QUARTERLY PROGRESS REPORT

October 1 to December 31, 2012

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

Principal Investigators:

Leonel E. Lagos, Ph.D., PMP®

David Roelant, Ph.D.

Prepared for:

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

Introduction

The Applied Research Center (ARC) at Florida International University (FIU) executed work on five major projects that represent FIU-ARC's continued support to the Department of Energy's Office of Environmental Management (DOE-EM). The projects are important to EM's mission of accelerated risk reduction and cleanup of the environmental legacy of the nation's nuclear weapons program. The information in this document provides a summary of the FIU-ARC's activities under the DOE Cooperative Agreement (Contract # DE-EM0000598) for the period of October 1 to December 31, 2012.

Highlights during this reporting period include:

- Project 1 milestone 2012-P1-M15.2 was completed three days before the due date, and sent to DOE HQ and site personnel on 10/12/2012. Milestone 2012-P1-M2.2 was completed as well, and a summary document was sent to DOE HQ and site personnel on 11/9/2012.
- Project 2 milestone 2012-P2-M2 was completed on 11/30/2012, as scheduled, by the conclusion of testing on the formation of U (VI)-bearing precipitates using various Si:Al ratios in the presence of bicarbonate.
- Project 3 milestone 2012-P3-M1.2 was completed and a summary of the XPSWMM model's preliminary results was sent via email to the relevant DOE personnel.
- Project 3 milestone 2012-P3-M5.1 was completed and a summary of the Moab model's preliminary results sent via email to the relevant DOE personnel. A journal article entitled "Migration of VOC Plume in the Subsurface Domain at the Y-12 National Security Site" was also submitted and accepted by the Journal of Remediation, contributing to Milestone 2012-P3-M8.1 "Submit publications to relevant journals" which will be an ongoing process as research continues throughout 5/17/2013.
- Project 4 milestone 2012-P4-M2.1, marking the completion of the meso-scale testbed system demonstration, was completed on 11/23/12.
- The associated deliverable for Project 4 Task 2, a draft technical report for the meso-scale testbed system demonstration, was completed and submitted to DOE on 12/22/12. This report will be submitted to OSTI once it is finalized.
- Project 4 milestone 2012-P4-M3.5, deployment of the multiple SMS support for the D&D Hotline, was completed on 11/15/12. In addition, a deliverable for the Project 4 Task 3, draft summary report for mobile development research, was completed and submitted to DOE on 12/14/12.
- The following milestones and deliverables for Project 5 were completed and sent to DOE personnel by their due dates:
    - Milestone 2012-P5-M4: Summer Internships Reports
    - Deliverable: Summer 2012 Interns reports to DOE
    - Milestone: 2012-P5-M5: Selection of new DOE Fellows – Fall 2012

- Deliverable: List of identified/recruited DOE Fellow (Class of 2012)
- Milestone: 2012-P5-M6, Conduct Induction Ceremony – Class of 2012, was completed on November 13, 2012.
- Milestone 2012-P5-M7, submittal of student abstracts to the Waste Management Symposium, was completed on 12/28/12.

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 operational shortcomings in the current high-level waste processing strategy. The implementation of advanced technologies to address challenges faced with baseline methods is of great interest to the Hanford site.
Specifically, the use of field or *in situ* technologies, as well as advanced computational methods can improve several facets of the retrieval and transport processes of HLW. FIU has worked with site personnel to identify technology and process improvement needs that can benefit from FIU's core expertise in HLW. These needs are being addressed by the following tasks:

- Task 2: Pipeline Unplugging and Plug Prevention
- Task 12: Multiple-Relaxation-Time, Lattice Boltzmann Model for Multiphase Flows in Three Dimensions
- Task 15: Evaluation of Advanced Instrumentation Needs for HLW Retrieval
- Task 16: Computational Simulation and Evolution of HLW Pipeline Plugs (New Task for FIU Year 3)

Task 2: Pipeline Unplugging and Plug Prevention

Task 2 Overview

The objective of this task is to qualify (test & evaluate) pipeline unplugging technologies for deployment at the DOE sites. Due to the lack of maturity and/or success previously demonstrated by commercial technologies, FIU has focused on developing alternative unplugging approaches during FY10-FY11. The approaches included: 1) a Peristaltic Crawler that can maneuver in the pipeline within close proximity to a plug and provide various means to remove it; and 2) an Asynchronous Pulsing System (APS) that utilizes pressure pulses from both sides of the plug to break the bonds between the plug and the pipe wall. During FY11, efforts focused on improving the design for the crawler and validating both methods in lab scale and engineering scale test beds.

During FY12 (FIU Year 3), FIU will work with Hanford Site engineers to optimize the design of the crawler and maximize its capabilities. FIU will also investigate alternative pressure sources for the asynchronous pulsing system to increase its effectiveness at longer distances from the pipe inlet to the blockage. Efforts will focus on developing realistic test beds and evaluating the effects of pipe geometry and plug types on the systems' ability to unblock plugs. FIU will also work with Site engineers to identify potential opportunities to test the technologies in the field.

Task 2 Quarterly Progress

- For the peristaltic crawler subtask, the front and back rims were received from the manufacturer and the flanges on the outer bellow were machined to allow welding of the assembly. Figure 1-1 shows the front end of the crawler prior to assembly and the crawler unit after assembly. Once the unit was sent for welding, a previous version of the crawler was modified to test the functionality of the camera system inside the pipeline. The tether section, which includes the camera connector and the capsule containing the pneumatic valves, was adjusted to provide the necessary clearance inside the pipeline.

Figure 1-1. Front end prior to assembly (left) and assembled unit (right).

- Navigational tests were conducted and several sleeve configurations were tested to improve the crawler's navigational speed. The milestone titled Experimental Validation of Improvements to the Peristaltic Crawler System (2012-P1-M2.2) was completed. A summary document was provided that included experimental tests of the navigational speed of the crawler on a straight section using different sleeve thicknesses (Figure 1-2 left) and maneuverability tests of the crawler through a 90° Victaulic® elbow. The fastest speed recorded was 19 ft/hr and the time required to clear the elbow was 12 minutes. The camera mounted at the front of the unit provided clear images of the condition inside the pipeline (Figure 1-2 right).

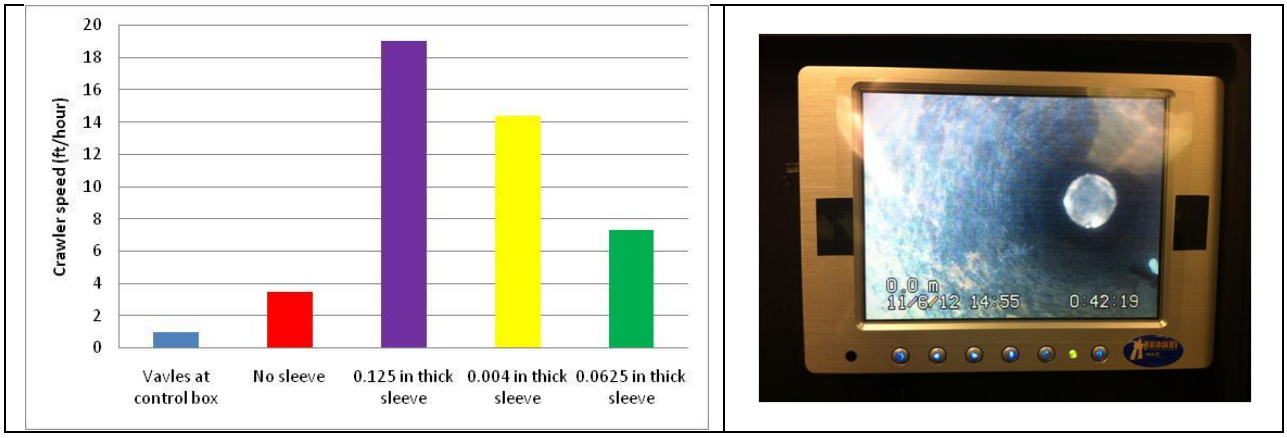


Figure 1-2. Speed of crawler using different sleeve configurations (left), screen capture of the carbon pipe section (right).

- Navigational and maneuverability tests were repeated using a crawler that has a smaller outer bellow thickness. Reducing the thickness of the outer bellow lowers the axial and radial stiffness of the unit, providing a larger displacement per cycle and improving the turning maneuverability of the crawler. The experimental tests were conducted using a

testbed consisting of two 3 ft pipeline sections connected by a 90° Victaulic® elbow. The recorded speed of the crawler in the straight section was 30.6 ft/hr (a significant increase from the previous 3.50 ft/hour recorded with the thicker wall outer bellow). The time required to clear the elbow was approximately 11 minutes. For this bellow, there was no need for using a sleeve to aid in the compression of the crawler, which was not the case with the thicker bellow.

- For the APS subtask, vacuum tests were executed to determine relationship between vacuum pressure and residual air in addition to obtaining corresponding pressure vs. volume curves. These tests were useful in determining the necessary vacuum system required in order to mitigate any entrained air in the pipeline prior to flooding. The results from these tests will be used for vacuum sizing.

- The development of system response (calibration) curves was completed. Calibration curves will be used to size upgrades to the current configuration as well as design for alternative methods of system pulsation. Moreover, the calibration curves also aid in determining the system static pressure pre-sets necessary for larger lengths of pipe and un-quantifiable amounts of air. Initial calibration tests have been conducted on air quantities varying from 0 - 1% in 0.1% increments. Curves have been developed for up to 3.5% air. Testing will continue until air quantities of 5% are reached.

- Research began on the development of an alternate pulsing system. Initial tests were conducted on a small positive displacement pump arranged with two solenoid valves; one on the discharge side of the pump and another on the suction side. By sequentially operating the valves, a positive pressure pulse is delivered to the pipeline that is then followed by a suction phase. The benefit of utilizing a pump as the pressure source instead of a piston is that the pump will provide more flexibility in the volumetric flow during the pressure and suction phases. Results from the initial tests proved to be successful and work has now begun on configuring a large progressive cavity pump to perform large scale testing on the pipeline.

Task 12: Multiple-Relaxation-Time, Lattice Boltzmann Model for High-Density Ratio, Multiphase Flows

Task 12 Overview

The objective of this task is to develop stable computational fluid dynamics models based on the multiple-relaxation-time lattice Boltzmann method (MRT LBM) that can be used to generate computer simulations relevant to the waste mixing operations. The research focus is to improve the knowledge base of modeling multiphase flow systems found in HLW tanks. Specific applications include modeling air sparger systems used in tank mixing. Understanding the fluid mechanics of the air sparger system will aid in the design and proper operation of hybrid pulse jet mixer/sparger units. 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.

During FY12 (FIU Year 3), the 3D parallel LBM code developed at FIU during FY11 will be used to obtain large scale simulations of bubble generation and liquid mixing in tanks. In order to

generate the computational domains with complex geometries, a computer interface will be produced that can convert CAD data into voxels that LBM code can read. Appropriate wall boundary conditions will be implemented in the LBM code that will result in correct wetting characteristics of the fluid phases with the solid surfaces. Finally, the applicability of the LBM method for non-Newtonian flows will be investigated and possible solutions will be proposed. FIU also will work with Site engineers to integrate the modeling findings with specific field operations which will assist in the overall performance of the operation being modeled.

Task 12 Quarterly Progress

- The boundary condition for the Lattice Boltzmann Model **(**LBM) code that is responsible for the adhesion force exerted on the liquids by the solid surfaces was investigated first. The method chosen to achieve this calculates the force on the solid surfaces in the normal direction to the surface is given by

$$\mathbf{F}_w = -\rho K_w \hat{\mathbf{n}},$$

which was then inserted in the lattice Boltzmann equation as a body force. For the accurate calculation of the forcing term, the normal vector at the solid nodes needed to be calculated accurately. Since the voxelized geometries in 3D that were translated into the LBM computational domain appeared as a staggered representation, the calculation of the actual normal vector for the smooth solid surface needed special attention. The method chosen for the normal vector calculation evaluated the moving average of the normal of the lattice nodes along the surface within a specified radius of interest and corrected the directions of the normal vectors based on the contributions of the lattice nodes surrounding the target node within the zone of influence. Figure 1-3 shows the result of the weighted averaging procedure applied to a cylinder where the normal vectors are shown with red arrows. A subroutine has been added to the LBM code that could perform the above described procedure.

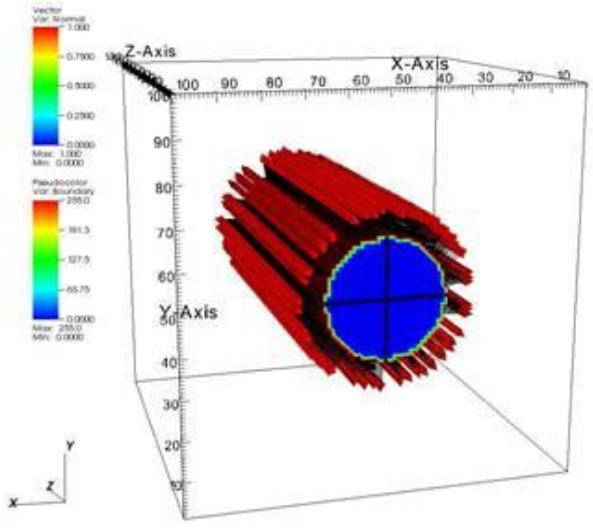


Figure 1-3. Weighted averaging procedure applied to a cylinder.

- Later, the wall adhesion boundary condition implemented in the LBM code was evaluated for accuracy. The force on the solid surfaces ($\mathbf{F}_w = -\rho K_w \hat{\mathbf{n}}$,) was made to repel or attract the liquid phases depending on the sign of the K_w parameter. The prestreaming, poststreaming and the hydrodynamics subroutines of the code were updated by inserting the calculation of the F_w force and including it in the calculation of the collision part of the lattice Boltzmann equation.

  In order to test the performance of the implementation of this forcing term, a numerical problem was generated in the computer where a semi-circular droplet was placed on a flat solid surface in a computational domain filled with a lighter medium. Under a zero gravitational field, the initial droplet was left to stabilize. Depending on the value and sign of the K_w parameter, the initial contact angle of the droplet (90°) was expected to converge to a value larger or smaller than 90°. Figure 1-4 shows that for a value of K_w =0.001, the contact angle of the droplet is 77.5° while Figure 1-5 shows that for K_w =-0.001 the contact angle obtained becomes 102.5°.

  The initial results indicated that the forcing term implemented in the LBM code could simulate the effects of hydrophobic and hydrophilic surfaces.

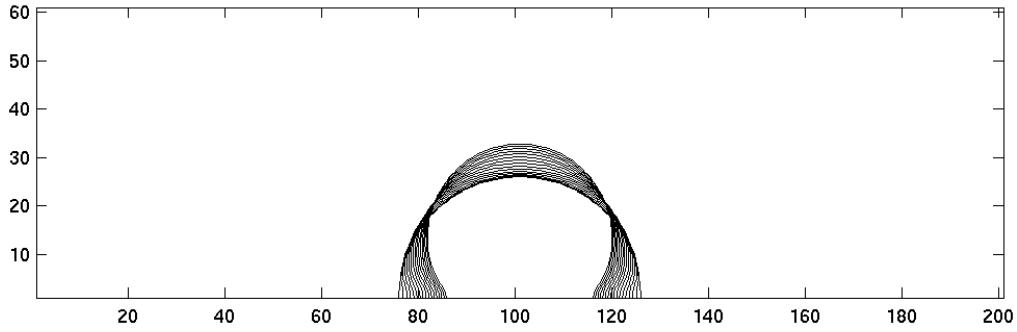


Figure 1-4. Convergence of contact angle using Kw = 0.001.

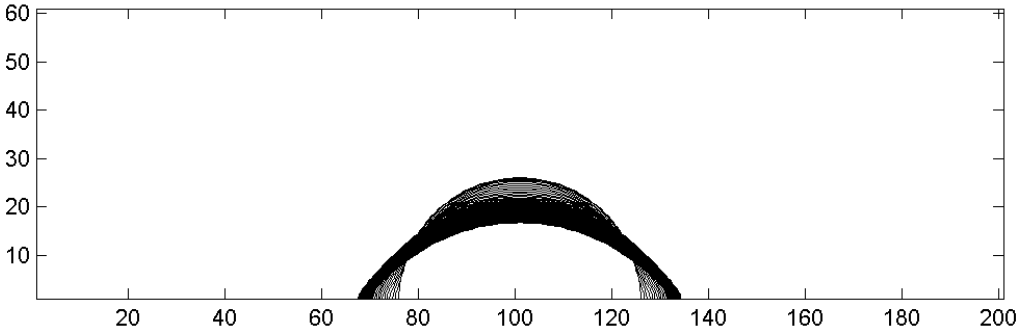


Figure 1-5. Evolution of droplet on flat surface using Kw = -0.001.

