QUARTERLY PROGRESS REPORT April 1 to June 30, 2015

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

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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 planned period of performance for FIU Year 5 under the Cooperative Agreement was May 18, 2014 to May 17, 2015. However, DOE EM proposed a no cost extension to extend the end of the period of performance for a period of two months, until July 20, 2015. FIU subsequently requested an additional no cost extension to extend the end of the period of performance of FIU Year 5 to August 28, 2015, in order to complete the DOE Fellow summer internships and additional research and experimental work in the current performance year. The activities described in this summary are included in the FIU Year 5 period of performance. In addition, some of the milestones and deliverables anticipated within original FIU Year 5 period of performance have been adjusted to reflect the new end date. Completion and deliverable of FIU Year 5 Year End Reports have been reforecast for August 28, 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 April 1 to June 30, 2015. Highlights during this reporting period include:

Project 1:

• Due to changes in personnel and reduced funding levels for the year, a number of deliverables have been reforecast. After discussions with our DOE-EM representative, the deliverables associated with Tasks 2.2, 17.2, 18.2 and 19.1 will be incorporated into the Year End Report. For Task 18.1, the sonar malfunctioned during testing and due to lengthy delays in getting the system repaired, these deliverables will be incorporated into next year's Project Technical Plan.

Project 2:

• A deliverable, a progress report on sorption properties of the humate injected into the subsurface system (subtask 2.3), was completed and sent to DOE HQ and the SRNL site contacts on April 3, 2015.

Project 3:

- Milestone 2014-P3-M6, meeting and presentation of project progress at SRS, which was reforecast to April 13, 2015, was completed with a visit by FIU researchers to SRS and hosted by SRNL personnel.
- Due to the no cost extension, several of the report deliverables have been reforecast to incorporate additional data and results acquired during the extended period of performance. The new submission dates are as follows: Technical Report for Task 1 "Modeling of the migration and distribution of NOM injected into subsurface systems", due 6/3/15, reforecast to 7/6/15; Technical Report for Task 2 "Surface Water Modeling of Tims Branch", due 6/10/15, reforecast to 7/17/15; Technical Report for Task 3

"Sustainability Plan for the A/M Area Groundwater Remediation System", due 6/17/15, reforecast to 7/31/15.

Project 4:

- Milestone 2014-P4-M1.1, importing the 2015 data set for waste forecast and transportation data into WIMS was completed on May 14, 2015.
- Two deliverables, the technical report and the Tech Fact sheet for demonstrated technologies, were completed for the FX2 advanced fogging agent technology demonstration and submitted to DOE and the collaborating sites (SRNL and INL) on May 15, 2015.
- Milestone 2014-P4-M2.2, draft test plan for baseline incombustible fixatives, has been reforecast to July 2, 2015 due to FIU's no cost extension, allowing time for FIU to fully collaborate with and incorporate SRNL input into the test plan.
- Milestone 2014-P4-M3.5, adding D&D knowledge to Wikipedia through editing 4 articles, was completed and a summary report submitted to DOE on May 8, 2015.
- Another deliverable, updating the D&D KM-IT Tech Fact Sheet was completed and submitted to DOE on May 15, 2015. In addition, a deliverable on the metrics report on outreach and training for D&D KM-IT was completed and submitted to DOE on May 8, 2015.
- Two workshops (deliverables under the D&D KM-IT task) were completed; one was held at the FIU exhibition booth during Waste Management 2015 in Phoenix, AZ, in March and the second was completed at the EPRI Decommissioning Workshop in Orlando, FL, in June.

Project 5:

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

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. Completion and deliverable of FIU Year 5 Year End Reports have been reforecast for 08/28/15 to reflect the new end date of the performance year.

Task	Milestone/ Deliverable	Description	Due Date	Status	OSTI
Program-wide (All Projects)	Deliverable	Draft Project Technical Plan	06/18/14	Complete	
	Deliverable	Monthly Progress Reports	Monthly	Complete	
	Deliverable	Quarterly Progress Reports	Quarterly	Complete	
	Deliverable	Draft Year End Report	Reforecast to 08/28/15	Reforecasted	OSTI
	Deliverable	Presentation overview to DOE HQ/Site POCs of the project progress and accomplishments (Mid-Year Review)	11/21/14*	Complete	
	Deliverable	Presentation overview to DOE HQ/Site POCs of the project progress and accomplishments (Year End Review)	06/30/15*	Complete	

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

Project 1 Chemical Process Alternatives for Radioactive Waste

Project Manager: Dr. Dwayne McDaniel

Project Description

Florida International University has been conducting research on several promising alternative processes and technologies that can be applied to address several technology gaps in the current high-level waste processing retrieval and conditioning strategy. The implementation of advanced technologies to address challenges faced with baseline methods is of great interest to the Hanford Site and can be applied to other sites with similar challenges, such as the Savannah River Site. Specifically, FIU has been involved in: analysis and development of alternative pipeline unplugging technologies to address potential plugging events; modeling and analysis of multiphase flows pertaining to waste feed mixing processes, evaluation of alternative HLW instrumentation for in-tank applications and the development of technologies, 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

This performance period effort on the asynchronous pulsing system (APS) included the evaluation of the experimental data obtained from recent testing. The analysis has initially focused on the testing that was conducted at 1 Hz. The analysis is intended to assist in the explanation of unplugging times for the trials conducted with various amount of air entrained in the system. Pressures at the pistons were compared to the pressures at the plug faces to understand the overall change in pressure along the pipeline. In most cases, some amount of amplification was observed between the inlet and plug face, even with the air entrained. It should be noted that our test system is inclined similar to the cross-site lines. This means that air on the P4-P6 side resides next to the piston face and air on the P1-P3 side resides on the plug face. The variability of the location of the air entrained could explain some of the variability seen in the data. Additionally, the APS control system is designed to compensate for air by increasing the static pressure, further complicating the evaluation of the data. Lastly, variation in temperature throughout the course of testing also changes the pressure in the line dramatically.

Figure 1-1 shows an example of one trial data set and how it was analyzed. Pressure peaks for representative sections of the testing show how the pressure at the inlet (1, 4) compared to those at the plug face (3, 6). The average of the peak difference was determined, indicating the level of amplification for each test trial.



Figure 1-1. Example data sample to evaluate line pressure.

Table 1-1 shows the representative pressure differences from each of the trials at 1 Hz. All pressures are in psi. In general, as air increased, the time to unplug also increased. FIU would expect that the pressure amplification would decrease with increasing amounts of air. However, due to the aforementioned reasons, some variability was observed. The pressure peak differences appear similar in magnitude with the exception of the half-stroke case on the P4-P6 side. In this trial, virtually no amplification was observed.

Amount Air	Unplugging Time	Ave P1 Peak	Ave P3 Peak	Ave P1-P3 Amplitude	Ave P4 Peak	Ave P6 Peak	Average P4-P6 Amplitude
No Air	6 hours	207.7	218.1	10.4	211	203.8	7.2
Half Stroke Air	5.5 hours	189.5	205.8	16.4	189.2	179.6	9.6
	8 hours	216.9	225.9	9	184.9	184.9	0.1
Full Stroke Air	9.5 hours	231.9	241.4	9.6	144.6	133.1	11.4

Table 1-1. APS Unplugging Trials for 1 Hz

During the data analysis of the experimental data obtained from recent testing, it was observed that various factors affected the results of the testing, including piston drift, the temperature of the pipeline, and amount of air within the pipeline as well as variability in the strength of the plug.

Each pump's piston position is controlled by the computer via LabView. By obtaining feedback readings from the pressure transducers, the piston position transducers, and the desired pressure pulse profile, the control software determines the starting position and how far and how fast to drive each piston forward. The controls try to maintain a desired static pressure within the pipeline by moving the piston forward to compensate for drops in pressure. The piston can drift from its nominal state due to this compensation as well as high frequency pulsing that does not allow the piston enough time to return to its original starting position.

As mentioned previously, the temperature of the pipeline can significantly affect the unplugging results. As the ambient temperature of the pipeline increases, the water in the pipeline increases due to the large amount of volume in the system. As this temperature increases, the water itself tries to expand but is restrained because of the small (or no amount) of air in the system; therefore when temperature in the pipeline is increased slightly, the pressure in the system will increase greatly. Temperature in the system varies with ambient temperature, weather conditions,

etc. and is amplified by the black iron pipes that compose the system. The results of the temperature variation cause large variability in the pressure waves that are sent through the system, changing the amplification of the waves as well as the amplitude. Temperature also has a significant effect on the variability of the starting pressure in the system along with the amount of air entrained.

The volume of air within the pipeline can adversely affect the efficiency of the system. When the pipeline temperature is increased (due to environmental conditions), existing air pockets within the system are more easily removed. This is due to the expansion of the air pockets, which allows them to travel to the highest points in the pipeline section where purge valves are located to expel the air. However, variability in ambient temperature proves to be an obstacle when performing air mitigation techniques. It is important to note that the complete removal of air from the pipeline is very difficult in terms of our air mitigation practices; therefore, variability will exist between unplugging tests conducted with different amounts of entrained air.

Another parameter that can affect unplugging results is the variability of the plug. Initial blow out tests ranged from 400 to 600 psi. Upon testing, it was observed that the success of making this plug was significantly impacted by the plug material, development procedure and conditions. For instance, mixing for a prolonged or shortened time would yield different shear strengths for the same composition. Pressure blowout tests were conducted on a variety of 3-ft kaolin-plaster plugs in order to verify that the plugs could withstand a maximum static pressure of 400 psi. Results showed that the optimal plug had a composition of 30% kaolin, 35% plaster and 35% water (by weight) with a 24 hour "wet cure" time (wet curing involves keeping the plug in a moist environment). Results from initial blow out tests showed that the plugs could withstand pressures from 400-600 psi, where any pressure exceeding 400 psi was optimal for testing.

Subtask 2.2: Computational Simulation and Evolution of HLW Pipeline Plugs

Efforts for this task included investigating the 2D and 3D turbulent flow based settling dynamics of particles in different geometric sections in pipes. Initially, 2D pipe sections with L sections, U-sections and constrictions along with sharp and curved bends (elbows) were investigated. Later on, this was extended to a detailed 3D investigation of settling dynamics.

A vertical section (L-section) and a section with constriction in the pipe diameter were considered. Settling characteristics were studied using COMSOL multi-physics software version 4.4 for each of the two cases. The mixture model-turbulent flow module in COMSOL was used for simulations and in all cases a velocity of 0.5 m/s was used. Densities of the solid particles and fluid were taken as 6300 kg/m³ and 1000 kg/m³, respectively. Solid particles were 45 μ m in diameter and their volume fraction was 2.9%. In the case of the vertical section, the diameter of the pipe was kept constant at 3 in. while in the other trial, the diameter was reduced from 3 in. to 0.75 in.

The results obtained are shown in Figures 1-2 through 1-5. Figure 1-2 (left) shows the dispersed volume fraction of the solid particles in the vertical section (red color indicates the deposition of solids). Figure 1-2 (right) gives a detailed view of the deposition of the particles in the bend region. Figures 1-3 (left) and 1-3 (right) represent the deposition of the solids in the constriction geometry of the pipe. It is evident that most of the particles are deposited in the pipe section with higher diameter and only a few are carried after the constriction. Hence, this could be a region for potential plug formation.



Figure 1-2. Settling of solids in a vertical section (left), detailed view (right).



Figure 1-3. Settling of solids in a constriction (left), detailed view (right).

Figure 1-4 represents the surface velocity profile in the vertical section. As seen in the detailed view (Figure 1-4 (right)), there is an increase in the velocity after the bend region. The surface velocity profile for the constriction section is shown in Figure 1-5. It is evident that the change in diameter results in an increase in the surface velocity of the mixture.



Figure 1-4. Velocity profile in the vertical section (left), detailed view (right).



Figure 1-5. Velocity profile in constriction (left), detailed view (right).

FIU then expanded the investigation to include the settling of solids in a complex pipe geometry including vertical sections, bends and constrictions. This effort focused on investigating the 2D turbulent flow based settling of solids in circular pipes with mixing of flows and variation in geometric sections. A T-section, a U-section and a geometry including corners and U-sections were studied.

Densities of the solid particles and fluid were taken as 6300 kg/m^3 and 1000 kg/m^3 , respectively. The flow velocities were varied from 0.5 m/s to 2.0 m/s. Two different diameters of solid particles were considered: 45 µm and 200 µm. The volume fraction was varied from 2.9% to 10%. Geometry of the pipe sections were based on the standard 3-inch schedule 40 pipe dimensions.

Sample results obtained are as shown in Figures 1-6 through 1-10. Figure 1-6 shows the dispersed volume fraction of the solid particles in the vertical T-section (red color indicates the deposition of solids). It is to be noted that the flow is input from both sides of the T-section. It mixes at the junction and the combined mixture flows through the outlet at the bottom. Figure 1-6 also gives a detailed view of the deposition of the particles in the T- region. Figure 1-7 represents the surface velocity profiles in the vertical T-section. As seen in Figure 1-7 (detailed view), there is an increase in the velocity after the flow combines from both sides at the T-junction.



Figure 2-6. Settling of solids in a T- section (left), detailed view (right).



Figure 1-7. Velocity profile in a T- section (left), detailed view (right).

Figure 1-8 represents the dispersed volume fraction and the surface velocity profile in the narrow section respectively. The fluid enters on the left side and exits on the right side. As seen in Figure 1-8 (left), there is settlement of solids in the bend regions. Also from Figure 1-8 (right), it is evident that the bends result in slight changes in velocity before the flow stabilizes after a certain length of the pipe. A pipe section with bends, U-section and sharp corners is studied to determine the effect of settling due to complexities in the geometry of the pipes. The finite element mesh for the pipe section is shown in Figure 1-9 (left) and the velocity profile is shown in Figure 1-9

(right). As seen in Figure 1-9, there is a greater increase in the velocity at sharp corners when compared to that on the curved bends. The settling of solid particles is shown in Figure 1-10 for two different velocities (0.5 m/s and 2 m/s). Also the solids volume fractions considered were 2.9% and 10%. It is to be noted that in the case of lower velocity, the deposition was seen in the elbow section, straight section and the U-section of the pipe. Increasing the velocity to 2 m/s resulted in very less deposition at the straight and U-sections. In this case, volume fraction was also increased by 10%.



Figure 1-8. Settling of solids in narrow section (left), velocity profile in narrow section (right).



Figure 1-9. Finite element mesh (left), velocity profile (right).



Figure 1-10. Settling of solids in pipe for 0.5 m/s (left), settling of solids in pipe for 2 m/s (right).

The effort on this task also included extending the 2D investigations to the 3D turbulent flow based settling of solids in circular pipes with complex pipe geometric sections. A 3D pipe geometry including horizontal, vertical and inclined sections along with elbow sections was created and modeled for the dynamic settling characteristics of solids.

A Solidworks rendering of the developed pipe model is shown in Figure 1-11 (left). The nominal diameter of the pipe is 3 inches and the loop consists of five 90° elbows with a long radius. There

are five straight sections and one angular section in the loop, along with four vertical elbows and one horizontal elbow. The lengths of the straight sections are varied to predict the change in volume fraction of the particles flowing through the pipe loop.



Figure 3-11. Pipe model (left) and finite element mesh (right).

The COMSOL multi-physics software version 4.4 was used to simulate the flow characteristics in the pipe model. A finite element (FE) mesh was generated (Figure 1-11, right); an FE is a physics controlled mesh consisting of 3D tetrahedral elements.

After the FE mesh was generated, the multiphase fluid flow module was used for modelling. Solid liquid mixture models under turbulent flow conditions were considered. The Rans k- ε model was chosen for turbulence and the Schiller-Naumann model was chosen for slip. A step function was used to introduce solid waste particles into the pipe loop at the inlet. Initial and inlet flow conditions were specified along with the outlet pressure condition. Densities of the solid and fluid particles were taken as 3147 kg/m³ and 1000 kg/m³, respectively. The flow velocities were varied from 0.5 m/s to 2.5 m/s. Solid particles with a diameter of 45µm were considered. Their volume fraction was varied from 2.9% to 10%.

The sample results obtained are shown in Figures 1-12 and 1-13. Figure 1-12 (left) shows the distribution of the dispersed volume fraction in the pipe loop for the case with flow velocity of 2.5 m/s and an initial solids volume fraction of 2.9%. It is evident from Figure 1-12 (left) that the volume fraction is higher (indicated by red) at the bends (elbow sections) than it is in the straight sections. The values of the volume fraction ranged from 2.9% to 8.9%. Hence, the elbows are regions of potential plug formations. Also, it is to be noted that the intrados of the elbows show larger deposition when compared to the extrados. This is due to the local changes in flow velocities and gravity effect.

Figure 1-12 (right) represents the distribution of volume fraction for the case with a flow velocity of 1 m/s and an initial volume fraction of 2.9%. It is evident from the figure that a decrease in velocity by 1.5 m/s did not result in a significant change in the dispersed phase volume fraction and thus in the settlement of particles. The volume fraction in this case ranged from 2.9% to 9.1% and the pattern for volume fraction distribution remained the same as in the previous case.



Figure 1-12. Settling of solids in pipe section (left - 2.5 m/s, right - 1.0 m/s).



Figure 1-13. Settling of solids in pipe section (10% volume fraction).

In order to consider the effect of the initial volume fraction on the settling dynamics, the volume fraction of the solids was chosen as 10% with a velocity of 2.5 m/s. Results obtained for the dispersed phase volume fraction of the solids in the pipe section are shown in Figure 1-13. As seen in the figure, the volume fraction of the solids increased from 10% to 27%. The highest value is at the elbows (indicated in red). The dispersion is similar to the previous cases. However, in this particular case, the settlement of solids at the bottom of the straight sections was observed to be higher. This is due to the higher volume fraction values.

The results obtained in the 2D and 3D simulations for the settling dynamics are promising and serve the objective of investigating the actual settling of solids in the plug formation process.

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

During this performance period, FIU initiated verification of Star CCM's ability to model non-Newtonian fluid. The experimental data to which Star CCM will be compared to is documented in "Pipe flow of a thixotropic liquid" (Presti and Escudier, 1995). RANS modeling of this work has already been performed by Bechtel. The same approach will be replicated in order to quickly gain an understanding of the RANS modeling of non-Newtonian pipe flow. This will be achieved by creating a user defined function for the dynamic viscosity as follows:

Viscosity modeling: $\tau = \tau_y + K \gamma^n$

$\tau_{Y}(Pa) = 4.42, \quad K(Pa \ s^{n}) = 0.242, \quad n = 0.534$

where the constants are obtained from the experimental work, leaving the viscosity as a function of the strain rate γ . Proper geometry and mesh sizes have been implemented in accord with the work of Bechtel (2015). To maintain compliance with the reference computational analysis, FIU performed its grid independency study of the same geometry and boundary conditions using the RANS modeling approach on a finer computational grid; FIU is in the early stage of progress in the present task. Results of this grid independency test, as shown in Figure 1-14, indicate that there was no significant difference in results for decreasing cell size, validating the current size. However, there are clear discrepancies between the experimental data and the laminar/turbulent profiles obtained from STARCCM+. This was mitigated by running the simulation for more time steps to allow the critical variables, such as viscosity, to stabilize and converge to steady values (Figure 1-15). Figure 1-16 shows the convergence of the simulation results to the experimental values at T=1 second under turbulent flow conditions. Velocity profiles still need to converge but good agreement is seen between the experimental work and the one performed on STARCCM+.



Figure 1-14. Profile of axial velocity at Reynolds = 550 (left) and Reynolds = 25300 (right).

@ T= 1.001 s



Figure 1-16. Velocity profile at Reynolds 25300 at 1.001 sec. (top right) and strain rate (bottom right).

In the next step, the QDNS module of the STARCCM+ was used to avoid scale-averaging (occurs in RANS) necessary to improve viscosity predications. FIU then conducted a sanity check on the QDNS in a simple approach targeting pipe flow simulation of water, as a Newtonian fluid. An inlet turbulence was added to the boundary conditions in order to reach a sustained source of turbulence. Due to the lack of information about inlet conditions in the experimental and numerical references (Eggels et al., 1993; Eggels et al., 1994; Komen et al., 2014; Shams et al., 2012; and Westerweel et al., 1996), recommended values in the literature were used for the turbulent parameters. An estimate for the inlet turbulent intensity was obtained by analyzing the referenced DNS data available in the literature. The following figures show the flow in the presence and absence of the sustained source of turbulence.



Figure 1-17. Simulation results in absence (a&c) and presence (b&d) of sustained turbulence at the pipe inlet.

Several locations along the pipe were selected for data measuement, aiming to demonstrate the fully developed condition of the flow. Simulation results at two locations (e.g., 0.9 L and 0.74 L, and T=5.0 sec) demonstrate that flow is fully developed inside the pipe. However, the results represent a maximum relative error of 30 percent.



Figure 1-18. Q-DNS simulation results in the pipe with 2,189,373 grid elements at T=0.5 sec, velocity profile (left) and contour of axial profile (right).

The time-averaging procedure was established through creation of points at the measurement location (0.7 L from the inlet) in a traverse direction across the pipe. The simulation results from the pipe flow with almost 2.2 m grid cells were averaged over 9 seconds and are shown below. Agreement with the experimental data could be further improved by using the originally recommended grid size of 3.56 million, which will be pursued and reported later. Simulation against longer times is in progress to obtain better agreement.



Figure 1-19. Simulation results in the pipe with 2,189,373 grid cells averaged in [5-9sec]. Velocity profile on left and point data for velocity on the right showing establishement of turbulence in the domain.

