QUARTERLY PROGRESS REPORT

July 1 to September 30, 2014

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

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Prepared for:

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



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 July 1 to September 30, 2014. Highlights during this reporting period include:

Program-wide:

- FIU received comments from DOE HQ and site contacts on the FIU Year 5 Project Technical Plans. FIU incorporated the suggested revisions, developed resolutions to the comments, and sent the PTPs back to the DOE on July 30, 2014.
- FIU began developing the Renewal Application for the new Cooperative Agreement that would begin in May 2015 at the conclusion of the current FIU Year 5. FIU held discussions with DOE EM as well as site contacts on their high priority technical needs to guide the proposed scope of work for the new CA.

Project 1:

• No milestones or deliverables were due for this project during this quarter.

Project 2:

• Milestone (2014-P2-M6), completing preparations for the microcosm experiments prepared with SRS sediments using sulfate additions, was originally due on September 12, 2014. This date was re-forecasted to October 13, 2014 to provide SRNL the time needed to collect, analyze for potential radioactivity, package, and ship the sediments to FIU. This milestone delay was discussed with SRS site contacts and communicated to DOE HQ via email on September 5, 2014.

Project 3:

- The final technical reports for Project 3, Tasks 1 & 2, associated with the FIU Year 4 Carryover Work Scope, were completed and submitted to DOE-ORO as well as DOE-HQ on July 31, 2014.
- FIU visited SRS on August 5-6, 2014, and attended a series of meetings with SRNL contacts to discuss current FIU Year 5 work scope as well as potential scope for the next five years, completing milestone 2014-P3-M5. In addition, two (2) abstracts were submitted to Waste Management Symposia 2015 based on research related to Project 3, meeting a project deliverable.
- A summary report on Green and Sustainable Remediation and its application to DOE EM Sites was submitted to DOE HQ and site contacts on September 26, 2014. The report summarizes GSR and describes the application of SiteWise[™], providing an example of SiteWise[™] implementation at the Savannah River Site (SRS). This concludes the Project 3 FIU Year 4 Carryover Work Scope.

• The Project 3 Task 1 (Subtask 1.1) milestone (2014-P3-M1) and its associated deliverable "Work plan for experimental column studies," was completed and submitted to DOE HQ (EM-12) and site contacts on 9/26/14.

Project 4:

- FIU milestone 2014-P4-M3.2 was met on September 5, 2014, with the development and deployment (for DOE review) of a popular keyword display on the homepage of D&D KM-IT. In addition, a deliverable under Project 4, a metrics definition report on D&D KM-IT outreach and training activities, was sent to DOE on September 30, 2014.
- The two D&D KM-IT Workshops to DOE EM staff at HQ were originally planned by the end of August and September. These workshops are being coordinated and re-scheduled based on the availability of DOE EM staff.

Project 5:

• No milestones or deliverables were due for this project during this quarter.

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
	Deliverable	Draft Project Technical Plan	06/18/14	Complete	
	Deliverable	Monthly Progress Reports	Monthly	On Target	
Program-wide (All Projects)	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*	On Target	
	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, 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

A topical report describing the evolution and testing of the asynchronous pulsing system was submitted to EM-21 and site contacts on June 16, 2014 for review.

July was focused primarily on acquiring and installing components necessary to modify the asynchronous pulsing system (APS) for the next phase of testing as well as verifying that the system is fully functional. The previous design utilized pipe unions to mount the plugs in the pipeline. These fittings eventually would require resurfacing as well as increased torqueing every time the plug was replaced. This lead to long preparation times for each test. The current redesign utilizes the use of flanges on the plugs. The use of flanges allows for the quick installation and removal of the plugs without loosening other joints along the pipeline. This will reduce the preparation time which will allow for additional testing. In addition, the system was checked for any faults since it had not been operated in 2 months and concerns about moisture infiltration into the electronics had arisen. All moisture barriers were checked due to the impending wet season. Also, during a routine check, it was found that a dynamic transducer had been physically damaged. A replacement dynamic transducer was ordered.

August's work was focused on acquiring and installing components found to be damaged during the modification of the APS test loop as well as verifying that the system is fully functional. A replacement dynamic transducer was received and installed and all sensors were recalibrated. The system was leak tested at high pressures and all leaks were addressed. Verified control code for the air mitigation methods to be employed during system air removal operations. Tested plugs were manufactured from materials left over from previous tests. However, during blowout tests, the plugs were only able to withstand 75 psi. In order to be useful for testing, the plugs need to be able to withstand approximately 300 psi. In the past, lower blowout pressures were obtained due to the plaster being exposed to moisture. New materials were ordered.

September's APS work included dealing with issues involving plug manufacturing and obtaining consistent results. From previous testing it was determined that the desired plugs would withstand a minimum blowout pressure of 300-350 psi. In resuming plug manufacturing for this last phase of the project, consistency in plugs has reduced as plug fabrication personnel have changed. We have been attempting to determine which variables could affect the results, such as curing time and mixing speeds. Two plugs were manufactured from the same batch, with one being installed on the test loop while the other was subjected to a quality control blow out test. The latter plug blew out at 250 psi which was below our initial criteria for unplugging in a pipeline but we decided to use it to begin establishing procedures for when the manufacturing begins to yield desired results. As part of the installation process for a line with no air entrained, the plug was subjected to the following events in order (and repeated 3 times):

- 1. Filled pipeline at a static pressure of 55 psi. In the past, this process would take one hour since the isolation valves had failed. New valves have been installed and this should reduce the fill time as they prevent the influx of air into the larger portion of system that occurs between plug installations. This reduction in time minimizes pre-loading the plugs for extended periods of time.
- 2. Applied air removal pulses. This process requires pulling a vacuum generated by the pistons followed by moving the pistons at specific frequencies for a total of 75 cycles. These cycles are low compared to previous tests (required 3000 cycles before failure); however, we have no data on the effect of pulsing at a vacuum. These tests should aid in determining if the air removal pulses pre-fatigues the plug. This is critical as the scope of determining the effects of air of the plug removal process could be affected.
- 3. Removed air that has traveled to the exhaust ports. The air removal pulsing allows for pockets to enlarge due to the vacuum and move along the pipeline. Once the air accumulates at one of the risers, we open the water entry valve and begin opening all the exhaust ports so the air can be removed as water flows out of the pipeline.

Once the air removal process was completed, we ran a test with parameters used previously that would have taken 1 hour to unplug. However, the plug yielded after only about 3 minutes. Since the previous blowout test indicated that this plug may not have been strong enough, we cannot determine at this time whether the air removal pulsing has pre-fatigued the plug or if the absence of air in the system increased the efficiency of the system, allowing the plug to fail faster. Once the cause of the short blowout duration is determined, experimental testing is expected to continue.

For the peristaltic crawler subtask, a small test loop with schedule 40 pipe was assembled to determine if the smaller diameter pipe improved the response of the rubber cavities. During the prior attempts of large scale testing, it was observed that the crawler's rubber prematurely failed due to overextension from the slightly larger diameter pipe. The testbed consists of three straight sections (two 21 ft long and one 12 ft long) coupled together with 90° elbows. In order to use existing resources, the two 21-ft sections were coupled using a threaded-to-Victaulic connectors and the 12-ft section was grooved at the ends. Figure 1-1 shows the experimental testbed.



Figure 1-1. Experimental testbed using the schedule 40 pipe sections.

Additionally, different vacuum pump configurations were evaluated to replace the damaged unit which is required to provide compression of the bellow. Previous experiments showed that continuous use of the vacuum pump caused the oil in the pump to saturate, resulting in damage to the internal seals. A vane pump could prevent air moisture accumulation but does not provide a deep vacuum (27.5 in Hg) when compared to a rotary vacuum pump (29 in Hg). Not providing a full vacuum to the system will aversively affect the navigational performance of the crawler. It was determined that adding a stage containing a large desiccant prior to the air reaching the vacuum pump will make it possible to use a rotary pump with no long-term damage.

Three vacuum pumps used on previous DOE tasks were located and tested to replace the damaged vacuum pump. The desiccant system will also be upgraded using a system obtained from another project. The final configuration will consist of a rotary pump to create a full vacuum (29 in Hg) coupled to a moisture collecting unit. Additionally, the equipment for powering the PLC (DIN-Rail Mount AC to DC transformer) was selected and quoted and is awaiting procurement. Efforts also included the assembly of the system with the new improvements and writing a test plan for experimentally testing the PLC in the 54-ft testbed.

Finally, the fitting connecting the air compressor to the crawler's tether was replaced and clamps and gaskets were added to all fittings to prevent leaks. The current crawler unit includes a clamp/cable system that limits the extension of the bellow. This was installed to reduce the chance the bellow will fatigue. Although the extension of the bellow can reach 4 inches per cycle of operation, it was set to allow the bellow to extend 1 inch. The cycle was set to 32 seconds with 22 seconds of compression for this set of tests.



Figure 1-2. Crawler set-up.

Initial dry run tests were conducted and the crawler initially traveled at approximately 5 ft/hr. This was approximately half of what the speed should be based on cycle time and extension. Investigations have been started to determine the cause of the reduced speed. It is likely that the bullet valve seals have a slight leak, allowing for the positive pressure to reduce the effectiveness of the vacuum during the compression cycle.

FIU Year 4 Carryover Work Scope

Subtask 2.2: Computational Simulation and Evolution of HLW Pipeline Plugs

During July, a 3-D single phase $k-\omega$ turbulence model was developed to ascertain its numerical accuracy. A quantitative assessment of the results was done by comparing the so-called diametrical pressure coefficient, c_k , to an engineering correlation outlined in the work by Homicz et al. The definition of c_k is:

$$C_{k=\frac{p_0-p_i}{\frac{1}{2}\rho U^2 a v g}} \tag{1}$$

where p_o and p_i are the pressures where the outer and inner radii of the bend intersect the symmetry plane, respectively. The diametrical pressure coefficient is commonly measured at half the bend angle, in this case at 45°. Figure 1-3 shows a surface plot of the pressure in a plane at 45°; p_o and p_i are the maximum and minimum values of the pressure in Figure 1-3, respectively, which gives $p_o - p_i \approx 1.88 \times 10^4$ Pa. Since U_{avg} is 5 m/s, Eq. (1) evaluates to 1.56.



Figure 1-3. Pressure in a plane at 45°.

The pressure coefficient result of the numerical model was computed to be 1.56 and was found to be in close agreement with that obtained from an engineering correlation calculated at 1.42.

Efforts were also focused on simulating a precipitation event in a multi-phase model. The chemical reaction interface and the mixture interface were coupled and the coupled physics were integrated. The model underwent convergence; however, inaccurate data related to mass fractions of the dispersed phase was observed. The equations underlying the physics are in the process of being investigated.

During August, the numerical validation of the 3D single phase $k-\omega$ turbulence model included quantitative assessment of results comparing the computed friction factor of the numerical model with that obtained from R.H. Perry et al.³

The numerical model equation for friction factor, f_f, related to the head loss, h_L, is

$$f_{f=\frac{\Delta p}{2\rho U_{avg}^2}\frac{D}{L}}$$
(2)

where, L is the length of the pipe segment, g is the gravity constant, U_{avg} is average velocity, D is the diameter of the pipe and Δp is the pressure drop over the pipe segment.

The numerical friction factor was computed to be 8 x 10^{-3} . This was compared with the following correlation for the friction factor through a curved pipe given by R.H. Perry et al.²

$$f_{f=\frac{0.079}{Re^{0.25}} + \frac{0.0073}{\sqrt{Dc/D}}}$$
(3)

The computed friction factor was 7.6 x 10^{-3} . The difference of 5.3% was within the expected range of accuracy.

During September, the validated 3D k- ω turbulence model was integrated with the multi physics model,, simulating settling conditions in a horizontal pipe. The slurry flow in a horizontal pipeline was computed 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/m³ 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. The mesh used to partition the model domain into sub-domains consisted of rectangular elements as shown in Figure 1-4. The mesh size used was extremely coarse.



The settling of solids in a pipe was simulated via transient simulation. The slice plot as shown in Figure 1-5 shows the dispersed solids volume fraction in a pipeline and where the settling occurs as characterized by the red and yellow colors in the plot below.



Figure 1-5. Dispersed volume fraction.

During the next performance period, a mesh analysis will be conducted, creating virtual scenarios with different mesh types and sizes.

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

FIU had numerous conversations with Joel Peltier from Bechtel, Chris Guenther from NETL and Rod Rimando at DOE in regards to the CFD task at FIU that aims to advance the modeling capabilities of DOE for the non-Newtonian fluid mixing at the Hanford Waste Treatment and Immobilization Plant (WTP).

As per our conversations so far, all parties have come to a conclusion that FIU will use the Star-CCM+ software as the framework to build the modeling capability for multiphase turbulent flows to model the mixing performance of pulse jet mixers (PJMs) at WTP. It is understood that such a CFD package that can perform large scale simulations of highly turbulent fluids jetting in a liquid-solid mixture that exhibits Bingham plastic behavior doesn't exist and the effort to get to that level will take a couple of years. FIU will first build a knowledge and expertise on the current capabilities of the Star-CCM+ software for single-phase flows with Newtonian and non-Newtonian fluids and study the theory of the RANS approach for multiphase flows in order to improve the turbulent Bingham fluid model.

The FIU team will consist of Dr. Gokaltun, and possibly 1 PhD and 1 undergraduate student who will be trained on the Star-CCM+ software. The students will be hired as DOE Fellows in the Fall 2014 semester and the student applications are being received at this time. Dr. Gokaltun will attend a 3-day online training on the Star-CCM+ software on Oct 7-9, 2014. Once the students are hired, he will train the students as well on the software and they will be able to use it in their research. Contact with the Cd-Adapco company has been initiated in regards to the licensing information for the Star-CCM+ software and the computer hardware requirements necessary to produce simulation results in a reasonable amount of time. The DNS approach is known to necessitate large amounts of computer memory due to the large number of grid elements in the computational mesh. FIU has started to receive quotes from a server builder for a small scale computer cluster that could satisfy the requirements of the DNS modeling approach.