- After verifying the results of the wetting method in LBM for 2D serial code, the implementation of solid surfaces with wetting boundary conditions was started for

the 3D parallel LBM code. The code previously used periodic boundary conditions on the edges of the computational domain; therefore, the exchange of the information between processors during the parallel computation had to be modified in order to properly implement the no-slip boundary condition as well as the contact force applied on the fluids by the solid surfaces. A numerical problem was simulated with periodic boundaries on the sides of the domain where a solid block was placed in the interior of the domain (Figure 1-6). The purpose of this test was to separate the errors received from the code that may be due to improper implementation of message passing between the compute nodes. Currently, the bounce-back boundary condition is being evaluated using this test case after which the surface wetting will be evaluated. Once the results are verified for this case then the domains with closed sides will be considered.

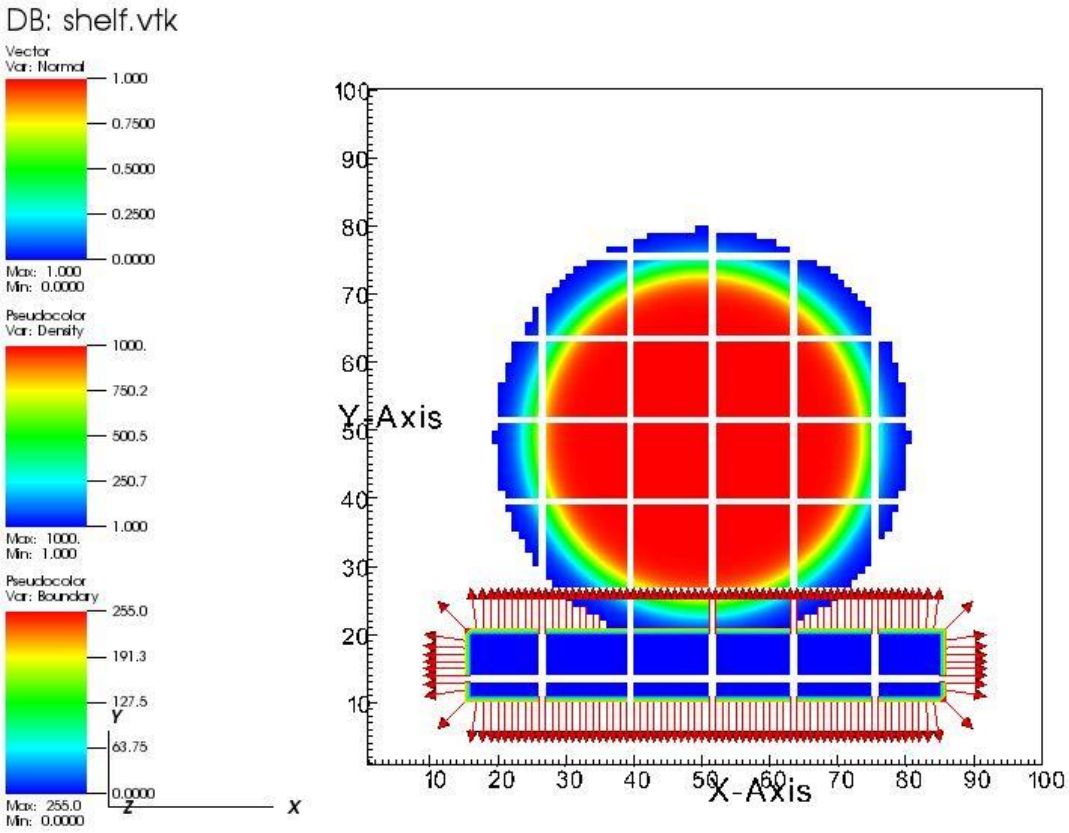


Figure 1-6. Droplet-surface interaction simulation with periodic boundary conditions.

Task 15: Evaluation of Advanced Instrumentation Needs for HLW Retrieval

Task 15 Overview

The objective of this task is to evaluate the maturity and applicability of commercial and emerging technologies capable of addressing several instrumentation needs for DSTs that will be

used for HLW mixing and transport to WTP. Efforts will be focused on the instrumentation needs for tank AY-102; however, the lessons learned will be applicable to other tanks and sites.

During FY12 (FIU Year 3), based on the test results of the ultrasonic spectroscopy system (USS), FIU will evaluate the candidate technologies selected during the FY10 technology search and evaluation process, with a focus on those technologies that showed limited research and development activities during the initial search. Second, a lessons-learned document will be prepared to address technical and operational issues in the development of an in-tank bulk density meter. This meter will be a simplified version of the in-tank solids monitor (ITSM) already developed by FIU during FY09.

Task 15 Quarterly Progress

- ITS submitted their final report to FIU which contained results and analysis from all testing completed. In general, the report stated that further testing was needed to resolve continued discrepancies between the reproducible performance of the system for simple mixtures, and the unstable measurements when interrogating complex mixtures. The primary cause of such behavior continues to be the effective size of the ultrasound transducer, where the trade-off between echo sensitivity and pulse strength must be analyzed in order to determine the optimal transducer size. The attenuating effects of the complex mixtures – and the expected Hanford tank waste – will significantly impede potential ultrasound in-tank technology until this engineering challenge is addressed. FIU prepared and submitted a summary document for milestone 2012-P1-M15.2, highlighting the results and providing recommendations.
- FIU was contacted by WTP engineers on the possibility of using the solid-liquid interface monitor (SLIM) developed at FIU to determine the amount of solids remaining on the bottom of a staging tank after a pulse jet mixing cycle which is intended to remove the waste. Discussions between FIU and WTP engineers still continue.

Task 16: Computational Simulation and Evolution of HLW Pipeline Plugs (New Task)

Task 16 Overview

The 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 rigid and flexible piping, with a focus on the multi-physical (chemical, rheological, mechanical) processes that can influence the formation. During FIU Year 3, based on data collected from a literature review of recent research conducted, this task will create a multi-physical model that simulates the formation of a pipeline plug, and looks at the influence of pipeline geometry/configuration on the plug development process. The task will utilize lessons learned from pipeline unplugging testing at FIU, as well as data collected during development of simulated plugs, to develop the model. Ultimately, the task will create several lab-scale tests to verify simulation results, and develop guidelines to address plug evolution, and allow site operators to modify the retrieval parameters in the event of a possible plug formation process.

Task 16 Quarterly Progress

- A literature review on the correlations used to predict pressure drop and concentration profile in slurry pipelines was conducted. The correlations were divided into two major classes such as empirical correlations and semi-empirical correlations. The empirical correlations approach included generalizing the known correlations for some parameters by dimensional analysis, without providing an insight into the flow mechanism_(e.g. Newitt et al.1955; Zandi & Govatos, 1967; Turian & Yuan, 1977; Ghanta, 1999 and many others). The semi-empirical correlations approach included the basic equations of motion and numerical solving them with the help of physical /mathematical assumptions for different terms. Most of the correlations had been developed based on limited data on materials having same sized or narrow size-range particles and hence would fail to predict accurately for Hanford waste. However, the Wasp model (1977) was the first which developed a pressure drop model by taking into account the concentration profile. This semi-empirical model is distinct from other pressure drop correlations in a sense that it tries to incorporate the underlying physics in its model development as well as is versatile and can be applied with some modifications over a wide range of slurries. Because of this, it has been used very successfully for the past 30 years for Newtonian slurries.
- An additional literature review focusing on the lines plugged due to sodium salts at Hanford was also conducted. Reviewing previous line plugging events revealed that a majority of the plugs formed were due to phosphate salts. This led to a review of the phosphate solubility studies. Phosphate solubility experiments were carried out as a function of temperature and sodium concentrations on simulated waste by (Herting 1987). The author observed that phosphate salts precipitated as pencil shaped solids at low sodium concentration (<5 M), needle shaped crystals at medium sodium concentration (5 < [Na] < 10M) and chunks at high solids concentrations (>10 M). A simple model was created that can determine phosphate solubility due to temperature change at a give molarity of sodium and is currently used to predict on-site evaporator performance in Hanford Tank Farms.
- Efforts have also been geared towards investigating the available multi-phase waste transport models and their applicability in predicting critical velocity/plug formation in pipelines relevant to Hanford waste. The Delta Q Program offered by Helix Technologies allows calculating critical settling velocity for slurries with varied particle size distributions within 5% of those calculated from the Environmental Simulation Program used by Hanford. However, the code is one-dimensional and does not consider the potential reacting nature of the flow and heat transfer while inputting the model requirements for predicting plug formation. Another code used by PNNL for multi-phase modeling is TEMPEST. A drawback with the TEMPEST code is that it lacks capabilities for particle tracing, particle growth kinetics, particle/particle interaction, and changes in bulk viscosity due to solids formation. Researchers at Mississippi State University have used code PHOENICS to create a 1-D CFD model to compute critical velocity and stationary bed profiles as a function of the flow velocity, particle size distribution, solid and liquid densities, viscosity, and volume percent solids. The code showed good agreement with the experimental data on simulated tank wastes from FIU; however, the code does not include chemical kinetics.

- COMSOL Multiphysics software is a powerful tool that can simulate plug formation by coupling waste fluid dynamics to waste chemistry. Current research undertaken at FIU aims to use COMSOL to predict plug formation by investigating the particle settling behavior, predicting critical velocity and concentration profiles of slurries with varied PSD relevant to Hanford waste. Work has been initiated in understanding the particle tracing module of the software.

Milestones and Deliverables

The milestones and deliverables for Project 1 for FIU Year 3 are shown on the following table. Summary documents for milestones 2012-P1-M15.2 and 2012-P1-M2.2 were completed on time and sent to DOE HQ and site personnel on 10/12/2012 and 11/09/2012, respectively.

FIU Year 3 Milestones and Deliverables for Project 1

Task	Milestone/ Deliverable	Description	Due Date	Status	OSTI
Task 2: Pipeline Unplugging and Plug Prevention	2012-P1-M2.1	Complete engineering scale pipeline unplugging using the asynchronous pulsing system	5/10/2013	On Target	
	Deliverable	Summary Document for 2012-P1-M2.1	5/10/2013	On Target	
	2012-P1-M2.2	Complete experimental validation of improvements to peristaltic crawler	11/09/2012	Completed	
	Deliverable	Summary Document for 2012-P1-M2.2	11/09/2012	Completed	
	2012-P1-M2.3	Complete engineering scale pipeline unplugging testing using the modified peristaltic crawler	5/03/2013	On Target	
	Deliverable	Summary Document for 2012-P1-M2.3	5/03/2013	On Target	
Task 12: Multiple-Relaxation-Time, Lattice Boltzmann Model for High-Density Ratio, Multiphase Flows	2012-P1-M12.1	Integration of mesh generation with appropriate boundary conditions in the 3D MRT LBM for simulation in complex geometries	5/16/2013	On Target	
	Deliverable	Summary Document for 2012-P1-M12.1	5/16/2013	On Target	
	2012-P1-M12.2	Investigation of multiphase LBM models for Non-Newtonian fluids and turbulence modeling	5/16/2013	On Target	
	Deliverable	Summary Document for 2012-P1-M12.2	5/16/2013	On Target	
Task 15: Evaluation of Advanced Instrumentation Needs for HLW Retrieval	2012-P1-M15.1	Complete Phase II candidate technology testing at Vendor facility	8/15/2012	Completed	
	Deliverable	Summary Document for 2012-P1-M15.1	8/15/2012	Completed	
	2012-P1-M15.2	Complete USS analysis and recommendations for Hanford	10/15/2012	Completed	
	Deliverable	Summary Document for 2012-P1-M15.2	10/15/2012	Completed	
Task 16:	2012-P1-M16.1	Complete literature review on plug	1/31/2013	On Target	

Computational Simulation and Evolution of HLW Pipeline Plugs		prevention methods			
	Deliverable	Summary Document for 2012-P1-M16.1	1/31/2013	On Target	
Project-wide	2012-P1-M1.0	Waste Management Symposium 2013abstract submitted	8/17/2012	Completed	OSTI[1]
	Deliverable	Draft Project Technical Plan	06/18/2012	Completed	
	Deliverable	Quarterly Progress Reports (all tasks and projects combined)	Quarterly	On Target	
	Deliverable	Draft Year End Report	06/28/2013	On Target	OSTI

Work Plan for Next Quarter

- Task 2: FIU will complete additional calibration curves for the APS to extrapolate the relationship between entrained air and pressure degradation. In addition, several transient tests will be performed to determine the pressure overshoot caused by the drive phase, and how that compares to the static pressure readings found during the calibration curves experiment. The pressure overshoot, and its effects in the presence of air, will allow FIU to develop an additional parametric relationship for system control and monitoring. Finally, the alternative pressure source will be tested on a larger scale loop.
- FIU will initiate the design of the test bed to perform the experimental testing of the Peristaltic Crawler System on an engineering scale pipeline (500 ft approximately). Improvements on the manifolds that hold the bullet pneumatic valves will be investigated to eliminate potential air leaks. The programmable logic controller software will also be optimized to provide faster navigational speed, this includes a secondary sequence specifically programmed to increase the speed of the unit when turning through 90° elbows. A second crawler unit will be fabricated and additional bellows will be procured to perform experimental pressurization/depressurization fatigue tests. Lastly, the system will be integrated into a skid for ease of transportation and deployment.
- Task 12: FIU will complete the verification of the wall boundary conditions in the 3D MRT LBM code in order to generate simulations with complex geometry from voxelated data and wetting of droplets on solid surfaces with various hydrophobicity properties. For this purpose, the dynamic simulations of bubbles and droplets in domains with solid boundaries will be simulated. The results will be presented in a poster at the Waste Management Symposium. The literature review for turbulence modeling for multiphase LBM will also be initiated.
- Task 15: FIU will meet with Hanford engineers to determine other tasks that can be performed in the area of HLW instrumentation.
- Task 16: FIU will review the Particle Tracing Module of COMSOL which will include particle tracing, particle growth kinetics and particle-particle interactions. This information will assist in incorporating particle deposition in the model. Efforts will also

[1] Announcement of published journal or conference paper will be submitted to OSTI

focus on simulating a spherical particle falling in water in a 3" horizontal pipe and determining its terminal velocity.

Project 2
Rapid Deployment of Engineered Solutions to Environmental Problems

Project Manager: Dr. Leonel E. Lagos

Project Description

This project focuses upon delivering solutions to environmental challenges at the DOE Hanford Site. During FY12 (FIU Year 3), FIU ARC is providing support on uranium contamination and remediation at the Hanford Site with research under Project 2. This project includes two subtasks: Subtask 1.1 – Sequestering Uranium at the Hanford 200 Area by In Situ Subsurface pH Manipulation using Ammonia (NH3) Gas; and Subtask 1.2 - Investigation on Microbial-Meta-Autunite Interactions - the effect of bicarbonate on the autunite mineral microbial dissolution and U (VI) biouptake by Arthrobacter G968.

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

Task 1.1 Overview

This task is being developed to evaluate the role of major pore water cations and anions on the U (VI) sequestration process in the presence of bicarbonate and calcium ions and study their effects on the mineralogy of formed precipitates after NH_3 (5% NH_3 in nitrogen) injection. The study will also examine the solubility of formed uranium precipitates under environmental conditions relevant to the Hanford vadose zone. Solubility studies will be conducted over the pH range of 6-11 in the presence of bicarbonate, calcium, and major pore water constituents such as sulfate, nitrate, Mg, and chloride. Studies will analyze mineralogical and morphological characteristics of precipitates by means of XRD and SEM-EDS to confirm the identity of the solid phase before and after solubility experiments. X-ray photoelectron spectroscopy (XPS) analysis will help in chemical identification of the samples' constituencies and uranium oxidation state to determine the mechanisms of U incorporation within a material.

Task 1.1 Quarterly Progress

- Experiments on the determination of the structure and composition of U-bearing precipitates changing over time were continued. The samples belonging to the 2nd batch prepared at the end of June were decanted after being kept for 3 months in the "mother solution", and precipitates were extracted and then placed in the incubator for drying. Also, 3-month samples belonging to the 3rd batch were decanted, and precipitates were extracted and then placed in the incubator for drying. During the reporting time, samples from the 3rd batch placed for drying were numbered as #1, #2, #3, #4, and #5 after 2 days, 2 weeks, 1 month, 2 month, and 3 month from the initial day of sample preparation, respectively.

- Two sets of precipitates belonging to the 2nd batch were evaluated by scanning electron microscopy and energy dispersive spectroscopy (SEM/EDS). Within this batch, half of the precipitates were prepared from solutions amended with 3 mM bicarbonate (HCO_3^-) while the rest were done with 50 mM HCO_3^-. The second set of precipitates from 2nd batch was formed by using solutions prepared by the same method with the addition of 5 mM of calcium. Before drying, the samples were kept in solution for 3 days, 2 weeks, 1 month, 2 months, and 3 months. The samples evaluated by SEM/EDS included the 3 mM and 50 mM HCO_3^- Ca-free versions kept in the "mother" solution for 3 days, 2 months, and 3 months. The analysis was repeated using Ca-bearing samples kept in the solution for 2 and 3 months.
- SEM imaging was performed using backscattered electron detection mode, allowing areas with higher atomic numbers to appear brighter. This helped in identifying locations of highest uranium concentration. EDS spectra of these "hot spots" were used to confirm uranium content (See Figure 2-1).