By accepting the performance of the QDNS module of the STARCCM+, the progress was followed by proposing a modification method to viscosity to be used in the QDNS non-Newtonian fluids simulations. Literature contains a number of viscosity models proposed for the flow of non-Newtonian fluids (Thomas, 1963a&b, Soto and Shah, 1976, Wilson and Thomas, 1986). According to Escudier and Presti (1996), Soto and Shah (1976) improved the theory for the Herschel-Bulkley fluid in the entrance region of the flow. Wilson and Thomas (1986) improved the theory of the power-law and Bingham plastic categories for the log-law region of the velocity profile towards better prediction of the wall friction coefficient. This modification reflected an enhancement of viscosity effects at the small time and length scales of the dissipative micro-eddies. Herein, our attempt is to use the fundamental theory of the non-Newtonian fluids which relates the stress to strain rate in order to obtain a modification that spans the entire computational domain. Figure 1-20(a) shows the fundamental stress-strain diagram of the Bingham plastic material. According to Wilson and Thomas (1986), one can define the coefficient α as the ratio of the area under the Bingham plastic curve to the area under the Newtonian curve in Figure 1-20(a). By using this coefficient, it is possible to modify the viscosity, μ , in an iterative and corrective fashion. The explanation of this procedure is that one can start with a viscosity obtained from a non-precise method, such as the Herschel-Bulkley method, and obtain the entire flow field. In the next step, at the end of each iteration, the graph in Figure 1-20(a) a can be reconstructed and α can be obtained. The correction to the viscosity can then be obtained using the expression, $\mu_{\text{micro eddies}} = \alpha * \sigma/(du/dy)$, where, σ is the shear stress. This correction is performed to update the entire field of velocity and the iterative procedure will continue until convergence is attained. In this approach, the correction can be applied to only small or micro-size eddies which are present in the entire computational domain. Figure 1-20(b) shows the distribution of micro or dissipative eddies in the computational domain, embracing the inner and outer layers of the boundary layer and in the core flow.



Figure 1-20. Characteristics of the non-Newtonian fluids: (a) typical rheogram (b) eddy size in turbulent flow.

To separate the small/micro/dissipative eddies from the rest of eddies, one possible solution is to identify them by the rate of dissipation of energy. According to Tennekes and Lumley (1972), the cascade of turbulent energy declares that dissipation occurs in small eddies. Thus, they are named "dissipative eddies." Our attempt involved the use of the direct definition of dissipation rate of energy as $\varepsilon = 0.5*\tau^*(du/dy)$ (Wilson and Thomas, 1986) in the QDNS flow simulation of the Bingham plastic material. Since all of these quantities are known a priori in the computational domain, it is possible to calculate and apply the corrections to any range of scales. This brings up a thresholding on the dissipation rate and the hypothesis can be represented by Eq. 1.

$$\tau = \begin{cases} \tau_{cor.} = \tau_{int.} = \tau_Y + K \gamma^n & \epsilon < \epsilon_{\rm THS} & \text{Eq. 1} \\ \\ \\ \tau_{cor.} = \alpha * \frac{\tau_{int.}}{(\frac{du}{dy})} * \left(\frac{du}{dy}\right) = \alpha * \tau_{int.} & \epsilon \ge \epsilon_{\rm THS} \end{cases}$$

In these expressions, a good initial starting point can have $\tau_{y}(Pa) = 4.42$, $K(Pa s^{n}) = 0.242$, and n = 0.534.

To make the proposed method implementable, FIU introduced the following step-by-step approach:

- Initialize the solution
- Use Hershel-Bulkley for the entire domain (Viscosity modeling: $\tau = \tau_y + K \gamma^n$)

 $\tau_{v}(Pa) = 4.42, \quad K(Pa \ s^{n}) = 0.242, \quad n = 0.534$

- Create the shear stress vs strain rate curve obtained from the entire domain
- Calculate the α from the above curve
- For the scales with dissipation rate (0.5 $\mu_{\text{H-B}} (du_{l}/dx_{k}) (du_{l}/dx_{k})$) > threshold, use the $\mu = \alpha * \mu_{H-B}$ (According to Wilson, 1987)

FIU also investigated the more theoretical aspects of the proposed model and the possibility of

implementing the proposed model in the STARCCM+. The challenge in this approach is finding the updated area of the stress-strain rate envelope through numerical integration over the entire domain.

Testing of the suggested hypothesis is pending upon approval and issue of a valid license for the STARCCM+. Recently, FIU has completed its purchase of the STARCCM+ license and this application will be accessible very soon. However, a search on the feasibility of numerical integration of stress-strain in the STARCCM+ has encountered 2nd and 4th-order Runge-Kutta schemes using the temporary stored values of the stress and strain in each iteration of the computation.

Subtask 17.2 References

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Task 18: Technology Development and Instrumentation Evaluation

Task 18 Overview

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

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

FIU's 3-D sonar was repaired by its manufacturer, Marine Electronics, and received back at FIU. A second CFD study was performed to analyze and optimize mixing with the larger pump, new shaft and rotating 3-head nozzle system. Water will be injected into the bottom of the tank via the rotating nozzles and the shape of the nozzle heads have been studied for improved mixing. A new mixing configuration was designed and parts were ordered and installed. The experimental setup was nearly completed with a structure of U-channels framed around the tank to allow for the sonar and the pumping and mixer system to be bolted to it. A photograph of the tank and structure is shown in Figure 1-21.

FIU performed additional research on how to operate the 2-D sonar (Imaginex Inc). The system is more complicated than the 3-D sonar. New test plans have been drafted for the 2-D and 3-D sonar due to the new experimental test setup and in order to get additional data points on the cutoff density of kaolin clay. Kaolin clay will be added in increments until the tank floor cannot be imaged at a distance from the sonar of 4 ft due to scattering from suspended particles. At this point, the sonar will be lowered to 3 ft from the tank floor cannot be imaged. Tests will be completed for 4, 3, 2 and then 1 foot distances. Grab samples of the suspended Kaolin will be collected to measure percent solids by volume and compared to that calculated based upon water and Kaolin input into the tank.



Figure 1-21. New structure around the test tank for mounting sonar and rotating mixer.

In addition, several tests completed on the 3-D sonar will be performed on the 2-D sonar scans (e.g., 20-30 seconds) to allow comparison of their performance. Past mixing tests with the 2-D sonar always used several 2-D scans which required several minutes for excellent images. These short scans will be the first such tests on this 2-D sonar. If successful, then results from the 2-D sonar for the current test tank and test matrix can be compared to that of the 3D sonar. Figure 1-22 shows photographs of the hollow rotating shaft with 2 nozzles attached.



Figure 1-22. A rotating shaft with opposing nozzles for mixing solids in the test tank (left); the rotating bearing close up (right).

Eric Berglin (PNNL) reached out to FIU to ask for all information on the SLIM monitor, current tasks and system as well as several earlier prototypes and numerous test results. FIU sent Year End Reports, technical reports, presentations and papers on the SLIM system. There is an interest in the results of the current testing on the sonars. Eric Berglin and Carl Lanigan (PNNL) have identified sonar testing they would like to see implemented at FIU, related to WTP mixing tanks.

If the FIU sonars meet performance requirements, then there would be interest in testing the sonar at PNNL on their tank and mixer setup in order to ascertain that the pulse jet mixers will indeed mix and suspend all solids in all HLW slurries to be received at WTP. Ultimately, the goal is to test the envelope of HLW conditions in a test tank at PNNL and ensure that the solids are always mixed. Understanding the operating conditions of the mixers for the entire envelope of waste conditions would mean that the sonar would have completed its mission and mixing would always be effective and hence the sonar would not be needed in the actual HLW mixing tanks.

FIU discussed the performance metrics and data quality objectives with Eric Berglin and Carl Lanigan (PNNL). Eric and Carl sent FIU a PNNL package on behalf of the Waste Treatment & Immobilization Plant (WTP) single high solid vessel design effort to formally request a near-term "capability assessment" of FIU instrumentation to address any or all of the three measurement challenges (bottom mobilization, bulk or slurry mobilization, and relative concentration of gas bubbles) related to vessel mixing. The measurement challenges are associated with full-scale non-hazardous material testing of the mixing system design. WTP measurement needs pose challenges (e.g., vessel configurations: enclosed metal tank with internal structure; fluid conditions: opaque and periodic/cyclic flows) and will likely require customized techniques to obtain the desired data. PNNL requires responses to this challenge and related vendor information to be provided by July 15, 2015.

In addition, FIU will add a few additional tests to its sonar test plan being executed this summer in order to measure image resolution and test the system's ability to image bubbles. PNNL has sent the challenge document to many vendors of technologies and expects to test the best candidates in their test tank system over the next year.

Subtask 18.2: Development of Inspection Tools for DST Primary Tanks

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

During this performance period, FIU made progress in both obtaining further results and in the development of a full-scale test bed. The engineering scale test bed was designed in SolidWorks, as can be seen in Figure 1-23. Note that the test bed pictured is an 8 ft. long section of the entire assembly. The test bed was designed to be modular so that specific sections may be tested for portability. This section uses select pine boards (0.75"x 1.5"x 8' and 0.75"x 3.5'x 8'), a carbon steel flat bar (0.25"x 2.5"x 8'), an acrylic plastic sheet (.093"x 3.5"x 8'), galvanized steel angles and wood screws (#6 x 1/2"). This test bed was designed with the goal in mind of being dimensionally accurate and includes the 90° turn, which is critical for testing.



Figure 1-23. SolidWorks model of test bed.

Using a scale with a resolution of 1 gram, maximum pull force tests were conducted with the inspection tool. The setup for this test can be seen in Figure 1-24. As pictured, the scale was initially on the same surface as the inspection tool; however, it was noted that this was causing the hook to impose a moment about the rear of the body, effectively reducing the normal force and traction on the front wheels. This produced varying results and did not accurately simulate the tank conditions. When deployed, the inspection tool will travel upside-down, causing the tether to hang down and have a vertical force on the inspection tool; the scale was raised 1.25" to simulate this. Making the change in height also took care of the traction loss of the front wheels and produced more accurate and consistent results. It is worth noting that despite this test being conducted with the inspection tool upright, the inspection tool's weight (16.7 gf as tested) is considered negligible compared to the force of the 4.53 lb magnet.



Figure 1-24. Maximum force testing.

FIU also built a full-scale test bed to emulate the first 17 ft of a channel in the refractory pad of tank AY-102. The primary goal for the initial testing is to evaluate the performance of the inspection tool and demonstrate its ability to provide visual feedback. The test bed is comprised of two channels with carbon steel tops spliced together, each with a 1.5 in \times 1.5 in cross-section area to mimic the geometry of a refractory pad channel (Figure 1-25). Multiple experiments were conducted using the test bed to demonstrate the inspection tool's ability to navigate the length of the test bed and to determine tether loads. Based on initial testing and comments provided by

WRPS engineers, additional design challenges have been identified and modifications are currently being proposed and evaluated.



Figure 1-25. The inspection tool navigating inside the test bed (left) and pulling the tether (right).

The initial tests demonstrated that the inspection tool had enough power to pull the tether which was comprised of the camera cables and power line. Other observations from the testing identified areas for improvement:

- The refractory walls created were not exactly 1.5 inches in width, which will be similar to the wall conditions expected in the tank. Occasionally, the rubber wheel would rub against the plastic wall, creating a friction load that the unit could not overcome.
- The inspection tool had difficulty navigating through the ridge created between the two sections of the testbed.
- The motors of the inspection tool were affixed in a manner that if any of the motors failed, the entire tool would have to be discarded. Modifications to the design should allow the parts to be replaced.

In this performance period, a modified unit was designed in Solidworks to address the aforementioned issues and is shown in Figure 1-26.



Figure 1-26. Solidworks rendering of the modified design.

In order for the inspection tool to have more clearance and a greater ability to avoid obstacles, larger wheels must be used. The selection of off-the-shelf-wheels is very limited. The current

wheels are 14 mm in diameter and 4.5 mm in width. A wheel bore of 20 mm must be maintained if the same motors are to be used. The 4.5 mm width appears to be adequate.

The current inspection tool has one large magnet located in the middle of the unit. The new design will have 3 magnets along the length of the inspection tool to ensure an even balance of normal force and to overcome obstacles easier. The approximate cumulative magnet strength is to stay the same, as it has provided enough normal force for sufficient traction but not too much to strain the motors with rolling resistance.

To restrict movements of the motors and camera without using a glue to permanently mount them to the body, slots will be created for the parts and set-screws will be used to keep the parts from moving relative to the body. All parts of the design which require a press-like fit (nuts, motors, camera, etc.) have a clearance of 0.05 mm.

The new modifications were introduced to the design based on the testing conducted. The primary objective of the modifications was to come up with a version of the inspection tool that allows for the replacement of the electrical components. In the initial design, a permanent adhesive was used to secure the DC motors. This arrangement, although practical, did not allow for the replacement of motors in the event that one failed. In this situation, the entire inspection tool would become non-functional. The initial prototype also struggled to overcome small obstructions, which was identified as a result of small wheels being used.

In the modified design, each of the four DC motors rest on a 6-mm diameter half cylindrical case with 18 radial grooves and a 1 mm \times 0.5 mm cross section (Figure 1-27(a)). Once all the DC motors are positioned, a second component (Figure 1-27(b)) which has all four upper half cylindrical spaces with radial grooves is placed on top. Three screws (12 mm \times 2.75 mm) fasten the top component of the main body by passing through the built-in holes and reaching to the bottom of the main body where bolts are inset into 12 mm \times 4.75 mm hexagonal spaces. The radial grooves with predetermined clearances should provide enough friction to prevent the motor from free spinning.



Figure 1-27. (a) The main body of inspection tool; (b) part used for securing motors.

The modified version of the inspection tool is shown in Figure 1-28. The design also includes an increase in the radius of the wheels and the addition of two extra magnets. These modifications will decrease the chance of the inspection tool being blocked by obstacles resulting from debris or welding sections of the tank bottom.



Figure 1-28. Solid works drawing of the modified version of inspection tool.

An additional effort is being given to developing an inspection tool that can navigate and provide visual feedback through the 4" air supply pipe that leads to the tank central plenum of AY-102.

One of the issues FIU focused on for this task was redesigning and strengthening the gripper. Additionally, the maximum gripping force was analytically estimated, and pneumatics were added to the design. The original gripper was designed to be manufactured with a metal, and the 3D printed version of it is not strong enough to endure functional tests. Therefore, its structure was reinforced as shown below in Figure 1-29. The use of thermoplastic 3D printed parts has the potential to expedite the manufacturing process of the new crawler.



Figure 1-29. Original design (left) and strengthened redesign (right).

The maximum theoretical gripping force F_{max} was estimated using the gripper free body diagram shown below. In which, the tether dragging force T must be held by the frictions F, between the gripper claws and the pipe, during the peristaltic movement; the radial compression forces C counterbalance themselves.



Figure 1-30. Gripper free body diagram.

Based on the body static equilibrium:

$$\sum F_x = 0 \Longrightarrow F = \frac{T}{n}$$

where *n* is the number of claws, and the maximum gripping force F_{max}^* per claws is:

$$F_{max}^* = \mu_s N$$

where μ_s is the coefficient of static friction of the surfaces in contact, and:

$$N = C$$

The radial compression forces C were determined using the individual claw free body diagram shown below in Figure 1-31. In which, the pneumatic actuator opens and clamps the claws with a force A equal to:

$$A = \pi b^2 p$$

where b is the bore of the cylinder, and p is the supplied air pressure. Based on the claw static equilibrium:

$$\sum M_o = 0 \Longrightarrow P_y(s+a) + Fl_2 - Nl_1 = 0$$

where s is the pneumatic piston stroke, a, l_1 , and l_2 are functions of the mechanism geometry. P is the normal force transmitted to each claw by the pin attached to the pneumatic piston assembly:

$$nP_x = A + T \Longrightarrow P_x = \frac{A + T}{n}$$

The normal force per claw is then:

$$N = \frac{(s+a)}{n \tan \phi \, l_1} (A+T) + \frac{l_2}{l_1} F$$

Finally, the maximum total theoretical gripping force is:

$$F_{max} = n \cdot \mu_s \left[\frac{(s+a)}{n \tan \phi l_1} (A+T) + \frac{l_2}{l_1} F \right]$$

or

$$F_{max} = \mu_s \left[\frac{(s+a)}{\tan \phi \, l_1} (\pi b^2 p + T) + \frac{l_2}{l_1} T \right]$$

where the angle ϕ is:

$$\phi = \pi - (\beta + \theta)$$

The angle β is constant, and the angle θ can be calculated applying the *Law of Sines* to the triangle ΔOMW shown in Figure 1-31 as well:

$$\frac{s+a}{\sin\beta} = \frac{x}{\sin\theta} \Longrightarrow \theta = \sin^{-1}\left(\frac{x\sin\beta}{s+a}\right)$$

x can be also calculated applying the *Law of Cosines* to the same triangle $\triangle OMW$:

$$(a+s)^2 = x^2 + a^2 - 2ax\cos\beta$$

which leads to a second order polynomial equation:

$$x^{2} - 2a\cos\beta x + a^{2} - (a+s)^{2} = 0 \implies x = \frac{2a\cos\beta \pm \sqrt{(2a\cos\beta)^{2} - 4[a^{2} - (a+s)^{2}]}}{2}$$

The positive root is the solution for x.



Figure 1- 31. Individual claw free body diagram (top) and gripping mechanism actual geometry (bottom).

The computed results of the maximum total theoretical gripping force are presented below in Figure 1-32. The preliminary results show that by using a claw with a rubber coated tip, the gripping mechanism could hold a maximum tether force of around 33 pounds in a pipe with 3 inches in diameter, and around 110 pounds in a pipe with 4 inches in diameter. These values need to be experimentally confirmed. A priori, they seem adequate for the proposed inspection at the Hanford Site.



Figure 1-32. Maximum theoretical gripping force.

During this performance period, FIU also analyzed the path through the air supply lines that the crawler would have to traverse. The proposed ventilation header of the AY-102 tank at Hanford is about 100 feet from grade, down through one of the drop legs and then lateral to the center bottom of the tank. As clarified below in Figure 1-33, the four 4-inch diameter drop legs all branch from the *"header ring"* with a 3-inch pipe, which then transitions to the 4-inch pipe. All pipes are schedule 40 with long radius elbows.



Figure 1-33. The proposed robotic inspection at Hanford site.

A functional crawler prototype was built, assembled and tested, conducting preliminary functional tasks. Figure 1-34 below shows the updated crawler design and Figure 1-35 shows the front camera.



Figure 1-34. Crawler final design.



Figure 1-35. 1.0 megapixel 720p camera.

The prototype, shown in Figure 1-36, not only was able to successfully crawl through 3-inch diameter pipes in horizontal and vertical positions, but was also able to negotiate through elbows. The crawler grip seems satisfactory to perform the proposed inspection task. However, more elaborate tests will be conducted to experimentally verify the maximum gripping force, theoretically predicted.



Figure 1-36. Crawler prototype.

FIU also modified the crawler motion system to be fully automated. The system consists of:

- four pneumatic actuators
- an air pressure regulator
- four 120 volts pneumatic two-way control valves
- a relay bank, and
- an embedded system

To produce the crawler peristaltic movement, the pneumatic actuators are controlled by valves connected to a relay bank, which is controlled by an embedded system using digital ports. Figure 1-37 shows the setup.



Figure 1-37. Crawler locomotion system.

The embedded system utilized is the BeagleBoard Black (www.beagleboard.org). The BeagleBoard Black is a low-power open-source hardware single-board computer produced by Texas Instruments, which has the following characteristics:

- AM335x 1GHz ARM® Cortex-A8 processor,
- 512MB DDR3 RAM,
- 4GB 8-bit eMMC on-board flash storage,
- 3D graphics accelerator,
- NEON floating-point accelerator,
- 2x 200MHz ARM7 programmable real-time coprocessors,
- 10/100 Ethernet and USB connections,
- 4 Timers,
- XDMA interrupt,
- 65 GPIO pins,
- 8 PWM outputs,
- 7 12-bit A/D converters,
- 3.4" $\times 2.1$ " board size, and
- Linux operational system

Currently, crawling routines are being implemented and tests are being performed. Shortly, the crawler will be able to carry out automatic pipe inspections. Several kinds of suspension mechanisms are also still being investigated with the objective of keeping the crawler at center while crawling through pipes and fittings, which will minimize the dragging and the bulldozer effect in the front camera.

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

Subtask 19.1: Pipeline Corrosion and Erosion Evaluation

FIU continued to evaluate different brands of ultrasonic sensors that can be used for measuring the thickness of 2- and 3-in diameter pipes. A majority of the companies that carry relevant transducers did not have products that met the requirements needed. In particular, most sensors evaluated required the use of a liquid couplant. For our application of long-term real-time measurements, only a dry couplant is practical. After discussions with WRPS engineers, FIU decided to purchase an Olympus 45MG Digital Ultrasonic Thickness Gage. The system is a dual crystal transducer that comes with a two-step reference block and a liquid couplant sample. Representatives of Olympus did not recommend the unit with dry couplant; however, a dry couplant was purchased for evaluation. Figure 1-38 shows the system being tested on a long radius, a short radius and Vitaulic elbows. Preliminary measurements indicate that the liquid couplant provides accurate readings and errors are obtained with the dry couplant.



Figure 1-38. Ultrasonic sensor measurements of various elbows.

WRPS visited FIU in May 2015 to assist with the assessment of the sensor and provided recommendations on the path forward. Some of their comments and recommendations are as follows:

- 1. Prefer for FIU to investigate conventional sensors
- 2. Frequency of 5 MHz for the sensor
- 3. Prefer a sensor suitable for the 2-inch diameter pipes
- 4. Investigate and develop a new dry couplant

Based on the recommendations from WRPS, the ultrasonic properties of new materials were investigated for potential use as dry couplants. A brief literature review along with a market survey was conducted with the result that polymers and rubbers are the most promising options.

An elastomer couplant (in the form of aqualene) was tested as the first polymer based dry couplant. Aqualene was purchased by FIU from Olympus. Various measurements were made on carbon steel and cast iron pipe elbows and a reducer section using the Olympus UT sensor (45MG digital ultrasonic thickness gauge – D790 SM). Both the liquid gel couplant and dry couplant were used and the readings were compared. Sample results are as tabulated in Table 1-2. The readings obtained from the gel were accurate whereas those obtained using the dry couplant were inconsistent. As shown in the table, the percent error varied from 18% to a maximum of 45%. Possible reasons could be the geometry, acoustic property mismatch, low signal attenuation through the material, air gaps and/or the pressure exerted on the sensor.