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.

Task 18 Quarterly Progress

FIU Year 4 Carryover Work Scope

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

Limited Area View Algorithm

During July, an additional software algorithm code was developed to allow for a "Limited Area View" of imaged sections of each scan. The limited area view reduces the area viewed during each scan and therefore limits extra post processing of data that is outside the area of interest. Recall that in the proposed application of FIU's Solid-Liquid Interface Monitor (SLIM) in Hanford's mixing tanks, the area of interest is the area between pulsed jet mixers and constitutes only a few square feet of the tank floor. This algorithm will improve the volume calculation of each scan by eliminating the processing of data from areas where no solids are expected but errors in the measurement of the bare floor would add increased error to the total volume calculated for solids on the tank floor. False height measurements above the tank floor can arise from sonar reflections off the tank wall or off solid particles suspended in the liquid or from any double scattering of sonar echoes. Based on the broader algorithm used to interpolate each ping detected by SLIM, this new algorithm will increase the quality and accuracy of the interpolation by removing erroneous spikes due to the mechanisms described above for sonar pings that can result in false height calculations.

Examples of How the Limited Area View Algorithm Works

This algorithm removes sonar data points from the beginning and end of each swath that are outside the area of interest, focusing directly below the sonar since the sonar will be positioned directly over the small area of interest wherein solids might accumulate.

In the example below, a 60° swath arc scan with 34 pings was used. This scan was one where the brick was centered directly under the sonar. The algorithm removes data that is outside the small area of interest. Simultaneously, the algorithm filters the sonar data to correct values that are out of range and that would cause errors in the interpolation algorithm. Figure 1-6 is an image wherein all of the past filtering algorithms have been applied. Yet, the calculated solids volume in the area surrounding the brick is undesirable and reduces the accuracy of the volume due to errors in the sonar data that show as reflections high above the floor (or as spikes).



Figure 1-6. Sonar image processed with all data points.

As extraneous sonar data points are removed, the image is focused on the smaller area of interest as shown in Figure 1-7. In this image, note the immediate change in height of solids as depicted by the changed default color scale. The area around the brick in now a dark shade of blue depicting a distance of 680+ millimeters away from the SLIM sonar in comparison with the image in Figure 1-6 which had 660-675 millimeters from the sonar.



Figure 1-7. Limited area view on the area of interest after 4 data points removed per swath.

Figure 1-8 shows an image where sufficient sonar data points have been removed to start to lose the data from the brick or the area of interest. Processing of the sonar data can be optimized to allow imaging of only the area of interest as shown in Figure 1-9.



Figure 1-8. Sonar image with 8 data points removed with part of brick cutoff.



Figure 1-9. Optimal image with 6 sonar data points removed.

Kaolin Property Testing

Research on the on the properties of kaolin was conducted. FIU has purchased kaolin from Edgar Minerals, Inc. The chemical name for this kaolin is kaolinite which is part of the hydrous aluminum silicate chemical family and its product name is EPK Kaolin, pulverized Kaolin.

The MSDS information provided by manufacturer (*Edgar Minerals, 651 Keuka Rd. Edgar, FL 32640, (352) 481-2421*) may be found in PDF format at the following webpage: http://edgarminerals.com/Sites/48/Downloads/Kaolin%20MSDS%2001-01-2013.pdf Unless otherwise stated, the information on kaolin described below and on this task is from the manufacturer's MSDS document.

Kaolin Research Summary

Safety: Kaolin, also known as Kaolinite, is known to contain small amounts of crystalline silica. This chemical is found in kaolin in concentrations of 0.1-4.0%. Crystalline silica is known to be a carcinogen when inhaled or ingested and can have several side effects. Safety precautions to be followed during work at FIU with kaolin in liquid slurries include:

- Use NIOSH approved dust respirator when levels exceeds TLV, 0.05mg/m³.
- Keep containers firmly closed when not in use and avoid the release of the chemical into air.
- If chemical is to be released into open air, ensure proper ventilation.
- Wear eye protection while handling material at all times.
- Use of impermeable gloves and eye protective glasses are highly recommended.

Chemical Properties Summary - The settling time for kaolinite is dependent on the solid concentration (% kaolinite within the fluid), the ionic strength of the kaolin and the pH of the water.^[1] Research shows that as the concentration of kaolin in an aqueous solution of water increases, the settling time will increase as well almost at a linear rate, assuming the pH of the aqueous substance is 7. The Hanford and Savannah River Site high-level radioactive waste (HLW) are highly alkaline (pH >14). In alkaline solutions, kaolin settles as dispersed particles when ionic strength is low. When ionic strength is increased in alkaline solutions, kaolinite particles settle in flocculated form. Results also show that as the solid concentration increases, the settling rate decreases due to the buoyancy effect.

Work cited: 1. Kaya, Abidin, Ali Hakan Ören, and Yeliz Yükselen. "Settling of Kaolinite in Different Aqueous Environment." *Marine Georesources & Geotechnology* 24.3 (2006): 203-18. Web. <u>http://www.ameltech.com/docs/Marine_Georesources_Aug_20062.pdf</u>.

Kaolin Settling and Flow Characteristics Testing

Testing of the pulverized kaolin clay material purchased from Edgar Minerals was conducted to help measure the settling rate and thereby understand flow characteristics of these micron-sized particles in water. Kaolin particles are often used as a surrogate for flow simulations of Hanford high-level radioactive waste (HLW) which has similar particle size and flow characteristics. Data collected and analyzed will enable simulation of flow of this specific form of kaolin in water within our test tank (dimensions of 36 inches in diameter and 84 inches in height). Another goal of this experiment was to help FIU determine the type of pump and nozzle as well as their setup in the tank to ensure complete mixing and a uniform density of entrained kaolin particles during various experimental tests.

A 2-liter beaker was used for our testing and scale-up calculations are underway. With a proportional volume of water and volume of kaolin, the settling time and behavior for the kaolin was studied. Our experimental test plan includes measurements from 0% to 30% (by volume) of kaolin in water-kaolin slurry. The kaolin purchased, CAS no. 1332-58-7, has a density of 2.6 g/cm^3 .

Results from the experiment showed the expected linear correlation between the concentration of kaolin in water (or volume %) and the settling time of the kaolin. When ionic concentration is low (pH~7), the particles will be seen in a dispersed form and thus settle in accordance with Stokes' sedimentation law.

Experimental Setup and Final Planning for Sonar Tests with Suspended Kaolin Particles

During the month of September, a pump system was designed, acquired and installed in the test tank to mimic Hanford mixing tank operations. The goal of the experiment is to measure the sonar's resolution and to determine the critical suspended kaolin particle volume percentages that obscure the sonar signal for 1, 2, and 3 feet separation between the sonar and the 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 with the mixing stopped and before all the rapidly settling particles settle to the floor.

The installed pump system consists of a 2 horsepower centrifugal pump, 2 hoses and a 3-way split head nozzle. The pump has been placed outside of the tank and the output hose connects the pump to the 3-way split head nozzle. The input of the pump is connected to an intake on the opposite side of the tank but at the same level. The pump system has been tested and the desired dynamic fluid movement has been achieved. The photograph below in Figure 1-10 shows the 3-way nozzle and the pump intake inside the test tank.



Figure 1-10. Three-way nozzle and pump intake inside the test tank.

In addition, a structure with unistrut components has been designed 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 must hold SLIM within 3 degrees of the perpendicular in order to reduce errors due to an offset angle. Various designs were considered with special consideration in regards to stability against movement and still allowing access to the water surface in the tank.

FIU Year 4 Carryover Work Scope

Subtask 18.2: Development of Inspection Tools for DST Primary Tanks

Initial efforts during this reporting period focused in completing the design and starting building the first functioning prototype. After calculating the tolerance stack-up for fit form and function of the assembly, changes were made to account for the resolution of the rapid prototype printer. A section of the assembly was fabricated and the gears and motor were assembled (Figure 1--11 left). Once the motor was energized, it was determined that friction between the ABS parts and metal gears prevented the wheel from turning. Methods for reducing the friction and increasing the torque delivered by motor were investigated; they included resizing the casing of the inspection tool to accommodate a larger motor. Additionally, the control systems for the motors were successfully tested using an Ardurino microcontroller (Figure 1--11 right).



Figure 1-11. ABS prototype, gears and motor and microcontroller connected to motor.

Based on further observations and comparisons to the finite element analysis (FEA) model, it was determined that the size of motor selected cannot deliver the power required in a non-ideal scenario. An alternative design was proposed which uses worm gears to allow accommodating the motors vertically. This new configuration is expected to allow for a motor size of approximately 0.5" in diameter. Using two of these motors (one for each side of the tank) will significantly increase the power available to overcome friction forces.

For the month of September, we redefined our efforts to focus on designing an inspection tool that can 1) travel through the first seventeen feet of the 1.5 inch by 1.5 inch channel, 2) minimize the damage to the refractory material, and 3) provide a tether as means of retrieval in case of malfunction.

The modified design includes a body frame that is 1 inch in width and 0.6 inch in height, giving it ample space to travel through the channel. It houses four motors, giving power to four wheels. It also contains a magnet on top of the frame in order to hold the device upside down and travel through the slots without touching the refractory pad. This design is similar to our initial device but it contains two extra motors and the gears were eliminated to minimize inefficiencies. Moreover, the wheels are offset in order to fit the motor in the width direction to connect directly to the wheels. A first prototype is being constructed to validate the principles of operation and

determine if the motors will provide enough torque. Currently, the cables powering the unit create loads that are significant and will ultimately need to be minimized.

Another aspect of the design that was improved was the motor. The initial motor utilized was a Digikey motor that only provided 0.014 ozs of torque. After continued investigation, a coreless brushed DC motor that is slightly larger with a 6-mm diameter and 21.9-mm length was obtained. While the new motor requires updates to the design, it now provides 8 oz of torque. This significant increase in torque should allow the vehicle to travel the 17 ft of the refractory pad in addition to the load provided from the cable tether. This torque is possible because the gearbox attached to the motor contains planetary gears with a 136:1 gear ratio.

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 an initial set of data of thickness measurements taken from components in the POR 104 Valve Pit and information regarding how the locations were selected.

Recommendations based on the literature review included:

- 1. Sensors should be located at a minimum of 3 points on the pipe.
- 2. For elbows, sensor arrays should be located at 30, 45 and 60 degrees.
- 3. The sensors should be located at 0, 90 and 270 degrees on the bend where 0 degrees represents the outer-most radius.
- 4. A sensor array should be placed no further than one diameter length after the bend.

Information regarding design inputs for the POR 104 Valve Box pipes included:

- Critical velocity of slurry waste 6 ft/s (63 gpm)
- Flow rate for slurry waste ~100 gpm
- Viscosity 10 cp
- Density 2.6 $slug/ft^3$
- 2 in schedule 40 stainless steel nominal thickness of 0.156 in





Initial thickness measurements are included in Table 1-1. Additional data will be supplied by the site engineers and with nominal data, erosion patterns will be obtained. Note that some of the sensors failed to produce thickness measurements. FIU will follow up with site engineers to determine how to handle the missing data.

Location	Thickness (in)	Retest Thickness (in)
A1	0.157	0.157
A2	0.126	0.126
A3	0.157	0.157
B1	0.153	0.153
B2	0.142	0.139
B3	0.234	0.249
C1	0.155	0.164
C2	0.136	0.136
C3	0.15	0.15
D1	0.151	0.152
D2	0.15	0.151
D3	0.153	0.153
D4	Nonfunctional	Nonfunctional
E1	Nonfunctional	Nonfunctional
E2	Nonfunctional	Nonfunctional
E3	Nonfunctional	Nonfunctional
F1	0.158	0.157
F2	0.155	0.155
F3	0.16	0.162
G1	0.175	0.164
G2	0.15	0.151
G3	0.15	0.15
H1	0.148	0.149
H2	0.153	0.151
H3	0.156	0.156
H4	0.158	0.152
J1	0.153	0.153
J2	0.151	0.152

Table 1-1. Initial Thickness Measurements for the POR104 Valve Box

During August, additional thickness measurements were received from the engineers at Hanford for 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. Figure 1-14 and Figure 1-15 show the locations of the measurements for both sets of nozzles.



Figure 1-15. Measurement locations for Nozzles B and C.

Data analysis of the nozzles has been initiated. Some of the figures provided below show the variations in thickness from the elbow section of Nozzle B. As noted previously, the nozzle has three sections including a straight section defined by a Purex nozzle, a long radius elbow and a straight pipe section. Figure 1-16 shows the individual measurements plotted along the radial position. As expected, the cross sections have similar trends with lower thickness near the

bottom of the pipe. The longitudinal averages demonstrate that most of the measurements are above the nominal thickness for the pipe. Figure 1-18 shows the individual longitudinal measurements. Some of the data was not obtainable; however, there are two typical trends that can be observed. The averages at each longitude location are all above the nominal thickness, indicating no wear or erosion.





Figure 1-18. Longitudinal measurements in the elbow of Nozzles B.





Figures provided below show the variations in thickness from the elbow section of Nozzle E. As noted previously, the nozzle has three sections including a straight section defined by a Purex nozzle, a long radius elbow and a straight pipe section. Figure 1-20 shows the individual measurements plotted along the radial position. As expected, the cross sections have similar trends with lower thickness near the bottom of the pipe. The longitudinal averages demonstrate that most of the measurements are above the nominal thickness for the pipe. Figure 1-21 shows the individual longitudinal measurements. Some of the data was not obtainable; however, there are two typical trends that can be observed. The averages at each longitude location are all above the nominal thickness, indicating no wear or erosion.



Figure 1-21. Longitudinal measurements in the elbow of Nozzle E.



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

The 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. 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.

A test plan was previously developed by Sandia National Laboratory but never executed. Due to experimental testing location limitations, our research will not include radiation exposure testing. The aging experiments will be limited to various combinations of simultaneous exposure of caustic solutions, high temperatures and high pressure stressors. Evaluation of baseline materials will be conducted and compared with materials that have been aged with the various stressors.