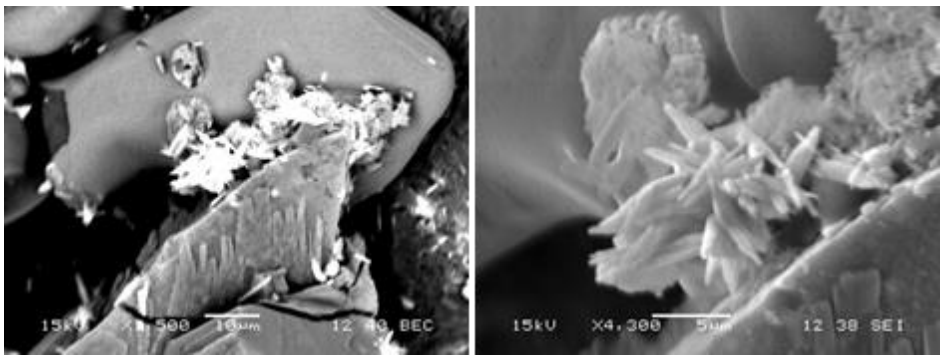


Figure 2-1. Backscatter (left) and scanning electron (right) images of the 3 day - 50mM HCO_3 sample (No calcium present)

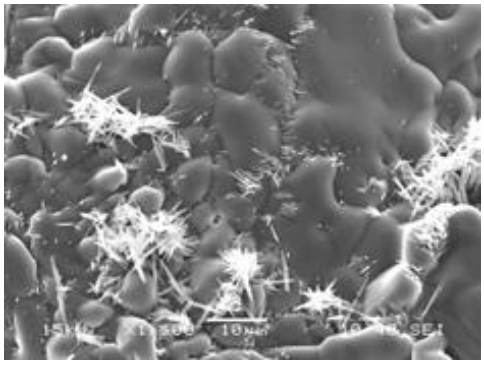


Figure 2-2. Scanning electron images of the 2 month - 50mM HCO_3 – 5mM Ca sample

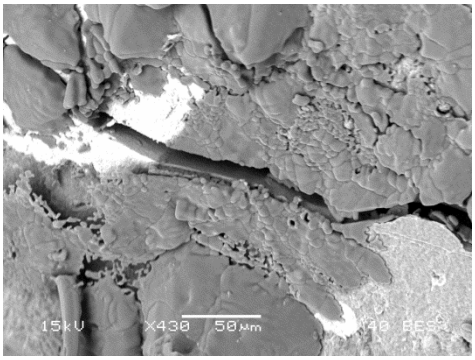
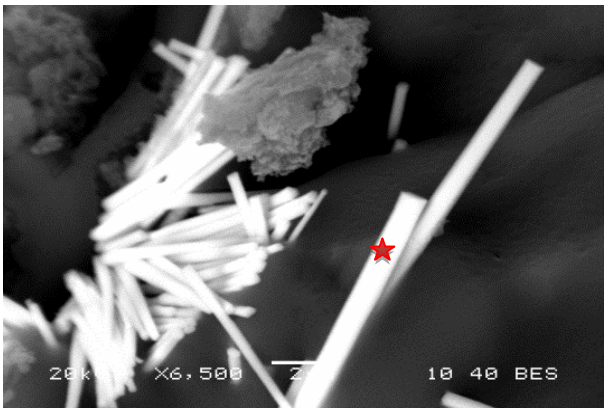


Figure 2-3. Backscatter image of the 3 month - 50mM HCO_3 – 5mM Ca sample

- In the 3 month-50 mM HCO_3-5 mM Ca sample, the uranium was found in a highly incorporated form without evident sign of crystal features (Figure 2-3). In the 2 month

sample of the same component ratio, elaborate crystalline structures were found (Figure 2-2).

- Completed experimental run that includes 5 mM of magnesium (Mg) in the synthetic mixture amended with 0 and 2.9 mM of bicarbonate for six different Si/Al ratios (1, 10, 20, 30, 40, and 50) and finalized TOC and KPA analysis for these sets. Prepared set for 25 and 50 mM HCO_3 and after keeping for 2 days in the incubator/shaker, samples were centrifuged and supernatant solutions were processed with KPA for U (VI) and TOC content.
- Additional samples from the two sets of precipitates were evaluated by scanning electron microscopy and energy dispersive spectroscopy (SEM/EDS). The sets represented the effect of time left in solution on the morphology of the precipitate produced by pH manipulation in the pore water simulation. Within one set, half of the precipitates were prepared from solutions with 3 mM bicarbonate (HCO_3^-) while the rest were done with 50 mM. The second set of precipitates was formed using solutions prepared by the same method with the addition of 5 mM of calcium. Before drying, the samples were kept in solution for 3 days, 2 weeks, 1 month, 2 months, and 3 months.
- The backscatter electron detection was used to predict where the locations of highest uranium concentration would be based on the higher intensity produced in areas of higher average atomic number, Z. The EDS spectra of these "hot spots" were used to confirm uranium content (Figures 2-4, 2-5, and 2-6). Prior analysis showed that crystalline uranium structures were only present in the high bicarbonate (50 mM HCO_3) samples. For this reason, the samples evaluated were limited to the 50 mM HCO_3^- versions of the 2 week and 1 month samples with and without calcium present for a total of 4 samples. Additional micrographs were produced for a precipitate formed with the same constituents as the samples of interest but without uranium.



Element	Wt%	At%
CK	07.11	11.31
NK	10.08	13.75
OK	45.29	54.07
NaK	22.06	18.33
AlK	00.30	00.21
SiK	01.49	01.01
ClK	00.00	00.00
UM	13.13	01.05
KK	00.46	00.22
CaK	00.09	00.04
Matrix	Correction	ZAF

Figure 2-4. Backscatter image and elemental content of the 1 month - 50mM HCO3 bearing

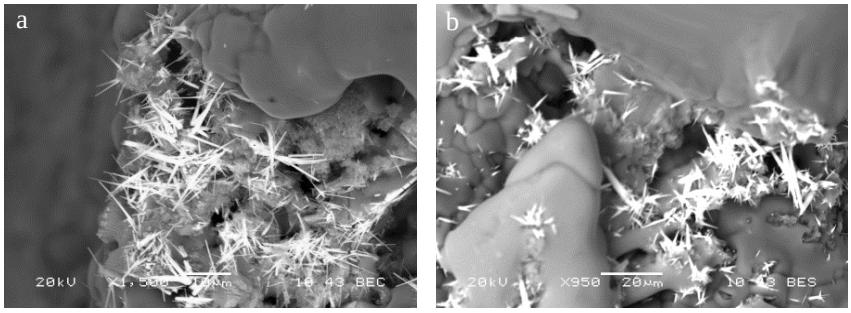


Figure 2-5. Two weeks - 50mM HCO_3 samples without (a) and with (b) Ca

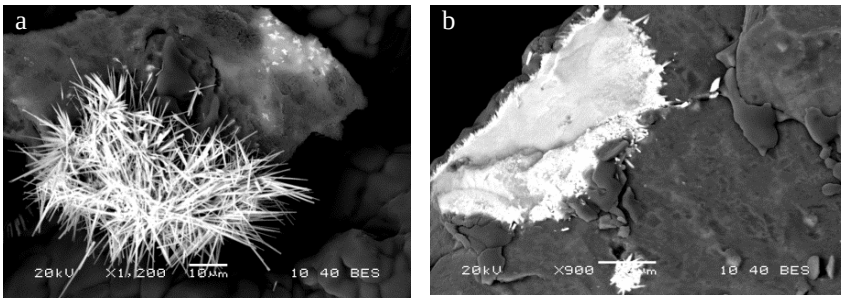


Figure 2-6. One month - 50mM HCO3 samples without (a) and with (b)Ca

- The resultant EDS data is being evaluated to find any correlation between the presence and concentration of the elements like uranium, potassium, carbon, and silicon. The relationship between the amount of time in solution and uranium content and crystal formation is also being investigated. Completed experimental run that includes 5 mM of magnesium (Mg) in the synthetic mixture amended with 25 and 50 mM of bicarbonate for six different Si/Al ratios (1, 10, 20, 30, 40, and 50) and finalized TOC and KPA analysis for these sets. Prepared set for 75 and 100 mM HCO_3 and after keeping for 2 days in the incubator/shaker, samples were centrifuged and supernatant solutions were processed with KPA for U(VI), inorganic carbon (IC) content and Si, Ca, Mg, and Al via ICP-OES.
- Two manuscripts were submitted to the Chemical Geology Journal for potential publication. The first manuscript "Effect of bicarbonate on the dissolution of sodium meta-autunite" examined the role of low concentrations of aqueous bicarbonate (0.5 mM – 3 mM) on the dissolution kinetics of synthetic Na-autunite in the pH range of 6 - 11 and a temperature range of 5 - 60^{o}C. The experiments were accomplished through a series of dissolution tests conducted via single-pass flow-through (SPFT) reactor using a mixture of carbonate and TRIS (tris hydroxymethyl aminomethane) as buffer solutions at various pH and temperatures. The rate of uranium release from Na-autunite was found to be directly correlated to increasing concentrations of bicarbonate. However, at higher pH, the effect of bicarbonate was reduced. The rate of uranium release in the range of bicarbonate concentrations tested showed little to no temperature dependency. The second finalized manuscript, "Comparison of the kinetic rate law parameters for the dissolution of natural and synthetic autunite in the presence of bicarbonate ions" presents results on the study of the effect of aqueous bicarbonate (0.5 mM – 3 mM) on the rate of uranium release from Ca–autunite. The experiments were accomplished through a series of dissolution tests conducted in the pH range of 7 - 11 and temperature variations from 5^{o}C to 60^{o}C via SPFT reactor using a mixture of carbonate and TRIS (tris hydroxymethyl

aminomethane) as buffer solutions. The study compared the rate of uranium release from Ca-autunite and thermodynamic rate law parameters, such as activation energy (Ea), enthalpy (ΔH), and pseudo-equilibrium constant (Kg) with similar parameters obtained for Na-autunite for better prediction of the bicarbonate impact on the U(VI) release during the dissolution process. The discussion on the results provides an explanation for the higher stability of Na-autunite. The results of the study are necessary for conducting effective remedial actions at Hanford and other sites contaminated with uranium and for forecasting the migration of uranium in the subsurface. The literature search confirmed that this is the first investigation that has quantified the kinetic rate law parameters of Na-autunite and Ca-autunite in bicarbonate-bearing solutions under wide temperature and pH ranges. Announcement of the journal articles will be submitted to OSTI once published.

- The doctoral dissertation manuscript of Ravi Gudavalli was approved by the FIU Graduate School for graduation in the Fall 2012 semester.

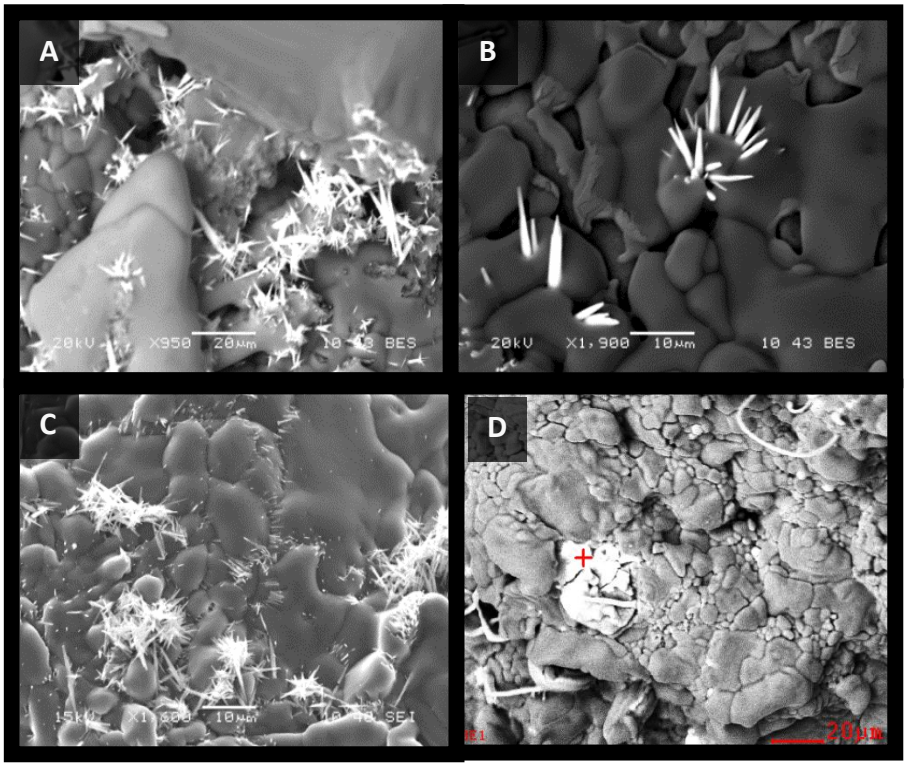


Figure 2-2. Precipitates formed from solutions containing calcium (5mM) and high bicarbonate (50mM) concentration after 2 weeks (A), 1 month (B), 2 months (C), and 3 months (D).

- Experimental sets containing 5 mM Ca and high bicarbonate concentrations (50 mM) were performed. Data were collected by scanning electron microscopy and energy dispersive spectroscopy (SEM/EDS) and then evaluated and organized for inclusion in the upcoming progress report. The data represents the effect of time left in solution and other variables, such as bicarbonate (HCO_3) concentration, on the morphology of the uranium-bearing precipitates experimentally produced by pH manipulation. The micrographs produced were prepared using both secondary electron and backscatter electron collection modes. The bright areas of higher average atomic number were further

evaluated by EDS analysis to confirm increased uranium concentration, compared to the rest of the precipitate. It is apparent that after a 2 week stay in solution, the uranium has localized into crystal-like structures (Figure 2-7A) which are scattered around the precipitate. The timeline, from two weeks to three months (Figure 2-7D), is being used to provide an explanation of how the precipitate is changing with time in solution. In addition to the qualitative changes, data from EDS analysis of uranium- rich areas is being considered in order to characterize the change of elemental content with respect to time.

- Work was also initiated on a new batch of samples that contains 10 mM of calcium (Ca) to study it effect on the removal of U (VI) after ammonia gas pH manipulation in the synthetic solutions mimicking conditions found in the vadose zone at the Hanford Site 200 Area. Previous experiments were conducted using 5 mM of Ca; however, the average concentration of Ca 9.7 mM was found in the porewater composition in the sediment layers of borehole 299-E33-45 where the highest concentrations of U (VI) were observed (Serne et al. 2002). Experimental samples were prepared from stock solutions of Al (50mM), Si (422 mM), and HCO_3 (400 mM). No magnesium was added to this set. The samples contained 0 mM, 2.9 mM, 25 mM, 50 mM, 75 mM and 100 mM of HCO_3, with Si/Al ratios of 1, 10, 20, 30, 40, and 50 each (a total of 36 samples). The final volume of each sample has been adjusted to 50 mL with the addition of deionized water. The pH of the solutions has also been adjusted to a value of 8.0 by the titration of nitric acid. Samples with synthetic mixtures are ready for the ammonia gas injection and addition of UVI). The results of these experiments will be reported in the next monthly report.
- Continued review of uranium solubility literature for the preparation of isopiestic method laboratory set up. Placed an order for a metal pressure pot that will be used as an isopiestic apparatus and Omega's 5 psia high accuracy piezoresistive pressure transducer PX419-005AV-XL to measure a vapor pressure of solutions.
- Graduate students Claudia Cardona, Paola Sepulveda and Robert Lapierre prepared presentations for the ARC graduate evaluation committee based on the research conducted for the project 2 during Fall 2012.

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

Task 1.2 Overview

The objective of this task is to examine microbial- uranium interactions that include biodissolution of autunite mineral and bio-adsorption of uranium (VI) in the presence of bicarbonate ions. The experiments will involve oligotrophic microbial species *Arthrobacter* spp. that have previously been isolated from Hanford Site soil to study their influence on the dissolution of meta-autunite. Our previous results showed that the *Arthrobacter* G975 strain bioenhanced the dissolution of the natural Ca-autunite in the presence of various concentrations of bicarbonate up to 10 mM and was able to dissolute U(VI) even while not in direct contact with the mineral. Cells exposed to U (VI) in the presence of bicarbonate were more active in TOC degradation compared to those without bicarbonate, attained higher cells densities, and colonized deeper and larger regions of autunite crystals. The study planned for 2012 will attempt to

examine mechanisms of bacterial dissolution of autunite mineral to understand the interaction of the microorganisms with the meta-autunite.
In addition, experiments on the mechanisms of U bioleaching from autunite mineral will include autunite dissolution in the low-phosphorous growth media substrate augmented with various concentrations of bicarbonate, which is left after culturing G975 and G968 strains. These experiments will supplement a study conducted with cultureware where autunite and bacteria were separated by a 0.45 um membrane and help to understand if organic acids produced by microorganisms may play a role in the solubilization of U (VI). Post-experimental assessment of bacteria and mineral will apply SEM-EDS and FIB/SEM methods to characterize bacteria uranium interactions during U (VI) leaching as well as possible biogenic transformations that might occur during the dissolution.