Gel Couplant			Dry Couplant		Error (%)	
(Glycerin)			(Aqualene)		(Aqualene)	
	Тор	Extrodus	Тор	Extrodus	Тор	Extrodus
90° Elbow (carbon steel)	0.239	0.210	0.312	0.310	30.5	44.8
90° Elbow (cast iron)	0.265	0.250	0.320	0.320	20.8	26.4
	Diameter	Diameter	Diameter	Diameter	Diameter	Diameter
	(Smaller)	(larger)	(Smaller)	(larger)	(Smaller)	(larger)
Reducer (carbon steel)	0.235	0.275	0.301	0.325	28.1	18.2

Table 1-2. Results of Thickness Measurements using UT Sensor and Couplants

Different hydrophilic polymers (water based polymers) are being currently investigated as potential dry couplant materials based on the literature. These are a unique group of plastic materials characterized by compatibility with water. Water acts as a plasticizer and after swelling, they transform from a glass state to high-elastic rubber-like state. They exhibit high elasticity and flexibility and hence are suitable for complex geometries and surface roughness, avoiding the air gaps in UT measurements. Swelling with water increases their acoustic properties to closely match those of water and, hence, are suitable for high frequency ranges. These polymers with equilibrium water content ranging from 10% to 98% by wet weight have been investigated for ultrasonic applications at frequencies ranging from 1 MHz to 25 MHz.

Nitrile rubber material was also investigated as a potential dry couplant. A sample thin sheet of nitrile rubber was used as a dry couplant to measure the thickness of a carbon steel pipe section of nominal diameter 3" and average thickness of 0.19". It was observed that by using the nitrile rubber material alone, no signal was captured by the sensor, but the nitrile sheet along with the gel couplant (glycerene) provided by the manufacturer gave an exact reading. Also, as a next option, the nitrile rubber sheet was placed on top of the acqualene dry couplant and the combination was used to measure the thickness. In this case, a reading was observed but with an approximate error of 20%. It was concluded that nitrile rubber alone is not a feasible option but has potential when combined with acqualene since it does not interfere with the signals. We are currently further investigating this option.

Vacuum sealing was investigated as a possible method for sealing dry couplants to avoid the air gap between the couplant and the test piece. Initial vacuum tests were conducted using a vacuum bag and also using a nitrile bag. The experimental set up for the vacuum sealing test conducted using a nitrile bag is shown in Figure 1-39. As seen in the figure, a sample of dry couplant - acqualene was placed on the test piece and air was pulled using a vinyl pipette tip and a tube combination. The UT sensor was placed on top of the set up and readings were taken. It was observed that the thickness readings did not have much influence from the vacuum sealing.

Currently the option of vacuum sealing a thin layer of acqualene with the test piece is being investigated. Also, the following rubber materials and hydrophilic polymers are being investigated for testing:

- 1. Hydrophilic polymers
 - a. Polyhydroxy ethyl methacrylate with 38% of water content
 - b. Copolymer of N-vinyl pyrolidone and 2-hydroxy ethyl methacrylate with 42% of water content
 - c. Poly hydroxyl ethyl methacrylate with 49% of water content
 - d. Terpolymer based on glyceraol methacrylate with 59% of water content
 - e. Copoplymer of N-vinyl pyrrolidone and methyl methacrylate with 75% of water content
- 2. Rubbers
 - a. Nitrile rubber
 - b. Polyisoprene rubber
 - c. Polymethyl methacrylate (PMMA) based rubbers



Figure 1-39. Vacuum bag sealing using a nitrile bag.

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

The purpose of this task is to support the integrity assessment of hose-in-hose transfer lines (HIHTL) and Teflon gaskets and to improve the existing technical basis for their evaluation. FIU efforts during this reporting period included design and selection of the flow loop's main components. These components include the tanks, pumps and heaters which were ordered and received. The three tanks, shown in the Figure 1-40, will hold the caustic material at three separate temperatures (70°F, 130°F and 180°F) which will be regulated via thermostatically controlled tank heaters (Figure 1-41). The tanks will be held in a fume hood and placed on a spill containment skid for health and safety purposes. Three separate loops will be manufactured containing sections of a HIHTLs and gaskets and O-rings. Separate specimens will also be placed directly in the tanks for aging and subsequently tested for degradation of material properties.


Figure 1-40. Tanks and pumps on spill containment skid.



Figure 1-41. Thermostatically controlled tank heater.

Additional efforts were focused on procuring HIHTL specimens. Previous correspondence with Riverbend indicated that their price for the couplings and their installation would be significantly greater than the allowable budget. Various elements such as lower quality assurance of the couplings and the use of carbon steel will reduce the cost significantly. Even with the cost reduction, modifications to the test plan will likely have to be made. The test plan calls for the aging of 27 HIHTL specimens, with approximately 5 additional needed for baseline and initial testing. It is likely that the 60 day aging parameter will be removed, leaving the 180 and 360 day exposures with three operating temperatures. An additional specimen may be used at the upper temperature limit for 60 days to determine if 60 days of aging causes any reduction in strength. If so, potential tests in the future could be used to complete the test matrix.

Representatives at WRPS were able to locate a 864 in. HIHTL that will be used to create our specimens (see Figure 1-42). After discussions with representatives from Riverbend, it was decided that FIU will use 26-inch specimens with the fitting adding another 2 inches on each side. The HIHTL sample does have a kink in the line that extends approximately 18 inches which leaves 846 in. of usable line. Although FIU would potentially be able to manufacture 32

specimens from this length, limitations in the budget will allow for only 24 test specimens. The test matrix will likely be reduced by eliminating the aging for 2 months. FIU will continue with the 6-month and 1-year aging. One sample coupon may be evaluated after 2 months with elevated temperature to determine if a 2-month exposure has any effect. If it does, then next year's scope will include the completion of the predefined test matrix. FIU is in the process of getting the sample shipped to Riverbend to be cut and fitted with the fittings.



Figure 1-42. Hanford HIHTL to be used to create test specimens.

After continued discussions with representatives from Riverbend, a quote was finally issued for 24 test coupons with a 2-inch Safe-T-Chem hose with SST, MNPT swaged end fittings. Riverbend will hydro-test each coupon up to 850 psi to ensure integrity. The length of the specimens will depend on the usable hose obtained by WRPS.

Additionally, FIU had discussions with representatives from PNNL regarding support for a number of our current tasks. The discussion included how PNNL could support our testing with information on the aging of rubber materials exposed to radiation. Radiation exposure is an additional aging stressor that FIU does not currently have the capabilities to test.

Milestones and Deliverables

The milestones and deliverables for Project 1 for FIU Year 5 are shown on the following table. Due to changes in personnel and reduced funding levels for the year, a number of deliverables have been reforecast. After discussions with our DOE-EM representative, the deliverables associated with Tasks 2.2, 17.2, 18.2 and 19.1 will be incorporated into the Year End Report. For Task 18.1, the sonar malfunctioned during testing and due to lengthy delays in getting the system repaired, these deliverables will be incorporated into next year's Project Technical Plan.

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	Reforecast- Included in Year-End Report	
	Deliverable	Draft summary report for subtask	04/01/15	Reforecast-	OSTI

FIU Year 5 Milestones and Deliverables for Project 1

		2.2.1		Included in Year-End Report	
Task 17: Advanced Topics	2014-P1-M17.2.1	Complete computational fluid dynamics modeling of jet penetration in non-Newtonian fluids	05/11/15	Reforecast- Included in Year-End Report	
for Mixing Processes	Deliverable	Draft topical report for subtask 17.2.1	05/15/15	Reforecast- Included in Year-End Report	OSTI
	2014-P1-M18.2.1	Complete development of first prototype of the inspection tool	12/19/14	Complete	
Task 18: Technology Development and Instrumentation Evaluation	Deliverable	Draft summary report for first prototype (subtask 18.2.1)	01/30/15	Reforecast- Included in Year-End Report	OSTI
	2014-P1-M18.1.1	Complete pilot-scale testing of SLIM to assess imaging speed and ability to estimate volume of solids on tank bottom during mixing operations	02/20/15	Reforecast into next year's PTP	
	Deliverable	Draft summary report of pilot scale testing of SLIM (subtask 18.1.1)	03/13/15	Reforecast into next year's PTP	OSTI
	2014-P1-M18.2.2	Complete analysis design and modifications to the peristaltic crawler	03/20/15	Reforecast- Included in Year-End Report	
Task 19: Pipeline Integrity and Analysis	Deliverable	Final Deployment Test Plan and Functional Requirements for SLIM (subtask 18.1.2)	05/15/15	Reforecast into next year's PTP	
	2014-P1-M19.2.1	Complete test plan for the evaluation of nonmetallic components	11/14/14	Complete	
	Deliverable	Draft experimental test plan for subtask 19.2.1	11/14/14	Complete	OSTI
	2014-P1-M19.1.1	Complete data analysis of the C- Farm POR 104 Valve Box	05/01/15	Complete	
	Deliverable	Draft summary report for subtask 19.1.1	05/01/15	Reforecast- Included in Year-End Report	OSTI

Work Plan for Next Quarter

- Project-wide:
 - Draft the Year End Report (YER) for FIU Year 5 (May 2014 to August 2015).
 - Draft the Project Technical Plan (PTP) for FIU Year 1 (FY15) of the renewal period of performance.
- Task 2:
 - The APS task will be ending at the end of the current year, FIU Year 5 (August 2015). The remainder of this year will be used to complete the analysis and write the YER.
 - The computational simulation task will be ending at the end of the current year, FIU Year 5 (August 2015). The remainder of this year will be used to complete the 3D simulations, showing the effects of complex geometry on plug formation and to write the YER.
- Task 17:
 - FIU will test the proposed hypothesis in RANS and QDNS simulations. First, the control zones of the computational domain (potential zones for viscosity modification) will be identified using thresholding of the dissipation rate and viscosity. The areas will be compared in RANS and QDNS simulations to evaluate the degree of effectiveness of the thresholding mechanism. Later, the impact of modifying viscosity on the improvement of agreement between numerical and experimental values (axial mean velocity profiles) will be evaluated. In parallel, the definition of the strain rate in Kolmogorov scales will be modified in the STARCCM+ QDNS and the same procedure will be applied to evaluate the agreement between numerical and experimental values.
- Task 18:
 - For the SLIM subtask, FIU will repeat earlier tests on the 3D profiling sonar imaging objects such as a brick to ensure the system has the same image resolution now after repairs as compared to earlier studies done in 2014 and January 2015. We will also execute the test plan of imaging the bottom of a test tank as micron-sized particles of kaolin clay are added in specific increments (e.g., 0%, 2%, 5%, 10%, 15%, 20%, 25%, and 30% solids suspended in the water by volume). FIU will additionally investigate the ability of the sonar to image solids layers as thin as 2 mm and to image bubbles, relevant to the PNNL test tank challenge.
 - For the refractory pad inspection tool, the primary goal of our efforts in the next quarter will focus on implementing design modifications that have been identified in order to achieve the desired reliability of inspection tool. The experiments will be conducted in order to resolve possible issues such as reduction of contact force with the inspection tool and wall, and wheel design improvement to provide sufficient traction force while being able to avoid obstacles. FIU will also evaluate the performance of the new design which has eliminated the use of adhesive to secure the motors.

- For the crawler, the tether design will be finalized and tested under several conditions involving varied pipe sizes, lengths and fitting configurations. Other tests will also be executed to estimate the tether dragging forces required for the proposed robotic inspection of the ventilation header in the AY-102 tank at Hanford. If necessary, the crawler grippers will be redesigned to comply with it. Additional functional tests will be conducted and the inspection tool will be tested for carrying out automatic pipeline inspections. Several kinds of suspension mechanisms are also still being investigated with the objective of keeping the crawler at center while crawling through different pipe sizes and fittings, which will minimize not only the crawler bouncing and dragging, but will also reduce the bulldozer effect and the accumulation of debris in the front camera.
- Task 19:
 - FIU will continue to investigate the potential dry couplant materials required for use with the sensors. The possibility of manufacturing some of them in-house will also be investigated if required. Additionally, the type and size of suitable sensors for mounting into 2" and 3" pipelines will be explored for design alternatives.
 - For the non-metallic materials task, FIU anticipates receiving the HIHTL coupons with the fittings installed from Riverbend. Due to modifications of the fittings, FIU will work with WRPS engineers to determine how best to integrate the EPDM O-rings and gaskets. With this finalized, the test loop will be completed. Burst pressure test procedures will be determined and initial baseline burst tests will be conducted. Aging of the specimens will also commence.

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
 - o 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.

Subtask 1.1 Quarterly Progress

FIU continued to perform research on the solubility of multicomponent solids via the isopiestic method. Two new reference standards, sodium (NaCl) and calcium chlorine (CaCl₂), were prepared in April to evaluate the reliability of measurements obtained from a newly fabricated isopiestic chamber. This step is necessary to gauge the accuracy of isopiestic measurements in the new chamber to conduct experiments using U-bearing multicomponent solids samples. Six samples of NaCl and three samples of CaCl₂ with varying weights were prepared from "ultra dry" grade chemicals. Then, each sample was amended with 20 uL of DIW and placed in the chamber. Table 2-1 presents information on the solute content in each crucible. After equilibration and sample weighing, the obtained values of water activity (a_w) for NaCl and CaCl₂ will be compared with data published in the literature. In addition, samples containing uranium were prepared; their composition and the procedure for preparation followed those used for previous experiments with the addition of 2 ppm of uranium.

 Table 2-1. Initial Samples Weights and Molality Calculations for Standards NaCl and CaCl₂ (a total of 300 uL were added to the system)

						Crucible+lid
Crucible	Standard	Crucible +	Standard	Solute	Pure Water	+ Standard
#	Sample	lid (g)	Weight (g)	Content (M)	Added (g)	(g)
13	NaCl	15.55070	0.15470	0.00265	0.0200	15.72540
15	NaCl	15.40052	0.23881	0.00409	0.0200	15.65933
20	NaCl	15.32886	0.41093	0.00703	0.0500	15.78979
21	NaCl	16.47894	0.85110	0.01456	0.0500	17.38004
22	NaCl	18.32013	1.53916	0.02634	0.0500	19.90929
23	NaCl	15.16116	2.36194	0.04042	0.0500	17.57310
24	$CaCl_2$	16.90778	0.01763	0.00016	0.0200	16.94541
25	$CaCl_2$	16.66326	0.05610	0.00051	0.0200	16.73936
26	$CaCl_2$	19.63735	0.07249	0.00065	0.0200	19.72984

FIU continued the evaluation of the XRD data on uranium- bearing samples. The experimental patterns were compared against the known patterns for various uranyl carbonate minerals using Sigma Plot software. Matches were mostly found for alkali metals uranyl carbonate such as cejkaite (sodium uranyl carbonate, Na₄UO₂(CO₃)₃), grimselite (hydrated potassium sodium uranyl carbonate, K₂Na₂(UO₂)(CO₃)₃), and agricolaite (potassium uranyl carbonate, K₄UO₂(CO₃)₃). Sample preparation will be repeated to improve the representativeness of and ability to characterize the samples. A presentation of the progress on Task 1.1 during the current performance year was prepared for the annual DOE Review for the project.

After discussions with DOE and PNNL contacts, new approaches for the characterization of samples prepared by the laboratory scale application of the ammonia gas remediation method were explored. It was determined by meeting with representatives of the FIU AMERI facility that the radiochemical nature of our produced samples would disqualify them from use with the instrumentation we were interested in. It was further determined that PNNL's Environmental Molecular Sciences Laboratory (EMSL), which features a radiochemistry annex furnished with

equipment dedicated to studying the chemistry of actinides such as uranium, was best suited for the desired analyses. Two representatives were contacted to discuss the facility requirements and capabilities as well as the objectives of the project. With the backing of those science contacts, a rapid access proposal was drafted for submittal to EMSL where it will be considered. This proposal is currently being revised prior to submission.

FIU continued testing in May to determine if the newly fabricated isopiestic system remains stable and sealed with time. Nine crucibles were prepared with various molalities of NaCl and CaCl₂ reference standards and monitored for a period of two months to determine if the system can achieve equilibrium and if the measurements for water activities and osmotic coefficients are reliable. This step is necessary to gauge the accuracy of isopiestic measurements using a new chamber prior to FIU starting to conduct experiments with U-bearing multicomponent solids samples. Molality measurements of six NaCl samples showed very high values, preventing the use of literature data to find osmotic coefficients; so, all calculations for testing on the system reliability was conducted based on three CaCl₂ samples. For each trial of sample weighing, water mass added to the system before and after the sampling event was calculated. The first two measurements suggested that the water mass inside the system was increased by 4-18%, which might be due to incomplete sealing of the chamber or water gain or loss during the sample weighing process. This also affected the variability between water activity values between the CaCl₂ samples calculated in the range of 2.3-3.5%. The third to last measurement showed that 9% of moisture was lost from the system, which might also have occurred during sample weighing or chamber degassing. Water activity values for the last measurement were in the range between 0.9-2%, which is slightly lower than previous results. FIU will evaluate the integrity of the chamber seal and will initiate preparations of U-bearing samples to evaluate for their solubility.

Continued monitoring of the newly fabricated isopiestic system allows for the gauging of the accuracy of isopiestic measurements taken from the new chamber prior to FIU starting the experiments with U-bearing multicomponent solids samples. Molality measurements of six NaCl samples still showed very high values, preventing FIU from determining the osmotic coefficient values from literature. So, all calculations for the testing of the system reliability were conducted based on three CaCl₂ standard samples. At the end of each sample weighting trial, the water mass added to the system before and after the sampling event was calculated. These measurements suggested that water losses due to sample weighing were in the range of 1.3-2.9%. Water activity values were in the range between 0.32-1.52%, which is slightly lower than previous results. In addition, FIU initiated preparations of U-bearing samples to evaluate for solubility. Eight samples of 10 mL were prepared with 2 ppm of U(VI) in tarred crucibles and kept at 30°C for drying. The concentration of sodium silicate and aluminum was unchanged for all samples, 100 mM and 5 mM, respectively. Four samples were prepared with 3 mM bicarbonate and amended with 0 mM, 5 mM, 10 mM and 15 mM of calcium chloride. Another four samples were prepared with 50 mM of bicarbonate and amended with the same concentrations of calcium chloride as the 3 mM bicarbonate samples. Isopiestic measurements will start as soon as the samples are dried. Calcium chloride will be used as a standard to obtain isopiestic measurements.

A presentation outlining recent progress and future plans for the project subtask concerning the characterization of uranium-bearing solid phases was prepared and presented to PNNL collaborators. Included in the presentation were the details of altered sample preparation methods which included modifications suggested by the same PNNL contacts with experience with the project. The primary changes in these new methods will center on the isolation of the solid phase

in a way that will prevent the formation of an erroneous secondary phase, irrepresentative of the system being studied. Sample preparation is underway and is anticipated to be ready for analysis very soon.

The proposal for gaining access to PNNL's Environmental Molecular Sciences Laboratory (EMSL) facility was revised and completed for submission. The proposal draft was sent to PNNL for comments and suggestions. FIU initiated preparations of samples for this analysis, which will require some special preparations including the use of an epoxy mold for mounting. A vendor for the mounting materials was identified and contacted after dialogue with EMSL's science contact for the electron microprobe. The samples will be prescreened at FIU via SEM/EDS and SRD analysis and selected samples will be stored for shipping to EMSL.

Dr. Hope Lee and Brady Lee from the Energy and Environment directorate at the Pacific Northwest National Laboratory visited FIU on May 22. Dr. Hope Lee gave a talk as part of the DOE Fellow Lecture Serious on the history of PNNL, and provided an overview of the Hanford site research efforts on remediation of radionuclides. Her presentation was followed by a discussion with ARC leadership and key scientists on the ideas for growth of student mentoring relationships with PNNL and technical exchange on the project. DOE Fellows Robert Lapierre, Claudia Cardona and Sandra Herrera gave presentations on the research they are conducting for the Hanford Site projects.

DOE Fellow Claudia Cardona is interning with PNNL and working under the mentorship of Dr. Jim Szecsody. Claudia is involved in a NH₃ gas injection field experiment and is doing some lab work with sediments from that site. In addition, she is using Geochemist Workbench software to predict uranium speciation in conditions of varying pH, ions and bicarbonate concentrations.

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

In April, FIU started preparations of the media leaching solution amended with bicarbonate to be used in the autunite mineral biodissolution experiments. All solutions were buffered with 0.02M Na-Hepes buffer with pH adjusted to 7.0. The concentration of sodium lactate ($C_3H_5NaO_3$, 60% w/w) was 0.024 mol/L. The solution was divided into four 250-mL flasks and sterilized by autoclaving. As the experiment is based on the investigation of bacteria interactions in the presence of different bicarbonate concentrations, each autoclaved flask was amended with potassium bicarbonate salt to have 0, 3 mM, 5 mM and 10 mM of bicarbonate and then the

solutions were filter-sterilized into sterile 250-mL bottles. These bottles were stored in the anaerobic chamber until initiation of the experiments.

In addition, FIU tested the applicability of the whole cell protein determination according to BCA (Pierce) bacterial cells protein analysis for the autunite biodissolution experiments. For that, a fresh culture of facultative anaerobic bacteria *Shewanella Oneidensis MR1* was grown in two 15-mL tubes filled with LB liquid media. The tubes were placed into the incubator for two days at 30° C (Figure 2-1).



Figure 2-1. Tube with bacterial culture grown in LB liquid media.