FIU has held conference calls with site engineers to discuss specifics about the test plan. It was suggested that FIU should focus on providing a fundamental analysis of the aging effects and the synergistic effects from the multiple stressors. Details including configuration specific testing and coupon testing has been discussed but needs to be finalized. This will significantly influence the number of specimens tested, the cost for testing and the timeline for completing the tests.

During September, engineers from FIU traveled to Hanford to discuss the current and future status of all tasks. A number of site engineers were present for the meeting specifically coordinated for this task. Extensive time was spent discussing the path forward for this task, including the specific materials to be tested. Research previously conducted by Dr. Lieberman includes testing on hose-in-hose transfer line (HIHTL) materials that focused on the effects of temperature and pressure. One additional test was conducted with caustic material in conjunction with elevated temperature and pressure. It was not clear from the meeting what the cost benefit would be for FIU to conduct additional tests with the HIHTLs, if radiation was not included. WRPS engineers will meet to discuss the issue and provide guidance on how to proceed. FIU will continue to develop a test plan for synergistically testing gaskets and o-rings with three of the stressors. We will incorporate HIHTL testing in the initial draft of the test plan, which may be modified at a later date, depending on the guidance provided by WRPS.

The test plan will emulate the test plan previously developed by Sandia National Laboratory with the exception of aging the materials with radiation. Testing will be conducted in two general stages. Initially, the materials will be aged using combinations of elevated temperature, pressure and exposure to caustic material. Degradation of the material will then be quantified via various types of material testing as well as leak testing. FIU is currently planning on testing samples in service configurations as well as coupon samples. Current test methods and standards listed in the Sandia plan are currently being investigated to determine optimal procedures for our current plan.

Milestones and Deliverables

The milestones and deliverables for Project 1 for FIU Year 5 are shown on the following table. No milestones or deliverables were due for this project during this quarter.

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	2014-P1-M17.2.1	Complete computational fluid dynamics modeling of jet	05/11/15	On target	

FIU Year 5 Milestones and Deliverables for Project 1

for Mixing		penetration in non-Newtonian fluids			
Processes	Deliverable	Draft topical report for subtask 17.2.1	05/15/15	On target	OSTI
	2014-P1-M18.2.1	2014-P1-M18.2.1 Complete development of first prototype of the inspection tool		On target	
	Deliverable	Draft summary report for first prototype (subtask 18.2.1)	01/30/15	On target	OSTI
Task 18: Technology Development and Instrumentation Evaluation	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	On target	
	Deliverable	Deliverable Draft experimental test plan for subtask 19.2.1		On target	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 to determine the source of inconsistencies in the plug strength manufactured from kaolin and plaster of Paris. A number of samples will be made to assure minimal variation. Tests will then continue with various amounts of air entrained in the pipeline.
 - For the peristaltic crawler, the bullet valves will be evaluated and the experimental testing of the crawler will be extended to fully flooded conditions. The performance of the crawler will be evaluated for navigational speed and durability. If no other problems are observed, testing will continue with the large scale system.
 - For the computational simulation of plug formation subtask, 3D models will be completed. Work will continue with the analysis of the settling dynamics as a function of operational parameters such as solids volume fraction, particle size, liquid and solids density, etc.
- Task 17:
 - FIU is in the process of acquiring the Star-CCM+ software license and establishing the high performance computing (HPC) requirements that the direct

numerical simulations will require. CD-Adapco has provided recommended computer configurations for similar applications and FIU is working with the IT department for the cost of building such a multi-CPU system. These activities will be completed in the next quarter and single-phase flow simulation 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. A literature review of turbulent flow with Bingham fluids will be simultaneously conducted.

- Task 18:
 - The current test plan will be refined with the addition of the specific pump system and resent to Hanford site engineers on October 31 for review. Meanwhile, initial testing of the sonar with suspended kaolin will be initiated in order to bracket the upper percent solids that obscure the sonar signal. Measurements will be taken at the highest pump power settings to determine: (1) the maximum % volume of solids the pump can entrain in the liquid; and (2) the critical % volume of solids that masks the sonar from imaging the settled solids layer when the sonar is exactly 1 meter from the solids layer. Upon determination of these upper bounds, the test plan execution will commence and the data will be analyzed by the modified imaging software and volume calculation algorithms
 - For the inspection tool task, the new motor and the corresponding wheels will be incorporated into the design during the next performance period. A microcontroller will also be integrated into the design for control of the four motors. Currently, power is supplied separately to each motor. This simplification was done to validate the use of the motors.

Task 19:

- Data from components in the POR 104 Valve Pit will be compiled and analysis will be completed. Efforts will also continue to determine how the data compares to the existing analysis from previous work to provide a better understanding of the overall status of the waste transfer component integrity.
- The initial test plan for the nonmetallic materials testing and evaluation will be completed and submitted for review. It is anticipated that interested parties will provide feedback and we will work with site engineers to incorporate suggestions with the intent of finalizing the test plan. We will also start the process of determining what infrastructure is needed and the associated costs to conduct the aging and testing of the materials at FIU.

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 NH₃ 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 NH₃ Additions

Subtask 1.1: Sequestering Uranium at the Hanford 200 Area by *In Situ* Subsurface pH Manipulation using Ammonia (NH₃) 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°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

FIU continued studying the deliquescence behavior of multicomponent U(VI)-free precipitates created after NH_3 (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 composition of multicomponent precipitate samples was outlined in the June monthly report. Experiments were continued to test calcium chlorine (CaCl₂) and lithium chlorine (LiCl) reference standards, known for their high solubility. The most soluble is LiCl; its maximum molality to obtain osmotic coefficient value for the water activity calculations is 19.219 mol/kg. Pure water was added to the system to increase the humidity and locate water activity values closer to the eutonic point, where the lowest relative humidity coexists with a liquid solution. Results showed an incremental increase in sample water activities following the water addition when the system reached equilibrium.

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 1.573, respectively. For the LiCl, a_w values were found between 0.735 and 0.798 and the osmotic coefficient, phi, between 1.695 and 1.493. The molality values of duplicate standards ranged between 0.2% - 2.6%. Tables 2-1 and Table 2-2 display calculated water activities and osmotic coefficients values using the same equations as previously reported. Both standards showed an incremental increase in water activities as well as decreasing osmotic coefficients. Results showed that the samples haven't yet reached a eutonic point.

a _w CaCl ₂	Na ₂ SiO ₃ + Al(NO ₃)3+ KHCO ₃ (3mM)	Na2SiO3+ Al(NO3)3+ KHCO3 (50mM)	Na2SiO3+ Al(NO3)3+ KHCO3*(3mM) + CaCl2(5mM)	Na2SiO3+ Al(NO3)3+ KHCO3*(50mM) + CaCl2(5mM)	Na2SiO3+ Al(NO3)3+ KHCO3*(3mM) + CaCl2(10mM)	Na2SiO3+ Al(NO3)3+ KHCO3*(50mM) + CaCl2(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

 Table 2-1. Values for water activities, a_w, and osmotic coefficients, Ø, for standards (CaCl₂ and LiCl) and multicomponent samples

a _w LiCl	Na ₂ SiO ₃ + Al(NO ₃) ₃ + KHCO ₃ (3mM)	Na2SiO3+ Al(NO3)3+ KHCO3 (50mM)	Na2SiO3+ Al(NO3)3+ KHCO3*(3mM) + CaCl2(5mM)	$\begin{array}{c} Na_{2}SiO3+\\ Al(NO_{3})_{3}+\\ KHCO_{3}^{*}(50mM)\\ + CaCl_{2}(5mM) \end{array}$	Na ₂ SiO3+ Al(NO ₃) ₃ + KHCO ₃ *(3mM) + CaCl ₂ (10mM)	Na ₂ SiO3+ Al(NO ₃) ₃ + KHCO ₃ *(50mM) + CaCl ₂ (10mM)	Ø LiCi
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	1.347	1.841	3.268	2.392	2.640	3.015	1.465
0.795	1.466	1.901	3.497	2.478	2.786	2.991	1.470
0.798	1.330	1.792	3.408	2.381	2.700	2.964	1.493

Table 2-2. Water Activities, aw and Osmotic Coefficients, Ø for LiCl and samples

Figure 1 shows the osmotic coefficient for multicomponent samples as a function of water activities, aw, using $CaCl_2$ as a standard. From those measurements, the difference between water activities obtained for two standards was calculated as 0.97% (0.808 for $CaCl_2$ and 0.798 for LiCl), demonstrating the accuracy of such determinations via the isopiestic method. As water activities increased, a slight change in the slope in the curve representing the osmotic coefficient of the solution as a function of water activity was noted. The experiment is continuing to increase the relative humidity (water activity) in the system.



Figure 2-1. Osmotic coefficient for multicomponent samples as a function of water activities, aw, using CaCl₂ as a standard

A new set of multicomponent samples was prepared for the characterization studies to investigate the mineralogical and morphological characteristics of precipitates by means of X-ray diffraction (XRD) and scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS). The concentration of silica this time was reduced to 50 mM, and the concentration of U was increased up to 500 ppm. Sample tubes were left for 2 weeks to cure and monitoring of pH changes was performed. The XRD analysis will be performed in the month of October.

A DOE Fellow, Robert Lapierre, spent 10-weeks on a summer internship at PNNL performing research and assisting Dr. Jim Szecsody. Robert worked with Geochemist's Workbench and Visual Minteq to attempt to model the equilibrium reactions associated with relevant

experiments. These simulations are an attempt to predict the product phases in order to support other analytical findings.

During August, FIU continued to work with Visual Minteq and Geochemist's Work Bench to model the equilibrium reactions for the various changes in the experimental systems for this study. To evaluate the understanding and effectiveness of the updated Visual Minteq (v3.1) software, simulations were run to model the effect of increasing the concentration of NH_4^+ on pH in a solution with components similar to that which would be seen in sample preparations (Figure 2-2). Similar simulations were used to observe the effects that modifying pH, using NH_4^+ concentration, had on the silicates in solution (Figure 2-3). More simulations, including uranium speciation changes, have been attempted with varying degrees of success. Complications currently being addressed with the speciation software include the inability to use the precipitation function and the lack of thermodynamic information for some of the anticipated phases.



Figure 2-2. Relationship between pH and [NH₄⁺]



Figure 2-3. Speciation of Silicates vs pH

On September 18-19, engineers from FIU traveled to Hanford and PNNL to present an overview of Project 2, including background, relevant past performance, planned deliverables and milestones and discuss the current status of the FIU Year 5 scope of work related to the Hanford Site. FIU, together with the PNNL site contacts, Jim Szecsody, Nik Qafoku and Brady Lee, also discussed the renewal application for the FIU proposed scope for 2015-2020. In addition, FIU engineers attended a conference for the National Association of Black Geoscientists, 33rd Annual Technical Conference "Environmental Innovation - Collaborations for the Future" in Richland, WA. Two DOE Fellows, Christian Pino and Robert Lapierre, were awarded funding to attend the event and present their ongoing EM research. Christian Pino gave an oral presentation, "Use of XRF to Characterize Pre-Hanford Orchards in the 100-OL-1 Operable Unit," showing soil sampling results he obtained via an XRF analyzer during his 2014 summer internship for evaluating levels of lead and arsenic in the soil still present from lead arsenate pesticide historically used by orchardists. Robert Lapierre also gave an oral presentation on the research involving the attempts at characterization of the uranium phases produced by the proposed NH₃ injection for vadose zone remediation. The conference proved to be a valuable opportunity to network with peers who could provide input, advice, and constructive criticism on the research and presentations for both students. Aside from the conference, Robert worked on preparing a technical report detailing the results of his summer internship. The report was written with scrutiny towards omitting a sizable portion of the work done that was determined to be inappropriate for public release. With the exclusion of this portion of the research, the scope of the report was limited to the study and application of geochemical modeling software, such as The Geochemist's Workbench, and the development of the research experimental plan. The latter of these two objectives involved networking with some of the Pacific Northwest National Laboratory scientists most knowledgeable on the subject from past and current projects.

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

FIU continued work on two manuscripts written in collaboration with PNNL researchers. Changes were incorporated to the manuscript on the "Effect of Bicarbonate on the Microbial Dissolution of Autunite Mineral." Changes were also incorporated into the second manuscript, titled, "The Effect of Uranium on the Bacterial Viability and Cell Surface in the Presence of Bicarbonate Ions." The text was reframed: more experimental details were included in the write up, new bacteria profile plots were drawn to improve the graphics and to make sure all samples presented were evaluated with the same magnification. Images from the optical fluorescence microscope of the Live and Dead assay were reprocessed to improve clarity. The methodology on atomic force microscopy was updated and more details and discussions were added to the text in the results and discussion sections. The revision of these two manuscripts was finalized and the manuscripts were prepared for the submission to the peer-review.

The work under this subtask also included maintaining the equipment to keep the bacteria frozen, obtaining laboratory supplies to conduct the microbial experiments, and preparation of the Shewanella bacteria culture for freezing at -80C. Shewanella oneidensis MR1 was obtained from PNNL and FIU initiated preparation of stock using LB media for future freeze stocks from that.

FIU hired a master's level student from the Environmental Engineering Department, Sandra Herrera, to work on the effect of facultative microorganisms (e.g., Shewanella) on the dissolution of autunite mineral in the presence of the bicarbonate ions. Sandra started learning procedures for culture maintenance and currently is taking FIU Health and Safety training to be able to work in the laboratory.

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

On August 5-6, staff from FIU visited SRNL and presented an overview of Project 2, including background, relevant past performance, planned deliverables and milestones and the current status of the FIU Year 5 scope of work related to SRS. FIU, together with the SRS site contacts, Miles Denham and Brian Looney, took a tour of the F/H area remediation sites and Tims Branch. The discussion was extended to the renewal application for the FIU DOE proposed scope for 2015-2020.