Task 1.2 Quarterly Progress

- The dissolution experiment using cultureware was restarted due to the fact that preliminary KPA results indicated that the data points were too high, and did not correlate with previous data conducted with a different bacterial strain. To restart the experiment, Hepes buffer media was made from 5% minimal PTG media consisting of 5 g/L peptone, 5 g/L tryptone, 10 g/L glucose, 0.6 g/L $MgSO_4.7H_2O$, and 0.07 g/L $CaCl_2.2H_2O$. Yeast extract due to the high phosphorus content was not included in the media. The media was prepared in deionized water (DIW), autoclaved at 121^oC, 15 psi for 15 minutes, and allowed to cool down to about 30^oC. Then, the media solution was equally distributed between four 250-mL bottles and separately amended to contain 0, 3, 5 and 10 mM of $KHCO_3$. Media pH in each bottle was adjusted to pH 7.5 with 0.1 mol/L HCl or NaOH and buffered with 20 mM 2-(2-hydroxyethyl)-1-piperazine ethanesulfonic acid sodium salt hydrate (HEPES-Na). Each bicarbonate media solution was filter-sterilized (0.2 µm) and kept refrigerated until the time of the experiment. Sterile 6-well cell culture plates with inserts were used in the non-contact bioleaching experiments where natural Ca meta-autunite and bacteria cells were kept separately. A 3.2 mL aliquot of sterile media was dispensed in the appropriate well and 2.5 mL inside the insert receptacle. The total volume inside each well added up to 5.7 mL. The cultureware inserts have 0.4 µm cylindrical pores that transverse the membrane and only allow the diffusion of soluble uranium. Ten mg (10 mg) of sterilized autunite powder was added to the bottom of the well. The wells were numbered and organized in the following order: 0 mM HCO_3: wells 1, 2, 3, 4; 3 mM HCO_3: wells 5, 6, 7, 8; 5 mM HCO_3: wells 9, 10, 11, 12; 10 mM HCO_3: wells 13,14,15,16; and wells 1, 5, 9 and 13 are abiotic controls to compare results with bacteria-bearing wells.
- Due to contamination of agar plates, a fresh set of bacterial stock was re-plated and grown in liquid media to check for both viability and contamination. New HEPES media from 5% minimal PTG media consisting of 5 g/L peptone, 5 g/L tryptone, 10 g/L glucose, 0.6 g/L $MgSO_4.7H_2O$, and 0.07 g/L $CaCl_2.2H_2O$ was made. Yeast extract due to the high phosphorus content was not included in the media. Media was prepared in deionized water (DIW), autoclaved at 121^oC, 15 psi for 15 minutes, and allowed to cool down to about 30^oC. Then media solution was equally distributed between four 250 ml bottles and separately amended to contain 0, 3 mM, 5 mM and 10 mM of $KHCO_3$. Media

pH in each bottle was adjusted to pH 7.5 with 0.1 mol/L HCl or NaOH and buffered with 20 mM 2-(2-hydroxyethyl)-1-piperazine ethanesulfonic acid sodium salt hydrate (HEPES-Na). Each bicarbonate media solution was filter-sterilized (0.2 µm) and kept refrigerated until the time of the experiment. The bioleaching experiment with inserts was run one final time; however, due to time constraints, only the abiotic control samples were used. Sterile 6-well cell culture plates with inserts were used in the non-contact bioleaching experiments where natural Ca meta-autunite and bacteria cells were kept separately. The total volume inside each well added up to 5.7 ml. The cultureware inserts have 0.4 µm cylindrical pores that transverse the membrane and only allow the diffusion of soluble uranium. Ten mg (10 mg) of sterilized autunite powder was added to the bottom of the well. The samples were labeled as follows:

0mM HCO_3: well 1

3mM HCO_3: well 5

5mM HCO_3: well 9

10mM HCO_3: well 13

Periodically, 20 µl samples aliquots were taken according to the sampling schedule and ashed on a hot plate in the presence of concentrated plasma grade nitric acid and hydrogen peroxide solutions. Wet digestion in seven mL scintillation glass vials was continued until a dry white precipitate was obtained, then vials were dry ashed in a furnace at 450^{o}C for 15 min. This experiment continued into the second week of December, where KPA analysis was performed.

- Silicon wafers were prepared and cleaned for future AFM imaging. The wafers were suspended in isopropyl alcohol and placed in a sonicator for two minutes; the same was repeated in an acetone bath, methanol bath, and water bath, each for two minutes. Simultaneously, 2% 3-aminopropyltriethoxysilane (AMPTES) was prepared by adding 0.2 mL of 3-aminopropyltriethoxysilane to 10 mL of methanol. The wafers sat in a bath of this solution for 12 hours; afterwards, the wafers were removed from this solution and washed in three baths of methanol for 2-5 minutes each (without the sonicator). Once the wafers have been washed and fully dried (left overnight), a 10-20 microliter drop of bacteria was added on top of the wafer amended with AMPTES. This drop of bacteria can be left to dry overnight or dried using a low pressure air supply for about 10 minutes. Then it is ready for imaging.
- FIU repeated the bioleaching experiment with inserts no-bacterial controls. Sterile 6-well cell culture plates with inserts were used in the non-contact bioleaching experiments where natural Ca meta-autunite and bacteria cells were kept separately. A 3.2 ml aliquot of sterile media was dispensed in the appropriate well and 2.5 ml inside the insert receptacle. The total volume inside each well added up to 5.7 ml. The cultureware inserts have 0.4 µm cylindrical pores that transverse the membrane and only allow the diffusion of soluble uranium. Ten mg (10 mg) of sterilized autunite powder was added to the bottom of the well. Due to time constraints, only the control samples were used

  0mM HCO3: well 1

  3mM HCO3: well 5

5mM HCO3: well 9

10mM HCO3: well 13

Periodically, 20 µl samples aliquots were taken according to the sampling schedule and ashed on a hot plate in the presence of concentrated plasma grade nitric acid and hydrogen peroxide solutions. Wet digestion in seven mL scintillation glass vials was continued until a dry white precipitate was obtained, then vials were dry ashed in a furnace at 450oC for 15 min. KPA analysis was performed, most of the data showed that the system reached equilibrium. Two samples, however, had questionable results, the first sample had a uranium concentration of 0, which may be due to improper digestion, or the sample contained only small traces of uranium. Also, the last sample showed very high uranium concentrations which may be caused by evaporation within the well.

- In addition to the bioleaching experiment with inserts, preliminary AFM imaging was performed on bacteria containing bicarbonate. The solution for imaging contained: a 1 ppm U(VI) solution (Log7.5 bacterial cells was added to 4 mL of stock solution), 3712 µl of bacterial stock solution, 168 µl of uranyl stock solution, and 120 µl of fresh media. Preliminary imaging did not produce good results due to the medium used. The media contained phosphorus which interacted with uranium producing a precipitate. Future imaging will be conducted using synthetic ground water to eliminate organics from interfering with the images. Furthermore, a new batch of *Arthrobacter* strains, G968 and G975 were obtained. These strains underwent short term storage, plated and kept in the refrigerator and long term storage, underwent glycerol treatment to be kept in a -20°C freezer for future use.

- The manuscript entitled "Investigation on microbial dissolution of uranium (VI) from autunite mineral," submitted to the 2013 Waste Management Symposia and accepted for an Oral Session (#097), came back from peer review. The paper was accepted as is and is eligible for competing for the WMS Outstanding Paper/Presentation Award. Announcement of the conference paper will be submitted to OSTI once published.

Milestones and Deliverables

The milestones and deliverables for Project 2 for FIU Year 3 are shown on the following table. Milestone 2012-P2-M2, completion of testing on the formation of U (VI)-bearing precipitates using various Si:Al ratios in the presence of bicarbonate, was completed by 11/30/12.

FIU Year 3 Milestones and Deliverables for Project 2

Task	Milestone/ Deliverable	Description	Due Date	Status	OSTI
Task 1.1: Sequestering Uranium at the Hanford 200 Area Vadose Zone by *In Situ* Subsurface pH Manipulation Using NH3 Gas	2012-P2-M2	Completion of testing on the formation of U(VI)-bearing precipitates using various Si:Al ratios in the presence of bicarbonate	11/30/2012	Completed	
	Deliverable	Subtask 1.1 Progress report on over time morphological changes of U-bearing precipitates' via SEM/EDS.	1/11/2013	On Target	

Task 1.2: Investigation on Microbial-Meta-Autunite	2012-P2-M3	Completion of AFM assessment on bacteria exposed to U (VI) in bicarbonate-bearing solutions.	4/30/2013	On Target	
	Deliverable	Subtask 1.2 Progress report on AFM assessment on bacteria exposed to U(VI) in bicarbonate-bearing solutions	4/30/2013	On Target	
Project-wide	Deliverable	Draft Project Technical Plan	6/18/2012	Completed	
	2012-P2-M1	Waste Management Symposium 2013 abstract(s) submitted	8/17/2012	Completed	OSTI[2]
	Deliverable	Draft Year End Report	6/28/2013	On Target	OSTI
	Deliverable	Quarterly Progress Reports	Quarterly	On Target	

Work Plan for Next Quarter

- Task 1.1: Finalize experiments for the removal of U using a synthetic groundwater composition in the presence of 10 mM Ca and continue uranium-bearing precipitates characterization studies. Complete progress report on over time morphological changes of U-bearing precipitates' via SEM/EDS. Continue assessment of previously prepared uranium-bearing precipitates via SEM/EDS and XRD.
- Task 1.2: Finalize dissolution experiments with G968 strain using culture cells inserts and focus on AFM measurements to monitor changes at the nanoscale level in G968 cell surface topography before and after the cells exposure to uranium in the presence of bicarbonate ions.
- Work on the FIU's Year 4 Continuation Application for our DOE-FIU Cooperative Agreement for Project 2. Update all fact sheets for the project for upcoming WM conference.

[2] Announcement of published journal or conference paper will be submitted to OSTI

Project 3
Remediation and Treatment Technology Development and Support

Project Manager: Dr. Georgio Tachiev

Project Description

The overall objective of this project is to provide technical assistance and perform research in support of the remediation efforts at the Oak Ridge Reservation. Student support for research at the Moab Site will also be provided. Research efforts will be executed in collaboration with DOE EM and DOE ORO and will be closely aligned with the ASCEM program objectives. The numerical modeling and experimental work will provide a better understanding of the fate and transport of inorganic and organic pollutants.

Task 1: East Fork Poplar Creek Model Update, Calibration & Uncertainty Analysis

Task 1 Overview

For Task 1, FIU will use the numerical model of EFPC to determine the impact of remediation alternatives on the complete hydrologic cycle, the transport overland and in surface water and rivers, sediment transport and reactions, and mercury exchange with sediments. The research will be coordinated with the site and ORNL personnel. The major objective of this task is to provide analysis of the coupling between hydrology and mercury transport within the context of decreasing the risk of D&D activities. The major deliverable of this task will be numerical and stochastic analysis of observed and computed time series for flow and contaminant concentration for NPDES-regulated outfalls within the watershed. Model simulations will be used to account for a range of hydrological impacts related to planned remediation alternatives.

Task 1 Quarterly Progress

- ***Subtasks 1.1 & 1.2***
  - The EFPC model is currently being modified to decrease simulation time. Test simulations have been and will continue to be performed throughout the next month.
  - Continued literature review on the concept of stochastic analysis and probability distributions in an effort to further understand the analytical approach taken in analyzing model simulation results and observed data.
  - Continued working on the thesis draft pertaining to the work being conducted under Project 3 Task 1.
  - Presented conference paper at the 9th International Symposium on Persistent Toxic Substances held at the Miami Airport Marriott on October 26, entitled “Hydrologic and Kinetic Parameters Impacting the Total Mercury Transport within the EFPC

Watershed, Oak Ridge Reservation". Announcement of the conference paper will be submitted to OSTI.

- Added groundwater monitoring wells to the model along EFPC, and determined the model's performance along a set of transects beside EFPC.
- Developing MATLAB scripts to extract observed and computed data and provide statistical analysis for model performance.
- Developing MATLAB scripts for reading and extracting concentration data along EFPC.
- Executed several simulations and evaluated results for flow and depth to phreatic surface. Concluded that well timeseries need to be updated to include more observation points if possible. Calibration is needed for the groundwater wells with recorded values of depth to phreatic surface.
- Observation stations show a captured base flow but inconsistency in capturing peak flows. A contributing factor may be the drainage within this area. This will be explored by comparing locations relative to known outfalls or drainage structures to determine which model changes or updates would be adequate. Figure 3-1 is an example of station EFK 23.4.

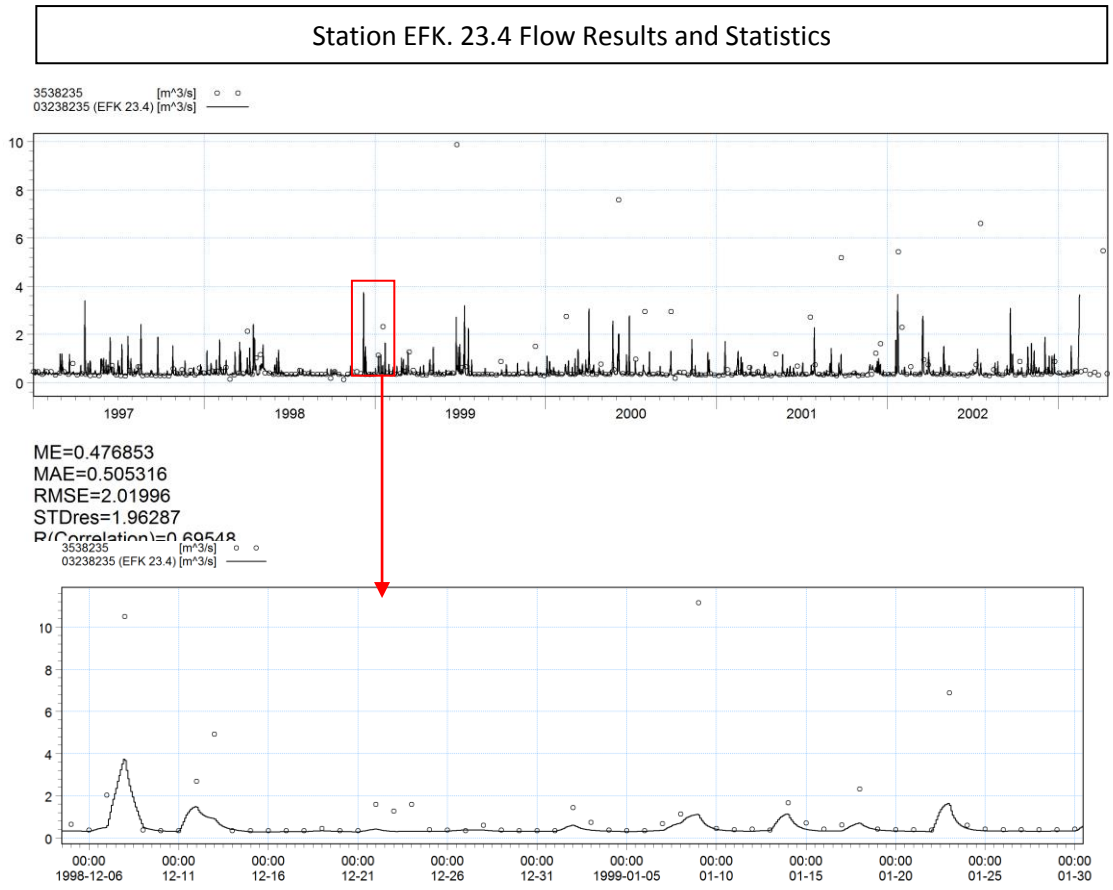


Figure 3-1. Flow Results and Statistics

- Repeated a 10 year simulation (12/1/1996 – 2006) which originally failed, then implemented a series of corrective actions (i.e. resolved cross section errors and modified boundary conditions).
- Checked simulations results. There was a failure at 62.1% of simulation, near the end of the river network, so specific cross-sections were expanded to increase water flow in that portion of the watershed and eliminate error No. 25. These changes were successful in reducing the numerical instabilities, so water movement simulations were completed for the full 10 year period.
- Repeated water quality simulation which originally failed because boundary conditions included 6 concentration components for Ecolab. Concentration components were removed, leaving only 1, however simulation duration estimate excessively high, so currently reviewing to determine which module is slowing down the simulation (MIKE SHE or MIKE 11).