After two days, the culture was centrifuged and the pellet was washed with DIW water and resuspended in 1.5 mL of DIW water. The washing procedures were repeated twice. After washing, the cells were counted via hemocytometer and 1.2 mL from each vial was extracted into the 1.5-mL microcentrifuge tubes to be used for the Bicinchoninic acid (BCA) protein assay. Cell density concentration in vial #1 was calculated as 884,210,526 cells/mL and in vial #2 as 877,419,355 cells/mL. Following the protocol procedures, the cells were lysed by boiling at 100°C for 10 min and then cooled on ice. The lysate in different dilutions was used for the protein analysis and values were correlated with the cell densities prepared at specific dilutions.

The BCA Protein Assay combines the reduction of Cu^{2+} to Cu^{1+} by protein in an alkaline medium with the highly sensitive and selective colorimetric detection of the cuprous cation (Cu^{1+}) by bicinchoninic acid. Using reagents included in the BCA protein assay kit, the working reagent was prepared by mixing 50 parts of solution 1 and 1 part of solution B. The WR solution was used to build a calibration curve using albumin as a standard. Once a calibration curve was prepared, the WR was mixed with lysate taken at various dilutions at 20:1 ratio, incubated at $37^{\circ}C$ in a water bath (Figure 2-2), cooled on ice and the absorbance was measured at 562 nm via a spectrophotometer UV-VIS. Since this protocol was not sensitive for the small cells densities ranging between log 6-log 7 cells/ mL, another calibration curve was prepared by following micro BCA protocol at 1:1 ratio between the WR and sample volume. Figure 2-3 presents a calibration curve using concentrations of the albumin standard ranging between 0.1-20ug/L.



Figure 2-2. Water bath with dilutions for calibration curve.



Figure 2-3. Calibration curve for protein analysis.

Figure 2-4 shows the correlation between cell densities vs. protein content.



Figure 2-4. Correlation between cell density of Shewanella Oneidensis MR1 and protein content.



Figure 2-5 shows the same correlation in the cell density range between log 5.94-log 6.3 cell/mL.

Figure 2- 5. Correlation between Shewanella Oneidensis MR1 cell density at low concentrations (log 5.9-6.34 cells/mL) and protein content.

Another manuscript by DOE Fellow Paola Sepulveda-Medina, Yelena Katsenovich, Vishal Musaramthota, Michelle Lee, Brady Lee, Rupak Dua, and Leonel Lagos titled, "The effect of uranium on the bacterial viability and cell surface morphology using atomic force microscopy in the presence of bicarbonate ions," prepared in collaboration with PNNL, was published in the *Research in Microbiology* journal. The paper is available online at the following web address: doi:10.1016/j.resmic.2015.03.003

FIU started preparations for the Live/Dead assay in May using procedures modified from the LIVE/DEAD® BacLight Bacterial Viability Kit (Molecular Probes, L-7012) protocol. This assay can illustrate the effect of varying concentrations of bicarbonate ions on the viability of bacterial cells after exposure to uranium. The experiments were focused on the preparation and

microscopy analysis of uranium-free control alive and dead bacterial samples. Preparations for this assay included cell culturing in the LB media and then, after centrifugation, re-suspension of a cells' pellet in 2 mL of the synthetic groundwater solution (SGW). Next, the cells were counted and diluted to log 6 cells/mL density in the suspension. The cell suspension prepared in the SGW solution was then equally divided between two tubes. Samples prepared for killed bacteria were kept for 15 min in 15 mL of 70% isopropyl alcohol and then the pellets were re-suspended in 1 mL of SGW to wash out the alcohol solution after centrifugation. Both killed and alive samples were mixed with 3 uL of a dye mixture composed of SYTO 9 and propidium iodide from the LIVE/DEAD® BacLight Bacterial Viability Kit. Samples were incubated for 15 min in the dark and filtered through black polycarbonate filter (Whatman #110656) via a vacuum filtration system. Samples were then washed with 1 mL of DIW water and placed on the slide with one drop of mounting oil. Samples were covered with the coverslip and observed via fluorescence microscope. The results of the microscopy analysis suggested that more time is required to kill bacteria in a preparation of a "dead" sample. FIU started preparation of new control Live/Dead samples following the same procedures, but keeping bacteria overnight in the isopropyl alcohol solution for the preparation of a "dead" sample and then checking the sample under the light microscope.

FIU completed preparations for the autunite dissolution experiments in the presence of anaerobic Shewanella oneidensis MR-1. To prevent microbial contamination during sampling events, the experiment will be conducted in sacrificial 20-mL glass scintillation vials. Each vial is filled with 18 mg of autunite powder to provide a final U(VI) concentration of 4.4 mmol/L and 10 mL of sterile media solution amended with 0, 3, and 10 mM KHCO₃. Each set prepared using a specific bicarbonate concentration includes sacrificial bacteria-inoculated vials prepared in duplicate and abiotic controls. Samples will be sacrificed at specific time intervals according to the sampling schedule. In addition, to allow the media solutions to equilibrate with the autunite, three abiotic samples were prepared at each bicarbonate concentration and will be taken every 5 days before bacteria inoculation. The interval of time between sampling events after the media equilibrates with the autunite and bacteria inoculation will be about 4-5 days; duplicate bacteria-inoculated vials will be used and an abiotic vial will be used as a control for each set. The total number of sacrificial vials for the duration of experiment was calculated as 99. All prepared glass vials containing 18 mg of autunite were covered with plastic caps and autoclaved for 15 min at 121°C to ensure sterile conditions. After autoclaving, each sample was aseptically amended with 10 mL of the bicarbonate-bearing media solutions stored in an anaerobic chamber (Figure 2-6).



Figure 2-6. Sacrificial vials inside the anaerobic glove box, prepared to conduct the autunite biodissolution experiment.

Task 2 Quarterly Progress

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

Supplementing the previous experiment that was conducted using ICP analysis, the same experimental samples were used to conduct a KPA analysis in this part of the investigation to determine the influence of sodium silicate on the removal of uranium concentrations in the aqueous phase via precipitation. The existing batch samples contained 60, 70, 80, and 90 parts per million of sodium silicate solution in addition to soil from the Savannah River Site (SRS), synthetic ground water, and 0.5 ppm of uranium (VI). In total, 14 samples were created, including two control samples where no silicates were introduced, and monitored for a period of four days.

Over the course of the four days, the pH values were monitored to ensure the values reflected the concentration of sodium silicate present in each sample. An increase in the sodium silicate concentration correlated to an increase in the sample pH value. Figure 2-7 displays the pH values taken from the samples over the four-day period.



Figure 2-7. The pH value of each sample for each day recorded, according to the concentration of sodium silicate present.

From the analysis, we observed that the 0 and 60 ppm sodium silicate concentrated samples showed no variation over time and maintained a relatively low pH throughout the experiment. The samples containing 70, 80, and 90 ppm of sodium silicate observed an initial spike in their pH values, followed by a gradual decrease to a pH range of between 6.5 and 8.

From each of the 14 samples, two additional aliquots were extracted. One set of the aliquots underwent a filtration process using a 0.45 μ m PTFE filter and the other set of samples did not. Both the non-filtered and filtered samples were then diluted 1:10 with 1% nitric acid in preparation for the kinetic phosphorescence analysis. Using the KPA instrument, FIU measured the uranium concentrations present in both the filtered and non-filtered samples, which allowed for the determination of the percentage of uranium precipitate removed from the aqueous phase via the filtration process.

The percent of uranium removed via precipitation can be observed in Figures 2-8 to 2-11. Each figure represents a distinct sodium silicate concentration. The values in each of the graphs are classified by the mobility of the uranium particles; the smallest particles (shaded in green) are considered the most mobile given that they are smaller than the soil pore size at SRS, and the larger macro-colloidal particles (both red and blue) are classified as immobile since they are larger than the soil pore size at SRS (0.40 μ m). Therefore, the percent of uranium removal can be interpreted by the combination of both the red and blue shaded areas on each graph since the red (particles that are greater than 0.45 μ m) and the blue (precipitated particles) are no longer present in the aqueous phase.



Figure 2-8. Percent of uranium removed over a three-day period for the sodium silicate concentration of 60 ppm.



Figure 2-9. Perent of uranium removed over a three-day period for the sodium silicate concentration of 70 ppm.



Figure 2-10. Percent of uranium removed over a three-day period for the sodium silicate concentration of 80 ppm.



Figure 2-11. Percent of uranium removed over a three-day period for the sodium silicate concentration of 90 ppm.

From the graphs, we can conclude that the sodium silicate concentrations of 70, 80, and 90 ppm did not show a significant variation in the percent removal, although all three seemed slightly more successful in percent of uranium removal than 60 ppm of sodium silicate. Therefore, we can also conclude that 70 ppm of sodium silicate appeared to be the optimal concentration, given that 80 and 90 ppm failed to show a proportional increase in effectiveness based off an increase in concentration.

Reverting back to the first part of the experiment, ICP analysis was used to determine the concentration levels specific to silica and iron present in each sample. The results of the analysis are presented in Figure 2-12 and Figure 2-13 for each the non-filtered and filtered samples.



Figure 2-12. The percent of silica present in the supernatant solution of non-filtered samples for the three days in which data was collected.



Figure 2-13. The percent of silica present in the supernatant solution of filtered samples for the three days in which data was collected.

The results from this experiment show that the silica concentrations are relatively consistent throughout the 3 day period in both the filtered and non-filtered samples. The values for the non-filtered samples were only slightly higher due to the presence of both colloidal and soluble silica. Overall, nearly 90% of silica was quantitatively removed from the aqueous phase.

Figure 2-14 represents iron (Fe) concentrations over the experimental period for each sodium silicate concentration used. Each concentration displays the results for both filtered and non-filtered samples.



Figure 2-14. The iron concentrations for both filtered and non-filtered samples, during the 3-day period of the experiment respective to each sodium silicate concentration used.

This analysis indicated that small amounts of iron leached from the soil into the solution, with a natural standard concentration (with no silicate present) of 0.16 ppb. It was also observed through this analysis that iron concentrations were significantly higher in non-filtered samples versus samples that underwent the filtration process. This implies that small amounts of iron remained on the filter, indicating that Fe may have combined with the macro-colloidal particles greater than 0.45 μ m in size.

Batch experiments were then performed in polypropylene vials, which contained 400 mg of SRS soil (fraction 0.18 < d < 2mm) and 20 ml of synthetic groundwater imitating the water composition of SRS (initial pH 3.5) with 0.5 ppm of U(VI). The samples were spiked with 70, 80 and 90 ppm of sodium silicate and two samples served as controls (no sodium silicate was introduced) and were equilibrated on a platform shaker (110 rpm) for a period of 30 days at room temperature. Over the course of 30 days, the pH was monitored; U(VI), Fe and Si concentrations in the supernatant were determined periodically for a period of 9 days. In a similar fashion to our previous experiments, the metals concentration in the supernatant was determined by isolating aliquots without any further treatment as well as by isolating aliquots and filtering them through a Teflon filter (0.45µm). U(VI) was analyzed using kinetic phosphorescence analysis (KPA) and Fe and Si concentrations were determined by means of inductively coupled plasma – optical emission spectrometry (ICP-OES). Results are shown in Figures 2-15 through 2-18.



Figure 2-15. pH variance as a function of time for different sodium silicate concentrations



Figure 2-16. Percentage of different forms of U(VI) as a function of time for treatment with 70 ppm sodium silicate. Precipitate, colloidal form (average size larger than 0.45 μm) and soluble form are represented by red, green and blue color respectively.



Figure 2-17. Percentage of different forms of U(VI) as a function of time for treatment with 80 ppm sodium silicate. Precipitate, colloidal form (average size larger than 0.45 µm) and soluble form are represented by red, green and blue color respectively.



Figure 2-18. Percentage of different forms of U(VI) as a function of time for treatment with 90 ppm sodium silicate. Precipitate, colloidal form (average size larger than 0.45 μm) and soluble form are represented by red, green and blue color respectively.

The results indicated that the fractions of U(VI) remain stable within a period of 9 days. Approximately 50-55% of the U(VI) is in the precipitate form; 20% is found in a colloidal form retained by a 0.45μ m filter; and 25-30% remains in soluble form. Given the rather large size of the colloidal particles that include U(VI), it is presumed that the mobility of these particles is

going to be rather limited and, therefore, the removal of U(VI) from the aqueous phase accounts for ~70% (the sum of the precipitate and colloidal form percentages). These results are in accordance with theoretical calculations based on speciation software that predict ~60% of U(VI) at circumneutral pH will be removed from the aqueous phase through precipitation in the form of $UO_2(OH)_2 \cdot H_2O$ (Figure 2-19).



Figure 2- 19. Speciation diagram for the conditions studied: Savannah River Site synthetic groundwater. The solubility of atmospheric CO₂ has been considered (Chemical Equilibrium Diagrams Hydra-Medusa software by Swedish Royal Technical Institute KTH).

FIU continued the experiments to study the effect of sodium silicate additions on the immobilization of U(VI). Batch experiments were performed in polypropylene vials, which contained 400 mg of SRS soil (fraction 0.18 < d < 2 mm) and 20 ml of synthetic groundwater, imitating the water composition of SRS (initial pH 3.5), with 0.5 ppm of U(VI). The samples were spiked with 70, 80 and 90 ppm of sodium silicate and two samples served as controls (no sodium silicate was introduced) and were equilibrated on a platform shaker (110 rpm) for a period of 30 days at room temperature. Over the course of 30 days, the pH was monitored; U(VI), Fe and Si concentrations in the supernatant were determined periodically for a period of 9 days. In a similar fashion to our previous experiments, the metals concentration in the supernatant was determined by isolating aliquots without any further treatment as well as by isolating aliquots and filtering them through a Teflon filter (0.45µm). U(VI) was analyzed using kinetic phosphorescence analysis (KPA) and Fe and Si concentrations were determined by means of inductively coupled plasma – optical emission spectrometry (ICP-OES).

The results of Si present in the aqueous phase are presented in Figure 2-20.



Figure 2-20. Percentage of Si removed from the aqueous phase as a function of time for different sodium silicate concentrations.

As it can be seen in Figure 2-20, after an equilibration time as low as 2 days, \sim 85% of Si is removed from the aqueous phase. This experimental result approaches the theoretical values of dissolved (\sim 30%) and solid form silica (\sim 70%) based on speciation calculations, as shown in Figure 2-21.



Figure 2-21. Silicon species as a function of pH for the conditions studied: Savannah River Site synthetic groundwater in the presence of 90 ppm sodium silicate (Chemical Equilibrium Diagrams Hydra-Medusa software by Swedish Royal Technical Institute KTH).

As far as iron is concerned, there seems to be a correlation between the addition of sodium silicate and the "leaching" of iron in the supernatant. More specifically, the addition of sodium silicate seems to incur iron release in the aqueous phase, but the concentration of sodium silicate added does not seem to play any role (Figure 2-22). Furthermore, there is a significant difference in the amount of iron detected in the aqueous phase between not filtered samples and filtered samples (0.45 µm Teflon filters).



Figure 2-22. Iron concentration in the aqueous phase as a function of sodium silicate addition for not filtered samples (blue) and samples filtered through 0.45µm filters (orange).

After filtration, the levels of iron in the aqueous phase are very low, comparable to those of the control samples with no addition of sodium silicate (~180 ppb) whereas, before filtration, the concentration of iron is approximately at 1.8 ppm. These results imply that iron in the aqueous phase is associated with the formation of colloidal particles, since it is retained largely by a 0.45 μ m filter.

FIU Year 4 Carryover Work Scope

During April, unfiltered aliquot samples on experiments with 50 ppm HA were collected from the batches 2, 3, 5, and 6 from pH 3 to 8. Samples were prepared and analyzed using KPA and ICP for concentrations of uranium, iron and silica.

The uranium (VI) removal in unfiltered samples was found to be similar to that of the filtered samples; the highest removal of uranium was observed at the lowest pH (pH 3) and U removal showed a downward trend as pH reached 8. As expected, a higher removal was seen for sediment-containing batches 5 and 6, which might be explained by the increased availability of binding sites. The highest value for U removal of 71.83% was found at pH 3 and the lowest value for U removal of 33.00% was found at pH 8. Batches 2 and 3 showed the highest U removal, on the level of 45.01%; however, this value decreased to 18.16% at pH 8. The overall removal of U(VI) for unfiltered samples was found to be lower than for filtered samples since the filtration process also removes some semi-soluble components. With unfiltered samples, any U(VI) associated with colloids that may be removed from suspension via filtration would remain and be analyzed, thus decreasing the percentage of U removal compared to filtered samples.

Silica removal for unfiltered samples from batches 2 and 3 gave a downward trend with the highest removal at pH 3 (94.55% removal) and slowly decreasing towards pH 8 with 44.04% removal. Batches 5 and 6 remained fairly consistent at an average of ~60% removal. When compared to previously filtered samples, the removal of Si remained fairly constant for all batches with some slight deviation seen at pH 8; the unfiltered non-sediment samples (2 and 3) yielded a higher U removal percentage than those containing sediments.

Sample- Description, pH 3	U(VI) Avg Removal, %	Std Deviation	Si Avg Removal, %	Std Deviation	Fe, ppm	Std Deviation
Batch 2	31.8	4.57	94.55	1	No Se	diment
Batch 3	44.28	2.75	No Si	NA	No Se	diment
Batch 5	71.83	1.32	72.68	7.42	0.85	0.52
Batch 6	64.53	2.69	No Si	NA	0.62	0.06
Sample- Description, pH 4	U(VI) Avg Removal, %	Std Deviation	Si Avg Removal, %	Std Deviation	Fe, ppm	Std Deviation
Batch 2	44.98	0.5	88.92	1.37	No Se	diment
Batch 3	45.01	4.38	No Si	NA	No Se	diment
Batch 5	52.94	4.02	66.69	2	0.44	0.02
Batch 6	60.77	3.76	No Si	NA	0.51	0.07
Sample- Description, pH 5	U(VI) Avg Removal, %	Std Deviation	Si Avg Removal, %	Std Deviation	Fe, ppm	Std Deviation
Batch 2	37.55	1.66	84.02	0.29	No Sediment	
Batch 3	18.24	1.67	No Si	NA	No Se	diment
Batch 5	40.66	8.17	65.53	2.61	0.49	0.06
Batch 6	40.12	2.76	No Si	NA	0.43	0.03
Sample- Description, pH 6	U(VI) Avg Removal, %	Std Deviation	Si Avg Removal, %	Std Deviation	Fe, ppm	Std Deviation
Batch 2	28.27	6.27	76.77	1.86	No Sediment	
Batch 3	26.88	1.18	No Si	NA	No Se	diment
Batch 5	25.71	3.6	54.81	5.2	0.53	0.02
Batch 6	36.06	2.34	No Si	NA	0.44	0.02
Sample- Description, pH 7	U(VI) Avg Removal, %	Std Deviation	Si Avg Removal, %	Std Deviation	Fe, ppm	Std Deviation
Batch 2	22.92	7.99	60.24	4.4	No Sediment	
Batch 3	24.76	0.59	No Si	NA	No Se	diment
Batch 5	22.6	1.83	60.42	1.47	0.63	0.03
Batch 6	33.93	2.94	No Si	NA	0.55	0.04
Sample- Description, pH 8	U(VI) Avg Removal, %	Std Deviation	Si Avg Removal, %	Std Deviation	Fe, ppm	Std Deviation
Batch 2	21.4	0.12	44.04	14.01	No Sediment	
Batch 3	18.16	3.24	No Si	NA	No Se	diment
D-4-1. 5	33.02	0.87	55 71	476	0.72	0.02
Batch 5	55.02	0.07	55.71	1.70	0=	

Table 2-2. Percentage of U(VI) and Si Removal, Fe Concentrations for Unfiltered Samples









Figure 2-25. Silica removal for the filtered samples.

The removal of uranium (VI) from 50 ppm HA unfiltered samples (Figure 2-26) was compared to that of the 10 ppm HA unfiltered samples (Figure 2-27). The 10 ppm HA solution showed significant removal at an alkaline pH, unlike the 50 ppm HA solution, which showed a greater removal in the acidic pH. It is postulated that HA concentration of 10 ppm is too low to cause significant interactions between colloidal Si and HA to occur. However, further research is needed to test this hypothesis.





Figure 2-27. Uranium (VI) removal at 10 ppm HA, unfiltered.

Silica removal for unfiltered 50 ppm HA samples (Figure 2-28) in Batch 2 gave a negative trend with the largest removal of 94.55% observed at pH 3. The U removal was shown to decrease to 44.04% as pH increased up to pH 8. A similar trend was seen for the 10 ppm HA unfiltered samples for Batch 2 (Figure 2-29) prepared without sediments where U(VI) removal decreased from 87.68% to 38.05%. However, U(VI) removal for the sediment-bearing Batch 5 remained constant at ~80%. For both HA concentrations, U(VI) removal for Batch 2 decreased steadily while remaining near a constant value for Batch 3.



Figure 2-28. Silica removal at 50 ppm HA, unfiltered samples.



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

In the month of April, XRD analyses were conducted on the Batch 2 microcosm samples to search for matches with the ferrous carbonate mineral, ankerite. Possible matches, which were slightly shifted from the maximum intensity peaks, were found on the graphs for Batch 1-Set 2 (Figure 2-30), Batch 2-Set 1 (Figure 2-31), and Batch 2-Set 4 (Figure 2-32) at ankerite's highest intensity peak at a 2-Theta angle of 30.7°; however, no distinct matches were found in any of the samples.



Figure 2-30. Batch 1- Set 2 vs Ankerite.





Figure 2-32. Batch 2- Set 4 vs Ankerite.