FIU Year 4 Carryover Work Scope

During this reporting period, FIU initiated U(VI) adsorption experiments with 50 ppm HA and 3.5 mM colloidal silica solution in the pH range of 3-8. Triplicate samples of Batches 2 (silica, HA and U) and 3 (HA, U) were prepared by mixing humic acid, colloidal silica oxide and uranium solutions as per Table 2-3. The pH of the samples was later adjusted between 3-8 using 0.01M HCl and 0.1M NaOH. Samples were placed on a shaking platform for over 3 days at 1000 rpm and were then centrifuged at 2700 rpm and 22°C for 30 min. Samples for the batch 2 (silica + humic acid) and 3 (humic acid) from pH 3 through 8 were filtered using a 0.45µm filter. Samples were diluted 1:10 using 1% HNO₃ and analyzed by using kinetic phosphorescence analyzer (KPA) in order to determine the concentration of uranium remaining in solution to calculate the percent uranium removal using the two different conditions from batch 2 and 3. The results obtained from the analysis are shown in Table 2-6 for the 50 ppm humic acid.
Table 2-3. Sample Composition										
				Consti	tuents					
Batch #	SiO ₂	Humic Acid	Uranium U(VI)	Vol of 0.01M HCl*	Vol of 0.01M NaCl*	Water H ₂ O	Initial pH*	Total Volume		
	mL	mL	mL	mL	mL	mL	Log(H)	mL		
				рН 3						
Batch #2	2.1	10	0.04	2.9	0	7.86	6.31	20		
Batch #3	0	10	0.04	2.7	0	9.96	6.37	20		
				pH 4						
Batch #2	2.1	10	0.04	0.67	0	7.86	6.36	20		
Batch #3	0	10	0.04	0.67	0	9.96	6.4	20		
				pH 5						
Batch #2	2.1	10	0.04	0.3	0	7.86	6.34	20		
Batch #3	0	10	0.04	0.34	0	9.96	6.5	20		
				рН б						
Batch #2	2.1	10	0.04	0.04	0	7.86	6.38	20		
Batch #3	0	10	0.04	0.12	0	9.96	6.6	20		
				pH 7						
Batch #2	2.1	10	0.04	0	0.26	7.86	6.35	20		
Batch #3	0	10	0.04	0	0.32	9.96	6.53	20		
				pH 8						
Batch #2	2.1	10	0.04	0	0.1	7.86	6.17	20		
Batch #3	0	10	0.04	0	0.07	9.96	6.42	20		

*Average value of triplicate samples

Higher percentages for removal of uranium were observed when the samples were filtered compared with unfiltered samples. When the samples were filtered, the colloidal silica particles and humic acid molecules bonded to uranium that were suspended in solution were removed, increasing the percentage of uranium removed for the filtered samples. Colloidal silica particles and humic acid molecules tend to aggregate at low pH because the surface of these molecules have very little charge, allowing the aggregation and precipitation from the solution; if uranium binds to the charges present at the surface of silica and humic molecules, it will neutralize those charges, allowing the aggregation. When the pH is increased (Table 2-4), less uranium is removed, and the possible explanation for this is that silica and humic molecules at higher pH will contain more negative surface charges and uranium will not be able to neutralize all these charges; so, the silica and humic acid molecules will repel each other. Also, when the pH is increased, the uranium species that starts to dominate have negative charges, so uranium will not be able to bind to humic molecules due to electrostatic repulsion. The results for the 50 ppm humic acid were compared with previous results (10 ppm humic acid) at similar conditions. Clearly, the use of higher concentration of humic acid decreases the removal of uranium from solution. This experiment will be repeated to insure the accuracy of the results. Another set will be initiated using soil samples according to the experimental matrix.

		Uranium (%	Removal %)*
рН	Batch	Filtered	Unfiltere d
		50 pp	om HA
2	2	35.58	24.32
5	3	27.61	19.97
Λ	2	21.76	18.57
4	3	13.22	15.83
F	2	19.29	16.99
5	3	9.6	11.66
6	2	12.71	9.87
0	3	12.5	9.99
7	2	13.14	8.92
/	3	12.32	-3.55
Q	2	20.74	15.55
0	3	14.73	12.11

Table 2-4. Percent of Uranium Removal from Solution in the Presence of 50 ppm Humic Acid

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

X-ray diffraction (XRD) analysis is a necessary step to determine if fine clay fractions will reveal ferrous iron solid phases such as pyrite and siderite. In preparation for this step, DOE Fellow Aref Shehadeh undertook XRD training at the FIU Advanced Materials Engineering Research Institute (AMERI) Lab. The training provided instructions on safety, operation, and analysis procedures and demonstrated XRD analysis of powders; a similar procedure to the clay fraction XRD analysis.

X-ray diffraction (XRD) analysis was conducted on the fine clay fractions of previously collected soil samples. The soil samples tested were from a depth of 65-68 feet with the expectation that they would reveal matches with quartz, goethite, kaolinite, montmorillonite, mullite, and/or muscovite. The sample was tested over a 2-theta range from 2.5° to 90°, with a 0.02° step size and 3 seconds count per step. The results were not conclusive due to either errors during sample preparation or a fault in the XRD equipment. Another XRD analysis was conducted for the same sample to determine if the stated minerals are present before soil treatment with molasses. The sediments tested were previously sieved at 63 mm, 125 mm, and 180 mm. Sieving was a necessary step to remove larger quartz particles which shield the finer clay fractions in XRD analysis. The results indicated that the sediments contained quartz, kaolinite, montmorillonite, and goethite (see figures below). All grain sizes tested had visible peaks for the clay fractions and thus it was determined that 180 mm sieved sediments will be used in the upcoming microcosm study.



Figure 2-4. XRD Results for Soil Samples from a Depth of 65-68 Feet.

The microcosm study will be used to determine if soil treated using a basal medium solution augmented with sulfate and molasses would arise in siderite and pyrite in the reducing zone and if any mineralogical changes occurred in sediments during the re-oxidation period. Based on a literature review, the optimal range of sulfate addition is 10-20 ppm per liter of basal medium. In anaerobic conditions, sulfate-reducing bacteria will reduce sulfate to sulfide, which in turn precipitates when reacted with ferrous iron. With the addition of a sulfate salt, it is expected that more ferrous iron precipitates will form in the soil. In addition, it is expected that there will be an increase in the pH and alkalinity of the soil, due to the release of HCO_3^- in the microbial reduction process.

The basal medium solution was prepared and consists of (in g L⁻¹ deionized water) NaHCO₃ 1.5, NH₄Cl 0.2, K₂HPO₄ 3H₂O 0.1, KH₂PO₄ 0.055, resazurin 0.001 as a redox indicator, Na₂S 9H₂O 0.039 as a sulfur source and reductant, and MgCl₂ 6H₂O 0.1. In addition, a 5 mL L⁻¹ trace metal solution was added. The trace metal solution consists of (in g L-1) FeCl₂ 4H₂O 0.005, MnCl₂ 4H₂O 0.001, Kl₂DO 0.001, H₃BO₃ 0.0006, ZnCl₂ 0.0001, NiCl₂ 6H₂O 0.0001, Na₂MoO₄ 2H₂O 0.0001, and CaCl₂ 2H₂O 0.002. In this study, the basal medium will also consist of 10-20 ppm of sulfate salt. We expect that the addition of the sulfate salt will result in more ferrous iron precipitates detected via XRD analysis.

New SRS sediments were received on September 29, 2014, and sieved through 180 μ m in preparation for the microcosm study. Soil preparation was on progress to meet a milestone for completing the microcosm set up by October 13, 2014.

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

Hansell Gonzalez, a DOE Fellow, conducted experiments on humic acid sorption under the mentorship of Dr. Miles Denham at SRS. In July, humate injection for the three remaining type of sediments was performed using the 1000 ppm humate stock solution. Six different concentrations of humate (50, 100, 150, 200, 250, 300 ppm) were tested. The pH of the samples was adjusted to 4 to simulate the SRS groundwater environmental conditions. The samples were placed in the shaker for 24 hours, and then centrifuged at 2700 rpm for 30 minutes. The next step was the analysis of the supernatant of the samples using a UV-VIS spectrophotometer in order to determine concentrations that were sorbed by the sediments. Once the analysis was finished, the liquid from the samples was transferred to vials. The second part of the experiment was the desorption studies. The centrifuge tubes containing just the sediment and the humate that was sorbed were filled with deionized water at pH 4 to the same volume (20 ml). The samples were shaken for 24 hours and then centrifuged at 2700 rpm for 30 minutes. After that, the supernatant was analyzed to determine concentration, E_4 / E_6 ratio (this ratio tells whether the fraction in solution contains fulvic or humic acid), and E_{ET} / E_{BZ} ratio, which is the ratio showing the degree of substitution in the aromatic rings.

During August, Hansell finalized the experiments on humic acid sorption by measuring the concentration of humate in the desorption experiments conducted for four types of sediment samples. In addition, E_4/E_6 and E_{ET}/E_{BZ} ratios, which correspond to the molecular size and degree of substitution, respectively, were measured using the same instrument for both the sorption and desorption experiments. Upon obtaining all data, the analysis and interpretation of the results have been initiated. Several models were researched that could best explain the adsorption behavior of the humate to the sediments. It was found that Langmuir and Freundlich isotherms best represented the experimental data. The data was plotted using both models and, according to the results, data on the sorption behavior of humate to the sediments are presented in the sorption behavior of humate with four different types of sediments are presented in the Hansell's internship report. The desorption studies suggest some humate is desorbed from the sediment after four sequential desorption experiments. The percentage of desorption was also varied for each type of sediment. Calculated data for humate desorption are shown in Table 2-5.

The sorption experiments using humate at different pH values will be continued at FIU. To be able to measure humate concentration and evaluate for the fraction of humic molecules, FIU obtained a quote for the Termo Scientific Spectrophotometer, Genesys 10S UV-VIS and Visionlite 5 software. The same instrument was used for humate analysis by Hansell Gonzalez at SRS.

Tuble 2 cr	Task 2-5. Concentration of Humate Kemaining in the Sond Huse arter Four Desorption Experiments									
	Sorption	First Desorption	Second Desorption	Third Desorption	Fourth Desorption					
Sample Name	Concentration [ppm]	Concentration [ppm]	Concentration [ppm]	Concentration [ppm]	Concentration [ppm]					
B1S1 300ppm	95.248588	73.466938	65.218381	59.017338	56.794323					
B1S2 300ppm	71.380423	49.286771	39.400203	28.655629	25.555108					
B1S3 300ppm	71.575425	52.952797	43.20273	33.160161	30.488643					
B2S1 300ppm	141.99041	118.161246	107.845675	102.288137	99.88962					
B2S2 300ppm	136.471872	108.352678	92.850071	84.289512	79.375478					
B2S3 300ppm	146.026938	114.690222	100.221122	90.588056	87.097532					
B3S1 300ppm	95.61909	80.779488	75.592452	73.778939	72.023927					
B3S2 300ppm	96.633097	81.09149	76.118956	74.110442	72.296929					
B3S3 300ppm	94.176081	78.458973	74.227444	72.277431	70.834421					
B4S1 300ppm	191.18925	159.170029	136.978876	124.674291	111.316699					
B4S2 300ppm	153.066487	114.690222	95.385089	84.153012	72.082429					
B4S3 300ppm	119.194753	79.004976	57.203826	39.595205	29.474635					

Table 2-5. Concentration of Humate Remaining in the Solid Phase after Four Desorption Experiments

During the month of September, FIU received sediments from Savannah River Site and the UV-Vis spectrophotometer for the continuation of the humate sorption experiments. The experimental plan was also discussed. First, sediments have to be disaggregated with a mortar and pestle using minimal force to keep the original texture of the sediment and avoid as much change as possible. After disaggregation, the sediment will be sieved to a particle size of ≤ 2 mm. Also, some preliminary experiments will be done with just humate solution and UV-Vis spectrophotometer in order to determine the different factors that could potentially affect the measurement of the humate concentration, such as pH and other parameters.

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

Task 3 Overview

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

Task 3 Quarterly Progress

FIU continued to review literature and the procedures which will allow the determination of ammonia gas partitioning and solubility. It was found through the review of existing literature on ammonia gas (NH₃) interactions with soil systems that research has predominantly focused on agricultural systems and the effects on crops due to volatilization rates as well the ammonianitrogen contained in fertilizers and the process of plant uptake. Although the presence of bicarbonate in soils is referenced in studies, ammonia buffering conditions have not been investigated much, leading to insufficient availability of data. On the other hand, similar investigations using phosphorus have been previously conducted to evaluate the effects of such parameters as well as aspects of the soil/gas interactions. Despite these experiments, the quantification of gas dose to counteract buffering has not been possible. These investigations, however, proposed the use of proportional studies in which the amount of the injection and bulk density of the soil as well as depth or rate of equivalence would be taken into account. Such methods could be applied to the investigation of ammonia gas injections.

Literature reviewed to determine the appropriate experimental methods proposed the use of electrochemical measurements using a simple design work-cell to determine the solubility of gases in solutions. This experimental method recommends the use of potentiometric sensor studies for the determination of gas partitioning. In subsequent reports, the solubility of ammonia gas was explored to confirm partitioning of NH₃ into water. These experiments relied on NH₃ gas bubbled into water with specific pH, temperature, and electrical conductivity monitoring. Further investigation of experimental methods suggests headspace gas chromatography, specifically E-HSGC (equilibrium headspace gas chromatography) and more recently the VPC (vapor phase calibration) method. The E-HSGC can be used to obtain physico-chemical data based on the system's partitioning phases, and the VPC method offers an additional means for quantitative analysis of the gas phase by means of external calibration in which K can be derived or calculated by differences found between the peak areas within the sample volume variation against a referenced standard. Results of such studies have been found useful in the determination of a wide range of partition coefficients, as well as useful for fully automated procedures.

Following the scope of the investigation, FIU continued to review literature and procedures on analysis of NH₃ in the presence of bicarbonate-bearing media under the influence of different pH and temperature conditions. These reviews helped to narrow down possible methods or procedures to analyze NH₃ in the aqueous solutions. It was found through these reviews that potentiometric studies using an ion-selective electrode may be implemented in order to obtain the desired information on the system. This method (EPA approved 350.3) seems to be more effective for this task due to the ample range of measurement (0.01 to 17000 mg/L) of ammonia available for the ion-selective Thermo Scientific Orion ammonia electrode. In addition to this, the results are not affected by the samples' turbidity or color, which eliminates the necessity for distillation processes.