- ***Subtask 1.3a: Surface Water Flow and Contaminant Transport Model of ORNL 4500 Area***
  - Conducted preliminary calibration of model for steady uniform flow using constant rainfall intensity and currently checking it via mass balance equations.
  - Provided analysis of the water balance for each catchment.
  - Determined the response of the model for a set of Manning's parameters to simulate the uncertainty in pipe condition, provided comparative runs for one year and determined the probability exceedances for each flow event.
  - Conducted preliminary calibration of model for unsteady non-uniform flow where the rainfall intensity varies with time.
    - Data for Outfall 211 is scarce. There is no timeseries information available for Outfall 211; however, there were a few samples (flow rates measured once per day) made available for calibration of the model.
    - The sample taken on May 12, 2009 was chosen for this preliminary calibration where the precipitation for May 11, 2009 and May 12, 2009 was retrieved from the ORNL website. Precipitation near Outfall 211 is monitored by ORNL's Tower C.
    - Obtained 60 min, and 24 hour precipitation data from ORNL's website, generated several models for selected periods of time, and developed inputs for yearly simulations using 60 minute time intervals, and simulations for 1999-2012 using 24 hour time intervals.
  - Conducted sensitivity analysis by running multiple simulations of monthly rainfall varying the Manning's n coefficient (0.011-0.017).
  - Completed milestone 2012-P3-M1.2 "XPSWMM Model Preliminary Results Summary". A summary report of the XPSWMM model's preliminary results was sent via email to the relevant DOE personnel.

- Refined the model and ran yearly simulations varying Manning's n coefficient and infiltration parameters.
- A Master's thesis is being developed based on this project work. An extended thesis proposal was presented and approved by the graduate committee.
- A sensitivity analysis where Manning's coefficient, and infiltration methods were varied in order to evaluate the sensitivity of the model on the parameters. The first analysis was for the Manning's coefficient variations (0.011-0.017, 0.035). Pipe 26 (P-26), the last pipe prior to discharging via Outfall 211 (OF-211), was analyzed for comparison. The probability exceedance (PE) curve in the figure below indicates there were minute variations between the variations. Manning's coefficient of 0.014 and the evaporation default of 0.1"/day were held constant for the simulations.
- The second sensitivity analysis was conducted for various infiltration methods: Green Ampt, Horton, and Uniform Loss. Typical values of clay loam soils were utilized for the infiltration methods were used as shown below.
- A study of contaminant transport within the ORNL area was conducted using the XPSWMM model. The model was run based on the following assumptions:
    1. No loss in the system (i.e. infiltration, evaporation).
    2. Tracer is conservative.
    3. The conservative tracer is added at nodes B-4501 and I-10.1 with constant concentration and flow of 1 mg/L and 0.1 cfs respectively.
    4. 1 year rainfall with 15 minute intervals.
- These assumptions (1 & 2) were made so that the model's mass balance could be checked or calculated and easily compared to the analytical calculations.
- The model produced identical results to the analytical calculation results for both tracer mass loading and concentration. This indicates that the model has the capability and potential to be used to study contaminant transport.
- The resulting tracer concentration, tracer mass loading and hydrographs at Node B-4501, I-10.1, and MH211-3 are shown in the figures below.

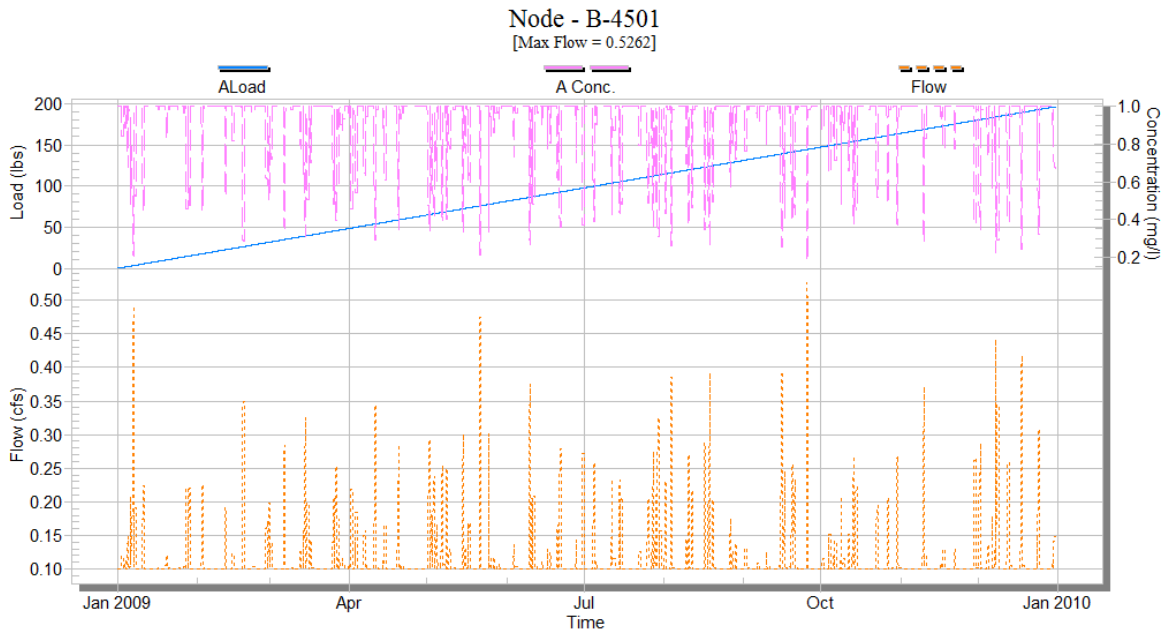


Figure 3-2. Tracer concentration, tracer cumulative load (196 lbs), and the flow hydrograph at Node B-4501

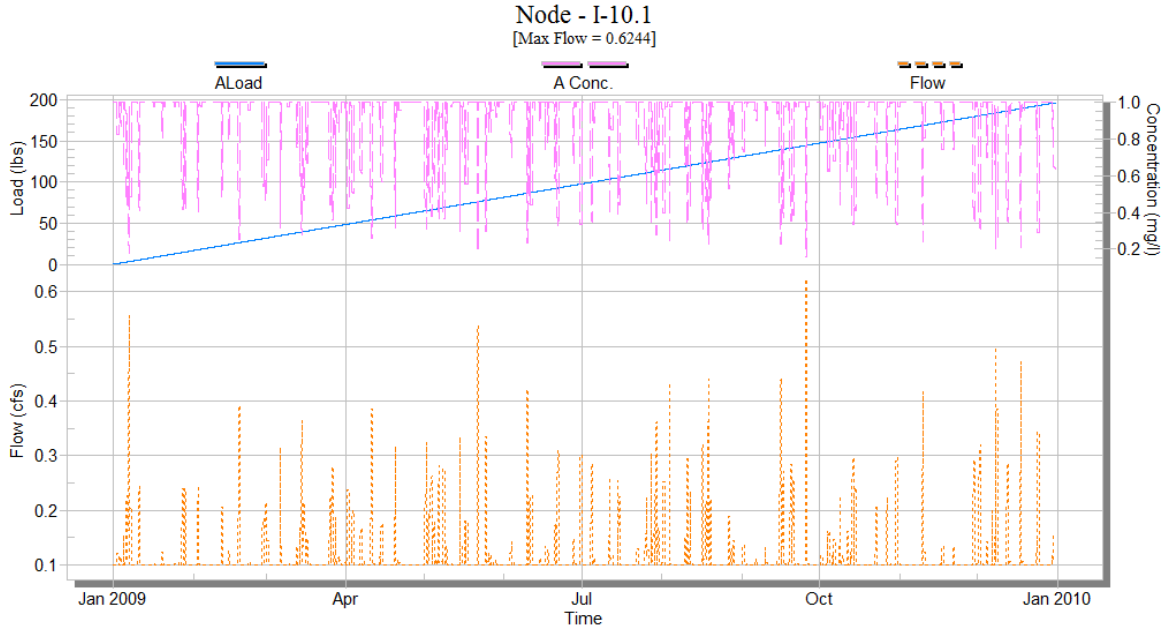


Figure 3-3. Tracer concentration, tracer cumulative load (196 lbs), and the flow hydrograph at Node I-10.1

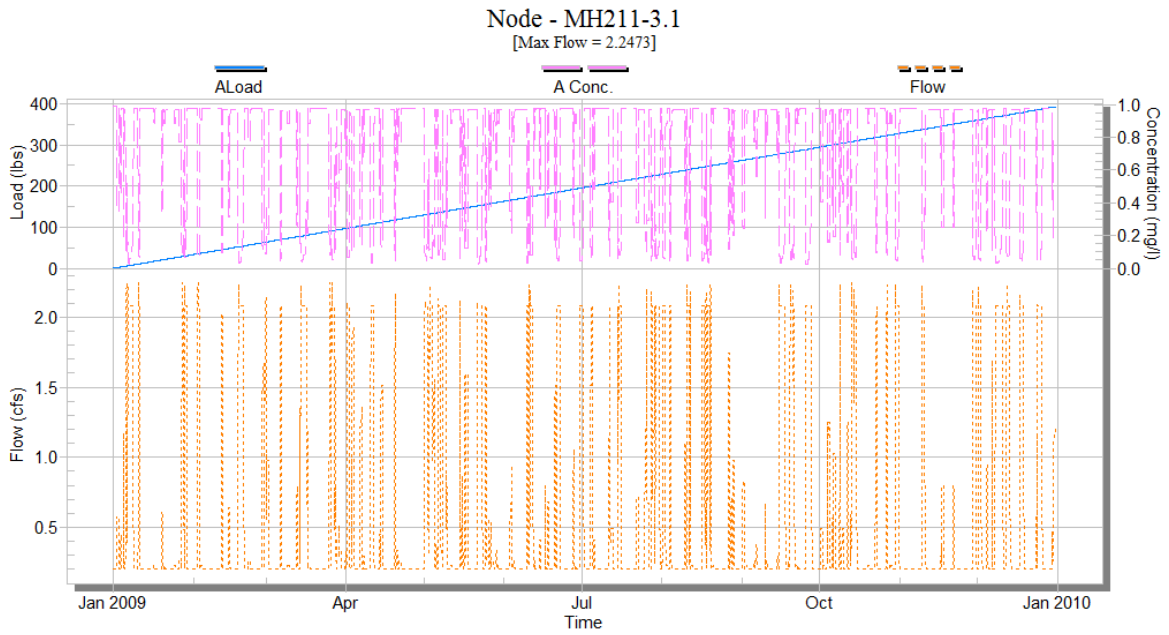


Figure 3-4. Tracer concentration, tracer cumulative load (393 lbs), and the flow hydrograph at Node MH211-3.1

- Currently, the model is being calibrated by comparing OF-211 data provided by ORNL. This is being conducted by simulating actual rainfall data from Tower C through the XPSWMM model and comparing the 5-minute intervals time series data provided by ORNL at OF-211 and 5-minute interval time series XPSWMM results.

- ***Subtask 1.3b: Surface Water Flow and Contaminant Transport Model of Y-12 NSC***
- The test model (small portion of Y-12 NSC) was run with the following model conditions:
    - Rainfall data of Y-12 was replaced with SCS data (1 month).
    - The IDF data and IDF table were created and input into the model.
        - Some data was not available and had to be assumed.
        - Assumptions include 25-yr, 50-yr and 100-yr return periods.
    - The site elevation was exported from GIS in the form of contours.
    - Sub-catchments were adjusted according to land uses.
    - Node and pipe elevations were adjusted according to the GIS contours.
    - The model was run with a 1 month, 5 year return period.
        - Flow results are being analyzed.
        - Dynamic Plan View was used to examine the flooding nodes or the points at which water was lost from the system.

        - The design tool was used to calculate the pipe sizes then simulated in the model again to make sure that all the nodes were not getting flooded. Thus, the final designate pipes can carry the flow without flooding.
    - The Y-12 model was expanded to cover more area of the site. The model was run with the following model conditions:
        - The steady state rainfall was input to test the accuracy of the flow hyetograph.
            - The flow hyetograph output corresponding to the steady state rainfall results were examined.
        - Model was run with 1 year (2009) rainfall data.
            - Dynamic Plan View was used to examine the flooding nodes or the point that the water was lost from the system.
            - The design tool was used to calculate the pipe sizes then simulated in the model again to ensure that all the nodes were not being flooded. Thus, the final designate pipes will be able to carry the flow without flooding.
- The study conducted in Subtask 1.3a was carried out to determine the XPSWMM model's capability and potential to be used to study contaminant transport in the ORNL area. Based on the successful results obtained, the same process is being duplicated for the Y-12 NSC.

Task 2: Simulation of TMDL for the Entire EFPC

Task 2 Overview

Task 2 will provide numerical analysis of contaminant flow and transport within the EFPC watershed and will determine the impact of model parameters on NPDES and TMDL regulations. During FY2012 (FIU Year 3), the objective will be to determine the effect of the hydrological events (including changes in hydrology caused by D&D activities on the site) on contaminant loading (changes in external and internal loading in time and space), and how imminent ecosystem restoration may affect existing contaminant pools.

Task 2 Quarterly Progress

- Updated the library of MATLAB scripts and added capabilities for generation of timeseries plot and probability exceedance plots for comparison of observed and computed data. The scripts allow for considerable data reduction and storage of only selected results.
- Updated the EFPC model.
- Completed an article for the WM2013 conference. The article uses modeling results to provide analysis of the efficacy of stabilization in place with hydrologic isolation for remediation of mercury contaminated areas in EFPC. Announcement of the conference paper will be submitted to OSTI once published.

- Mercury sources at the former Building 81-10 area, where mercury was previously reported, were modeled using a telescopic refined mesh with boundary conditions extracted from the watershed model.
- Modeling on a watershed scale indicated that only source excavation for soils/sediment in the vicinity of UEFPC had any effect on mercury flux in surface water.
- The simulations showed that colloidal transport contributed the largest fraction (up to 85 percent) of the total mercury flux leaving the UEFPC watershed under high flow conditions.
- Simulation of dissolved mercury transport from liquid elemental mercury and adsorbed sources in soil at former Building 81-10 indicated that dissolved concentrations are orders of magnitude below a target industrial groundwater concentration beneath the source and would not influence concentrations in surface water at Station 17.
- This analysis addressed only shallow concentrations in soil and the shallow groundwater flow path in soil and unconsolidated sediments to UEFPC.
- The simulations showed that mercury in soil is highly adsorbed and transport in the groundwater system is very limited under porous media conditions and particularly if there are no strong ligands present to change the dissolution equilibrium.
- Provided stochastic analysis of load reduction resulting from two hypothetical remedial actions that included: i) hydrologic isolation of soil contaminated with mercury (hydrologic isolation assuming impervious surface and no infiltration from rainfall) and ii) assuming a cutoff wall along contaminated areas which would prevent horizontal groundwater flow).
- A series of simulations were performed to analyze each of the two actions above. Each of the simulations included variation of several major parameters, such as hydraulic conductivity of the upper layer, and hydrologic parameters of the vadose zone.
- The analysis compared the loads at Station 17 and the associated uncertainties and the loads at the exit of the watershed (STA EFK 6.4)
- Developed probability exceedance curves for each scenario; this data provided additional insight of the effect for the entire range of hydrologic regimes (very wet to very dry conditions). This approach provided characteristics of the hydrology which limits the amount of overland flow over site surfaces, and limits the infiltration of rainwater through areas with underlying mercury contamination.
- Continued simulations were performed to analyze each of the two actions above. The data is in process of analysis to determine the effect of variation of hydraulic conductivity of the upper layer, and hydrologic parameters of the vadose zone on the probability exceedance curves describing the load, the concentration and the flow volumes through 6 benchmarking stations along EFPC (including Sta 17 and Sta EFK 6.4 at the watershed exit).
- Summarized the results for each scenario related to the variation of hydrologic conditions to provide understanding of the effects of surface water on contaminant mobilization and transport within the watershed.

- Conducting analysis of the floodplain along EFPC and developing correlations between measured concentrations of mercury in soil, groundwater and surface water along the EFPC and flooding patterns during intense rainfalls.

Task 3: Parameterization of Major Transport Processes of Mercury Species

Task 3 Overview

The proposed FY2012 (FIU Year 3) scope for this task will focus on further understanding of the important processes in modeling the cycling of Hg in aquatic ecosystems. Experiments will be conducted to determine 1) effects of various environmental factors (pH, Eh, mineral oxides, water content, NOM (natural organic matter)) on the percentage of legacy Hg species available for methylation and demethylation in sediment, and 2) effects of DOM (dissolved organic matter) and other complexing reagents (e.g., Cl^-) on the dissolution of cinnabar, and through which process these factors affect the dissolution of cinnabar. In addition, experiments will be carried out to investigate the effects of DOM and Cl^- on the dissolution of cinnabar.