ICP was conducted to repeat samples from Batch 2 and determine the soluble iron concentrations. Three of the Batch 2 samples (Sets 2, 3, and 4) had previously returned inconclusive results and it was decided that the samples would require a lower calibration curve. The soluble Fe²⁺concentrations for the Batch 2 samples were recorded in Table 2-3, along with iron concentrations determined for Batch 1. Overall, Batch 2 samples had a lower average iron concentration of 4522.52 ppb in comparison to Batch 1 (6111.53 ppb), which is believed to have been caused by the formation of iron precipitates. However, their weight percentage may be too low to be detected via XRD. The lower average soluble iron concentration of Batch 2 is mainly due to Set 3, which had an uncharacteristically low iron value of 893.27 ppb. It was noted that in both batches the highest concentrations of iron were found in the samples inoculated with 5 mL of anaerobic sludge taken from the wastewater treatment anaerobic digester. It was also observed that concentrations for all of the samples were found to be lower than those which were recorded in the previous microcosm study presented in the 2013 Year End Report. The average concentration for both of the current batches combined was found to be 5317 ppb, while in the previous study it was recorded as 57691 ppb. This might be due to a difference in the sample preparation for ICP analysis. Further tests will help to determine the cause of this difference.

Description	Fe Concentration (ppb)	
Batch 1 (Set 1-1)	1650.87	
Batch 1 (Set 1-2)	13312.80	Average
Batch 1 (Set 1-3)	8462.03	7808.57
Batch 1 (Set 2-1)	4705.95	
Batch 1 (Set 2-2)	4757.76	Average
Batch 1 (Set 2-3)	5815.26	5092.99
Batch 1 (Set 3-1)	5730.32	
Batch 1 (Set 3-2)	4343.13	Average
Batch 1 (Set 3-3)	5349.70	5141.05
Batch 1 (Set 4-1)	5494.83	
Batch 1 (Set 4-2)	6118.96	Average
Batch 1 (Set 4-3)	7596.79	6403.53
BATCH 1 Average	6111.53	
Batch 2 (Set 1)	5748.89	
Batch 2 (Set 2)	4255.69	<u> </u>
Batch 2 (Set 3)	893.27	Average
Batch 2 (Set 4)	7192.26	4522.52
BATCH 2 Average	4522.52	

Table 2-3. Soluble Iron Concentrations

Sulfate analysis via ion chromatography using the supernatant solutions collected from the microcosm samples is currently in progress. Future work will include speciation modeling via Minteq software to determine the percent of major species distribution and finalizing sulfate analysis.

FIU also conducted data analysis of ICP/OES results on ferrous iron. The samples varied in the range of 6-13 ppm in the ferrous iron concentrations, with the greatest amount reaching 13,312.8 ppb in Batch 1, Set 1-2. It was noted that Batch 1 samples previously inoculated with the anaerobic bacteria (Sets 1 and 4) had the highest average iron concentrations in comparison to those which were not inoculated. It is believed that iron-reducing bacteria may have biodegraded molasses using ferric iron as a terminal electron acceptor, which would explain the higher soluble ferrous iron concentrations in these samples. When comparing the samples without bacteria (Sets 2 and 3), it was observed that the ferrous iron concentration was almost identical. This suggests that hydrogen sulfide generated after sulfate reduction might not complex with the ferrous iron due to the acidic conditions created in the microcosm samples.

Overall, the Batch 2 samples had a lower average iron concentration (4,522.5 ppb) in comparison to Batch 1 (6,111.5 ppb), which is believed to have been caused by the formation of iron precipitates, which may be too low in concentration to be detected via XRD. The lower average soluble iron concentration of Batch 2 is mainly due to Set 3 which had an uncharacteristically low iron value of 893.3 ppb; making it the lowest concentration from any of the Batch 1 or 2 samples. It was noted that as in Batch 1, the Batch 2 samples with the highest concentrations of iron were found in the samples inoculated with 5 mL of anaerobic bacteria (Sets 1 and 4).

The average ferrous iron concentration in the samples amended with sulfate for Batch 1 and Batch 2 combined was found to be 5,726.5 ppb. The average ferrous iron concentration in the samples which contained no sulfate for Batch 1 and Batch 2 combined was found to be 4,907.5 ppb. While it was expected that samples containing sulfate would have a lower ferrous iron concentration, it is believed that the acidic conditions hindered the formation of any iron-sulfide precipitates. Sample preparation for sulfate analysis is in progress and the data will be presented in the next monthly report.

DOE Fellow Aref Shehadeh is currently interning at the Savannah River Site (SRS) located in Aiken, South Carolina. Aref is working under the mentorship of Dr. Miles Denham SRNL. Aref is involved in the experiments mimicking remediation of iodine-129 (I-129) in the SRS F-Area caused by a large radionuclide plume stemming from an old seepage basin. Dr. Denham has proposed the use of silver chloride (AgCl) to react with the I-129 in the sediments to create a binding effect and prevent further spreading of the plume. Aref is researching the mechanisms of the I-129 binding to the silver chloride particles, their particle size and structure, created in a laboratory setting, and is helping determine the optimal concentration of AgCl to be used in future *in situ* remediation efforts.

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

During the month of April, the kinetic experiments of Huma-K at a concentration of 50 ppm were completed. These experiments allowed for optimizing the sorption experiment until the sorption of Huma-K onto SRS sediments reached equilibrium. First, one gram of SRS sediment was placed in centrifuge tubes. Then, 50 ppm of Huma-K was added to each centrifuge tube with a total volume of 19 ml. Then, the pH of the solution was adjusted to pH 4, and DI water was added to reach a final volume of 20 mL in each tube. The samples were then placed in a shaker. At predetermined time intervals, the samples were withdrawn and centrifuged. The concentration of the supernatant was measured by UV-vis spectrophotometer. The results are shown in Figure 2-33.



Figure 2-33. Humate sorbed over time on SRS sediments.

It is clearly seen that after 4 days, the concentration of Huma-K sorbed to SRS sediments at pH 4 does not change, meaning that sorption has reached an equilibrium. FIU plans to repeat the same experiment at pH 9 to determine if the equilibrium is attained in the same time interval or if it needs more time at a different pH value. Also, FIU started the preparation of samples to determine whether centrifugation removes some of the humic molecules and if the removal is significant. These results will be compared with samples that were not centrifuged but filtered using 0.45 μ m and 0.2 μ m filters.

FIU efforts in May were dedicated to researching the literature to find different kinetic models that could best represent the kinetic experiments. Kinetic models offer valuable information about the rate of the reaction and the reaction mechanism involved in the sorption process. With the data obtained from the adsorption kinetics, the sorption and diffusion processes can be evaluated by using the mathematical kinetic models shown in Table 2-4.

Kinetic model	Equation	Linear equation	Rate constant	Amount adsorbed at equilibrium	Plot	R ²
First-order	$q_t = q_e e^{-k_1 t}$	$ln[q_t] = ln[q_e] - k_1 t$	$K_1 = 1.1x10^{-3}$	$q_e = 508.2$	$ln[q_t] vs.t$	0.3682
Pseudo first- order	$q_t = q_e (1 - exp^{-k_{1p}t})$	$log(q_e - q_t) = log(q_e) - \frac{k_{1p}t}{2.303}$	$K_{1p} = 9x10^{-3}$	$q_e = 178.2$	$log(q_e - q_t) vs.t$	0.4797
Second- order	$q_t = \frac{q_e}{1 + q_e k_2 t}$	$\frac{1}{q_t} = \frac{1}{q_e} + k_2 t$	$K_2 = -2x10^{-6}$	$q_{e} = 500$	$\frac{1}{q_t} vs.t$	0.3161
Pseudo second- order	$\frac{\frac{dq}{dt}}{=k_{2p}(q_e-q_t)^2}$	$\frac{t}{q_t} = \frac{1}{k_{2p}q_e^2} + \frac{1}{q_e}t$	$K_{2p} = 4.26x10^{-4}$	<i>q_e</i> = 714.3	$\frac{t}{q_t} vs.t$	0.9995

 Table 2-4. Kinetic Order Reaction Models

The model that best fit the experimental data from the kinetic experiments was the pseudo second order model with a correlation coefficient R^2 of 0.9995. The pseudo second order model assumes that two reactions are happening. One of the two reactions in the pseudo second order model proceeds to achieve equilibrium very fast. The rate of the other reaction is significantly slower, taking longer periods of time. These two reactions can occur in series or in parallel. In the case of Huma-K, it could be assumed that two types of reactions are occurring (fast and slow). An example of a fast sorption reaction is adsorption through electrostatic attraction and inner sphere complexation. Carboxyl groups from humic molecules tend to be negatively charged and can be attracted electrostatically to the positive charges developed at the surface of the sediment particles in the fast reaction. Examples of a slow sorption reaction can be slow interparticle diffusion, formation of precipitates on surfaces, and adsorption on sites that have a large activation energy. At low pH values, humic molecules have less charge, so they can agglomerate and precipitate. This precipitation could be attributed to the slow reaction that is happening from the pseudo second order kinetic model.

During the month of June, the potentiometric titration experiment of HumaK and SRS sediments was performed in order to determine the point of zero charge and the protonation-deprotonation behavior of HumaK and Savannah River Site sediments. The potentiometric titration consisted of placing a specific amount of the material (HumaK or SRS sediments) dissolved in NaNO₃ in a

closed beaker. The solution was stirred constantly and nitrogen was introduced in order to remove CO_2 and to create an inert atmosphere. Once the pH of the solution containing the material was stable, NaOH was added to raise the pH to 11 and to deprotonate the functional groups present in the material. Once the pH was stabilized again, the titration was started by adding small quantities of HNO₃. After each addition of HNO3, the pH and the volume were recorded. The titration was ended at a pH around 3. In the case of the sediments, after the titration was finished, the supernatant was collected by vacuum filtration and titrated again. The purpose of the supernatant titration was to estimate the functional groups that may have leached from the sediment and could consume hydrogen ions.

The titration curves obtained from this experiment were: NaNO₃ electrolyte, HumaK (100 and 500 mg), SRS sediment (less than 2 mm), SRS sediment (less than 63 μ m), and quartz standard (Figure 2-34, Figure 2-35). In order to get just the [H⁺] consumed at the surface of the material, it was necessary to subtract the titration curve of the electrolyte (NaNO₃) from the material dissolved in the electrolyte. This was done by using data analysis software.



Figure 2-34. Titration curve of Huma-K

Figure 2-35. Titration curve of SRS sediments

The next step of the experiments will be to identify and compare the functional groups present in Huma-K and SRS sediment with literature references. Also, samples containing SRS sediments and Huma-K will be prepared and analyzed by means of FTIR in order to have a better characterization of these materials.

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

Multiple experiments were performed in April using 3 mM of sodium bicarbonate solutions. The pH, conductivity, and temperature were monitored during ammonia gas injection into solutions via an automatic syringe pump. Three experiments were performed and data for the pH evolution is presented in Figure 2-36. The pH of the solutions during three experiments exhibited a similar trend, increasing steadily with the increase in ammonia volumes injected. The increase in pH values were very minimal as the pH reached 10. Temperature data and conductivity data were not consistent between all three batches; even the trends of temperature and conductivity were not observed to be similar, the values differed significantly. The ammonia injection approach was modified to rectify the reproducibility of the data; instead of a beaker, a long glass column is being used and data on this new approach will be reported during next reporting period.



Figure 2-36. Solution pH evolution with the injection of ammonia gas.

During May, 5% ammonia was injected into a glass column containing 50 ml of 3 mM bicarbonate while monitoring pH and temperature. A glass column was used in order to monitor any differences compared to a beaker due a longer contact time between the ammonia and the solution (Figure 2-37). The temperature was recorded between 20.8 to 21.0 °C, consistent with previous results (Figure 2-38). Changes in pH followed a similar profile as previously seen, rapidly increasing to pH 9 after injecting 55 mL of NH₃ while 380 mL of NH₃ was needed to reach a pH of 10.



Figure 2-37. Ammonia volume injected vs. pH.



Figure 2-38. Ammonia volume injected vs. temperature.

The experimental setup for injection of 5% NH_3 (95% N_2) was modified in June to increase the reproducability and accuracy of the measurements. The following changes were made to the protocols:

- Additional conductivity standards were acquired (including 100 μ S/cm) to allow for calibration within the range of the measurements.
- Deionized water was degassed by bubbling N_2 and mixing for at least 60 minutes to remove CO_2 to allow for greater consistency in initial conditions and total carbonate concentrations.
- Sample size was increased to 100 mL in a 150-mL beaker to allow for comparison with previous published works and to increase contact time with the gas.
- Samples were pulled at various time points during injection and acidified with H_2SO_4 (1 mL concentrated H_2SO_4 per 50 mL of sample) for later analysis for total NH_3/NH_4^+ by ammonia gas-sensing electrode (Orion 9512BNWP) or colorimetric method.

These adjustments allow for greater reproducability in the data as shown in Figures 2-39 to 2-41 for injection of aliquots of 5% NH₃ (95% N₂) into 3 mM HCO₃⁻ solutions at ~21°C. The experimental setup is shown in Figure 2-42. As shown by the data below, the injection of 5% NH₃ (95% N₂) gas increases both the pH and conductivity of the system as the aqueous NH₃/NH₄⁺ concentrations increase. However, following injection of 5 mL NH₃ (100 mL of total gas), the rate of increase in both pH and conductivity begin to decrease. To reach a pH of greater than 10.0, at least 10 mL of NH₃ gas must be injected for 100 mL of 3 mM HCO₃⁻ solutions at ~21°C. Future experiments will manipulate the HCO₃⁻ concentrations up to 100 mM and for variable temperatures. In addition, speciation modeling (using Visual Minteq) and a literature review are in progress.

One additional change to the experimental setup is still in progress. A peristaltic pump (Masterflex digital L/S with size 14 tubing pump head) will be considered for further injection experiments, replacing the syringe pump used previously for injection. This will allow for calibration of a specific flow rate being injected as well as continuous injection of 5% NH₃ (95% N₂). These changes will allow for comparison with previously published data and greater ease in development of simple models. Future work will include repeating these open system injection experiments with HCO₃⁻ concentrations from 0 to 100 mM. Batch equilibrium experiments with similar conditions will also be completed for determination of Henry's constants with variable HCO₃⁻ from 0 to 100 mM, constant ionic strength of 0.2 M (as adjusted by addition of NaCl), constant temperature ~21°C, pH 11 (with the use of Piperidine buffer for pH 11.0), and variable NH₃ concentrations.



Figure 2-39. pH versus volume of NH₃ (mL) injected for triplicate experiments with 3 mM HCO3suspensions at ~21°C.



Figure 2-40. Conductivity (µS/cm) versus volume of NH₃ (mL) injected for triplicate experiments with 3 mM HCO3- suspensions at ~21°C.



Figure 2-41. Comparison of Trials 1-3 with the new setup (triangles) with previous measurements (circles).



Figure 2-42. Experimental design including 150-mL beaker placed in a temperature-controlled water bath with stirrer probe, conductivity electrode and pH electrode for measurement throughout injection of 5% NH₃ (95% N₂) into bicarbonate solutions.

Milestones and Deliverables

The milestones and deliverables for Project 2 for FIU Year 5 are shown on the following table. A deliverable, a progress report on sorption properties of the humate injected into the subsurface system (subtask 2.3), was completed and sent to DOE HQ and the SRNL site contacts on April 3, 2015.

Task	Task Milestone/ Description			Status	OSTI
	2014-P2-M5	Obtain anaerobic facultative microorganisms, Shewanella sp., from PNNL and complete preparations to set up autunite leaching experiments.	10/03/14	Complete	
Task 1: Sequestering uranium at Hanford Task 2: Groundwater remediation at SRS	2014-P2-M3	Completion of sample preparation using a reduced amount of silica (50 mM)	11/07/14	Complete	
	2014-P2-M4	Complete preparation of a draft manuscript on the removal of uranium via ammonia gas injection method	12/15/14	Complete	
		Completion of solubility measurements of U(VI)-free samples (FIU Year 5 scope) <u>and</u>			
	2014-P2-M1	Completion of solubility measurements using standards such as calcium chloride and lithium chloride to get better deliquescence predictions at low water activities values (carryover scope).	01/30/15	Complete	
	Deliverable	Prepare a progress report on the solubility measurements via isopiestic method (subtask 1.1)	02/16/15	Complete	OSTI
	2014-P2-M6	Complete preparations for the microcosm experiments prepared with SRS sediments using sulfate additions.	09/12/14 Re-forecasted to 10/13/14	Complete	
	Deliverable	Progress report on microcosm studies prepared with SRS sediments augmented with molasses and sulfate (subtask 2.2)	01/30/15	Complete	OSTI
	Deliverable	Progress report on batch experiments prepared with SRS sediments, colloidal Si and higher HA concentration up to 50ppm (carryover scope under subtask 2.1).	03/30/15	Complete	OSTI
	Deliverable	Prepare a progress report on sorption properties of the humate injected into the subsurface system (subtask 2.3)	04/03/15	Complete	OSTI
Task 3: Evaluation of ammonia for uranium treatment	2014-P2-M2	Completion of literature review on physical mechanisms associated with the fate of ammonia after injections into subsurface	10/31/14	Complete	

FIU Year 5 Milestones and Deliverables for Project 2

Work Plan for Next Quarter

- Draft the Year End Report (YER) for FIU Year 5 (May 2014 to August 2015).
- Draft the Project Technical Plan (PTP) for FIU Year 1 (FY15) of the renewal period of performance.
- Subtask 1.2 Complete preparations of uranium-bearing samples and initiate a new round of isopiestic measurements. Use CaCl₂ as a standard for isopiestic measurements.
- Subtask 1.2: Complete proofs of "imaging" manuscript after acceptance. Learn procedures for the protein analysis, develop a calibration curve and conduct experiments to find a correlation between protein and Shewanella cell concentrations. Continue with the autunite dissolution experiment and sampling of sacrificial vials inoculated with Shewanella cells. Start chemical analysis for collected samples.
- Subtask 2.1: Assess the potential of sodium silicate concentration to retain the pH values for a longer period. Investigate iron and aluminum concentrations in the aqueous phase leached from soil as a consequence of sodium silicate addition. Prepare 0.45 µm and 0.2 µm filters for SEM/EDS analysis and perform SEM/EDS analysis.
- Subtask 2.2: Complete sulfate and iron analysis to find mass balance of elements in the samples before and after treatment with molasses.
- Subtask 2.3: Initiate kinetic experiment of desorption of HumaK at pH 4. Conduct sediments characterization studies via FTIR and XRD analysis. Conduct literature research in order to identify peaks in the spectrum.
- Task 3: Continue testing of ammonia injection at 0, 3, 10 mM bicarbonate concentrations.
- Subtask 2.1: Continue study on the effect of colloidal silica and sediments collected from F/H area on uranium removal; prepare humic acid-free batches and study uranium removal in the presence of colloidal silica in the pH range between 3 and 8.

Project 3 Environmental Remediation Technologies (EM-12)

Project Description

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

FIU Year 4 Carryover Work Scope

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

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

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

Task 1 Overview

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

Task 1 Quarterly Progress

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

- Tests were run on the single column that was filled with SRS soil which involved pumping approximately 2L of DI water through the columns (bottom → top) over a period of 1 week to eliminate air trapped in the column. This also helped examine the pressure exerted on the tubing and connectors. This process was repeated running the water in the opposite direction (top → bottom) prior to and during bromide tracer tests.
- Humate injection scenarios were updated and a flow rate between 2 4 ml/min will be used based on preliminary tests carried out.
- Modifications were made to the column tubing to facilitate pulse injection of the bromide tracer via a syringe. A bromide tracer test was then performed on Column 1, previously filled with SRS soil, and saturated with DIW water using 3 ml of 1000 ppm bromide solution.
- Samples were collected at regular intervals and the concentration of bromide in the effluent solution was measured. Based on the concentration of bromide, breakthrough curves were developed and the cumulative mass of the tracer was calculated (Figure 3-1).



Figure 3-1. Test column filled with SRS soil (left); bromide tracer test breakthrough curves (right).

• A second column was filled with SRS soil, saturated with DIW similar to Column 1, and a bromide tracer test conducted. Data will be analyzed and reported.

- An artificial groundwater solution was prepared using 0.01 M NaNO₃ and the pH was adjusted to 3.5 using 0.1 M HNO₃. This AGW solution was used to precondition the column.
- The effluent pH of the preconditioned column was 3.76. Miles Denham (SRNL) suggested that the effluent pH might not reach the desired pH of 3.5 and recommended that the humate sorption/desorption experiment be performed at the current pH.
- Kiara Pazan (DOE Fellow) supporting this task presented a poster based on this research at the Life Sciences South Florida STEM Undergraduate Research Symposium hosted at Indian River State College on April 4, 2015.
- A bromide tracer test was performed on Column 1 previously filled with SRS soil and saturated with DIW water using 3 ml of 1000 ppm bromide solution.
- Samples were collected at regular intervals and the concentration of bromide in the effluent solution was measured. Based on the concentration of bromide, breakthrough curves were developed and the cumulative mass of tracer was calculated.
- Artificial ground water solution was prepared using 0.01 M NaNO₃ and the pH was adjusted to 3.5 using 0.1 M HNO₃. This AGW solution was used to precondition the column. (*The effluent pH of the preconditioned column was 3.76; however, Miles Denham(SRNL) suggested that the effluent pH might not reach the desired pH of 3.5 and recommended that the humate sorption/desorption experiment be performed at the current pH.)*
- After the pH of the effluent reached equilibrium, 5000 ppm of Huma-K solution was pumped into the column.
- After pumping approximately one pore volume (PV) of 5000 ppm Huma-K solution, approximately 3 PVs of pH-adjusted AGW solution were injected and effluent samples collected to measure humic acid concentration and pH.
- A second column was filled with oven-dried soil and then saturated. This was followed by a bromide tracer test, preconditioning with pH 5 AGW and a humate sorption/desorption process. Samples were then collected and analyzed for pH and HA concentration.
- Samples collected during experiments with Columns 1 & 2 were analyzed via a UV-Vis spectrophotometer for humic acid concentration.
- The technical report deliverable, due 7/6/15, was drafted based on the results obtained from the column experiments thus far and will be updated with additional results and data prior to submission.
- FIU continued the column experiments to study humate sorption using HumaK and SRS F Area sediments using simulated groundwater (SGW) solutions with pHs adjusted to 6 and 7. The data obtained will be compared to the data derived from previous experiments conducted with SGW solutions at pH 3.5 and pH 5.
- Column 3 was filled with oven-dried SRS soil and is being equilibrated with DIW. Artificial groundwater containing NaNO₃ will be added followed by either NaOH or HNO₃ to adjust the pH to pH 6.