In addition, colorimetric experiments such as the EPA Method 1960 are also under consideration and further research and literature reviews are under way to determine the effectiveness and reliability of these procedures. Method 1960 is predominantly used for the determination of ammonia in water including ground, drinking and surface water. This method involves distillation of the sample followed by analysis through a colorimetric analyzer. Ammonia concentration is then determined by the measurement of the indophenol blue formed with the interaction of alkaline phenol and hypochlorite.

Following the analysis of potential experimental procedures for this task, it was determined that a potentiometric study could be used to determine the reactions of ammonia gas and thus determine partitioning rates within bicarbonate media. This led to the selection of a preliminary method of analysis of ammonia gas by using ion-selective technology to ultimately determine the equilibrium concentrations between ammonia gas and the aqueous media.

The selected method of investigation consists of using a potentiometric study, as described by the EPA approved method 350.3, in which ammonia concentration and activity can be determined by using an ion-selective electrode (Thermo Scientific Orion VERSA STAR

pH/ISE/Temperature Module). Further investigation regarding gas/liquid equilibria is still needed in order to determine the point at which the different concentrations of ammonia gas and the aqueous media reach equilibrium. The ammonia-selective electrode uses a hydrophobic gaspermeable membrane that separates the sample solution from the electrode's internal solution of ammonium chloride. The solution's pH is then raised above pH 11, at which point the NH₃ diffuses through the electrode's membrane and changes the internal solution's pH and is sensed by the electrode. The potentiometric measurements are taken by using a pH meter with an expanded millivolt capability. This method is capable of detecting a wider range of concentrations of NH3-N in the media of 0.03 to 1400 mg NH3-N/L in aqueous solutions. The dissolution of ions affects the measurement capability but they are not affected by color or turbidity.

FIU acquired the Thermo Scientific Orion Ammonia Gas-Sensing Combination electrode and Versa Star Conductivity meter equipped with Vstar-ISE module to be able to measure conductivity, pH, ammonia and temperature values. The experimental 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 bench top meter. All instruments and modules have been attached and calibrated to standards prior to beginning the testing phase. Ammonia gas of 100% concentration has also been ordered and is due for delivery to FIU. Other instruments and components necessary for the experimental phase have also been acquired and they include Khloen pump syringes in 25 mL and 50 mL sizes, 2L PTFE Luer-Lok (TLL) gastight syringes and Cole-Parmer gas sampling bags (FEP – 5mil thickness/4.7 L). Preliminary testing and experimentation will begin by using lower concentration NH3 gas (5% and 10%) in aqueous media during October 2014. The results obtained during the preliminary phase will allow for better predictions of the methods required to analyze the ammonia gas reactions within the bicarbonate bearing solutions.

Milestones and Deliverables

The milestones and deliverables for Project 2 for FIU Year 5 are shown on the following table with status through September 30, 2014. Milestone (2014-P2-M6), completing preparations for the microcosm experiments prepared with SRS sediments using sulfate additions, was originally due on September 12, 2014. This date was re-forecasted to October 13, 2014 to provide SRNL the time needed to collect, analyze for potential radioactivity, package, and ship the sediments to FIU. This milestone delay has been discussed with SRS site contacts and communicated to DOE HQ via email on September 5, 2014.

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	On Target	
	2014-P2-M3	Completion of sample preparation using a reduced amount of silica (50 mM)	11/07/14	On Target	
	2014-P2-M4	Complete preparation of a draft	12/15/14	On Target	

FIU Year 5 Milestones and Deliverables for Project 2

		manuscript on the removal of uranium via ammonia gas injection method			
	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	01/30/15	On Target	
		predictions at low water activities values (carryover scope).			
	Deliverable	Prepare a progress report on the solubility measurements via isopiestic method (subtask 1.1)	02/16/15	On Target	OSTI
	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	Re- forecasted	
Task 2:	Deliverable	Progress report on microcosm studies prepared with SRS sediments augmented with molasses and sulfate (subtask 2.2)	01/30/15	On Target	OSTI
Groundwater remediation at SRS	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	On Target	

Work Plan for Next Quarter

- Subtask 1.2 Continue with multicomponent samples characterization studies to investigate the mineralogical and morphological characteristics as well as deliquescence behavior of multicomponent U (VI)-free precipitates. Initiate preparation of U(VI)-bearing samples.
- Subtask 1.2: Complete revision and submit manuscripts prepared based on the experimental results on G968 strain dissolution of autunite minerals and cells viability assessment to peer-reviewed journals. Complete set up of biodissolution experiments with autunite and initiate sampling and sample preparation for analysis.
- Subtask 2.2: Continue monitoring of evolution of samples pH amended with and without sulfate for ARCADIS work.
- Subtask 2.3: Complete preparation of soil and initiate sorption experiments with HA in the pH range between 4 and 9.
- Task 3: Set up experiment and initiate testing of ammonia concentrations at 0 mM of bicarbonate.
- Subtask 1.1: As part of the carryover scope, continue testing different standards such as calcium chloride and lithium chloride to get better deliquescence predictions at low water activities values. Prepare a new set of samples for testing of uranium-bearing precipitates via SEM/EDS and XRD.
- Subtask 2.1: As part of the carry over scope, continue sample preparation and analysis to explore the effect of the higher humic acid concentrations up to 50 ppm. The experimental matrix will be 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

FIU Year 4 Carryover Work Scope

Task 1. Technical Report for EFPC Model Update, Calibration and Uncertainty Analysis

The task was closed in April 2014. The final technical report was drafted and submitted on July 31, 2014. The final report contains a summary of the work completed for this project during this year and includes a description of the model for EFPC, a summary of completed simulations and results. The main emphasis of the report is on the work conducted during the last year and more specifically on the development of the kinetic model and the thermodynamic database for mercury speciation.

Subtask 1.1: Work plan for experimental column studies

- Communicated with Miles Denham via regular teleconferences to discuss specifications for the column studies, including parameters such as pH range, soil type, concentration of HumaK, column size, flow rate and soil particle size. It was suggested that a component in the Work Plan be added to specifically deal with calculations of flow rates and other relevant data parameters.
- The use of synthetic soil versus actual SRS soil was also further discussed. FIU ARC does not have a current soil permit required to get soil from outside FL shipped to FIU, so

various options are being considered in the interim during the process of permit renewal. Options being considered include: 1) the use of synthetic soil which will be made to mimic SRS soil conditions in the F/H Area study domain, or 2) the use of actual SRS soil from an uncontaminated area of the same aquifer as the study area which can be shipped to another laboratory within FIU that has a current soil permit.

- Continued review of approximately 150 documents received from SRS on data regarding SRNL for soils within the area, contaminants, and water quality data. Data obtained from SRS includes scientific articles, technical reports, presentations, and papers from the Waste Management conferences. The documents were classified into different areas and data is being extracted to understand the operating parameters of the proposed column studies. Additional journal articles have also been downloaded related to the contaminants of concern.
- A review of the biogeochemistry's significance on the fate and transport of metals in different soils has continued to determine potential soil substitutes to be used in the column studies, which will provide data that is similar to the soils at SRS. Use of soil from an uncontaminated zone within the same aquifer can be used an alternative for SRS soil.
- Completed development of a work plan for the experimental column studies to test the migration and distribution of humate injected into subsurface systems. The work plan has undergone FIU-ARC internal review as well as review by Miles Denham from SRNL. The work plan was submitted to SRS and DOE HQ (EM-12) on September 26, 2014.



Figure 3-1. Study of humic acid sorption/desorption in SRS soil.

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

Subtask 1.2, conducting column tests, will be initiated after completion of the work plan under Task 1, Subtask 1.1.

- The next step (i.e. Stage 1 in Figure 3-1) will involve performing calculations to determine concentrations of humic acid and flow rates using a spreadsheet provided by SRNL (Brian Looney) to support this phase of the project.
- Soil characterization will be performed for soil obtained from SRS. Parameters estimated during the characterization will be used in the spreadsheet to calculate concentration and flow rates.

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 GIS and hydrological data for development of a flow and transport model have been requested.

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

FIU Year 4 Carryover Work Scope

Technical Report for Simulation of NPDES- and TMDL- Regulated Discharges from Non-Point Sources for EFPC and Y-12 NSC

The task was closed in April 2014. The final technical report was drafted and submitted on July 31, 2014. The final report contains a summary of the work completed for this project during this year with the main emphasis on an update of the hydrological and water quality data from the outfalls at the upper portion of East Fork Poplar Creek (within the Y-12 NSC).

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

- Preparation work to receive and process the GIS data from SRS has been completed. FIU is prepared for the data to be uploaded to the FTP site from SRS; external drives were not allowed onsite SRS during FIU's visit in August.
- FIU provided clarification on a number of issues related to the GIS data in order for SRS to process the data, including:
 - The version of ArcMap being used by FIU which will determine the manner in which the data can be transmitted.
 - The preference to use a USGS watershed boundary vs the SRS IOU watershed boundary as it contains additional gauges, more refined boundaries, as well as better elevation data.

- The SRNL task lead, Brian Looney, also provided clarification for the inclusion of radiological survey layers as he thought they would be useful in providing some background uranium data.
- A list of relevant GIS data for this task was provided to SRNL by FIU-ARC to support the modeling work in Subtask 2.2. SRNL personnel have been working to acquire the appropriate security clearance and approvals to release this data. The data is expected to become available to FIU by the first week of October. Discussions still need to be held to determine the best means by which the data should be transferred given its size.

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

- Continued review of available data for collection of SRS site characterization data needed for the models.
- Data requirements of MIKE SHE and MIKE 11 were reviewed and are being compared to data currently available in reports and other literature.
- A document was compiled and sent to SRNL which outlines the parameter inputs and attributes for the model and GIS geodatabase development. The requested parameter inputs are shown in Table 3-1. The data requirements include shapefiles, gridded data, river data, and boundary data. Following the data requirements, discussions with site personnel will be initiated to determine what is currently available, what data can be obtained if needed, and the approach to filling any data gaps which may exist.
- Previous reports and literature of the hydrology, monitoring data, and conceptual model continue to be reviewed for the development (or update) of existing conceptual models.

1	1 0
Shapefile	
	Watershed boundaries
	Monitoring point locations
	River and stream network
Gridded Data	
	Topography (gridded or contours will work)
	Aerials
	Hydraulic conductivity (for each layer)
	Depth of the bottom of each subsurface layer
	Depth of each soil layer
	Soil layers (classifications)
	Vegetation (Manning's number will be assumed based on
	classifications)
River Data	
	Cross sections, Manning's number
	Boundary Data and/or Calibration Data
	Timeseries of river discharge and stage
	Timeseries of rainfall
	Timeseries of evapotranspiration
	Timeseries of groundwater levels
	Timeseries of additional data collected from monitoring points

Table 3-1. Parameter inputs and attributes for development of MIKE 11/MIKE SHE hydrological model

- FIU continued to research and integrate the information and data from over 100 publications sent to FIU by SRNL. This includes 6 new documents given to FIU during the visit to SRS on August 5-6, 2014.
- Progress on the modeling component of this task has been delayed while a new task lead is being sought. In the meantime, SRNL has been assisting FIU-ARC with the acquisition of relevant GIS data to support this task.

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

FIU Year 4 Carryover Work Scope

Task 3. Technical Report for Sustainable Remediation and Optimization: Cost Savings, Footprint Reductions, and Sustainability Benchmarked at EM Sites

A summary report on Green and Sustainable Remediation at DOE Sites with supplemental information on the use of SITEWISETM was submitted to SRS site contacts and DOE HQ (EM-12 & EM-13) on September 26, 2014. The genesis of this report was to summarize knowledge of GSR acquired by FIU in 2013 that formed the basis for implementation of SiteWiseTM at a DOE EM site. For this reason, while this report summarizes GSR, it also goes with greater depth into the application of SiteWiseTM in general, providing an example of SiteWiseTM implementation at the Savannah River Site (SRS). The report summarizes GSR and GSR tools and their application (see GSR Planning & Implementation flowcharts in Figures 3-3 and 3-3). There are a limited number of documents on GSR and its application since the concept and tools have been mostly developed over the past decade and are not widely implemented. For this reason, this report is meant as a primer. It is hoped that the section with key GSR resources (documents, webpages, and government leaders) might be especially useful for those wishing to learn about and apply GSR tools at their remediation sites. The Interstate Technology & Regulatory Council (ITRC) GSR training presentation, the U.S. Environmental Protection Agency (EPA) GSR and Green

Remediation documents and U.S. DOE reports and presentations were key sources for this summary report.

Subtask 3.1: Analyze Baseline.

The following work was completed during this reporting period:

- Analyzed all contaminant data sent on spreadsheets for several years of performance of the air stripper. Awaiting actual power of pumps or the theoretical horsepower of the pumps in order to calculate the contaminant removal efficiency over time as well as the energy efficiency of the system per unit volume of contaminant removed.
- FIU staff traveled to SRS to meet with SRNL scientists and view the air stripper, GRS, catch basins, remediation systems and Tims Branch to better inform the conceptual modeling and the efficiency calculations.
- Received the pump specifications from SRNL. This completes the data needed to complete calculations of the mass of TCE and PCE recovered over time and energy used for the air stripper operations. Analysis of TCE and PCE recovery in 1987 was completed as an initial analysis of the data. Analysis of all hours of operation from January 1987 through December 2012 (last month of data at FIU) is well underway and will be completed in early September. Work on June 1982 to December 1986 will follow and will require incorporation of new wells and more extensive testing phases of the system.
- Completed calculations of the contaminant recovery for the period (1987-2012) for each of the 18 recovery wells as well as the sum of all the wells. A plot of mass of contaminants recovered (and destroyed) over this 31-year period for all wells combined has been generated. Results were submitted to the Project 3 Task 3 lead at SRNL (Ralph Nichols) for review.
- Created flowcharts depicting the sequential steps in the planning and implementation of GSR. The flowcharts were included in the summary report and are shown in the following two figures.