Task 3 Quarterly Progress

- A new technique using isotope tracers has been developed to simultaneously determine the dissolution of cinnabar and re-adsorption of released Hg^{2+} on the cinnabar surface in October. $^{201}Hg^{2+}$ was spiked into the cinnabar-dissolution system and detected to monitor the adsorption of Hg^{2+} on cinnabar. Variation of $^{202}Hg^{2+}$ with time was measured to estimate the dissolution rate. Isotope dilution-flow injection ICP/MS was employed to measure concentrations of $^{201}Hg^{2+}$ and $^{202}Hg^{2+}$ in solutions. This technique is being validated and will be applied in measuring the dissolution of cinnabar and re-adsorption of released Hg^{2+} on cinnabar.
- Results of the preliminary experiment conducted in October showed that the background concentration of Hg^{2+} in the cinnabar suspension solution is too high. Efforts are being made to decrease the Hg background in cinnabar suspension solution by comparing different pretreatment procedures used for cleaning up cinnabar.
- A new technique, isotope dilutions (ID)-phenylation-purge and trap-ICP-MS, is being developed for analyzing organomercury species at trace levels. 199-labeled EtHg and 201-labeled MeHg have been synthesized in the past month.
- Experiments are being conducted to study the difference of reduced glutathione (GSH) and oxidized glutathione (GSSG) in promoting cinnabar dissolution.
- A new technique using isotope addition ($^{201}Hg^{2+}$) and isotope dilution ($^{199}Hg^{2+}$) is being validated and applied in measuring the dissolution of cinnabar and re-adsorption of released Hg^{2+} on cinnabar.
- A new technique, isotope dilutions (ID)-phenylation-purge and trap-ICP-MS, is being developed for analyzing organomercury species at trace levels. This method has been applied in detecting concentrations of MeHg and EtHg standards in water phase in the past month. The detection limit and recovery of this technique will be determined in the

coming month. The method will also be applied in analyzing organomercury species in sediment and fish samples.

- Experiments were conducted to study the difference of reduced glutathione (GSH) and oxidized glutathione (GSSG) in promoting cinnabar dissolution.
- Experiments are being conducted to test if eliminating oxygen during all of the pretreatment procedures can decrease the background of Hg^{2+} in HgS suspension solution.

Task 4: Geodatabase Development for Hydrological Modeling Support

Task 4 Overview

During FY11 (FIU Year 2), FIU developed a geodatabase to support the hydrological modeling work performed by FIU which serves as a centralized data management system, making terabytes of data generated from the simulations of contaminant fate and transport accessible to all users and facilitates storage, concurrent editing and import/export of model configuration and output data. The work for FY12 (FIU Year 3) will serve to extend the geodatabase capabilities by creating a model using ArcGIS Model Builder and Python scripting that will automate the process of querying the existing EFPC geodatabase and generating maps. This can then be further extended to facilitate online querying of the database using downloadable freeware and generation of maps, graphs and reports, to more easily share the data with other project stakeholders such as DOE personnel and ORR site contractors.

Task 4 Quarterly Progress

- Continued research and testing of various Python scripts for automated archival of interpolated raster images by date in a raster catalog.
- In the process of integrating Python scripts from an already existing model into the simplified model created to export maps generated from files within the ORR geodatabase in PDF format. This is in an attempt to further refine the model to enable users to export maps from an ArcMap document within a specified data frame.
- Developed model using ArcGIS ModelBuilder which iterates through selected features and exports the results in tabular format. This can be utilized to extract model input and output data contained in the geodatabase such as groundwater level, discharge and mercury concentration. Once the feature (e.g. GW well or outfall) has been selected, a field attribute such as station name is used to extract all the data for that station and export it as a .dbf table which can be opened using MS Excel.
- This model is currently being extended and refined to enable greater functionality by developing new or modifying and incorporating existing Python scripts for statistical analysis of the exported data. This will be especially useful for extracting and analyzing timeseries data used in the EFPC model. Once the model is completed, a ModelBuilder workflow diagram will be generated and documented.

- Continued with the development Python Scripts to extend and refine model by enabling data to be extracted from the ORR geodatabase and saved/exported as Excel or .txt files.
- A toolbox was implemented in ArcGIS which uses the scripts to analyze water stages in rivers, flow rates, groundwater levels and water quality data from wells and rivers.
- The toolbox was tested extracting and analyzing timeseries data used in the EFPC model. Once the model is completed, a ModelBuilder workflow diagram will be generated and documented.

Task 5: Student Support for Modeling of Groundwater Flow and Transport at Moab Site

Task 5 Overview

FIU, in collaboration with the DOE's Moab site, is using an existing groundwater numerical model to evaluate the tailings pore-water seepage in order to assist in effective dewatering of the tailings pile and to optimize the groundwater extraction well field as part of the DOE Uranium Mill Tailings Remedial Action (UMTRA) for the Moab site. The work was carried out with support from student interns who assisted in the collection of groundwater samples and site data and applied the existing groundwater and transport model (SEAWAT available from the public domain) to analyze the groundwater flow and transport data of the Moab site. The objective of this model is to analyze the nitrogen and uranium cycle in the environment and provide forecasting capabilities for the fate and transport of contamination within the Moab site and to provide information which can be used to determine the efficiency of remedial actions in reducing the concentration and load of contaminants and to assist DOE in deciding the effectiveness of remedial actions. Modeling is to be performed with MODFLOW, SEAWAT and FEFLOW as a benchmark. The main objective is to determine the effect of discharge of a legacy ammonia plume from the brine zone after the extraction wells and injection system have been shut off. The model will be used to predict capture zones for different operating scenarios, mass removal; and time to complete remediation.

Task 5 Quarterly Progress

- Summarized the analysis of the gravimetric moisture contents of more than 70 tailing samples at Moab for modeling. Using the data for unsaturated flow at the mine tailings. The hydrological model provided calculation about the distribution of moisture content in the soil column as a function of precipitation.
- The numerical model was modified to provide capabilities for analysis of the fluctuation of moisture content which was determined on a daily basis at different soil column heights. The purpose was to provide information about the exchange of flux between the unsaturated and saturated zones and therefore gain a better understanding of the vertical contaminant fluxes from the mine tailings to the subsurface flow, and subsequent horizontal transport to the river.
- Additional simulations were conducted to determine the transient drainage of moisture in the tailings by quantifying the vertical downward fluxes which are a result of drainage of the mine tailings.

- The model simulations were used to determine the fraction of precipitation infiltrating the tailings, the extent of infiltration, and the fraction of surface runoff during precipitation events.
- A series of probability exceedance figures were developed for each selected tailings layer to provide understanding of the behavior of the tailings during wet, median and dry conditions.
- The paper which was submitted to WM 2013 was additionally revised. The simulations were used to understand the dynamics of the system and changes in moisture and moisture flux. The following conclusions were derived:
    - The analysis considered the stochastic variation of all hydrological events that control flow and transport at the site. A unique modeling approach simulated the daily climatic conditions and determined the changes in moisture and moisture flux from the disposal cell for a period of ten years.
    - Modeling results indicated that increases in the saturated conductivity at the top of radon barrier do not influence flux from the tailings with time because the tailings behave similar hydraulically to the radon barrier.
    - The presence of a thin layer of low conductivity material anywhere in the cover or tailings restricts flux in the worst case to the saturated conductivity of that material. Furthermore, the precipitation is equivalent to the evapotranspiration losses from the surface layer.
    - Where materials are unsaturated at depth within the radon barrier of tailings slimes, conductivities are typically less than 10-8 centimeters per second.
    - If the low conductivity layer is deep within the disposal cell, its saturated properties are less likely to change with time.
    - The model confirmed the following trends:

        a) Infiltration and evapotranspiration: The accumulated infiltration is equivalent to the accumulated evapotranspiration, resulting in no water reaching the groundwater tailings under the conditions simulated (daily precipitation and evapotranspiration). In general, for the hydrologic conditions at the site, the water from precipitation infiltrates in the shallow surface zone, where it is lost from evapotranspiration.

        b) Extent of Infiltration: At a depth of 0.7 ft in the rip-rap layer (1st layer) the moisture content is very low, implying that there is a low possibility of water reaching past that layer (hydraulic conductivity is in the order of 10-10 m/s).

        c) Vegetation: The vegetation affects the rate of evapotranspiration, increasing the amount of evaporation thus reducing the amount of water that infiltrates through the layer.

        d) Land cover: The rip-rap rock cover variations in hydraulic conductivity ranges from 10^{-6} to 10^{-4}. There is no concern that rock rip-rap is increasing percent saturations and downward moisture flux.

- The significance of this modeling approach is that the stochastic variations of a variety of hydrologic events are taken under consideration and provide a better understanding of the flow and transport within the site. Therefore, both the operation and the maintenance of the disposal cells can be minimized if they are allowed to progress to a natural condition with some vegetation and soil genesis. Because the covers and underlying tailings have a very low saturated hydraulic conductivity after transient drainage, eventually the amount of moisture leaving the tailings has a negligible effect on groundwater quality. Although some of the UMTRA sites are not in compliance with the groundwater standards, the explanation may be legacy contamination from mining, or earlier higher fluxes from the tailings or unlined processing ponds. Investigation of other legacy sources at the UMTRA sites may help explain persistent groundwater contamination.
- A progress report was submitted which described the simulations and the main aspects of the model:
    - The existing model was revised and updated with additional information related to the current remedial actions which include injection, well withdrawal, and simulating the fate and transport of contaminants, including uranium and ammonia, in the subsurface domain at the Moab site in Utah and how density dependent flow is related to brines in the groundwater system beneath the site. Information such as ammonia surface water data collected between 2000 and 2002 were used in the analysis.
    - The existing Moab model was updated by implementing geostatistically interpolated ammonia and uranium plumes and current well operation data into the model to evaluate the effects of pumping on contaminant concentrations and determining potential surface water concentrations in riparian habitat areas for a range of operating conditions. The plumes of aqueous species of concern (nitrate, uranium) were developed with the width of the tailings that would be conservative.
    - After implementing plumes into the model as initial conditions, additional simulations were conducted to optimize mass removal and capture from the existing system. The ammonia transport was simulated by applying as a initial condition the ammonia plume (for a couple of cycles), and determining the yearly rise and fall in the river to determine if the ammonia concentrations moving up into the brine zone is due to the fluctuations of concentrations in the river.
    - The effects of the brine zone beneath the site on an overlying saline zone and the effect of discharge of a legacy ammonia plume from the brine zone after the extraction wells and injection system have been shut off and the spatial extent of the discharge zone for the ammonia legacy plume in the brine zone and its effect on natural flushing were determined.
    - A diversion ditch was added to intercept and extract water from the tailings. The ditch was implemented into the flow model (as drain cells) and by setting the head, levels will be set in each drain cell at the elevations of the drains.

- A new configuration was implemented that includes infiltration and provides information about the reoccurrence of the concentrations within the recharge assuming the existence of a freshwater lens.

- The effect of mixing water from the river and the diversion ditch was determined along with the benefits of running a diversion ditch and well extraction at the same time.

Milestones and Deliverables

The milestones and deliverables for Project 3 are shown in the following table. Milestone 2012-P3-M5.1 was completed and a summary of the Moab model's preliminary results sent via email to the relevant DOE personnel. A journal article entitled "Migration of VOC Plume in the Subsurface Domain at the Y-12 National Security Site" was also submitted and accepted by the Journal of Remediation, contributing to Milestone 2012-P3-M8.1 "Submit publications to relevant journals" which will be an ongoing process as research continues throughout 5/17/2013. Announcement of all conference papers and journal articles will be submitted to OSTI once published. Milestone 2012-P3-M1.2 was completed and a summary of the XPSWMM model's preliminary results was sent via email to the relevant DOE personnel.

FIU Year 3 Milestones and Deliverables for Project 3

Task	Milestone/ Deliverable	Description	Due Date	Status	OSTI
Task 1: EFPC Model Update, Calibration, Uncertainty Analysis	2012-P3-M1.1	Finalize XPSWMM model preliminary configuration parameters	9/14/2012	Completed	
	2012-P3-M1.2	XPSWMM model preliminary results summary	11/16/2012	Completed	
	Deliverable	Technical Report for the EFPC Simulations	3/1/2013	On Target	OSTI
Task 2: Simulation of NPDES- and TMDL-Regulated Discharges from Non-Point Sources for the EFPC and Y-12 NSC	2012-P3-M2.1	Presentation overview to DOE ORO/DOE HQ of the project progress and accomplishments	9/21/2012	Completed 8/21/2012	OSTI
	Deliverable	Technical Report for Simulation of NPDES and TMDL for EFPC and Y-12 NSC	4/16/2013	On Target	OSTI
Task 3: Parameterization of Major Transport Processes of Mercury Species	2012-P3-M3.1	Preliminary results summary of laboratory experiments	1/18/2013	On Target	
	Deliverable	Technical Report for the Parameterization of Major Transport Processes of Mercury Species	2/18/2013	On Target	OSTI
Task 4: Geodatabase Development for Hydrological Modeling Support	2012-P3-M4.1	Sample Python scripts and Model Builder process workflow diagram	2/1/2013	On Target	
	Deliverable	Technical Report for Geodatabase Development for Hydrological Modeling Support	4/1/2013	On Target	OSTI

Task 5: Student Support for Modeling of Groundwater Flow and Transport at the Moab Site, Utah	2012-P3-M5.1	Moab model preliminary results summary	10/19/2012	Completed	
	Deliverable	Technical Report for the Modeling of Groundwater and Flow and Transport at the Moab Site in Utah.	3/19/2013	On Target	OSTI
Project-wide	Deliverable	Draft Project Technical Plan	6/18/2012	Completed	
	2012-P2-M6.1	Waste Management Symposium 2013 abstract(s) submitted	8/17/2012	Completed	OSTI[3]
	2012-P3-M8.1	Submit publications to relevant journals	5/17/2013	On Target	OSTI
	Deliverable	Draft Year End Report	6/28/2013	On Target	OSTI
	Deliverable	Quarterly Status and Progress Summary Reports	Quarterly	On Target	

Work Plan for Next Quarter

- Task 1:
  - ***Subtasks 1.1 & 1.2***
    - Conduct the following:
      a. Simulations for flow
      b. Simulations for water quality
      c. ECOLAB simulation with no mercury input
      d. ECOLAB simulation with mercury concentration
      e. Simulated results comparison to observed data
      f. Modification of ECOLAB parameters as needed
      g. Additional simulations & calibration of ECOLAB parameters (if applicable)
    - Analysis/Result Comparison to Observed Data
      a. Stochastic Analysis of mercury load reductions effects
      b. Probability Exceedence Curves
  - ***Subtask 1.3a:***
    - Complete the evaporation portion of the sensitivity analysis.
    - Run 5, 10, 25, 100-year design storm simulation, analyze HGL, and suggest improvements if needed.
    - Introduce conservative contaminant into system at 10 varying locations.

[3] Announcement of published journal or conference paper will be submitted to OSTI

- Enter flow rate and concentration of conservative contaminant data into MATLAB in order to produce hydrographs and pollutographs for concentrations and loads as well as probability exceedance curves for the nodes. In addition, MATLAB will fit the data hydrographs and pollutographs to probability distribution functions.
- Complete hydrology and transport analyses and generate probability exceedance curves. This information will be incorporated as chapters of a graduate student thesis being conducted based on this research.

- ***Subtask 1.3b:***
  - Y-12 XPSWMM model
    - Use the provided data, if available, to calibrate and validate the model.
    - Conduct the Hg or contaminant transport studies, by integrating the sanitary mode into the model, using XPSWMM.
    - Run the model for different scenarios (different return period of rainfall).
  - Experimental work to determine the Hg selectivity coefficients (Ion Exchange) will be conducted at ORNL.
    1. To review previous studies for the different approaches to calculating the selectivity coefficient for Hg:
       a. Gaines & Thomas method
       b. Gapon method
       c. Vanselow method
    2. To determine Hg selectivity coefficient for Hg/cation sorption on the sedimentary minerals that are typically present in EFPC streambed (e.g. Clay, Kaolinite, etc.):
       a. Determine the selectivity coefficient for Hg/Ca ($K_{Hg/Ca}$).
       b. Determine the selectivity coefficient for Hg/Mg ($K_{Hg/Mg}$).
  - Mercury Bead Dissolution - Literature Review.
    1. To review previous studies and provide a mechanism of the processes controlling dissolution of mercury beads.
    2. To review previous studies reporting the conditions (or flow rates) for which the external diffusion process controls the dissolution rate (is rate limiting process):
       a. Determine the flux (W) and mass transfer coefficient (k_c) (between the outer layer and the bead surface) assuming validity of Fick's law.
       b. Determine the diffusivity of Hg, D_{Hg}, using the Frossling's correlation.

c. Construct the dissolution rate profile as a function of velocity (determine the effect of external diffusion).

3. To review previous studies reporting the conditions (bead particle size) for which the internal diffusion process controls the dissolution rate (is rate limiting process):
    a. Determine the internal diffusion coefficient (k_i).
    b. Determine effective diffusivity, D_e, respected to Fick's law.
    c. Determine the Thiele modulus which is a measure of the ratio of surface reaction rate to rate of diffusion through the mercury bead.
    d. Construct the concentration profile as function of the mercury bead particle size.
    e. Construct the rate profile as function of mercury bead particle size.

- Modeling will be conducted at ORNL using the PHREEQC model.
    1. To enhance the Hg database of the PHREEQC geochemical model by adding the experimental results (dissolution rate and ion exchange) into the model database.
    2. To evaluate and investigate the effects of mercury bead dissolution and sorption (Hg/cation exchange) on Hg fate and transport in EFPC.
    3. To provide a series of simulations using the enhanced PHREEQC model.

- Submit Deliverable "Technical Report for the EFPC Simulations", due 3/1/2013.