- Once the column is saturated, a tracer test will be conducted followed by the injection of humate.
- An order has been placed for a fraction collector to facilitate sample collection (Eldex.com) during the column experiments.
- A draft technical report based on the results obtained from column experiments at pH 3.5 and 5.0 with 5000 ppm of humic acid was completed and will be submitted to DOE and SRNL by 7/6/15.
- Brian Looney has reviewed the data and provided positive feedback. He noted a difference between the tracer test and organics which he found very interesting. Miles has not yet had an opportunity to review the data, but will do so in the coming weeks and provide his feedback.

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

This task includes modeling of the migration and distribution of humate injected into subsurface systems during deployment for in situ treatment of radionuclides, metals and organics. Relevant data derived from the column studies will be used for development of a flow and transport model. This task will be initiated this year with collection of GIS data and other relevant model parameters, incorporation of this data into the existing SRS geodatabase developed for Tims Branch, and geoprocessing of the data for hydrological model input. GIS data for the F/H Area has been requested. Further model development has been written into the FY15 (FIU Year 1) scope of the new 5-year DOE-FIU Cooperative Agreement.

Task 2: Surface Water Modeling of Tims Branch

Task 2 Overview

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

Task 2 Quarterly Progress

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

• The GIS metadata provided by SRNL in the form of XML files were appended to their associated GIS feature classes which are contained in the ArcGIS file geodatabase for SRS Tims Branch that was created by ARC researchers. The ArcGIS Diagrammer utility was then used to generate schema and data reports which will be incorporated in the final

Project 3 Year End Report due on 08/28/15. A snapshot of the data report can be viewed below in Table 3-1, which shows the various GIS files contained in the geodatabase, their geometry and geospatial extent as well as an image of the point, line or polygon feature.

• Several GIS maps of the Tims Branch watershed are being generated based on various classifications such as hydrology, geology, biota, contaminants, land use, etc.

 Table 3-1. Tims Branch Geodatabase Data Report Generated Using ArcGIS Diagrammer.

ArcGIS Diagrammer

Report Creation	n
Date	Wednesday, April 29, 2015
Author	Lawrence/ARC-2481F4A8 on ARC-2481F4A8
System	
Information	
Operating	Microsoft Windows NT 6 1 7601 Compies Deals 1
System	MICROSOIL WINDOWS INT 6.1.7001 SERVICE PACK 1
.Net Framework	2.0.50727.5477
Diagrammer	10.0.1.0
Geodatabase	
Workspace Type	File Geodatabase
File	G:\DOE_Project3\SRS_DATA\GIS\SRS_TimsBranch_GeodB\SRS_TimsBranch_GeodB.gdb

		Dat	a Report			
ObjectClass Name	Туре	Geometry	Subtype	Total	Extent	Snapshot
Admin_FC		-	*			
SavannahRiver_Tile_Layout5k	Feature Class	Polygon	-	11	425000 440000 3680000 3700000	
VGIS_BD_SRS_FACILITY_AREA	Feature Class	Polygon	-	8	430586.140000001 439393.098300003 3682286.0887 3692144.6029	8 4°
VGIS_BD_SRS_LINE_MEANDER	Feature Class	Polyline	-	1	422558.678800002 457132.343500003 3653704.0584 3696226.3696	· ~ /
VGIS_BD_SRS_LINE_MONMNT	Feature Class	Polyline	-	1	422561.7654 459782.053099997 3653704.0584 3696226.3696	5
VGIS_GD_USGS_QUAD_AREA	Feature Class	Polygon	-	4	418506.420599997 441962.053800002 3679193.1661 3707076.8547	
Biota_FC						
VGIS_FA_TES_SURVEY_AREA_SRS	Feature Class	Polygon	-	15	429282.7589 439738.627 3681375.1678 3689242.6089	
Buildings_FC						
VGIS_BG_BLDG_AREA_SRS_EXIST	Feature Class	Polygon	-	408	428936.980599999 439073.234700002 3682554.8745 3694379.5232	4.
VGIS_BG_BLDG_AREA_SRS_HIST	Feature Class	Polygon	-	0	No Extent	-

VGIS_BG_BLDG_AREA_SRS_SLAB	Feature Class	Polygon	-	130	430917.611400001 438229.777800001 3682719.6901 3689837.9162	ж
Contaminants FC		1			1	
soil_pollution_isoline_line	Feature Class	Polyline	-	158	420182.976300001 463525.929399997 3627602.9623 3697798.366	٩
VGIS_EH_GROUNDWATER_PLUME_I	Feature Class	Polygon	-	15	430356.490699999 439316.502099998 3681729.4108 3689044.2623	d . y.
VGIS_EH_GROUNDWATER_PLUME_R	Feature Class	Polygon	-	67	435969.029056848 439516.897500001 3681648.6829 3685081.0853	
VGIS_EH_GROUNDWATER_PLUME_VO	Feature Class	Polygon	-	99	429063.870012418 438783.884199999 3681945.3661 3690622.5819	\$
VGIS_EH_RAD_BISMUTH_LINE_1991	Feature Class	Polyline	-	2	427147.046800002 454710.122900002 3672771.9164 3696246.38	- Andrew
VGIS_EH_RAD_CESIUM_LINE_1985	Feature Class	Polyline	-	0	No Extent	-
VGIS_EH_RAD_CESIUM_LINE_1986	Feature Class	Polyline	-	0	No Extent	-
VGIS_EH_RAD_CESIUM_LINE_1991	Feature Class	Polyline	-	8	426678.031999998 461918.3763 3627932.9551 3692629.6357	R
VGIS_EH_RAD_CESIUM_LINE_1998	Feature Class	Polyline	-	10	421089.495399997 460325.316699997 3643919.5224 3697475.3544	No.
VGIS_EH_RAD_COBALT_LINE_1991	Feature Class	Polyline	-	8	427071.415899999 459261.2158999996 3638131.5585 3690052.3501	
VGIS_EH_RAD_COBALT_LINE_1998	Feature Class	Polyline	-	8	421015.569300003 461076.170400001 3643868.0309 3697755.3221	interest
VGIS_EH_RAD_GROSS_LINE_1991	Feature Class	Polyline	-	10	421210.122400001 463310.873599999 3627920.4882 3696556.7359	4
VGIS_EH_RAD_GROSS_LINE_1998	Feature Class	Polyline	-	14	420845.124700002 461128.2029 3643864.4219 3697782.3376	9
VGIS_EH_RAD_MANMADE_LINE_1991	Feature Class	Polyline	-	9	426386.369900003 460520.811800003 3628302.6972 3695430.353	10
VGIS_EH_RAD_MANMADE_LINE_1998	Feature Class	Polyline	-	13	421327.786700003 459252.686399996 3644073.4342 3696669.8163	\$
VGIS_EH_RAD_NATURAL_LINE_1991	Feature Class	Polyline	-	10	421217.369099997 463322.626900002 3627920.2418 3696556.7367	9

				420182.976300001	
	Feature	Polylino		e ^{463525.929399997}	100
VGIS_EN_KAD_POTASS_LINE_1991	Class	Polyine	-	° 3627602.9623	
				3696907 2158	8

- The geodatabase was updated to incorporate the metadata provided by SRNL as well as any additional metadata collected. ArcGIS Diagrammer was then used to create GIS Data and Schema reports which provide a list of all the GIS data stored in the geodatabase along with their spatial and attribute properties. These ArcGIS Diagrammer reports will be included in the final technical and Year End Report deliverables which will include a write-up of the work accomplished over FY14 (i.e., SRS geodatabase development, documentation of the geodatabase schema using ArcGIS Diagrammer, pre-processing of hydrological model data, development of process-flow models using ArcGIS ModelBuilder, preparation of maps of Tims Branch watershed to depict topography, hydrology, surface geology, soils, vegetation, Manning's roughness coefficient, paved runoff coefficient, etc.).
- Hydrological model development continued with respect to any necessary pre- and postprocessing of GIS data. Currently, a GIS shapefile of the water depth along the Tims Branch study area is being generated for input into the model.
- The final technical report deliverable is being drafted and will include a write-up of the work accomplished for this task during FY14: SRS geodatabase development, documentation of the geodatabase schema using ArcGIS Diagrammer, pre-processing of hydrological model data, development of process flow models using ArcGIS ModelBuilder, preparation of maps of Tims Branch watershed to depict topography, hydrology, surface geology, soils, vegetation, Manning's roughness coefficient, paved runoff coefficient, etc.

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

- ARC researchers (Dr. Mehrnoosh Mahmoudi and Angelique Lawrence) visited SRS on April 13-14, 2015. Meetings were held with SRNL personnel (Dr. Brian Looney, Dr. Miles Denham and Ms. Thelesia Oliver) to discuss project progress and proposed work scope for FY15 and the next DOE-FIU Cooperative Agreement 5-yr cycle. Discussions were also held regarding the arrangements being made for the upcoming student summer internships at the site.
- During the SRS visit, Dr. Mahmoudi and Ms. Lawrence toured the study area to gain a better understanding of the hydrology of the Tims Branch watershed (Figures 3-2 through 3-5). The locations visited include:
 - A/M Area (Air Stripper VOC/Hg treatment system, outfalls A14, A11, A11 LL Hg Sampling Location, Wetland Treatment System, outfall tributary, erosion (rip rap) site upstream of the weir, weir site)
 - Tims Branch (Beaver Pond 2, Steed Pond)
 - F-Area Field Research Site



Figure 3-2. Photo of Noosha Mahmoudi (left), Brian Looney (center) and Thelesia Oliver (right) visiting the location of the M-1 Air Stripper at SRS.



Figure 3-3. Photo of Noosha Mahmoudi (left), Brian Looney (center) and Thelesia Oliver (right) at the A-11 Low Level Mercury Sampling Location at SRS.



Figure 3-4. Photo of Angelique Lawrence at the A-11 Low Level Mercury Sampling Location at SRS.



Figure 3-5. Photo of Noosha Mahmoudi and Brian Looney exploring Tims Branch.

- Following the SRS site visit, modifications were made to the hydrological modeling strategy, including changes to the boundary conditions and other relevant parameters to reflect the actual topographic and hydrologic conditions observed.
- A progress update of the GIS and hydrological model development was presented to the SRNL technical lead for this task, Brian Looney. A phone discussion was held to discuss the Powerpoint presentation slides (Figures 3-6 to 3-11) that were sent via email with maps of Tims Branch and screenshots of the MIKE SHE model and ArcGIS geodatabase. Several of the slides presented are shown below. FIU received very positive feedback on the progress made to date and will be submitting a technical report in July.

ArcGIS ArcMap GUI showing (1) A/M Area, Tims Branch and several major tributaries with flow direction arrows, significant hydrologic and man-made features (e.g. ponds, weir, outfalls, etc.); (2) table of contents on the left serves as a legend for some of the features; (3) on the right, the SRS geodatabase structure can be viewed.



Figure 3-6. Map of the A/M Area, Tims Branch and several major tributaries.



Figure 3-7. Precipitation timeseries data from the 700-A rain gauge station at SRS A/M Area.



Figure 3-8. Geospatial map of Manning's M viewed through the ArcMap and MIKE SHE GUIs.



Figure 3-9. Land use/land cover maps as viewed through the ArcMap and MIKE SHE GUIs.



Figure 3-10. Preliminary development of the Tims Branch network file using MIKE 11.

Detailed cross-section data within MIKE 11.



Figure 3-11. Detailed cross-section data within MIKE 11.

- Development of the MIKE SHE model continued with refinement of the data being input into the model in order to fully implement the hydrological component of model development. The methodology employed will be detailed in the technical report deliverable due 7/17/15.
- FIU will complete the development and testing of the model to simulate the Tims Branch stream hydrology using MIKE SHE during the no cost extension of the performance year, including:
 - Preliminary short term surface flow simulation (1-3 days) with no rainfall and no groundwater
 - Model calibration
 - Simulation of surface flow during one single rainfall event (1-2 hours rainfall)
 - Development of the groundwater module (soil profile, water table, geological layers, etc.)
 - Integration of surface and groundwater modules
 - Simulation of coupled surface and groundwater flow for a longer period of time with no rainfall
- Although the focus of this task is on surface water modeling of Tims Branch, the groundwater module of MIKE SHE will be incorporated due to Tims Branch being influenced by the surface water/groundwater interaction. Contaminant transport in the groundwater, however, will not be modeled.

- Preliminary simulations of overland flow in Tims Branch were conducted this month using MIKE SHE for short periods of 1-2 days with 1-2 rainfall events. These were then repeated for longer periods of 1 month and 50 yrs. All simulations were conducted assuming dry land (i.e., no water).
- Four overland (MIKE SHE) simulations have been developed:
 - OL flow simulation for one single rainfall event, no initial depth, no ET, and no saturated/unsaturated zone
 - OL flow simulation for 50 years rainfall data, no initial depth, no ET, and no saturated/unsaturated zone
 - OL flow simulation for 2 months rainfall, no initial depth, no ET, and no saturated/unsaturated zone
 - OL flow simulation for 2 months rainfall, with 25 cm initial depth assumption in Tims Branch, no ET, and no saturated/unsaturated zone
- New simulations will be as follows:
 - OL flow simulation for 3 years period of rainfall (1993-1996), no initial depth, no USZ/SZ/ET
 - OL flow simulation for 3 years period of rainfall (1993-1996), with initial depth, no USZ/SZ/ET
 - OL flow simulation for 3 years period of rainfall (1993-1996), with initial depth, USZ/SZ/ET
- An abstract was accepted by the 2015 American Water Resources Association (AWRA) Annual Conference based on this research and a paper will be presented.

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

Task 3 Overview

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

Task 3 Quarterly Progress

Subtask 3.1: Analyze Baseline.

- Analysis was completed for the flow and recovery of TCE and PCE from the 18 recovery wells at SRS A/M Area from 1987-2012 (see sample figures below for wells RMW-1 and RMW-2). The volume of water pumped from each well every month during this period was plotted. In addition, the kilograms of TCE + PCE removed from each well for each month per 1000 gallons of water pumped was also plotted. Several insights were gained by FIU and SRNL researchers in viewing these 18 new plots related to efficiencies and characteristics of the various recovery wells.
- Additional analysis was completed on the electrical usage of pumps for the 18 recovery wells. There is not complete data on all of the current 18 pumps and no data on past pumps that may have been replaced. FIU is working with SRNL in order to ensure that the trends in electrical power usage over these 26 years of operation accurately shows trends and is conservative in electrical power usage. Continued analysis of the electrical power used by the groundwater pumps feeding the M1 Air Stripper and the electrical power of the M1 Air Stripper itself (blower). "As Built" documentation is needed from SRS to complete this analysis.
- SRNL, DOE EM headquarters are working on getting over 100 documents on the M1 air stripper released for FIU to review and to enable a Green and Sustainable Remediation analysis later in 2015.
- Prepared a presentation of studies completed to date on this task and began preparation of a publication on the latest analyses of TCE and PCE removed per 1000 gallons pumped from all recovery wells from 1987-2012. FIU also estimated enhanced recovery of TCE and PCE from recovery wells due to the heating of soil during the remediation operation of the dynamic underground stripping process (2005-2009).
- During the no cost extension period, FIU will complete an analysis of the enhanced recovery of TCE and PCE from a few wells that have enhanced recovery rates (kg/month) due to the heating of the subsurface in 2005-2009 from dynamic underground stripping operations. FIU will estimate the total extra mass of TCE and PCE that will be recovered through 2025, the date when subsurface temperature are expected to return back to ambient levels.
- FIU will also analyze documentation expected from SRS this summer and complete a preliminary Green and Sustainable Remediation analysis of the A/M Area Groundwater Remediation System.
- FIU participated in the June 2, 2015 webinar entitled, "An Introduction to Green and Sustainable Remediation (GSR): What, Who, Why, and How" and contacted the presenter, Gerald C. DiCerbo, in order to obtain a copy of the presentation.
- During the month of June, FIU began drafting the technical report for this GSR task due to DOE EM by July 31, 2015.
- Development of the annual report for this task was also initiated. This report will include all of the data, work, documentation, etc. developed on this task during the May 2014 to August 2015 performance period as well as summary information for the work completed on this task during 2013-2014.



Figure 3-12. Graph of RWM-1 water flow over time.



Figure 3-13. Graph showing Kg of TCE & PCE removed per 1000 gallons/month for RMW-1.



Figure 3-14. Graph of RWM-2 water flow over time.



Figure 3-15. Graph showing Kg of TCE & PCE removed per 1000 gallons/month for RMW-2.

- FIU completed exponential curve fitting for those recovery wells influenced by the 2005-2009 steam injection remediation process at SRS. The area of enhanced recovery under the graphs of monthly TCE and PCE recovery equates to the total mass of recovery due to this injection process. Since enhanced recovery is still being seen and will be for a number of years, an exponential curve was fit to the drop off in recovery over the past 2 years as well as for 2004-2005 (prior to steam injection).
- Natalia Duque (DOE Fellow conducting research on Tasks 2 & 3 under this project) traveled to SRNL in June for a 10-week summer internship related to sustainability and modeling a solar power system at SRS. She reported on her work so far with Ralph Nichols on the solar task. Analysis of some limited data has been completed and much more data is expected soon that would be analyzed later this summer.
- Yoel Rotterman (DOE Fellow conducting research on Task 3 under this project) traveled to DOE EM Headquarters in June for a 10-week internship working with Albes Gaona, (DOE EM Lead for Sustainable Remediation). He reported that his internship in Washington DC with DOE EM was going well. He attended a climate change/sustainability conference and is working with Albes Gaona on applying vulnerability assessment and mitigation analysis to an Oak Ridge project.

Milestones and Deliverables

The milestones and deliverables for Project 3 for FIU Year 4 are shown on the following table. Milestone 2014-P3-M6, meeting and presentation of project progress at SRS which was reforecast to April 13, 2015, was completed with a visit by FIU researchers to SRS hosted by SRNL personnel. Due to the no cost extension, several of the report deliverables have been reforecast to incorporate additional data and results acquired during the extended period of performance. The new submission dates are as follows: Technical Report for Task 1 "Modeling of the migration and distribution of NOM injected into subsurface systems", due 6/3/15, reforecast to 7/6/15; Technical Report for Task 2 "Surface Water Modeling of Tims Branch", due 6/10/15, reforecast to 7/17/15; Technical Report for Task 3 "Sustainability Plan for the A/M Area Groundwater Remediation System", due 6/17/15, reforecast to 7/31/15.

Task	Milestone/ Deliverable	Description	Due Date	Status	OSTI
Task 1: Modeling of the migration	2014-P3-M1	Completion of work plan for experimental column studies (Subtask 1.1)	9/30/14	Complete	
and distribution of NOM	Deliverable	Work plan for experimental column studies (Subtask 1.1)	9/30/14	Complete	
injected into subsurface systems	Deliverable	Technical Report for Task 1	6/03/15 Reforecast to 7/6/15	Reforecasted	
Task 2: Surface Water	2014-P3-M2	Completion of literature review (Subtask 2.2)	12/30/14 Reforecast to 3/31/15	Complete	

FIU Year 5 Milestones and Deliverables for Project 3

Modeling of Tims Branch	Deliverable	Literature review summary (Subtask 2.2)	12/30/14 Reforecast to 03/31/15	Complete	
	2014-P3-M3	Development of preliminary site conceptual model of Tims Branch (Subtask 2.2)	12/30/14 Reforecast to 03/31/15	Complete	
	Deliverable	Technical Report for Task 2	6/10/15 Reforecast to 7/17/15	Reforecasted	
Task 3: Sustainability	2014-P3-M4	Completion of Baseline Analysis (Subtask 3.1)	2/27/15	Complete	
Plan for the A/M Area Groundwater Remediation System	Deliverable	Baseline analysis summary (Subtask 3.1)	2/27/15	Complete	
	Deliverable	Technical Report for Task 3	6/17/15 Reforecast to 7/31/15	Reforecasted	
	Deliverable	Draft Project Technical Plan	6/18/14	Complete	
Project-wide	Deliverable	Two (2) abstract submissions to WM15	8/15/14	Complete	
	2014-P3-M5	SRS site visit and meeting	8/5/14	Complete	
	2014-P3-M6	Meeting and presentation of project progress at SRS	3/18/15 Reforecast to 4/13/15	Complete	

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

Work Plan for Next Quarter

Project-wide

- Draft the Year End Report (YER) for FIU Year 5 (May 2014 to August 2015).
- Draft the Project Technical Plan (PTP) for FIU Year 1 (FY15) of the renewal period of performance.

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

- A draft technical report based on the results obtained from column experiments at pH 3.5 and 5.0 with 5000 ppm of humic acid will be submitted to DOE and SRNL by 7/6/15.
- Additional column experiments will be carried out at varying pH values.
- Relevant data derived from the column studies will be used for development of a flow and transport model of HA. This task will be initiated this year with collection of GIS

data and other relevant model parameters, incorporation of this data into the existing SRS geodatabase developed for Tims Branch, and geoprocessing of the data for hydrological model input. GIS data for the F/H Area has been requested. Further model development has been written into the FY15 (FIU Year 1) scope of the new 5-year DOE-FIU Cooperative Agreement.

Task 2: Surface Water Modeling of Tims Branch

- Completion of the hydrological component of the integrated surface/groundwater model using MIKE SHE to depict seasonal variation of overland flow in Tims Branch.
- Conduct preliminary simulations of overland flow and surface water hydrology in Tims Branch.
- Submit technical report due 7/17/15.