Figure 3-2. GSR planning flowchart.



Figure 3-3. GSR implementation flowchart.

FIU Year 4 Carryover Work Scope

Task 4. Technical Report for Geodatabase Development for Hydrological Modeling Support

The task was closed in April 2014 and the final technical report completed and submitted as an Appendix to the FIU Year 4 Year End Report on 6/30/14. The report details the final work provided for this task. The task has provided support to the hydrological modeling work being performed by FIU-ARC at the Oak Ridge Reservation (ORR) through development of a GIS-based database (geodatabase) which provides an advanced spatial data structure for management, processing, and analysis of spatial and temporal numerical modeling data derived from multiple sources. ArcGIS ModelBuilder coupled with Python scripting was used to extend the geodatabase capabilities to more easily query data and automate many of the repetitive geoprocessing tasks required for pre- and post-processing of hydrological modeling data. Finally, a web-based GIS map which depicts hydrological modeling results was created so that project derived data can be more easily shared with project stakeholders including DOE personnel and ORR site contractors.

Milestones and Deliverables

The milestones and deliverables for Project 3 for FIU Year 4 are shown on the following table. ARC-FIU visited SRS on 5-6 August, 2014 and attended a series of meetings with SRNL contacts to discuss current Year 5 work scope as well as potential scope for the next five years. A tour on-site SRS of the areas where the collaborative research between ARC-FIU and SRNL is focused was also given, including the catch basins, air stripper, remediation systems and Tims Branch. This completed milestone 2014-P3-M5, "SRS site visit and meeting." In addition, two (2) abstracts were also submitted to WM15 based on research related to Project 3, which meets that deliverable.

The work plan for the experimental column studies being conducted under subtask 1.1 was completed and submitted to the relevant SRS and DOE-HQ (EM-12) contacts on September 30, 2014.

Task	Milestone/Deliverable	Description	Due Date	Status	OSTI
Task 1:		Completion of			
Modeling of		work plan for			
the migration	2014-P3-M1	experimental	9/30/14	Complete	
and		column studies			
distribution		(Subtask 1.1)			
of natural		Work plan for			
organic	Deliverable	experimental	9/30/14	Complete	
matter	Denverable	column studies			
injected into		(Subtask 1.1)			
subsurface	Deliverable	Technical Report	6/3/15	On Target	
systems	Deliverable	for Task 1	0/3/13	On Target	
Task 2:		Completion of			
Surface	2014-P3-M2	literature review	12/30/14	On Target	
Water		(Subtask 2.2)			

FIU Year 5 Milestones and Deliverables for Project 3

Modeling of Tims Branch	Deliverable	Literature review summary (Subtask 2.2)	12/30/14	On Target	
	2014-P3-M3	Development of preliminary site conceptual model of Tims Branch (Subtask 2.2)	12/30/14	On Target	
	Deliverable	Technical Report for Task 2	6/10/15	On Target	
Task 3: Sustainability Plan for the A/M Area Groundwater Remediation	2014-P3-M4	Completion of Baseline Analysis (Subtask 3.1)	mpletion of seline 2/27/15 alysis btask 3 1)		
	Deliverable	Baseline analysis summary (Subtask 3.1)	2/27/15	On Target	
System	Deliverable	Technical Report for Task 3	6/17/15	On Target	
	Deliverable	Draft Project Technical Plan	6/18/14	Complete	
	Deliverable	Two (2) abstract submissions to WM15	8/15/14	Complete	
	2014-P3-M5	SRS site visit and meeting	8/5/14	Complete	
Project-wide	2014-P3-M6	Meeting and presentation of project progress at SRS	3/18/15	On Target	
	Deliverable	Presentation overview to DOE HQ/SRNL of the project progress and accomplishments (Mid-Year Review)	11/21/14**	On Target	

Deliverable	Presentation overview to DOE HQ/SRNL of the project progress and accomplishments (Year End Review)	6/30/15**	On Target	
Deliverable	Draft Year End Report	6/30/15	On Target	
Deliverable	Monthly Progress Reports	Monthly	On Target	
Deliverable	Quarterly Progress Reports	Quarterly	On Target	

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

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

Work Plan for Next Quarter

Project-wide

- Submit two (2) technical papers to WM15 by 09/7/14.
- Prepare a presentation of the project progress and accomplishments for SRS/SRNL and DOE-HQ EM-12/13 (Mid-Year Review) by 11/21/14 (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 estimation of flow rate and concentrations to be used in the column studies.
- Begin laboratory preparation for column testing of the migration and distribution of humate injected into subsurface systems.
- Conduct column tracer test and collect relevant hydrological data for the subsurface properties required for development of a subsurface flow, fate and transport model of humic acid, including geological layers, hydraulic conductivity, porosity, bulk density, etc.

Task 2: Surface Water Modeling of Tims Branch

- GIS data for the Tims Branch watershed will be imported into ArcGIS. The path forward is to clip and preprocess this data for input into the hydrological model based on specified boundary conditions determined in coordination with the SRNL task lead.
- Progress on the modeling component of this task has been delayed while a new FIU-ARC task lead is being sought. In the meantime, SRNL will continue to work with FIU-ARC for pre-processing of the relevant GIS data in support of this task and to develop a detailed GIS-based representation of the Tims Branch ecosystem (Subtask 2.1)

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

- Natalia Duque and David Roelant will hold a conference call with Ralph Nichols, SRNL, to discuss missing and questionable data and a path forward.
- The call will focus upon a data analysis report of 18 recovery wells that was sent to Ralph Nichols (SRNL) and will include:
 - Table D-23 of detailed well reports for missing data for 1996-1998.
 - Wells 1-12 that are connected to the M1 air stripper.
 - The pilot air-stripper used onsite in 1985 was moved in 1986 and renamed the A2 air stripper. A2 was shut down but likely to restart as concentrations are rebounding since it was shut down. Wells 13-15 are on A2.
 - Ralph will put 1996-1998 reports (over 500 pages each) on the FTP site for FIU to download along with the monthly average precipitation from 1982 thru Dec. 2012.
 - FIU will review the 1996-1998 reports in October and locate all data that can be found for these years that is missing from the original spreadsheets received for the recovery wells.
 - Groundwater pump rates and total volume pumped will be plotted along with PCE and TCE recovered/destroyed for each of 18 wells and for all combined (1987-2012) by Nov. 5th.
 - In November, FIU will look into pump power and plot monthly electric power usage for 1987-2012. This will include analysis of pump efficiencies, pump replacements, electrical power used per month, etc.

Project 4 Waste and D&D Engineering & Technology Development

Project Manager: Dr. Leonel E. Lagos

Project Description

This project focuses on delivering solutions under the decontamination and decommissioning (D&D) and waste areas in support of DOE HQ (EM-13). This work is also relevant to D&D activities being carried out at other DOE sites such as Oak Ridge, Savannah River, Hanford, Idaho and Portsmouth. The following tasks are included in FIU Year 5:

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

Task 1: Waste Information Management System (WIMS)

Task 1 Overview

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

Task 1 Quarterly Progress

During this performance period, FIU performed database management, application maintenance, and performance tuning to the online WIMS in order to ensure a consistent high level of database and website performance.

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

FIU is reviewing the latest set of applications from FIU minority STEM students for the DOE-FIU Workforce Development Program. New DOE Fellows will be selected to support the research being conducted under this task, particularly on the organic semiconductor thin film research, the noncombustible fixatives research, and the fogging research and evaluation

Development of a Decision Model for Contamination Control Products

During FIU Year 4, FIU conducted a focused literature review (using D&D KM-IT, archived ALARA Reports, internet research, and vendor info) on contamination control products for radiological surface decontamination in support of the SRS 235-F Risk Reduction Project. The resulting summary report will help the project team develop their decontamination concepts for the PuFF process cells and define the out year's technical activities. FIU compiled data on each of the 40 products identified in the study and developed a matrix spreadsheet.

Due to the large variety of products available for decontamination, FIU began work on a decision making model. Criteria being taken into consideration include the type of radiation being encountered, the surface type, the location, and the isotopes involved. Each one of these criteria was then further expanded into sub-criteria in order to improve the accuracy of the model (Figure 4-1).

	Pair-Wise Comparison of Parameters							
					•			
Enter Number of Criteria :	5							
	Turneral	Contract				Manageland		
Parameters	Radiation	Properties	Location	Surface Type	Involved	Weight		
Type of Radiation	1.0	2.0	2.0	2.0	2.0	0.320		
Surface Properties	0.5	1.0	2.0	2.0	2.0	0.242		
Location	0.5	0.5	1.0	2.0	2.0	0.187		
Surface Type	0.5	0.5	0.5	1.0	2.0	0.143		
Itoropes Involved	0.5	0.5	0.5	0.5	1.0	0.108		
sum	3.0	4.5	6.0	7.5	9.0	1.0		
Consistency Che	ck							
Lambda max	5.22							
CI	0.05							
RI	1.12							
Consistency Ratio	0.05							
		F	^p air-Wi	se Com	parisor	of Sub	-Criteria	
					•			
Number of Sub Criteria:	3							
Type of Radiation	Alpha	Beta	Gamma	Weight				
Alpha	1.0	1.0	1.0	0.333				
Beta	1.0	1.0	1.0	0.333				
Gamma	1.0	1.0	1.0	0.333				
sum	3.0	3.0	3.00	1.0				
Consistency Che	ck							
Lambda max	3.00							
CI	0.00							
RI	0.58							
	0.00							

Figure 4-1. Preliminary work on decision model using pair-wise comparison of the criteria.

FIU is coordinating these efforts with SRS to identify the product search parameters based on project-specific needs and site applications. A selection of these search parameters will be 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.

During the month of July, code was created and debugged in Matlab which is capable of receiving user input related to the type of product needed and the application surface type; it then retrieves a list of decontamination products which fit the input criteria. A graphical user interface (GUI) was then created to make the application easy to use. This preliminary work on the decision model allows the user to upload Excel files, data files, and/or text files. The uploaded file is then displayed on a table and the user may do a keyword search for the application surface type or whether the product should be strippable or a fixative (Figure 4-2).



Figure 4-2. Decision Model created in Matlab

The project task team at FIU contacted Michael Serrato at Savannah River National Laboratory to gain insight on what the end users were looking for in the decision model. Several ideas were discussed, including what needs to be added to the list of criteria such as: level of contamination, delivery system, etc. As a result of this conference call, a visit to SRS was scheduled for August 5-6 for FIU to tour the site and meet with the manager of the SRS 235-F facility to discuss the decision model with the targeted end users at SRS. FIU visited SRNL and met with Mike Serrato as well as the technical team for the 235F facility. Based on these discussions, FIU began revising the Decision Model in order to fulfill the end users' requirements. Feedback for this task was received from the SRNL engineers/scientists who will perform the facility D&D. From this interchange of information, the updated Decision Model allows for 4 inputs from the user including: radiation type, surface type, application, and product category. The Decision Model output now consists of a list of products that fit any of the criteria, with the end goal that the

product which fits the most criteria is the best fit for the job. Further improvements will be implemented, such as the separation of the outputs, formating of the product list containing the essential information, and preliminary work on the web-based application.

FIU conducted bi-monthly phone calls with Michael Serrato at SRNL to follow-up with discussions from the onsite meeting and to discuss task progress.

FIU has also been contacting the product vendors to update and expand on the information in the contamination control products database. Figure 4-3 shows a partial screenshot of the data table.. FIU coordinated a conference call with an expert from one of the vendors who provided information on the combustion characteristics of specific fixatives used for contamination control. Planning and preparations were also began for developing a web application for the decision model.

Product Name	Manufacturer	Strippable	Application	Use	Cost	Coverage
DECON PEEL 5201 Halogen Free Prevents contamination	General Chem Corp.	Yes	Apply the product as received using an airless spray to proper thickness (recommended a minimun of 10 mils) may also be applied with a roller or brush. Aprox. I to 3 hour of drying time depending on the films thickness. The coating encompasses contaminants into the film mass. For airless equipment recommended to use a. 015 or. 017 nozzle at 1200-1500 psi. It is removed by peeling. More than one appliacation is recommended.	Used to inmobilize radioactive contamination, minimize exposure and facilitate consequent decontamination.	588.99 / gal	200 sqft/ gal at 8 mils.
DECON PEEL 2640 (a neutral pH version of 3900) Heavy Duty Decontamination pH Neutral Chemical, nuclear Equipment	General Chem Corp.	Yes	DeconPeel_2640 is normally used as received. Can be applied by an airless sprayer, a roller or a brush. Aprox. 1 to 3 hours drying time depending on film thickness.	Nuclear Equipment (Works best on Metals)	\$48.97/gal	aprox - coverage 200 sqft/ gal at 8 mils.
DECON KLEAN 5850	General Chem Corp.	Rinse	DeconKlean, liquid cleaner, can be used as received (highly concentrated) or dilute in water, depending upon the severity of the soils to be removed. When used with mechanical agitation as in a floor scrubber, DeconKlean can be diluted up to 5% (120).	Floors, walls and equipment (including tools). Clean of loose particles.	540. 35/gal	
DECON PEEL NUCLEAR 2050	General Chem Corp.	Yes	It can be applied by spray, roll or brush. The sprayed coating dries, depending on the film thickness, in 30 minutes to 4 hours.	Used to immobilize dispersible radioactive contamination deposited on buildings and equipment.	Approx. (\$47)gal)	50 sqft/gal

Figure 4-3. Partial Screenshot of the Data Table for Contamination Control Products

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

FIU conducted bimonthly phone calls with Michael Serrato at SRNL to discuss and refine the scope under this task. 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.