- Task 2:
    - Conduct 10 additional simulations with the EFPC model and provide analysis of the hydrologic conductivity of the Nolichucky Shale (mostly limestone and sandstone) on the exchange of contaminants with the river (EFPC).
    - Determine the flow in the unsaturated zone and the exchange between saturated and unsaturated zones during a range of stormwater events and provide information about the contaminant exchange between the two zones.
    - Provide analysis of the hydrologic regimes of Bear Creek and East Fork Poplar Creek, determine the extent of the floodplain and compare the published GIS data with flood maps and the model computed values. Analyze the extent of mercury contamination in the floodplain.
    - Summarize the simulations and the work of this task into a report.
- Task 3:
    - Submit Milestone 2012-P3-M3.1 "Preliminary results summary of laboratory experiments" due 1/18/2013.
    - Submit Deliverable "Technical Report for the Parameterization of Major Transport Processes of Mercury Species", due 2/18/2013.

- A new technique, isotope dilutions (ID)-phenylation-purge and trap-ICP-MS will be developed for analyzing organomercury species at trace levels. The detection limit and recovery of this technique will be determined. Application of this method in analyzing organomercury species in natural water, sediment, and fish samples will be conducted.
- The developed isotope dilution technique ($^{199}Hg^{2+}$) will be coupled with the isotope addition ($^{201}Hg^{2+}$) technique and used to simultaneously measure the dissolution of cinnabar and re-adsorption of released Hg^{2+} on cinnabar.
- A paper regarding the influence of thiols on cinnabar dissolution will be drafted.

- Task 4:
  - Submit Milestone 2012-P3-M4.1 "Sample Python scripts and Model Builder process workflow diagram" due 2/1/2013.
  - Conduct literature and Internet search of downloadable GIS freeware that can be used for querying the ORR geodatabase online.
  - Develop & test methodology for querying ORR geodatabase via online GIS freeware.
- Task 5:
  - Submit Deliverable "Technical Report for the Modeling of Groundwater and Flow and Transport at the Moab Site in Utah", due 3/19/2013.
  - Schedule a visit to the site to provide a presentation of work which was completed and discuss additional work with the model.
  - Extend the simulation period of the current model to 100 years and conduct long term simulations for each of the scenarios completed in the previous quarter.
  - Extract and analyze simulation data.
  - Summarize the simulations and the analysis and update the progress report.
- Project-wide:
  - Several papers and poster abstracts have been submitted to the Waste Management Symposium 2013 related to this project work. Staff and students will be attending and presenting their research at the conference Feb 24-28, 2013.

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 or international efforts being conducted by EM-2.1 with the Nuclear Decommissioning Authority (NDA) in England and the International Atomic Energy Agency (IAEA). Efforts on this project for FIU Year 3 include the following tasks:

- 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)
- An additional task from FIU Year 2, Task 4: IT Support to EM and DOE Sites, did not continue into FIU Year 3.

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

- The final paper related to this project task entitled, *Waste Information Management System with 2012-13 Waste Streams*, was submitted to the Waste Management Symposium 2013. Announcement of the conference paper will be submitted to OSTI once published.
- Performed database management, application maintenance, and performance tuning to the online Waste Information Management System (WIMS) in order to ensure a consistent high level of database and website performance.

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

Task 2 Overview

For FY12 (FIU Year 3)**,** FIU will focus on assisting DOE EM-13 in meeting the D&D needs and technical challenges around the DOE complex, including the following identified D&D needs: engaging with D&D organizations in the US and abroad to keep current and active in the identification of D&D technologies for the D&D complex as this interaction with DOE sites, DOE-HQ, contractors, focus groups and organizations will lead to the potential selection, evaluation, and deployment of D&D technologies with potential application/insertion to DOE project around the Complex. Information obtained through these efforts will directly benefit the D&D KM-IT performing technology development, demonstrations and deployments such as developing a technology prototype to remotely remove strippable coatings and decontamination gels; supporting Savannah River Site's *in situ* decommissioning efforts by evaluating several sensor network power and data transmission backbones that can be applied to a large-scale grouted structure and reviewing the software-based communication protocols required to gather and analyze data autonomously; collaborating with EFCOG in the development of Lessons Learned and Best Practices; and supporting the EM-2.1 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

- Final versions of two papers were submitted to the Waste Management Symposium 2013. Announcement of the conference papers will be submitted to OSTI once published. The papers include:
    - *Application and Removal of Strippable Coatings via Remote Platform*
    - *Sensor Network Demonstration for In Situ Decommissioning*

- FIU supported the troubleshooting of the ERT system in order to determine the cause of no communication between one of the multiplexers, and the main controller. Several troubleshooting attempts were unsuccessful, which will require that the ERT system be shipped back to INL in the coming weeks. FIU will continue its sensor system efforts with the use of the INL temperature system. The ERT sensor systems can be added later in the performance period. FIU will not include the system from MSU, as no funding is currently available for the sensor PI to provide support and input.
- FIU received approval from INL to integrate the developed Virtual Instruments (VI) with the temperature system. The VI was tested on a small scale local network, and was able to constantly log and display system-generated data.
- FIU received the photovoltaic (PV) system to power the sensor system located in the test cube. The footing design was modified after discussions with civil engineers, who recommended that based on the limited time that the system will be powering the sensor

systems, an alternative footing that can be removed would prove beneficial. With this in mind, a simple 2D Finite Element Analysis (FEA) of the A-frame supporting the PV panels was used to estimate the reaction forces and moments that would be generated by the array under a high wind load. These results were used to develop a system of ground stakes that could be used to support the reaction forces, and mitigate the reaction moments.

- FIU completed the setup and configuration of the photovoltaic (PV) system that will be used to power the ERT/TC system. The PV system will provide power up to 200W continuous, using a 1040W PV array and a 540 AHr battery bank. During testing, a faulty inverter was found on the system, which required that FIU request a new one from the vendor. The system is still operational, and being used to power the thermocouple and active tensionmeter (TC-AT) systems, as well as the weather station, and ancillary networking equipment in the container. FIU will add the ERT system to the PV network when INL can repair the existing communication issues with a faulty multiplexer.
- During this period, FIU continued monitoring the usage and performance of the PV power system to maintain stable operation of the sensor systems continuously. The PV system has encountered a generated two low-battery faults on the system during the course of operation; this was due to a 5-day period of cloudy weather (i.e. maximum PV array output less than 500 W). In order to allow for the batteries to fully charge, the ERT system was shut down for two days. This allowed the battery bank to charge up to a float mode.
- Also, FIU successfully completed the testing of the TC-AT Virtual Instruments (VI) developed in order to capture data from the systems (Figure 4-1). This VI was used to acquire the values, and load them into an array of shared variables that could be accessed through a client application or loaded into an automation industry-standard Open Platform Communications (OPC) server. In addition, the VI was then modified to run on a low-power controller. This controller was also programmed to capture data from the weatherstation and the power system. These datasets were also loaded into shared variables that could be accessed in a similar fashion to the TC-AT data. Finally, the integrated application was used to capture data from all systems in near real-time while all were in operation. The results could be seen on a client VI running on another computer located on another network. This completed the demonstration milestone 2012-P4-M2.1.
- The sensor data network is currently operational, and continues logging system(s) data. The network virtual instruments (VI) are being modified to improve communication, memory management and power management. In particular, the VIs are being modified to control acquisition state and sample rate depending on battery state of charge. This will allow better node autonomy depending on power system state. This will come in useful when the ERT is fully operational, as its use can be reduced depending on power system state.
- Finally, a demonstration report was submitted describing the details of the development and demonstration of the shared data network. This demonstration proved the capacity to develop a low-cost, integrated data network with the existing systems with minimal programming. This capability could be expanded to the other systems on the MSTB, and

can be used to develop an integrated sustainable monitoring system with the capacity to monitor and notify.

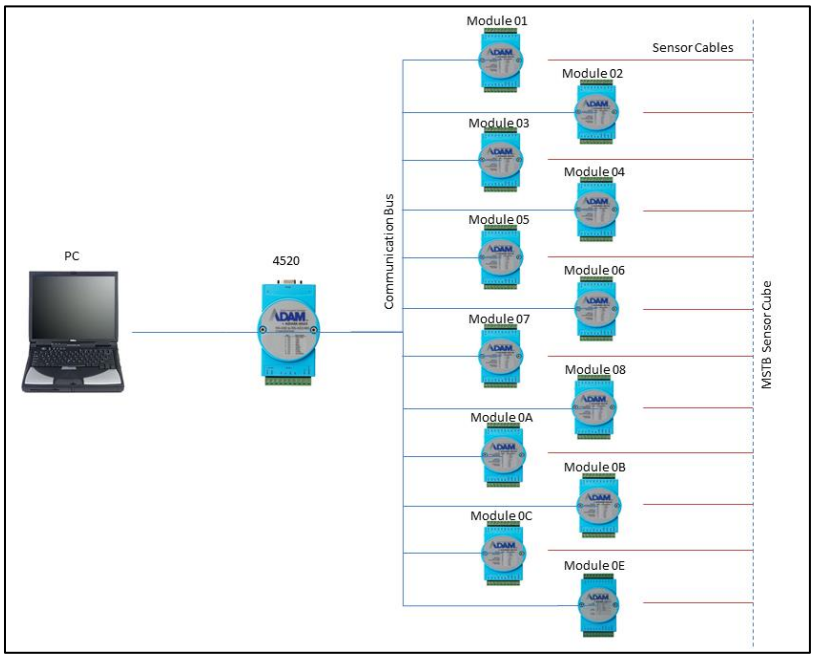


Figure 4-3. Diagram of INL's TC-AT System.

Carryover funding activity

FIU worked with the technology vendor, International Climbing Machine, to complete the Phase II feasibility study for the remote removal of strippable coatings. ICM has completed the testing activities for the Phase II feasibility study and sent a draft results report to FIU. FIU is reviewing the report.

Conclusions of the report include:

1) The brush with vacuum capture was effective at removing both manufacturers' materials tested and at removing them from both concrete and metal surfaces (Figure 4-2). This method is reliable and the average productivity of 45 square feet an hour for the small size brush tested was reasonable for field expectations. A larger, more powerful production brush would yield greater productivity.

Figure 4-2. ICM remote platform using a brush with a vacuum shroud to remove strippable coating from vertical surface.

2) The gripper / scraper method was also effective at removing both manufacturers' materials and at removing them from both concrete and metal (Figure 4-3). This method is particularly fast after an edge has been lifted and, duplicating the actions of a human manually removing the strippable coating, it can be pulled up in sheets. Thus, the average productivity of this method of 75 feet per hour was quite impressive. A tool designed with two gripper / scrapers and possibly an air ejector to help manipulate the sheets of strippable coating being removed will be features built onto a production unit. These features will address certain shortcomings noted in the testing and increase productivity.

Figure 4-3. ICM remote platform with a gripper/scraper tool to remove strippable coatings.

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 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

- The final version of the paper related to this project task entitled, *Knowledge Framework Implementation with Multiple Architectures*, was submitted to the Waste Management Symposium 2013. Announcement of the conference paper will be submitted to OSTI once published.
- Held bi-weekly teleconferences with DOE on project task status and action items.
- Added new vendors to the D&D KM-IT vendor module. As of January 9, the Vendor module includes a total of 601 vendors. Also continued adding technologies to the Technology module from technologies identified in the SRS ISSC newsletters and industry publications. The Technology module includes 549 technologies as of January 9, 2013.
- Search Engine Optimization process continues to be deployed on the D&D KM-IT web application.
- Drafted a 3rd quarter report on the web analytics for the D&D KM-IT website for the period of July through September 2012. The draft report was sent to DOE for review and comment on October 12, 2012. FIU subsequently received and resolved comments from DOE on this report.
- FIU successfully completed the deployment of the D&D Dictionary feature of D&D KM-IT onto the public server on October 25, 2012. The D&D Dictionary is integrated into the training module and allows users the option to list keywords or to view all. The system then displays the summary results with a "continue reading" link to the details page (Figure 4-4).

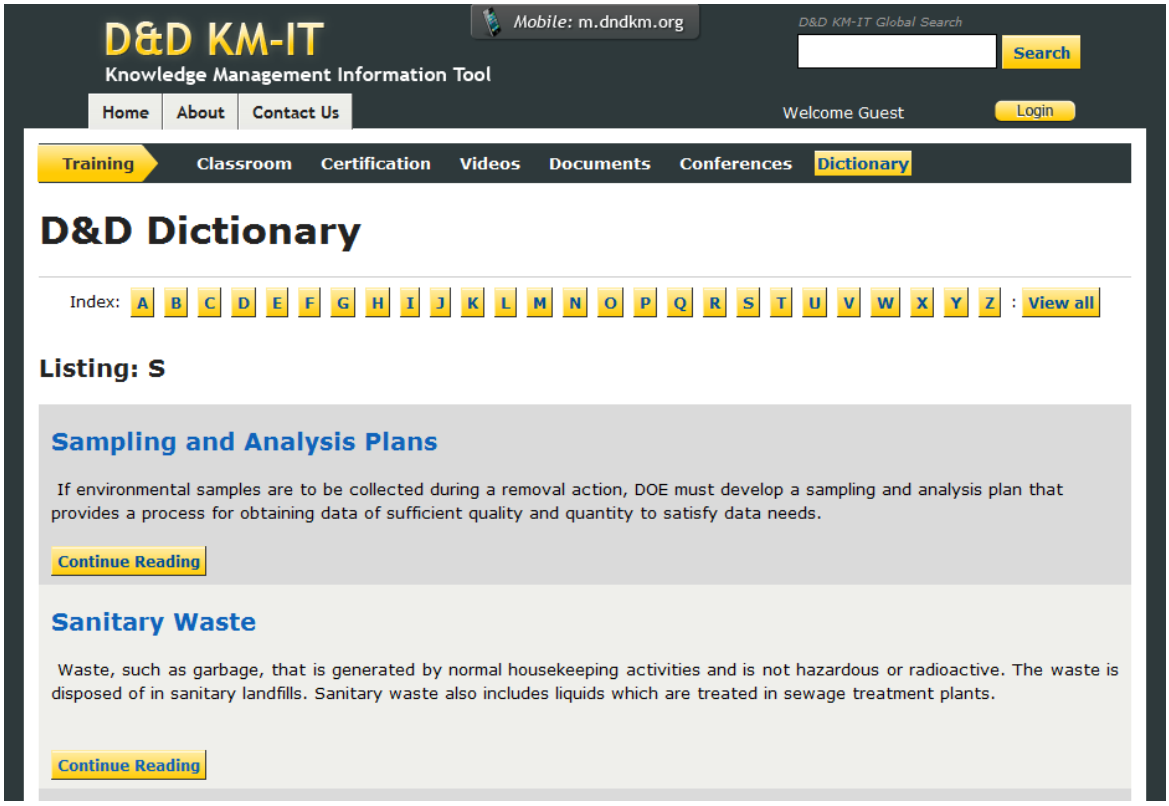


Figure 4-4. New D&D dictionary feature on D&D KM-IT.

- FIU deployed the global search feature onto the D&D KM-IT public server on October 25, 2012. The global search appears in the top right corner of the screen on all modules (Figure 4-5). A user can enter a search keyword and click the search button to be taken to the search screen displaying the matching results. This global search process searches through all the modules of KM-IT, including all the documents and KM-IT webpages.

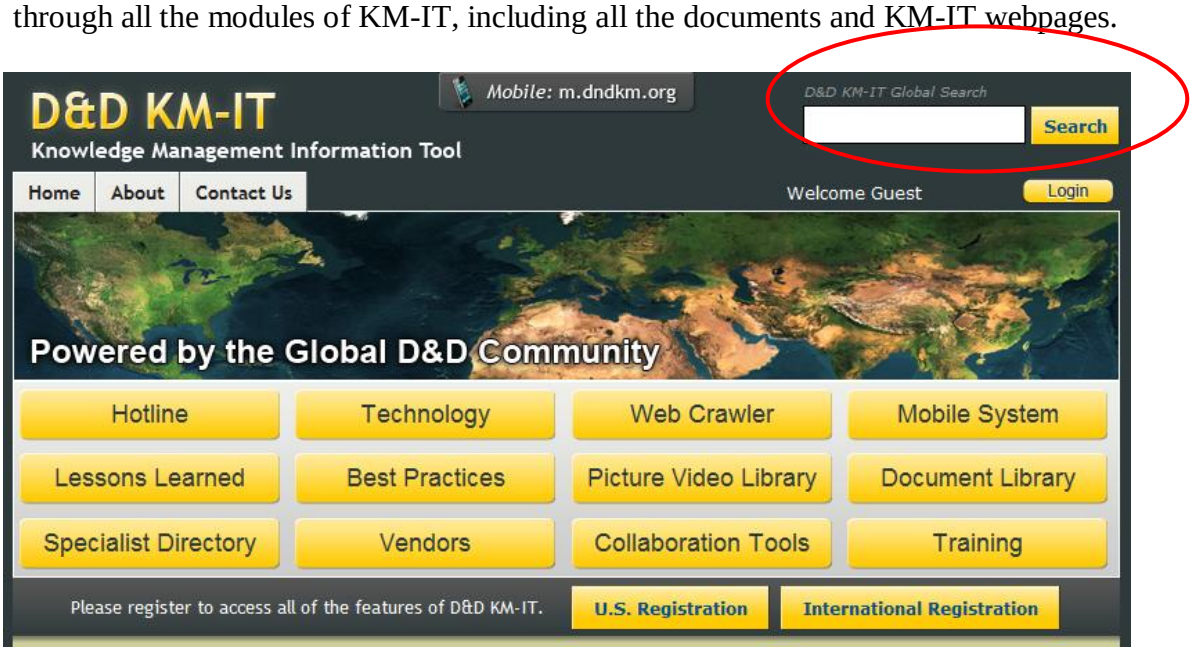


Figure 4-5. Global search feature has been added to D&D KM-IT.