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

- Complete an analysis of the enhanced recovery of TCE and PCE from a few wells that have enhanced recovery rates (kg/month) due to the heating of the subsurface in 2005-2009 from dynamic underground stripping operations. FIU will estimate the total extra mass of TCE and PCE that will be recovered through 2025 (date when subsurface temperatures are expected to return to ambient levels).
- Submit technical report on FIU analysis of TCE and PCE recovery since initial operations and progress on a Green and Sustainable Remediation analysis, due 7/31/15.
- FIU DOE Fellow will travel to SRS in August to view the air stripper and groundwater remediation system and to meet with site remediation engineers and collect documentation relevant to completing a preliminary Green and Sustainable Remediation analysis of the A/M Area Groundwater Remediation System by December.
- FIU will travel to SRS in September to meet with key SRNL scientists and SRNS remediation engineers in order to discuss the future options for the M Area air stripper and groundwater remediation system. This will be followed by a meeting to identify all remaining documents needed for the GSR option determined in the earlier meeting. The goal is to locate documentation during this trip and bring it back to FIU to allow for the GSR to be completed by December.

Project 4 Waste and D&D Engineering & Technology Development

Project Manager: Dr. Leonel E. Lagos

Project Description

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

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

Task 1: Waste Information Management System (WIMS)

Task 1 Overview

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

Task 1 Quarterly Progress

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

FIU received the new set of waste stream forecast and transportation forecast data from DOE as formatted data files on April 15, 2015. To incorporate these new files, FIU built a data interface to allow the files to be received by the WIMS application and imported it into SQL Server, the database server where the actual WIMS data is maintained. FIU completed the data import and deployed it onto the test server for DOE testing and review. FIU incorporated feedback from the data review and received approval to deploy the dataset on the public server. FIU incorporated DOE feedback from the data review and received approval to deploy the dataset on the public server. FIU incorporated because fully viewable and operational in WIMS on June 9, 2015. Figures 4-1 and 4-2 show screenshots of the new dataset in WIMS.

The timeline for these activities were as follows:

- FIU received the new dataset from DOE April 15, 2015
- FIU completed incorporated the data into WIMS, placed it on the test server for DOE review May 14, 2015
- DOE provided their review comments May 27, 2015
- FIU incorporated all changes from the review comments May 29, 2015
- DOE approved new data in WIMS for public server June 1, 2015
- New data live on WIMS public server June 9, 2015





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Figure 4-2. WIMS screenshots with 2015 dataset: Waste forecast data table.

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

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

In support of the development of a decision model for contamination control products, FIU is interacting with SRS to identify the product search parameters based on project-specific needs and site applications. The contamination control product list is continuously being updated by contacting new potential vendors and requesting the required information about their decontamination products.

The design and development the web-based fixative model application is in progress and will be completed in the next performance year. The design of the web-based database has been initiated and is ongoing. The database will be implemented in SQL server. Once the web-based application is complete, it will be made available through the D&D Knowledge Management Information Tool portal for beta testing and input from field site users.

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

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

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

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

FIU Year 4 Carryover Work Scope

Subtask 2.1.2: Fogging research and evaluation

FIU collaborated with SRNL and INL to perform a technology demonstration to test and evaluate the FX2 Advanced Fogging Technology, developed at INL, for potential implementation at the SRNL 235-F facility.

The FX2 technology testing and evaluation was performed from March 30 to April 3, 2015 at the ARC Technology Testing & Demonstration Facility in Miami where an existing hot cell mockup facility was modified to meet the objectives of the demonstration. Steve Reese from INL participated in the demonstration. Additional testing was performed prior to these dates (primarily the flammability tests) and a few final tests were completed in the following weeks.

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

- Ability to fix loose contamination to different types of surfaces (glass, concrete, steel, and plastic) and adhesiveness to the surface (Figure 4-3).
- Ability to cover locations outside of the direct line-of-sight of the fogger (Figure 4-4).
- Capacity to knockdown airborne particulates.
- Characteristic properties of the product:
 - Burn rate (ASTM E84)
 - Flammability (ASTM D3065)
 - Viscosity (ASTM D2196)
 - Surface Tension (ASTM D1331)
 - Density (ASTM D1475)
- Reactivity to flame and heat sources.
- Ability to shield against an alpha emitting point source.
- Coverage of surface area, as quantified via use of ImageJ software analysis.
 - Uses contrast analysis to determine coverage of the product.
 - Correlates radiation shielding to the coverage results.

Overall, the technology was capable of successfully achieving the objectives of this demonstration. The FX2 advanced fogging agent was very effective at reaching line-of-sight and non-line-of-sight areas. There did not appear to be any difference in the coverage achieved by the FX2 regardless of placement/location in the test facility. In addition, the advanced fogging agent demonstrated excellent fixing capacity for potential airborne particles such as dust and lint on metal, glass, plastic, concrete, and wood surfaces. The bond appeared slightly less durable on wood, but additional samples may be required before a definitive correlation can be made. The FX2 advanced fogging agent also demonstrated conclusive results in providing shielding against alpha sources as well as its non-flammability during the application phase. Finally, the commercial off-the-shelf Cyclone foggers appeared to do an excellent job at dispersing the FX2 advanced fogging agent in its current composition.



Figure 4-3. Applying compressed air to metal sample (left) and applying brush test to metal sample (right).

A few challenges were encountered during the demonstration. Initial test runs using a single Cyclone fogger in the hot cell mockup facility failed to achieve a uniform application of the FX2 fogging agent. Since the objectives of the technology demonstration were test the FX2 agent itself and not specifically the delivery device, additional test runs were performed to optimize airflow throughout the entire space in a uniform fashion. The final solution implemented included using two Cyclone foggers at the same height (53"), along the same wall and blowing diagonally across each other's stream. This set-up manipulated the air flow to move uniformly within the given space.

Another challenge faced was that a comprehensive NIST / ASTM standard for fixatives designed to operate in a radioactive environment does not exit. The requirement for a singular ASTM Standard was previously identified but apparently lost momentum before culminating in an accepted published standard. FIU recommends the development and establishment of standardized testing protocols and performance measures for fixatives and related contamination control products. The testing protocols that FIU implemented during this technology demonstration for the ability of a product to fix loose and potential airborne contamination, ability to effectively cover non-line-of-sight areas, and ability to shield against radioactivity, could be used to begin this process.

One innovative methodology employed by FIU during this technology demonstration was the implementation of ImageJ software to determine the percent of surface coverage by the fogging agent. The software performed well in this regard and provided standardized analyses for documenting the results of the demonstration. The use of ImageJ software is worth further consideration in future testing protocols.



Figure 4-4. Red-tinted FX2 agent covers all horizontal surfaces in 10'x15'x10' hot cell mockup after fogging (left). Fogged challenge sample located inside apparatus facing away from foggers (right).

Following the completion of the technology testing, FIU:

- Completed analysis of the results from the FX2 testing and evaluation.
- Completed development of the FX2 technology demonstration report and the DOE Tech Fact Sheet and submitted these to DOE EM, SRNL, and INL on May 15, 2015.
- Completed test site and ARC laboratory clean-up, packed and shipped fogging equipment back to INL.
- Developed and presented a research poster on this task for presentation at the EPRI Decommissioning Workshop in June in Orlando, FL (Figure 4-5).
- Reviewed and edited the videos taken during the testing for posting to D&D KM-IT.
- Started to identify publications and professional journals to develop abstracts to publish findings on FX2 test and evaluation.



Subtask 2.1.3: Incombustible fixatives

FIU discussed the research for this task via teleconference with Mike Serrato and Aaron Washington at SRNL on April 23, 2015. The main objective is to enhance the stabilization of radioactive contamination even if the facility is subjected to a fire. FIU worked with SRNL to identify a list of fixatives and similar products to be tested. FIU began working to develop a test plan to test these fixatives, first focusing on baseline testing for each fixative product used in isolation. Figure 4-6 shows photos of an intumescent coating reacting to a heat source. During this performance period, FIU:

- Completed the internal draft test plan for Phase I testing to support this task.
- Met with the FIU Radiation Safety Officer (RSO) to review the conceptual plan for testing incombustible fixatives with radioisotope-spiked coupons.
- Held a meeting the ARC D&D project team, FIU RSO, and SRNL to provide a briefing and reach consensus on the test plan objectives and methodologies.
- Research potential products for testing, including fixatives, strippable coatings, decontamination gels, and fire resistant coatings.
- Identified and developed a list of the selected products for testing in collaboration with SRNL.
- Completed revisions of the draft test plan for the Phase I testing based on internal ARC review/comments and sent the revised draft test plan to SRNL for review on June 10, 2015.
- Initiated drafting the Radioactive Materials Handling Form required by the FIU Radiation Safety Officer.



Figure 4-6. Intumescent coating reacting to flame / heat source. (Source: One Stop Shop in Structural Fire Engineering, Professor Colin Bailey, University of Manchester)

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

Task 3 Overview

The D&D Knowledge Management Information Tool (KM-IT) is a web-based system developed to maintain and preserve the D&D knowledge base. The system was developed by Florida International University's Applied Research Center (FIU-ARC) with the support of the D&D community, including DOE-EM (EM-13 & EM-72), the former ALARA centers at Hanford and Savannah River, and with the active collaboration and support of the DOE's Energy Facility Contractors Group (EFCOG). The D&D KM-IT is a D&D community driven system tailored to

serve the technical issues faced by the D&D workforce across the DOE Complex. D&D KM-IT can be accessed from web address http://www.dndkm.org.

Task 3 Quarterly Progress

FIU completed the development of a Google Web Analytic report for D&D KM-IT for the first quarter of 2015 (January to March) and submitted it to DOE on April 28, 2015. This report included information from Google Analytics and Google Web Master tools and a narrative to explain the results. The results reflect an increase in the major metrics. The largest increase was in the number of page views with a 239% increase over last quarter. The website traffic attributed to FIU doubled this quarter, a result of the increased web presence by FIU to integrate the NuVision/Cogentus robotic database into D&D KM-IT. While a typical quarter includes 5-6% of the visits coming from FIU, the FIU visits was tracked at 13% for this quarter. Also of interest, the user registration increased by 11% (from 652 last quarter to 725 this quarter) and the SMS registrations increased by 20% (from 69 last quarter to 83 this quarter). The main reason for this increase was the FIU participation in the Waste Management Symposium 2015 where the FIU team was able to engage with industry participants to demonstrate the functionality of D&D KM-IT and generate interest from users to become SMS. Conference participation continues to be one of the best platforms to bring industry awareness of the D&D KM-IT. Figure 4-7 shows an infographic of the web analytics for the first quarter of 2015.



Figure 4-7. Infographic for 2014 Q4 Based on Web Analytic Data for D&D KM-IT.

DOE Fellows and other FIU students are supporting D&D KM-IT by reviewing the information in the vendor and technology modules, updating contact information, and researching additional relevant D&D technologies offered by existing vendors. As of June 24, the system included a total of 1228 technologies (+45 from March) and 905 vendors (+7). This increase is primarily due to the continued completion of the integration of the robotics database, which is discussed below.

A database of robotic technologies, originally developed by NuVision/Cogentus, was sent to FIU from DOE, with a request to evaluate the potential for integrating the data into the D&D KM-IT framework for ongoing hosting/maintenance of the information. FIU first completed the research and updated the robotic entries that had missing data. The final 27 robotic technologies, for a total of 471 robotic technologies, were made live on the production server in April 2015.

FIU developed a draft newsletter to announce the availability of the robotic database in D&D KM-IT to all registered users. The draft newsletter was sent to DOE for review on April 22, received approval for distribution on May 28, and was distributed to D&D KM-IT users on June 10, 2015 (Figure 4-8). FIU also began development of the next newsletter for D&D KM-IT, highlighting the 1200 D&D technologies included.



Figure 4-8. Robotics Database newsletter for D&D KM-IT.

FIU also revised the DOE Fellows infographic to incorporate comments and feedback from DOE. A figure under Project 5 shows the current version of the infographic.

D&D knowledge management through contributions in Wikipedia was a part of the outreach and training (D&D community support) subtask. FIU completed the related milestone, 2014-P4-M3.5, and sent a draft summary report to DOE on May 8, 2015. The general D&D knowledge which has been gained through this project offers an opportunity to expand access to a broad audience via Wikipedia, which has a significant presence on the web, thereby offering greater opportunities for collaboration on D&D knowledge. ARC researched and targeted D&D information on Wikipedia where D&D KM-IT could provide additional relevant information while citing the source of the original information on D&D KM-IT. The information sources

focused on for this initial effort were the EFCOG lessons learned and best practices that have been developed in collaboration between FIU and EFCOG and published on D&D KM-IT.

During the completion of this task, four Wikipedia articles were edited with information. For each of these articles, relevant and significant text was added to the body of the article and a reference to the information source (e.g., lesson learned or best practice on D&D KM-IT) was included in the article's list of references. The edited Wikipedia articles included: 1) <u>Nuclear Power in the United States – Plant Decommissioning Section</u> with information from the best practice titled, "SRS P and R Reactor Disassembly Basin *In Situ* Decommissioning" 2) <u>Occupational Hygiene – Basic Characterization, Hazard Identification and Walk-Throughs Section</u> with information from the following best practice: "Historical Hazard Identification Process for D&D;" 3) <u>Asbestos Abatement – Removal Procedures Section</u> with information from the best practice titled, "Open Air Demolition of Asbestos Gunite by Using Track Mounted Wet Cutting Saw." and 4) <u>D&D KM-IT</u> with updated information.

FIU also completed the development of a metrics progress for outreach and training activities for D&D KM-IT and submitted to DOE on May 8, 2015. Also during this reporting period, FIU finalized the update of the DOE Technical Fact Sheet for D&D KM-IT and sent the document to DOE on May 15, 2015.

FIU prepared and submitted an abstract on the D&D KM-IT and international KM-IT tasks and submitted it to the EPRI Decommissioning Workshop for consideration. Upon acceptance, FIU developed a Powerpoint presentation and participated in the EPRI Decommissioning Workshop in Orlando, FL on June 15-16, 2015. During this conference, FIU participated in a panel discussion focused on U.S. Nuclear Plant Decommissioning Overview and provided an oral presentation on D&D KM-IT and the international KM-IT task (Figure 4-9).



Figure 4-9. Ms. Peggy Shoffner presenting D&D KM-IT at the EPRI Decommissioning Workshop.

FIU revised the D&D KM-IT overview presentation to incorporate comments received from DOE and to update the statistics included. The revised presentation was sent to DOE on 6/10/15 (example slide shown in Figure 4-10). This presentation will be used to brief DOE management during the planned D&D KM-IT Workshop to DOE HQ.

FIU also developed a quarterly update document for the *D&D KM-IT Strategic Approach for the Long-Term Sustainability of Knowledge* document. The strategic plan for D&D KM-IT is a living document. The projected schedule and status evolve over time as the recommended strategic approaches are implemented. The update document, which will be developed on a quarterly basis, provides an update to the table of recommended actions contained in the original document.



Figure 4-10. Example slide from D&D KM-IT Overview Presentation.

Milestones and Deliverables

The milestones and deliverables for Project 4 for FIU Year 5 are shown on the following table. Milestone 2014-P4-M1.1, importing the 2015 data set for waste forecast and transportation data into WIMS was completed on May 14, 2015. Two deliverables, the technical report and the Tech Fact sheet for demonstrated technologies, were completed for the FX2 advanced fogging agent technology demonstration and submitted to DOE and the collaborating sites (SRNL and INL) on May 15, 2015. Milestone 2014-P4-M2.2, draft test plan for baseline incombustible fixatives, has been reforecast to July 2, 2015 due to FIU's no cost extension, allowing time for FIU to fully collaborate with and incorporate SRNL input into the test plan. Milestone 2014-P4-M3.5, adding D&D knowledge to Wikipedia through editing 4 articles, was completed and a summary report submitted to DOE on May 8, 2015. Another deliverable, updating the D&D KM-IT Tech Fact Sheet was completed and submitted to DOE on May 15, 2015. In addition, a deliverable on the metrics report on outreach and training for D&D KM-IT was completed and submitted to DOE on May 8, 2015. Finally, two workshops (deliverables under the D&D KM-IT task) were
completed; one was held at the FIU exhibition booth during Waste Management 2015 in Phoenix, AZ, in March and the second was completed at the EPRI Decommissioning Workshop in Orlando, FL, on June 15.

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	Complete	
System (WIMS)	2014-P4-M1.2	Submit draft paper on WIMS to Waste Management Symposium 2015	Submit draft paper on WIMS to Waste Management Symposium 2015 11/07/14		
Task 2: D&D	2014-P4-M2.1	Preliminary decision model for contamination control products (subtask 2.1.1)03/06/15		Complete	
Support to DOE EM for	2014-P4-M2.2	Draft test plan for baseline incombustible fixatives (subtask 2.1.3)	Reforecast to 07/02/15	Reforecasted	OSTI
Innovation, Development, Evaluation	Deliverable	Lessons Learned and Best Practices	30 days after final approval from DOE & EFCOG	On Target	
and Deployment	Deliverable	Draft technical reports for demonstrated technologies	30-days after evaluation/demo	Complete	OSTI
Deployment	Deliverable	Draft Tech Fact Sheet for technology evaluations/ demonstrations	30-days after evaluation/demo	Complete	
	Deliverable	First D&D KM-IT Workshop to DOE EM staff at HQ	08/29/14**	Will be scheduled based on availability of DOE HQ officials	
	2014-P4-M3.2	Deployment of popular display on homepage of KM-IT to DOE for review/testing	09/05/14	Complete	
	Deliverable	Metrics Definition Report on Outreach and Training Activities	09/30/14	Complete	
Task 3: D&D Knowledge Management	Deliverable	Second D&D KM-IT Workshop to DOE EM staff at HQ	09/30/14**	Will be scheduled based on availability of DOE HQ officials	
Tool (KM-IT)	2014-P4-M3.1	Submit draft paper on D&D KM-IT to Waste Management Symposium 2015	11/07/14	Complete	
	2014-P4-M3.3	Deployment of lessons learned lite mobile application to DOE for review/testing	11/07/14	Complete	
	Deliverable	Preliminary Metrics Progress Report on Outreach and Training Activities	01/16/15	Complete	
	2014-P4-M3.4	Deployment of best practices mobile application to DOE for review/testing	01/16/15	Complete	
	2014-P4-M3.5	Four Wikipedia edits/articles	03/20/15 Reforecast to 05/15/15	Complete	
	Deliverable	First D&D KM-IT Workshop to D&D community	03/31/15	Complete	
	Deliverable	Second D&D KM-IT Workshop to D&D community	Reforecast to 6/30/15	Complete	

FIU Year 5 Milestones and Deliverables for Project 4

Deliverable	Metrics report on outreach and training activities	05/09/15	Complete	
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	Complete	

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

Work Plan for Next Quarter

- Draft the Year End Report (YER) for FIU Year 5 (May 2014 to August 2015).
- Draft the Project Technical Plan (PTP) for FIU Year 1 (FY15) of the renewal period of performance.
- Task 1: Perform database management, application maintenance, and performance tuning to WIMS.
- Task 2: Complete web-based preliminary decision model for the selection of contamination control products.
- Task 2: Complete preparations and execute the phase I test plan for evaluating a set of incombustible fixatives, selected by FIU and SRS.
- Task 3: Finalize D&D KM-IT website analytics report for the calendar year January to December 2014 time period as well as develop website analytics report for the second quarter (April to June) of 2015 and submit to DOE for review.
- Task 3: Perform outreach and training, community support, data mining and content management, and administration and support for the D&D KM-IT system, database, and network.

Project 5 DOE-FIU Science & Technology Workforce Development Initiative

Project Manager: Dr. Leonel E. Lagos

Project Description

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

Project Overview

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

Project Quarterly Progress

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

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

Three DOE Fellows graduated from FIU and participated during FIU's Spring 2015 graduation ceremony held during May 3-5, 2015:

- Christian Pino (Class of 2013) B.S. Chemistry
- Steve Noel (Class of 2013) B.S. Computer Science
- Maximiliano Edri (Class of 2014) B.S. Mechanical Engineering

DOE Fellow Steve Noel has accepted an offer of employment from Goldman Sachs. DOE Fellow Maximiliano Edri is planning to continue his education at FIU in pursuit of a master's degree. DOE Fellow Christian Pino is planning to continue his education at FIU in pursuit of either a Ph.D. degree or medical school.

DOE Fellows Aref Shehadeh (undergraduate in environmental engineering), Christian Pino (undergraduate in chemistry), Christine Wipfli (undergraduate in environmental engineering), and Kiara Pazan (undergraduate in environmental engineering) participated in the Life Science South Florida - 2015 STEM Undergraduate Research Symposia on Saturday, April 4, 2015, at Indian River State College Pruitt Campus. The DOE Fellows prepared and presented posters based on their DOE-EM research. Christine Wipfli (DOE Fellow - Class of 2014) obtained 3rd place for her poster entitled "Sodium Silicate Treatment for Uranium (VI) Removal and pH Stabilization of the Groundwater Systems at the F/H Area of Savannah River Site." The poster titles presented include:

- Monitoring Mineralogical Changes Occurring in Savannah River Site F-Area Sediments via Enhanced Anaerobic Reductive Precipitation Process Aref Shehadeh (DOE Fellow)
- Use of x-ray fluorescence to Characterize Pre-Hanford Orchards in the 100-OL-1 Operable Unit Christian Pino (DOE Fellow)
- Sodium Silicate Treatment for U(VI) Bearing Groundwater systems at F/H Area at Savannah River Site Christine Wipfli (DOE Fellow)
- Column Testing of the Migration and Distribution of Humate Injected into Subsurface Systems at Savannah River Site's F/H Area Kiara Pazan (**DOE Fellow**)



Figure 5-1. FIU DOE Fellows (Christine Wipfli, Kiara Pazan, Christian Pino, and Aref Shehadeh) along with Andres Arango, Alejandra Vivas, Elsa Bravo, and Lararo Mesa.



Figure 5-2. DOE Fellow Christine Wipfli awarded 3rd place for her research poster, pictured with DOE Fellows Program Director Leonel Lagos.