EFCOG Lessons Learned and Best Practices

FIU received notification that the DOE Energy Facility Contractors Group (EFCOG) DD/FE Working Group, as well as most of the other EFCOG working groups, are being discontinued and re-organized into a total of 4 working groups. FIU has been providing support to the DD/FE WG in the development of lessons learned and best practices for deactivation and decommissioning (D&D) throughout the DOE complex. The objective of these efforts is to capture previous work performed by the D&D community and facilitate the transfer of knowledge and lessons learned. DOE Fellows at FIU work closely with the DD/FE Working Group members as well as site contacts in the collection of information and the development of these documents. Once approved by EFCOG and DOE, these documents are made available via D&D KM-IT and the EFCOG website.

During this reporting period, DOE Fellows continued to assist EFCOG in developing Lessons Learned and Best Practices documents. A total of 9 Best Practices and Lessons Learned documents are final. During July, FIU received comments and suggestions from DOE on 2 best practices: 1) SRS R and P -Reactor Disassembly Basin In Situ Decommissioning, and 2) Use of a Remote Tapping Tool at Idaho National Laboratory to Minimize Worker Exposure and Avoid Future Contamination Accidents.

During August, FIU completed the revisions on the SRS best practice in coordination with the SRS site contacts and based on the comments received from the DOE review. This document was sent back to DOE on August 21 for final review and approval for publishing on the EFCOG and D&D KM-IT websites. FIU received approval from DOE and published the SRS best practice on D&D KM-IT and sent it to the EFCOG webmaster for publishing on the EFCOG website on September 3, 2014.

Two other best practice documents were sent to the new site point of contact at Hanford for review: 1) Use of Earthen Benches and other Technologies to Support River Structures' Demolition Activities; and 2) 327 Facility Source Term Stabilization and/or Removal Prior to Demolition. During September, FIU worked with the new site point of contact at Hanford to complete the revision of the two best practices. These documents were sent to DOE for review/approval on September 5, 2014.

FIU Year 4 Carryover Work Scope

Subtask 2.1.2: Fogging research and evaluation

FIU conducted bimonthly phone calls with Michael Serrato at SRNL to discuss and refine the task scope for both carryover tasks (fogging research and incombustible fixatives). The scope of work for this subtask was refined to include a comprehensive literature search and identification/selection of a technology/product for future operational performance test and evaluation. FIU also initiated planning with SRNL for a combined SNRL, INL, and FIU ARC conference at SRNL for late October to early November to further establish baseline, division of labor, and path forward for the SRNL related subtasks.

FIU contacted Rick Demmer at Idaho National Laboratory (INL) to set up a teleconference concerning the fogging research and evaluation task. INL has received

funding to execute a related research task and FIU plans to collaborate with INL where feasible to optimize the overall impact of their research and minimize any duplication of effort between FIU and INL.

Subtask 2.1.3: Incombustible fixatives

Through regular discussions with Mike Serrato (SRNL), FIU has further refined the task scope for the incombustible fixatives research to include a comprehensive literature search as well as a feasibility/cost/benefit assessment to support a decision on a potential expansion of the scope to include the development of a test plan, completion of phase 1 testing/evaluation of the selected fixative products for incombustibility characteristics, and completion of a technical report of the results.

During September, FIU continued a literature search in support of this subtask and pursued additional information on two identified potential technologies/products utilized in Japan following the events at the Fukushima Diiachi Plant. FIU also began to assess the requirements for performing testing/evaluation of incombustible fixatives at FIU, including locating an appropriate lab/facility for the testing, researching the additional health and safety requirements for working with high temperature and/or open flames, and contacting vendors who have performed similar testing to gather information. InstaCote Inc. was able to provide FIU with several reports with results of heat tests on materials and specimens.

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 July 24, August 21, September 11 and September 25, 2014.

During July, FIU worked with DOE on finalizing a strategic plan document for D&D KM-IT titled "D&D Knowledge Management Information Tool – A Strategic Approach for the Long-Term Sustainability of Knowledge." This paper offers a strategic vision for the long-term sustainability of knowledge through the D&D KM-IT by applying the system's assets together with good web practices; thereby, promoting and enhancing the collaborative sharing of knowledge and work experiences across the D&D community.

FIU also worked with DOE EM-13 to share approaches and lessons learned in developing web analytics for D&D KM-IT with the DOE Office of Learning & Workforce Development (HC-21). FIU participated in a meeting between FIU, EM-13, EM-72, and HC-21 on August 20 and gave a presentation via Adobe Connect, describing what web analytics are, how we use it in relation to D&D KM-IT, our methodology, and how we are applying and reporting based on the information gained (sample presentation slides provided in Figure 4-4).



Figure 4-4. Sample presentation slides on D&D KM-IT web analytics

Based on a recommendation from DOE, FIU updated the landing page of the D&D KM-IT Lesson Learned module (<u>http://www.dndkm.org/LessonsLearned/Default.aspx</u>) to include a description and link to the DOE Health, Safety and Security (HSS) Lessons Learned website. This resource is now conveniently located on D&D KM-IT so that it is easily available to users as shown in Figure 4-5. This resource can also be reached from the External Library section of the Document Library Module on D&D KM-IT.



Figure 4-5. Screenshot of the D&D KM-IT Lessons Learned landing page, showing the external link to the DOE HSS Lessons Learned database.

The IT team at FIU ARC implemented a solution in response to the recent announcement that there has been an increase in distributed denial of service (DDoS) attacks using spoofed recursive DNS requests. While all systems communication over the internet need to allow DNS traffic, the spoofed recursive DNS requests could allow the attacker to generate gigabits worth of DNS replies. The solution implemented by the FIU ARC IT team used Windows features for securing the DNS services as recommended by Microsoft.

FIU also explored the World's Nuclear News site as a potential source of information for data mining and D&D related news. This site has a D&D technologies section that has a similar focus as the D&D KM-IT Technology module. In addition, FIU is gathering and updating D&D KM-IT with D&D related news around the globe from multiple news sources.

FIU added the "Aging Infrastructure at DOE Sites" document to the Document Library module. This study was conducted to gather information on the issue of aging infrastructure across the DOE Complex. ARC researchers performed a literature/internet search and contacted the major DOE sites to determine what efforts are being implemented to:

- identify all the excess facilities,
- prioritize the maintenance/surveillance activities,
- prioritize D&D when funding becomes available, and
- whether they have used a commercial product or developed their own process for making these determinations.

FIU also responded to a DOE request for a summary of students who have provided support to D&D KM-IT since the project started. This list included the number of students by year and designation. There was also an internal list created with more detail which included names and the role each student played in the project.

FIU submitted a technical abstract on D&D KM-IT to the Waste Management 2015 Symposia on August 12, incorporated comments from DOE, and resubmitted the abstract to the conference.

FIU designed and developed a popular display for the homepage of D&D KM-IT. This milestone (2014-P4-M3.2) was completed and the link sent to DOE for review and testing on September 5, 2014. After receiving DOE approval, FIU made the new feature live on the public server on September 24, 2014. Popular keywords from the previous month's Google Analytics are utilized to highlight popular information on the D&D KM-IT homepage. The keywords are categorized and presented using dynamic tiles with corresponding images associated with the keywords. When a user clicks on each of the categories, the tiles rearrange themselves dynamically within the space allocated. The result is a slick and interactive way for users to access relevant information on D&D KM-IT (Figure 4-6).



Figure 4-6. New popular keyword display from D&D KM-IT homepage.

FIU completed and submitted the Google Web Analytic report for D&D KM-IT for the second quarter of 2014 (April to June) to DOE on September 12, 2014. This report included information from Google Analytic and Google Web Master tools and a narrative to explain the results. An infographic of the web analytic results is provided in Figure 4-7.



Figure 4-7. Infographic displaying web analytic results for 2nd quarter of calendar year 2014.

In addition, during September, FIU created a newsletter on fixatives and other contamination control products, an area of interest identified from the ongoing web analytics. The newsletter was sent to DOE on September 29, 2014, for review and approval to send out to all D&D KM-IT registered users. The draft newsletter is shown in Figure 4-8.

Also during September, FIU developed and submitted a summary report defining the outreach and training metrics that will be used this year. This document expands on the outreach and training activities for D&D KM-IT as described in the Project Technical Plan by defining specific metrics and capturing the tools and techniques that will be applied to track and report the results. Outreach and training is a critical element towards the long-term sustainability of knowledge and essential for the long-term strategic vision of D&D KM-IT, that it *will continue to grow and mature into a self-sustaining system through the active participation of the D&D community it was designed to serve.*



Figure 4-8. Screenshot of draft fixatives newsletter for D&D KM-IT user base.

Milestones and Deliverables

The milestones and deliverables for Project 4 for FIU Year 5 are shown on the following table. FIU milestone 2014-P4-M3.2 was met by September 5 with the development and deployment (for DOE review) of a popular keyword display on the homepage of D&D KM-IT. In addition, a deliverable under Project 4, a metrics definition report on D&D KM-IT outreach and training activities, was sent to DOE on September 30, 2014. The two D&D KM-IT Workshops to DOE EM staff at HQ, were originally planned by the end of August and September. These workshops are being coordinated and re-scheduled based on the availability of DOE EM staff.

Task	Milestone/ Deliverable	Description	Due Date	Status	OSTI
Task 1: Waste Information Management	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	
Winagement System (WIMS)	2014-P4-M1.2	Submit draft paper on WIMS to Waste Management Symposium 2015	11/07/14	On Target	
Task 2: D&D	2014-P4-M2.1	Preliminary decision model for contamination	03/06/15	On Target	

FIU Year 5 Milestones and Deliverables for Project	FIU	J Year 5	Milestones	and Delivera	bles for	Project 4
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Support to		control products (subtask 2.1.1)			
DOE EM for Technology Innovation, Development, Evaluation, and Deployment	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	
	Deliverable	First D&D KM-IT Workshop to DOE EM staff at HQ	08/29/14** Re-forecasted TBD	Re- forecasted	
	2014-P4-M3.2	Deployment of popular display on homepage of KM-IT to DOE for review/testing	09/05/14	Complete	
	Deliverable	Metrics Definition Report on Outreach and Training Activities	09/30/14	Complete	
	Deliverable	Second D&D KM-IT Workshop to DOE EM staff at HQ	09/30/14** Re-forecasted TBD	Re- forecasted	
	2014-P4-M3.1	Submit draft paper on D&D KM-IT to Waste Management Symposium 2015	11/07/14	On Target	
	2014-P4-M3.3	Deployment of lessons learned lite mobile application to DOE for review/testing	11/07/14	On Target	
Task 3: D&D Knowledge	Deliverable	Preliminary Metrics Progress Report on Outreach and Training Activities	01/16/15	On Target	
Management Information	2014-P4-M3.4	Deployment of best practices mobile application to DOE for review/testing	01/16/15	On Target	
Tool (KM-IT)	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: Submit technical paper on WIMS to WM15. Begin preparation of technical poster or oral presentation for the conference.
- Task 2: Florida International University will continue providing support to the Savannah River Site team for the SRS 235-F facility. FIU will continue to work on a decision model for mobile application use to better guide the product end users in the selection of the appropriate products depending on their specific needs and site application.
- 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 on the fogging research and evaluation to optimize the scope of work for overall impact of the research and minimize any duplication of effort between FIU and INL.
- Task 3: Complete draft of D&D KM-IT website analytics report for the July to September time period and submit to DOE for review.
- Task 3: Complete development of the lessons learned 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: Submit technical paper on D&D KM-IT to WM15. Begin preparation of oral presentation for the conference.

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

The DOE 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 the 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.

As a part of DOE Fellows program, all new fellows are required to take environmental health and safety (EH&S) training required by FIU to conduct research in the laboratories. All of the new DOE Fellows hired during the Spring/Summer completed the following training:

- Chemical Handling Safety
- Fire Safety
- Environmental Awareness PT1, PT2
- EPA: Hazardous Waste Awareness
- Hazard Comm. in sync with GHS
- Laboratory PPE
- Laboratory Hazard Awareness
- Small Spills and Leaks
- Radiation Safety

In addition, DOE Fellows Maria Diaz, Aref Shehadeh, Meilyn Planas and John Conley attended hands-on radiation safety training provided by FIU's radiation safety officer. The program director also conducted an orientation session for the new DOE Fellows. During the orientation, Dr. Leonel Lagos explained the features and benefits of the program as well as expectations, roles and responsibilities of the DOE Fellows.

The six new DOE Fellows (Class of 2014) developed brief biographies that will be posted to the DOE Fellows website: <u>http://fellows.fiu.edu/studentsBios.asp</u>.

The DOE Fellows summer/fall recruitment efforts were completed during this reporting period. Recruitment campaigns were conducted from July 28 to August 1, 2014, temporarily halted during the semester break between August 4 - August 23, resumed on August 25 and continued until September 26. Recruitment tables were placed at the College of Engineering and at the main FIU campus in the Physics & Chemistry building and Computer Science building and staffed with current DOE Fellows. A signup sheet was used to collect contact information from interested students. Program director Dr. Lagos visited classrooms, presented about the DOE Fellows program and collected contact information from interested students. An information session was held on September 10, 2014, to provide students with insights into the DOE Fellows program and answer any questions they might have. A total of 41 applications were received and are currently under review. Figure 5-1 shows DOE Fellows staffing one of the recruitment information tables.



Figure 5-1. DOE Fellows Aref Shehadeh and Dayron Chigin promoting the DOE Fellows program.

DOE Fellows Christina Pino and Robert Lapierre submitted abstracts, developed Powerpoint slides, and made oral presentations based on their DOE EM research by participating in the

NABG 33rd Annual Technical Conference (Environmental Innovation-Collaborations for the Future) held on September 17 - September 20, 2014, at Washington State University - Tri-Cities (WSU-TC) in Richland, Washington. The titles of the research presented at the conference by the DOE Fellows were:

- **DOE Fellow Christian Pino:** Use of XRF to Characterize Pre-Hanford Orchards in the 100-OL-1 operable unit
- **DOE Fellow Robert Lapierre:** Characterization of the Uranium-Bearing Phases Produced by Novel Remediation Technologies for Sequestration of Mobile Radiological Contaminants in the Hanford 200 Area Vadose Zone

Seven (7) DOE Fellows prepared research abstracts to submit to the FIU McNair Scholars Research Conference to be held at the main FIU campus on October 16 - 18, 2014. These Fellows also began developing their research posters to present at the conference.

