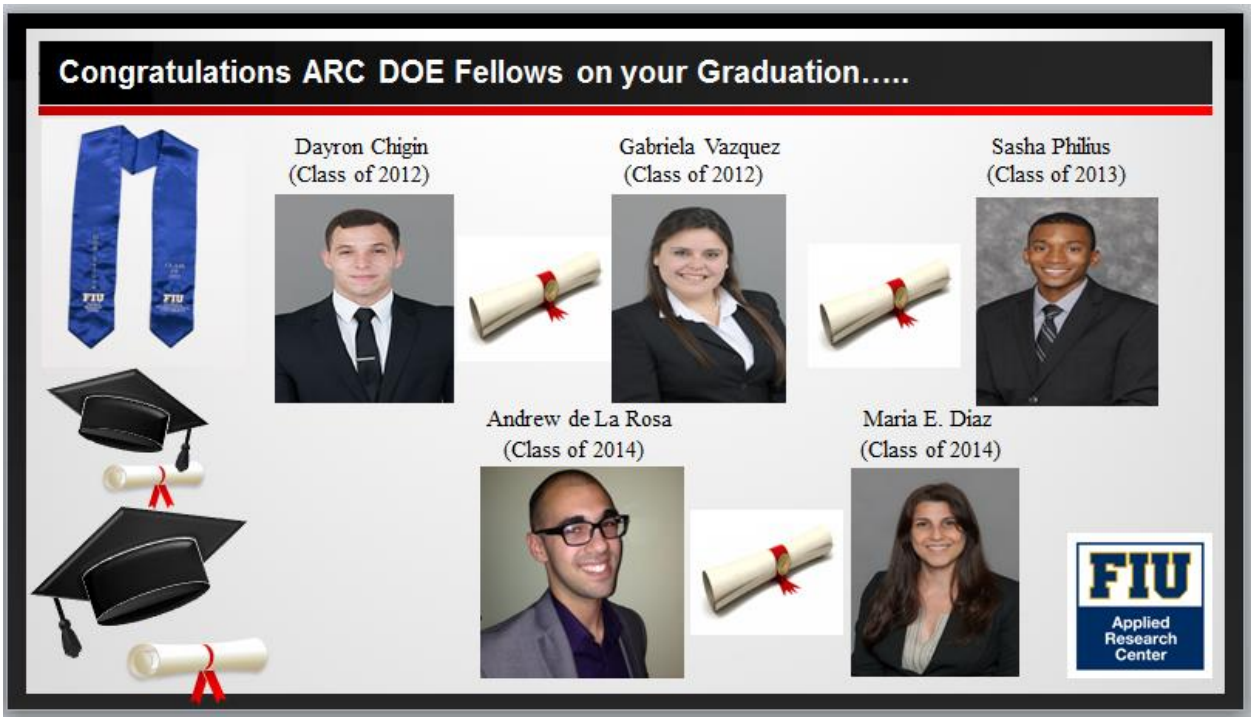


Figure 5-6. Graphic of congratulations for graduating DOE Fellows.

Two of these newly graduated DOE Fellows are continuing their education by pursuing graduate degrees at FIU:

- **Dayron Chigin** – M.S. student in electrical engineering
- **Andrew de La Rosa** - M.S. student in computer engineering

DOE Fellow Andrew De La Rosa wrote an article about technology awareness and was published in admitopia.com: http://admitopia.com/a-personal-awareness-in-technology/

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

Table 5-3. DOE Fellow Presentations during DOE Fellow Meetings

Student	Site	Mentor	Date
Christian Pino	PNNL, Richland, WA	Amoret Bunn	9/12/14
Hansell Gonzalez	SRNL, Savannah River, SC	Brian Looney/Miles Denham	10/03/14
Natalia Duque	DOE-HQ EM-13, Forrestal, Washington D.C.	Albes Gaona	10/10/14
Deanna Moya	DOE-HQ EM-12, Cloverleaf, MD	Justin Marble/Patricia Lee	10/24/14
Robert Lapierre	PNNL, Richland, WA	Jim Szecsody	10/31/14
Anthony Fernandez	WRPS, Hanford, WA	Ruben Mendoza	11/12/14
Steve Noel	SRNL, Savannah River, SC	Mary K. Harris	12/05/14
Sasha Philius	WTP (Bechtel), Hanford, WA	Brad Eccleston/Joel Peltier	12/12/14

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 with status through December 31, 2014. Milestone 2014-P5-M1 (draft summer internship reports) was completed and the reports were submitted to DOE on October 17, 2014. In addition, DOE Fellows for the Class of 2014 were selected (milestone 2014-P5-M2) and submitted to DOE on October 31, 2014. Milestone 2014-P5-M3 (conduct induction ceremony, class of 2014) was completed on November 13, 2014. Milestone 2014-P5-M4, submitting the student poster abstracts to the Waste Management Symposium 2015 was completed early, on December 20, 2014.

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

Work Plan for Next Quarter

- Continue research by DOE Fellows in the four DOE-EM applied research projects under the cooperative agreement and research topics identified as part of their summer 2014 internships.
- Coordinate travel for DOE Fellows to attend Waste Management 2015 Symposium.
- DOE Fellows to develop posters and present at student poster session at WM15.
- Begin Spring 2015 campaign to recruit DOE Fellows into the program.
- Begin coordination of internship placements for summer 2015 at DOE sites, national laboratories, DOE HQ, and DOE contractor locations.