In addition, DOE Fellows Ryan Sheffield, Max Edrei and Janesler Gonzalez presented their research posters at the ANS conference held at Texas A&M University College Station on April 9 - 11, 2015:

- Miniature Motorized Inspection tool for the Hanford DOE site Tank Bottoms **Ryan** Sheffield (DOE Fellow)
- FX2 Advanced Fogging System Janesler Gonzalez (DOE Fellow)
- Direct Numerical Simulation of Turbulent Multi-phase flow of a Bingham Plastic Maximiliano Edrei (DOE Fellow)



Figure 5-3. DOE Fellows presenting research posters at the American Nuclear Society conference.

FIU-ARC held the DOE Fellows lecture series on April 8, 2015 featuring Dr. Miles Denham from Savannah River National Laboratory (SRNL). The title of Dr. Denham's presentation was "Helping Nature Heal – Enhanced Attenuation." Dr. Denham discussed the soil and groundwater challenges/limitations at the Savannah River Site (SRS), remedy selection criteria, active and passive remediation technologies and enhanced natural remediation. He talked about the various technologies that are being applied at SRS to remediate contaminants such as uranium, strontium and iodine. After the lecture series, Dr. Denham toured the ARC laboratories where ARC scientists and researchers showcased various ongoing research activities to support DOE-EM's mission. Dr. Denham also participated in DOE Fellow Hansell Gonzalez's Ph.D. proposal defense titled "Unrefined Humic Substances as a Potential Low-Cost Remediation Method for Acidic Groundwater Contaminated with Uranium in Acidic Conditions."



Figure 5-4. Dr. Miles Denham (SRNL) presenting SRS research for the DOE Fellows lecture series.



Figure 5-5. Dr. Miles Denham (middle) with DOE Fellows and ARC staff.

On May 19, 2015, FIU ARC hosted a guest lecture as part of the DOE Fellows Lecture Series, featuring Mr. Dennis Washenfelder from Washington River Protection Solutions (WRPS). Mr. Washenfelder shared his experiences working on challenges they faced with waste transfer pipelines at Hanford's tank farms. FIU ARC hosted another guest lecture featuring Dr. Hope Lee, Environmental Scientist, from Pacific Northwest National Laboratory (PNNL) on May 22, 2015. Dr. Lee talked about the history of PNNL, current environmental issues and needs at the site, and remediation technologies being used to address these issues. Dr. Lee participated in lab tours and presentations by DOE Fellows.



Figure 5-6. Dr. Hope Lee with DOE Fellows and ARC staff.

DOE Fellows Spring recruitment efforts were conducted from April 20 to May 1 and from May 11 to May 22. Recruitment campaigns were conducted by placing recruitment tables at the College of Engineering and at the main FIU campus in the Physics & Chemistry building and Computer Science building. A large number of students showed interest in the program and a signup sheet was used to collect student information. Thirty-three (33) FIU students applied for the DOE Fellows program. The DOE Fellows selection committee, comprised of ARC researchers and staff, recommended 19 FIU students for formal interviews. These interviews were conducted from June 23 through July 6, 2015. Dr. Leonel Lagos (Program Director) subsequently asked for the committees input and recommendations to make the final selections and complete the recruitment process. Selected students will be contacted to initiate the hiring process.

DOE Fellow Claudia Cardona successfully defended her Ph.D. dissertation proposal defense titled "Uranium Sequestration by Subsurface pH Manipulation Using Ammonia Gas (NH3) Injection in the Vadose Zone of Hanford Site 200 Area" based on the DOE EM research she is conducting to support uranium remediation at PPNL via ammonia gas injection.

FIU also revised the DOE Fellows infographic to incorporate comments and feedback from DOE. Figure 5-7 shows the current version of the infographic.



Figure 5-7. DOE Fellows infographic.

The DOE Fellows program director finalized coordination with DOE-HQ, DOE sites, DOE national laboratories, and DOE contractors for placement of DOE Fellows for summer 2015 internships. A total of 15 DOE Fellows were placed for summer internships which will be conducted from June 1 to August 7, 2015. Figure 5-8 shows the DOE Fellows summer 2015 interns with program director, Dr. Leonel Lagos, and program coordinator, Dr. Ravi Gudavalli. Table 5-1 lists the summer internship assignments and a description follows.



Figure 5-8. DOE Fellows summer 2015 interns with Dr. Leonel Lagos (far left) and Dr. Ravi Gudavalli (far right).

Student	DOE Site	Mentor
Andrew De La RosaOak Ridge National Lab – Cyber & Information Security Research		Joseph Trien
Anthony Fernandez	PNNL, Richland, WA	Washington River Protection Solutions (WRPS)
Aref Shehadeh	SRNL, Savannah River, SC	Carol Eddy-Dilek/Brian Looney/Miles Denham
Christine Wipfli	DOE-HQ EM-12, Cloverleaf, Germantown, Maryland	Skip Chamberlain/Patricia Lee
Janesler Gonzalez	Idaho National Lab	Rick Demmer/Steve Reese
Natalia Duque	SRNL, Savannah River, SC	Ralph Nichols/Carol Eddy- Dilek/Brian Looney
Jesse Viera	Idaho National Lab	Rick Demmer/Steve Reese
John Conley	PNNL, Richland, WA	WRPS
Jorge Deshon	SRNL, Savannah River, SC	Miles Denham/Carol Eddy- Dilek/Brian Looney
Kiara Pazan	SRNL, Savannah River, SC	Miles Denham/Carol Eddy- Dilek/Brian Looney
Maximiliano Edrei	National Energy Technology Lab, Morgantown, WV	Chris Guenther
Meilyn Planas	Hanford, Richland	Terry Sams (WRPS)
Ryan Sheffield	DOE-HQ EM-20, Cloverleaf, Germantown, Maryland	Kent Picha
Yoel Rotterman	DOE-HQ EM-13, Forrestal, Washington D.C.	Albes Ganoa/John De Gregory
Claudia Cardona	PNNL, Richland, WA	Nick Qafoku

Table 5-1.	Summer	2015	Internshin	os for	DOE	Fellows
					202	

DOE FELLOW:	Andrew De La Rosa
LOCATION:	Oak Ridge National Laboratory, Oak Ridge, TN
MENTOR:	Dr. Joseph Trien

Andrew De La Rosa (DOE Fellow - Class of 2014) is working for the Computational Sciences and Engineering Division at the Oak Ridge National Laboratory (ORNL) in Oak Ridge, Tennessee during the summer of 2015. Under the mentorship of Dr. Joseph Trien, Andrew's main role is to learn and test the Hyperion toolset. The Hyperion Project's goal is to provide a software behavior computational algorithm designed to catch programs that are malicious. It is a tool comprised of programmable semantics and structuring based off the original code, by analyzing binaries and using mathematical precision to uncover the program's intended and unintended behaviors. The next generation of Hyperion is currently under development, where more powerful computational processing is performed as well as up-scaling for larger sized programs, while also implementing customization based on the user's preferences.

DOE FELLOW:Anthony FernandezLOCATION:Washington River Protection Solutions (WRPS), Richland, WAMENTORS:Mr. Ruben Mendoza and Mr. Gregory Gauck

Anthony Fernandez (DOE Fellow - Class of 2014) has been given the opportunity to intern for WRPS, a contractor for the Department of Energy whose focus is on managing the Hanford Tank Farms. Under the mentorship of Ruben Mendoza and Gregory Gauck, Anthony's main role is in single shell tank (SST) storage and monitoring at the Hanford Site. During his internship, Anthony will work hand in hand with the SST Design Authority Engineer to update all existing Dome Load Record Summary Sheets for all 149 SST's, update all existing round sheets to ensure accurate equipment calibration dates and update existing Enraf Reference Levels to be consistent with work to be performed. Anthony will also be working with the Tank Monitoring and Engineering Support (TMETS) group in the development of a management control system that will streamline SST monitoring requirements between different engineering groups in the organization.

DOE FELLOW:	Aref Shehadeh
LOCATION:	Savannah River Site, Aiken, SC
MENTOR:	Dr. Miles Denham

Aref Shehadeh (DOE Fellow - Class of 2014) is currently interning with the Department of Energy Office of Environmental Management (DOE EM) at the Savannah River Site (SRS) located in Aiken, South Carolina. Construction at SRS first began in the 1950's, with a total of five reactors producing base materials for nuclear weapons on the 310 square mile site. Since then, these reactors have been decommissioned and the site is now involved in an extensive clean-up/remediation initiative. Aref is working on this remediation initiative under the mentorship of Dr. Miles Denham with the Savannah River National Laboratory (SRNL). Dr. Denham received his Ph.D. from Texas A&M in geology and has been with SRNL for over 20 years, with a specialization in geochemistry of natural systems and remediation of metals and radionuclides. The project that Aref is working on involves the remediation of iodine-129 (I-129) in the SRS F-Area caused by a large radionuclide plume stemming from an old seepage basin. Dr. Denham has proposed the use of silver chloride (AgCl) to react with the I-129 in the sediments to create a binding effect and prevent further spreading of the plume. Aref will be researching the particle size and structure of AgCl, created in a laboratory setting, and will help determine the optimal size to use for future *in-situ* remediation. In addition, he will be observing whether the I-129 can bind to the entire AgCl particle or if it only reacts on the particle's surface.



Figure 5-9. DOE Fellows Aref Shehadeh and Kiara Pazan dressing out in PPE during their summer internship at SRS.

DOE FELLOW:Christine WipfliLOCATION:DOE-HQ Cloverleaf, Germantown, MDMENTOR:Mr. Skip Chamberlain and Mr. Kurt Gerdes

Christine Wipfli (DOE Fellow - Class of 2014) is working at the Department of Energy Headquarters office in Germantown, Maryland, during the summer of 2015. Under the mentorship of Skip Chamberlain (Senior Program Manager) and Kurt Gerdes (Director of the Groundwater and Soil Remediation Department), Christine is learning the operational activities required for managing the Office of Environmental Management's soil and groundwater remediation initiatives. One of her main projects is to develop case studies in conjunction with the Interstate Technology and Regulatory Council (ITRC), a national coalition of state regulators collaborating with federal regulatory agencies, technology institutions, tribes, and industry, that is dedicated to developing guidance for cost-effective and innovative solutions to environmental challenges. The case studies will elaborate on the enhanced attenuation remedial strategies implemented at various Department of Energy facilities including the Savannah River Site, Richland, Paducah, and Lawrence Berkeley National Lab. In addition to her internship activities, Christine is visiting the Hanford Site in Richland, WA, as well as the Savannah River Site in Aiken, South Carolina, to meet with key personnel involved in the soil and groundwater projects. Her objective is to gain insight on the contaminants of concern at each location and the implemented remediation strategies; additionally, to gain a better understanding of the technological developments for monitoring groundwater and soil data, the DOE-EM budget allocation process, and the overall organizational activities carried out to meet the sites' objectives and the DOE EM cleanup mission.

DOE FELLOW:Claudia CardonaLOCATION:Pacific Northwest National Laboratory, Richland, WAMENTOR:Dr. Jim Sczcsody

Claudia Cardona (DOE Fellow - Class of 2012) has been given the opportunity to intern with the Pacific Northwest National Laboratory (PNNL) located in Richland, Washington. Claudia is working with Dr. Sczcsody in the Research Technology Laboratory (RTL). She is working on an ammonia (NH₃) gas project where the NH₃ gas is utilized for uranium remediation in the vadose zone. Laboratory experiments underway include injecting 100% and 5% NH₃ into deionized water (DIW), Hanford groundwater and sediments to analyze the equilibrium for each also condition. Simulations being conducted using Geochemist are Workbench (GWB/Editions 5.0 and 10.0). The initial simulations performed for the Hanford groundwater conditions with uranium in solution include varying uranium concentrations, ion concentrations, and pH. GWB simulations are also being conducted to understand the NH₃ gas /liquid equilibrium by varying the pCO_2 values (-3.5, -2.8 and 2.0).

DOE FELLOW:	Janesler Gonzalez
LOCATION:	Idaho National Laboratory, Idaho Falls, ID
MENTORS:	Mr. Stephen Reese and Mr. Rick Demmer

Janesler Gonzalez (DOE Fellow - Class of 2014) is working under the mentorship of Mr. Stephen Reese and Mr. Rick Demmer at Idaho National Laboratory (INL) for 10 weeks, spanning the summer of 2015. INL is at the nation's forefront of nuclear energy research and development, focusing on topics that range from optimization of advanced nuclear fuel to nuclear nonproliferation. Janesler's scope of work includes decontamination and decommissioning efforts such as mercury abatement through the use of an advanced strippable fogging technology. Other projects include supporting the development of a scrubber designed for hazardous gas emissions from spent fuel and pyroprocessing for the extraction of useful materials in nuclear waste.

DOE FELLOW:	Jesse Viera
LOCATION:	Idaho National Laboratory, Idaho Falls, ID
MENTORS:	Mr. Stephen Reese and Mr. Rick Demmer

Jesse Viera (DOE Fellow - Class of 2014) is participating in a 10-week internship program at Idaho National Laboratory (INL), the nation's leading laboratory for nuclear energy research, testing, and development. Under the mentorship of Mr. Reese (Mechanical Engineer) and Mr. Demmer (Chemist), Jesse is pursuing projects supporting decontamination and decommissioning (D&D) efforts. These include a strippable coating development for fogging applications, a water security test bed, a spent fuel gas purifier, electrometallurgy techniques for treatment of spent fuel, and a mathematical model of decontamination gels. Jesse's background work includes testing and evaluation of fixative agents.

DOE FELLOW:	John Conley
LOCATION:	WRPS, Richland, WA
MENTORS:	Mr. Terry Sams and Mr. Dave Shuford

John Conley (DOE Fellow - Class of 2014) is working for the Mission Analysis Engineering team at the WRPS Sigma IV Facility in Richland, Washington, during the summer of 2015. Under the mentorship of Mr. Terry Sams and Mr. Dave Shuford, John's main role is to provide an engineering assessment of the chemical constituents within the low activity waste (LAW) passing through the stainless steel transfer lines, as well as to research how these chemicals corrode the pipelines.

DOE FELLOW:Jorge DeshonLOCATION:Savannah River National Laboratory, SCMENTORS:Mr. John Bobbitt and Mr. Steven Tibrea

Jorge Deshon (DOE Fellow - Class of 2014) is interning at Savannah River National Laboratory in Savannah River, South Carolina, during the summer of 2015. Jorge is helping John Bobbitt with a 3D virtual reality model of Building 235-F, specifically in the texture and lighting of the environment. Building 235-F is a Plutonium Fuel Form (PUFF) facility which was used to produce fuel for NASA's deep space probes. This fuel was produced through the grinding of plutonium-238 to produce a very fine powder and currently poses a risk as it is now airborne in the facility cells. The 3D virtual reality model will help emulate the work and prepare workers for the hazards within the facility by creating an immersive environment that can recreate real-life scenarios.

DOE FELLOW:Kiara PazanLOCATION:Savannah River Site, Aiken, SCMENTORS:Dr. Miles Denham and Ms. Margaret Millings

Kiara Pazan (DOE Fellow – Class of 2014) has been given the opportunity to intern with the Savannah River National Laboratory (SRNL) located in Aiken, SC. Under the mentorship of Miles Denham and Margaret Millings, Kiara will be processing diffusion samplers that were deployed in the F-Area to further test the effects on sorption of uranium by humate-loaded sediments. Diffusion samplers, which were filled with sediment and different humate concentrations, were deployed into a well to equilibrate with the groundwater. This method provides a major advantage as it can be performed in existing monitoring wells, rather than needing to perform additional drilling. She will analyze the groundwater, pore water, and sediment of the samplers for uranium, tritium, iodine (I-129), and total organic carbon (TOC). She will be looking at whether uranium sorption and I-129 vary for different initial concentrations of sorbed humate, as well as how much humate desorbed in actual groundwater conditions.

DOE FELLOW:	Maximiliano Edrei
LOCATION:	National Energy Technology Laboratory, Morgantown, WV
MENTOR:	Dr. Chris Guenther

Maximiliano (Max) Edrei (DOE Fellow - Class of 2015) is interning at the National Energy Technology Laboratory (NETL) in West Virginia during the summer of 2015. His ultimate goal

is to help test and study the performance of pulse jet mixers (PJM). This unique opportunity includes two components: experimental and simulation based research. For the experimental component, Max is working under the mentorship of Dr. Balaji Gopalan and is tasked with verifying the physical properties of granular materials that will be inserted into the PJM's while under operation in order to assess how well the fluid has mixed. This includes particle separation and sizing, density distribution analysis, and verifying viscosity. For the second research component, Max is working under Dr. Rahul Garg and is tasked with using computational fluid dynamics (CFD) to simulate a circular impinging jet on a flat surface. The goal will be to study the effects of varying the ratio of jet orifice diameter to the distance between jet orifice and the flat surface. This research will help verify if the current assumptions for modeling the PJMs is valid. With the culmination of his internship, Maximiliano will have contributed to the efforts of containing and transporting high level waste at the Hanford Site.

DOE FELLOW:	Meilyn Planas
LOCATION:	Washington River Protection Solutions, Richland, WA
MENTOR:	Mr. Terry Sams

Meilyn Planas (DOE Fellow - Class of 2014) is working for the Washington River Protection Solutions (WRPS) at the Hanford Site in Richland, Washington, during the summer of 2015. Under the mentorship of Mr. Terry Sams, Meilyn's summer internship will involve using infrared (IR) sensors to measure the temperature inside the double-shell tanks. These tanks must be kept at a certain temperature depending on the contents inside to prevent corrosion on the inside walls. The IR sensors will be placed in the annulus of the tanks and will measure the temperature on the outside of the tank wall. Through some calculations, the inside wall temperature will be determined using the coefficient of heat transfer, which will vary depending on the thickness of the steel wall. This analysis will extend the equipment lifetime and can be easily implemented into the regularly scheduled tank visits.

DOE FELLOW:Natalia DuqueLOCATION:Savannah River National Laboratory, SCMENTOR:Mr. Ralph Nichols

Natalia Duque (DOE Fellow - Class of 2013) has been given the opportunity to intern with Savannah River National Laboratory (SRNL), Office of Environmental Sciences, located in Aiken, South Carolina. Natalia is assisting Mr. Ralph Nichols with studying the coincidence of solar power generation with peak electrical demand in the southeastern United States. The data to be used in the analysis is from a 3MW solar farm with 40% of the photovoltaic (PV) panels' arrays using single axis tracking and 60% using fixed axis. The electrical generation between these two different arrays will also be compared. This study will ultimately evaluate the capacity value, the ability to reliably meet demand at peak electrical use when power is usually more expensive to generate.

DOE FELLOW:	Ryan A. Sheffield
LOCATION:	DOE-HQ Cloverleaf, Germantown, MD
MENTOR:	Dr. James Poppiti

Ryan Sheffield (DOE Fellow - Class of 2014) is working for EM-23's Office of Waste Treatment Plant and Tank Farm Program at the DOE-HQ Cloverleaf facility in Germantown,

Maryland, during the summer of 2015. Under the mentorship of Dr. James Poppiti, Ryan is learning about and analyzing the radiological release that took place at the Waste Isolation Pilot Plant (WIPP) last February in Carlsbad, NM. This site is half a mile underground in a salt bed and is the nation's disposal site for transuranic (TRU) waste. Ryan will be assisting Dr. Poppiti in publishing an article based on the events that took place during this release. Ryan will also be studying the different nuclear reprocessing methods performed at the Hanford Site, including PUREX, REDOX, bismuth phosphate, etc. to assist Dr. Poppiti in producing literature on these methods. Under John Moon, Ryan will also be assisting in the coordination of an Integrated Project Team (IPT) workshop at the Hanford Site.

DOE FELLOW:Yoel RottermanLOCATION:DOE-HQ Forrestal, Washington, D.C.MENTORS:Mr. Albes Gaona, and Mr. John De Gregory

Yoel Rotterman (DOE Fellow – Class of 2014) is working for the office of Environmental Management (EM) under the mentorship of Albes Gaona and John De Gregory. One project he is working on relates to sustainable remediation: the analysis of the performance and design of the current M1 air stripper system at the Savannah River Site (SRS) and the metrics for the wells on the system. Another project, under Deactivation and Decommissioning (D&D) and Facility Engineering, consists of the various technology applications that surveillance and maintenance of the facilities require to lower operational costs, improve efficiencies, and increase safety. He is also working on updating and improving Powerpedia (Media Wiki software platform) documents.

The Fellows continued their research during this performance period in the four DOE EM applied research projects under the cooperative agreement and research topics identified as part of their summer internships at DOE sites, national labs, and/or DOE HQ.

Milestones and Deliverables

The milestones and deliverables for Project 5 for FIU Year 5 are shown on the following table. 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	Complete	
Deliverable	Deliver Summer 2014 interns reports to DOE	10/17/14	Complete	
Deliverable	List of identified/recruited DOE Fellow (Class of 2014)	10/31/14	Complete	
2014-P5-M2	Selection of new DOE Fellows – Fall 2014	10/31/14	Complete	
2014-P5-M3	Conduct Induction Ceremony – Class of 2014	11/13/14	Complete	
2014-P5-M4	Submit student poster abstracts to Waste Management Symposium 2015	01/15/15	Complete	
Deliverable	Update Technical Fact Sheet	30 days after end of project	On Target	

FIU Year 5 Milestones and Deliverables for Project 5

Work Plan for Next Quarter

- Draft the Year End Report (YER) for FIU Year 5 (May 2014 to August 2015).
- Draft the Project Technical Plan (PTP) for FIU Year 1 (FY15) of the renewal period of performance.
- 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 internships.
- Complete DOE Fellow internships for summer 2015 at DOE sites, national laboratories, DOE-HQ, and DOE contractors.
- Begin preparation of summer internship technical reports.
- Begin preparation and coordination for the DOE Fellows Poster Exhibition & Competition.
- Complete hiring of selected new students from the Spring 2014 campaign into the DOE Fellows program. Assign mentors/supervisors from ARC scientists and engineers to each new DOE Fellow and conduct orientation sessions for the new Fellows.