In addition, 18 DOE Fellows began preparing research posters for the DOE Fellows Poster Exhibition/Competition to be held on October 23, 2014. The winners of this competition will be announced during the 2014 DOE Fellows Induction Ceremony on November 13, 2014.

DOE Fellow Meilyn Planas visited the Savannah River Site along with ARC staff to meet with SRNL engineers/scientists on the research work she is performing in support of Project 4, Task 2, on the contamination control product decision model.

The DOE Fellows completed their 10-week summer 2014 internships with DOE sites, DOE national laboratories, DOE contractors, and DOE-HQ and resumed their research activities at ARC. A total of 9 DOE Fellows interned this summer as detailed in Table 5-1.

	DOE Fellow	Location	Summer Site Mentor	
1	Deanna Moya	DOE-HQ EM-12, Cloverleaf, MD	Justin Marble/Patricia Lee	
2	Natalia Duque	DOE-HQ EM-13, Forrestal, Washington D.C.	Albes Gaona	
3	Carmela Vallalta	WRPS, Hanford, WA	Dennis Washenfelder	
4	Sasha Philius	WTP (Bechtel), Hanford, WA	Brad Eccleston/Joel Peltier	
5	Anthony Fernandez	WRPS, Hanford, WA	Ruben Mendoza	
6	Christian Pino	PNNL, Richland, WA	Amoret Bunn	
7	Robert Lapierre	PNNL, Richland, WA	Dawn Wellman/Jim Szecsody	
8	Hansell Gonzalez	SRNL, Savannah River, SC	Brian Looney/Miles Denham	
9	Steve Noel	SRNL, Savannah River, SC	Mary K. Harris	

 Table 5-1. DOE Fellow Interns, Locations, and Summer Mentors

The environmental research projects completed by DOE Fellows during the summer internships under the guidance of their site mentors as described below:

Deanna Moya (DOE Fellow - Class of 2013) is working for EM-12's Office of Soil and Groundwater Remediation at the DOE-HQ Cloverleaf facility in Germantown, Maryland

during the summer of 2014. Under the mentorship of Dr. Justin Marble and Dr. Patricia Lee, Deanna's main role is to learn and test the Advanced Simulation Capability for Environmental Management (ASCEM) toolset. The ASCEM Project's goal is to provide sustainable and cost effective solutions towards the DOE-EM cleanup mission. It is a tool comprised of advanced simulation capabilities that is used to understand and predict the subsurface flow and contaminant transport behavior in natural and engineered systems. With its modular and open source toolsets, ASCEM can provide standardized assessments of performance and risk analysis for EM activities, which ultimately aids in protecting human health and the environment for current and future generations.

Natalia Duque (DOE Fellow - Class of 2013) has been given the opportunity to intern with the Department of Energy, Office of Environmental Management (DOE-EM) Headquarters located in Washington, D.C. Natalia is assisting Mr. Albes Gaona and EM-13 in the development of its Green and Sustainable Remediation (GSR) and Sustainability Powerpedia pages, as well as in the development of the final GSR Catalog. During her internship, Natalia will also be working on the acquisition and analysis of data from the A/M Area located in Savannah River Site in order to identify opportunities for the incorporation of sustainability metrics in the environmental management decisions.

Carmela Vallalta (DOE Fellow - Class of 2013) is participating in an internship at Washington River Protection Solutions (WRPS), Hanford. Ms. Vallalta is working under the supervision of Mr. Dennis Washenfelder, and will prepare waste mitigation and annulus ventilation operating chronologies for the double shell tanks, beginning with the earliest tanks, AY-101 and AY-102.

Anthony Fernandez (DOE Fellow - Class of 2014) is at Washington River Protection Solutions (WRPS), Hanford. He is working with two engineering groups, Waste Transfer and Waste Storage, under the supervision of Mr. Ruben Mendoza. Currently Mr. Fernandez is updating the Single Shell Tank's (Enraf's) tank level, monitoring reference level documentation and supporting the baseline change requests to Enraf's levels. Anthony will be verifying and updating the waste transfer Safety Equipment Compliance Database, which requires review and comparison to various different design drawings and specifications. AutoCAD software will be used to create layout drawings of the waste transfer routes used in all the tank farms. Lastly, he will be tracking the changes necessary to overlay the ground penetrating radar scans onto the updated tank farm route maps.

Sasha Philius (DOE Fellow - Class of 2013) has been given the opportunity to intern with the Department of Energy's Office of River Protection (ORP) located at the Hanford Site, WA. Sasha is assisting Mr. Brad Eccleston and ORP in their partnership with Bechtel National Inc. to establish a new standard vessel design that would be capable of managing the most challenging waste slurries, with high solids and non-Newtonian fluid characteristics. In addition, he will accompany DOE staff in discussions related to vessel design features, test planning, and facility test readiness.

Robert Lapierre (DOE Fellow - Class of 2012) is on his second trip to the Tri-Cities. This summer Robert is working at Pacific Northwest National Laboratory with Dr. Jim Szecsody, studying the influence of NH_3 gas treatment on uranium remediation in Hanford vadose zone sediments. During summer 2012, Robert spent his summer as an

intern at Pacific Northwest National Laboratory (Richland, WA) under the guidance of Dr. Dawn Wellman of the Environmental Systems Group.

Christian Pino (DOE Fellow - Class of 2013) is working under the mentorship of Amoret Bunn at Pacific Northwest National Laboratory (PNNL). He is aiding Amoret in completing a pilot study focused on the environmental concentrations of lead in soil. Hanford site, before the land was owned by the government, used to be orchard fields where lead arsenate pesticides were applied. There is still residual lead from this use, and the fields are being surveyed in order to determine whether the lead still poses harm as its concentration may be above EPA's standard. If this is the case as expected, the end goal of the project will be to focus on remediation methods to bring these levels to a safe threshold.

Hansell Gonzalez (**DOE Fellow - Class of 2013**) is working at Savannah River National Laboratory under the mentorship of Dr. Miles Denham. During his internship, Hansell will study the effect of pH on the adsorption of humic substances on different sediments present at Savannah River Site. He will also analyze the ratio of absorbance of humate used during these adsorption experiments, at 465nm and at 665nm (E4/E6 ratio), to better understand the interaction of these heterogeneous humic substances with the sediments.

Steve Noel (DOE Fellow - Class of 2013) is participating in a summer internship at Savannah River National Laboratory (SRNL) under the mentorship of Mary Harris. His focus during the internship is to develop web applications for Savannah River National Laboratory, converting on-site desktop applications into web applications using the "Aptana" program. These web applications will enable employees across the DOE complex and national laboratories to use applications/software that were previously only available through on-site computers.

During August, these DOE Fellows returned to ARC and started drafting the summer internship technical reports based on the work they performed during their internships. The DOE Fellows and summer internship technical report titles are provided in Table 5-2.

DOE Fellow		Location	Report Title
1	Deanna Mova	DOE-HQ EM-12,	Advanced Simulation Capability for
1	Douiniu 1010 ju	Cloverleaf, MD	Environmental Management (ASCEM)
		DOE-HQ EM-13,	Sustainable Remediation and Literature Review
2	Natalia Duque	Forrestal, Washington	for Savannah River Site A/M Area
		D.C.	Groundwater Remediation System
3	Carmela Vallalta	WRPS, Hanford, WA	Analysis of Tank Chemistry Compliance with
5	Curineia Vanaria		Chemistry Specification in Double-Shell Tanks
4	Sasha Philius	WTP (Bechtel),	HVAC Design Assessments for the Hanford
-		Hanford, WA	Waste Treatment and Immobilization Plant
			Enraf & Densitometer Reference Level
5	Anthony Fernandez	WRPS, Hanford, WA	Updates for High-Level Nuclear Waste
			Tanks at Hanford Site
6	Christian Pino	PNNL, Richland, WA	Use of XRF to Characterize Pre-Hanford
0			Orchards in the 100-OL-1 Operable Unit

 Table 5-2. DOE Fellow Summer Intern Technical Reports

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

The DOE Fellows who participated in a summer internship are also preparing and presenting an oral presentation at the weekly DOE Fellows meetings. The schedule for these presentations is provided in Table 5-3.

Student	Site	Mentor	Date
Christian Pino	an Pino PNNL, Richland, WA Amoret Bunn		9/12/14
Deanna Moya	DOE-HQ EM-12, Cloverleaf, MD Justin Marble/Patricia Lee		9/12/14
Robert Lapierre	obert Lapierre PNNL, Richland, WA Jim Szecsody		10/3/14
Natalia Duque	DOE-HQ EM-13, Forrestal, Washington D.C.	Albes Gaona	10/17/14
Carmela Vallalta	WRPS, Hanford, WA	Dennis Washenfelder	10/31/14
Sasha Philius	WTP (Bechtel), Hanford, WA	Brad Eccleston/Joel Peltier	11/14/14
Anthony Fernandez	WRPS, Hanford, WA	Ruben Mendoza	11/21/14
Hansell Gonzalez	SRNL, Savannah River, SC	Brian Looney/Miles Denham	11/28/14
Steve Noel	SRNL, Savannah River, SC	Mary K. Harris	12/5/14

Table 5-3. Oral Presentations for Weekly DOE Fellow Meetings

FIU received notification that the DOE Energy Facility Contractors Group (EFCOG) DD/FE Working Group, as well as most of the other EFCOG working groups, are being discontinued and re-organized into a total of 4 working groups. FIU has been providing support to the DD/FE WG in the development of lessons learned and best practices for deactivation and decommissioning (D&D) throughout the DOE complex. The objective of these efforts is to capture previous work performed by the D&D community and facilitate the transfer of knowledge and lessons learned. DOE Fellows at FIU work closely with the DD/FE Working Group members as well as site contacts in the collection of information and the development of these documents. Once approved by EFCOG and DOE, these documents are made available via D&D KM-IT and the EFCOG website.

During this reporting period, DOE Fellows continued to assist EFCOG in developing Lessons Learned and Best Practices documents. A total of 9 Best Practices and Lessons Learned documents are final. During July, FIU received comments and suggestions from DOE on 2 best practices: 1) SRS R and P -Reactor Disassembly Basin In Situ Decommissioning, and 2) Use of a Remote Tapping Tool at Idaho National Laboratory to Minimize Worker Exposure and Avoid Future Contamination Accidents.

During August, FIU completed the revisions on the SRS best practice in coordination with the SRS site contacts and based on the comments received from the DOE review. This document was sent back to DOE on August 21 for final review and approval for publishing on the EFCOG and D&D KM-IT websites. FIU received approval from DOE and published the SRS best practice on D&D KM-IT and sent it to the EFCOG webmaster for publishing on the EFCOG website on September 3, 2014.

Two other best practice documents were sent to the new site point of contact at Hanford for review: 1) Use of Earthen Benches and other Technologies to Support River Structures' Demolition Activities; and 2) 327 Facility Source Term Stabilization and/or Removal Prior to Demolition. During September, FIU worked with the new site point of contact at Hanford to complete the revision of the two best practices. These documents were sent to DOE for review/approval on September 5, 2014.

Doc	BP/LL	Title	РОС	Status as of 9/30/2014
1	BP	Explosive Demolition of Buildings 337, 337B, and the 309 Stack at the Hanford's 300 Area	Daniel Beckworth, Bob Smith, Thomas Kisenwether	Final & Published
2	BP	Open Air Demolition of Asbestos Gunite by Using a Track Mounted Wet Cutting Saw	Rob Vellinger	Final & Published
3	BP	185-3K Cooling Tower Demolition	Bill Austin	Final & Published
4	BP	Historical Hazard Identification Process for D&D	Paul Corrado	Final & Published
5	LL	Closure of the Reactor Maintenance, Assembly, and Disassembly Facility and the Pluto Disassembly Facility at the Nevada National Security Site	Annette Primrose	Final & Published
6	LL	Unanticipated High Dose During the Removal of Wire Flux Monitor Cabling from the HWCTR Reactor Vessel	Bill Austin	Final & Published
7	LL	Radiological Contamination Event during Separations Process Research Unit (SPRU) Building Demolition	Mike Montini	Final, Publication on hold by POC request
8	BP	Structural Code Guidance for D&D Activities at DOE Facilities	Kirk Dooley	Final & Published

Table 5-4. Best Practices/Lessons Learned

9	BP	Electrical Code Guidance for D&D Activities at DOE Facilities	Kirk Dooley	Final & Published
10	BP	SRS R and P -Reactor Disassembly Basin In Situ Decommissioning	Jack Musall	Final & Published
11	BP	Use of Earthen Benches and other Technologies to Support River Structures' Demolition Activities	Bill Kirby/Scott Sax	Site POC revisions received and incorporated, sent to DOE for review/approval on 9/5/14.
12	BP	327 Facility Source Term Stabilization and/or Removal Prior to Demolition	Bill Kirby/Scott Sax	Site POC revisions received and incorporated, sent to DOE for review/approval on 9/5/14.
13	BP	Use of a Remote Tapping Tool at Idaho National Laboratory to Minimize Worker Exposure and Avoid Future Contamination Accidents	Kirk Dooley	EFCOG review comments incorporated and document sent to DOE on 6/26/14. DOE Comments received on 7/15/14. Revision in progress with site POC.

Milestones and Deliverables

The milestones and deliverables for Project 5 for FIU Year 5 are shown on the following table. No milestones or deliverables were due for this project during this quarter.

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

FIU Year 5 Milestones and Deliverables for Project 5

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.
- Complete and submit the DOE Fellow summer internship technical reports to DOE.
- Complete preparation/coordination and host the DOE Fellows Poster Exhibition & Competition on October 23, 2014.
- Complete selection of new DOE Fellows for the summer/fall recruitment period and submit list of selected DOE Fellows to DOE by October 31, 2014.
- Complete preparation/coordination and host the DOE Fellows Induction Ceremony Class of 2014 on November 13, 2014.