- FIU completed working with Sellafield Ltd on identified areas of collaboration within the scope of D&D KM-IT.
    - Links to D&D KM-IT have been placed on Sellafield internal sites.
    - Technical Centers of Expertise (CoEs) were invited/encouraged to register as subject matter specialist (SMS). The CoEs are Sellafield's community of recognized experts in a range of science and engineering subjects (similar to the subject matter specialists in D&D KM-IT). Four (4) SMS are currently registered from Sellafield Ltd.
    - Sellafield completed their review of the total of 23 D&D-relevant technologies that FIU extracted from the Sellafield report and integrated into KM-IT. These technologies have been made live to the public and can be displayed within the D&D KM-IT system by entering "Sellafield" into the Technology Module search feature.

- FIU successfully completed, deployed and tested the multiple subject matter specialists (SMS) support for the D&D Hotline. With this process, when the user submits the problem, the system administrator receives automatic notification. After reviewing the posted problem, the administrator triggers the multiple SMS emailing process which sends an email to all the registered SMS in the system. Once one or more solutions are received from the SMS, they are published in KM-IT and assigned to the expert who provided the solution.

Carryover funding activity

The D&D KM-IT team requested an audit of the system application and infrastructure by the FIU security team for vulnerability and issues with the system. An audit report was provided by the team And FIU has resolved all of the issues identified. A follow-up internal audit will be performed within the next few months.

The technology module's new template was completed and sent to DOE for review on September 5, 2012 and will be deployed on the public server once DOE review and approval is complete. The new look is based on new HTML5 standards, machine semantic friendly HTML structure, dynamic meta data, and a more intuitive layout with element placement based on Google Analytic data. The data descriptors used are compatible with Google, Yahoo, and Bing search engines. The HTML5 standard used will help future proof the tool as well as provide a more dynamic user experience, such as animations, few page loading events, access to sharing tools, and so on. Once DOE approves of the new template, it will be used throughout the rest of KM-IT to create a unified look and feel, a more dynamic user experience, and better search engine indexing. The new template features more dynamic logins, faster access to other modules via a module list dropdown, greater page width, and larger fonts with type enhancements for more readability.

Mobile development for the D&D KM-IT system is a challenging area because of the existence of multiple platforms, technologies, operating systems and hardware devices in the field. While the mobile application completed for D&D KM-IT last year (for the Vendor and Specialist Directory modules) used the standard web-based development process, FIU realized that a significant amount of research in the technology, platform, development processes and framework, etc., was needed for future D&D KM-IT mobile development. FIU completed the research work needed to establish the best development process for mobile systems which can be implemented in all the future modules of D&D KM-IT. This was done by developing the mobile vendor management module for two additional mobile platforms and evaluating its performance against the current standard web-based system. The best architecture will be used for the development of future D&D KM-IT mobile modules.

Service oriented architecture (SOA) is a development model for building distributed applications in a heterogeneous environment. This model depends on the transfer of messages between services and applications. The request and response messages used in the SOA model are either Extensible Markup Language (XML) or JavaScript Object Notation (JSON). This is a mature, widely distributed model that is now being utilized in mobile device development. To test the performance and viability for implementing the SOA model in the mobile development project for D&D KM-IT, three applications were created. The first, based on jQuery (a widely used JavaScript library), sends and receives messages via Asynchronous JavaScript and XML (AJAX); the second application is an ASP.NET C# application that interacts with the service via request made on the server hosting the application; the third application was built using the Android Operating System's (OS) environment, sending and receiving messages via a multithreaded send/receive class. The two former applications are accessible on mobile devices via the web browser, the latter is an application that runs locally on the device; all of the applications utilize the cloud to send and receive messages. The results of this test conclude that the native application running on the Android OS outperforms the other two applications by large margins. However, its viability is limited as there is a much higher development cost and upkeep compared to a browser based application. When comparing the two browser-based applications, the clear winner is the ASP.NET C# application; the ability for computation to be done on the server creates a very noticeable performance gap between it and the jQuery AJAX application. These results will ensure that the development process and environment used in the D&D KM-IT Mobile Application meet or exceed the standards and requirements of the D&D KM-IT. A draft summary report with the results for the mobile development research was completed and sent to DOE on 12/14/12. Figure 4-6 shows the client-server interaction between the different development methods.

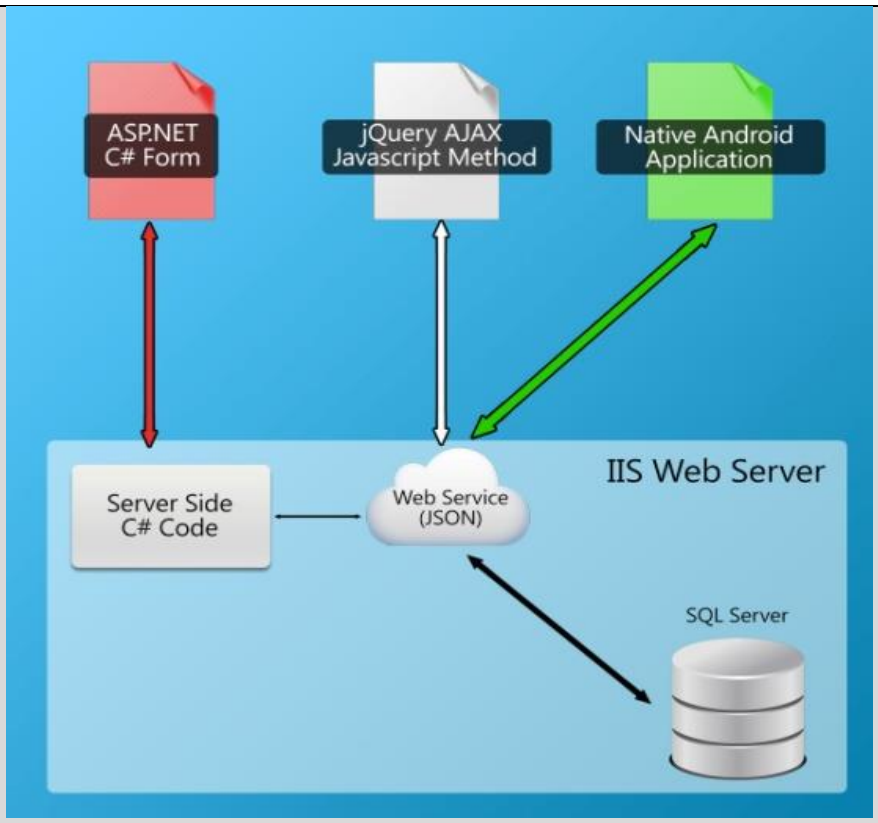


Figure 4-6: Client- Server interaction between different development methods

Milestones and Deliverables

Milestone 2012-P4-M2.1, marking the completion of the meso-scale testbed system demonstration, was completed on 11/23/12. In addition, milestone 2012-P4-M3.5, deployment of the multiple SMS support for the D&D Hotline, was completed on 11/15/12.

A deliverable for Task 2, a draft technical report for the meso-scale testbed system demonstration, was completed and submitted to DOE on 12/22/12. This report will be submitted to OSTI once it is finalized. In addition, a deliverable for the Task 3 draft summary report for mobile development research was completed and submitted to DOE on 12/14/12.

FIU Year 3 Milestones and Deliverables for Project 4

Task	Milestone/ Deliverable	Description	Due Date	Status	OSTI
Task 1: Waste Information Management System (WIMS)	2012-P4-M1.1	Import 2012 data set for waste forecast and transportation data	Within 60 days of receipt of data from DOE	Completed	
	2012-P4-M1.2	Import 2013 data set for waste forecast and transportation data	Within 60 days after receipt of data from	On Target	

			DOE		
	2012-P4-M1.3	Waste Management Symposium 2013 abstract submitted	08/17/2012	Completed	OSTI[4]
Task 2: D&D Support to DOE EM for Technology Innovation, Development, Evaluation, and Deployment	2012-P4-M2.1	Completion of Meso-Scale Testbed System Demonstration	09/30/2012 Re-forecasted to 11/23/2012	Completed	
	2012-P4-M2.2	Completion of preliminary prototype technology evaluation for remote removal of strippable coatings	04/26/2013	On Target	
	2012-P4-M2.3	Waste Management Symposium 2013 abstract submitted	08/17/2012	Completed	OSTI[5]
	Deliverable	Lessons Learned and Best Practices	30 days after final DOE/EFCOG approval	On Target	
	Deliverable	Draft technical reports for demonstrated technologies	30-days after evaluation/demo	On Target	OSTI
	Deliverable	Draft Tech Fact Sheet for technology evaluations/ demonstrations (ICM crawler)	30-days after evaluation/demo	On Target	
Task 3: D&D Knowledge Management Tool (D&D KM-IT)	2012-P4-M3.1	Deployment of SRS ISSC report integration to DOE for review/testing	07/13/2012	Completed	
	2012-P4-M3.2	Deployment of global search feature to DOE for review/testing	08/17/2012	Completed	
	2012-P4-M3.3	Waste Management Symposium 2013 abstract submitted	08/17/2012	Completed	OSTI[6]
	2012-P4-M3.4	Deployment of D&D dictionary module to DOE for review/testing	09/28/2012	Completed	
	2012-P4-M3.5	Deployment of the multiple SMS support for the D&D Hotline	11/16/2012	Completed	
	2012-P4-M3.6	Deployment of picture lite mobile application to DOE for review/testing	01/18/2013	On Target	
	2012-P4-M3.7	Deployment of technology lite mobile application to DOE for review/testing	02/15/2013	On Target	
	2012-P4-M3.8	User interface enhancement completion	04/12/2013	On Target	
	2012-P4-M3.9	Help videos development complete and sent to DOE for review	05/17/2013	On Target	
	Deliverable	Draft Summary Report for Mobile Development Research	12/14/2012	Completed	
	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 new module deployed	On Target	
Project Wide	Deliverable	Draft Project Technical Plan	6/18/2012	Completed	
	Deliverable	Draft Year End Report	06/28/2013	On Target	OSTI
	Deliverable	Quarterly Progress Reports	Quarterly	On Target	

[4,5,6] Announcement of published journal or conference paper will be submitted to OSTI

Work Plan for Next Quarter

- All tasks: present technical papers to the Waste Management Symposium
- Task 1: Determine expected delivery date from DOE of the 2013 data set for waste forecast and transportation data for WIMS.
- Task 2: Finalize report for meso-scale testbed system demonstration.
- Task 2: Finalize report for Phase II feasibility study for the remote removal of strippable coatings.
- Task 3: Deploy lite mobile applications for picture module and technology module to DOE for review/testing.

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 Student Career Experience Program (SCEP) or by getting directly hired by DOE contractors.

Project 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. Also, 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.

- The DOE Fellows finalized their DOE Fellows Summer Internship Reports (milestone 2012-P5-M4) which were sent to DOE on 10/19/12 (deliverable). These reports will also be submitted to OSTI. The table below shows the DOE Fellows, summer mentors, and report titles.

DOE Fellow	DOE Site/ National Lab/ Contractor	Location	Mentor	Technical Report Title
Janty Ghazi	DOE-HQ EM-23 (Tank Farm Program)	Washington, DC	James Poppiti	Hydrogen in Pipes and Ancillary Vessels (HPAV)
Claudia Cardona	DOE-HQ EM-12 (Soil/Groundwater	Washington, DC	Kurt Gerdes	Database of Groundwater Pump-and-Treat Systems

	Remediation			
Joshua Midence	Savannah River Site	Aiken, NC	Alex Cozzi	Saltstone Processing of Low-Level Waste at Savannah River Site
Eric Inclan	Oak Ridge National Laboratory	Oak Ridge, TN	Dr. Prashant Jain	Development of Pre-processing Software for Lattice Boltzmann Fluid Dynamics Solver
Jaime Mudrich	Oak Ridge National Laboratory	Oak Ridge, TN	Dr. Prashant Jain	Development of a Parallel, 3D, Lattice Boltzmann Method CFD Solver for Simulation of Turbulent Reactor Flow
Heidi Henderson	Oak Ridge National Laboratory	Oak Ridge, TN	Dr. Eric Pierce	Analysis of Oak Ridge National Laboratory Outfall 211 Contributing Drainage Areas
Revathy Venkataraman	Y-12 National Security Complex	Oak Ridge, TN	Emma Jones/ Jessica Metcalf	Y-12 EMBOS Medical Lab Interface Batch Loader
Ximena Prugue	Washington River Protection Solutions, Hanford Site	Richland, WA	Leo Thompson	Development of Mechanical Systems for Dry Retrieval of Single Shell Tank Waste at Hanford
Robert Lapierre	Pacific Northwest National Laboratory	Richland, WA	Dr. Dawn Wellman	Single Pass Flow-Through Testing of Metals
Lillian Marrero	Sullivan International Consulting	Chicago, IL	Jennifer Knoepfle	An Evaluation of Volatile Organic Compound Contamination at Two Superfund Sites
Elicek Delgado	Sullivan International Consulting	Chicago, IL	Jennifer Knoepfle	Metal Remediation of the Zinc Site

- Milestone 2012-P5-M5 was accomplished by the completion of DOE Fellows Fall 2012 recruitment process; more than 15 applications were received and evaluated. The table below shows the list of recruited DOE Fellows, class of 2012.

Name	**Major**
Nicole Anderson	Graduate Civil Engineering
Jennifer Arniella	Under Grad Mechanical Engineering
Francisco Bolanos	Under Grad Mechanical Engineering
Dania Castillo	Under Grad Civil Engineering
Dayron Chigin	Under Grad Electrical Engineering
Robert Lapierre	Under Grad Chemistry

Joel McGill	Graduate Environmental Engineering
Lucas Nascimento	Under Grad Electrical Engineering
Raul Ordonez	Under Grad Electrical Engineering
Valentina Padilla	Under Grad Environmental Engineering
Mariela Silva	Graduate Engineering Management
Gabriela Vazquez	Under Grad Mechanical Engineering
Revathy Venkataraman	Graduate Information Technology

- The DOE Fellows Poster Exhibition and Competition was held on October 17, 2012 (Figures 5-1 and 5-2). It showcased the research accomplishments of DOE Fellows in the areas of High-Level Waste, Soil and Groundwater, Deactivation & Decommissioning (D&D), and Information Technology (IT). Winners of the competition were announced at the DOE Fellows Induction Ceremony. Poster titles are shown in the table below.

DOE Fellow	**Poster Title**
Jennifer Arniella	High-Level Waste Pipeline Unplugging Technologies Asynchronous Pulsing System
Francisco Bolanos	Multiple-Relaxation-Time, Lattice Boltzmann Model for High-Density Ratio, Multiphase Flows
Claudia Cardona	The Effect of Ca Ions on the Removal of U(VI) at the Hanford Site 200 Area
Dania Castillo	Computational Simulation and Evolution of HLW Pipeline Plugs
Elicek Delgado-Cepero	Battery-less Wireless Sensors for Structural Health Monitoring for In Situ Decommissioning Tasks
Janty Ghazi	Hydrogen in Pipes and Ancillary Vessels
Heidi Henderson	ORNL Outfall 211 Stormwater Discharge and Chlorine Transport Model
Eric Inclan	Optimization of Asynchronous Pulsing Unit Operation
Robert Lapierre	Single Pass Flow-Through Testing of Metals
Lilian Marrero	An Evaluation of Volatile Organic Compound Contamination at Two Superfund Sites
Joel McGill	Degradation of Grout: Compressive Strength Comparative Analysis
Joshua Midence	Salt Stone Processing of Low Level Waste at Savannah River Site
Carol Moreno	Uranium Remediation in the Hanford 200 Area by In Situ Subsurface pH Manipulation Using NH3 Gas
Jaime Mudrich	PaRAllel Thermal-Hydraulics simulations using Advanced Mesoscopic methods
Lucas Nascimento	Acoustic Pulse Reflectometry For Identifying Pipeline Properties
Raul Ordonez	Sensor Network Energy Demand

Ximena Prugue	Development of a Mechanical-Based System for Dry Retrieval of Single Shell Tank Waste at Hanford
Paola Sepulveda	Investigation on Microbial Dissolution of Uranium (VI) from Autunite Mineral
Gabriela Vazquez	Peristaltic Crawler for Removal of High-Level Waste Plugs in Pipelines
Revathy Venkataraman	D&D Technology Services Development using Windows Communication Foundation on Cloud

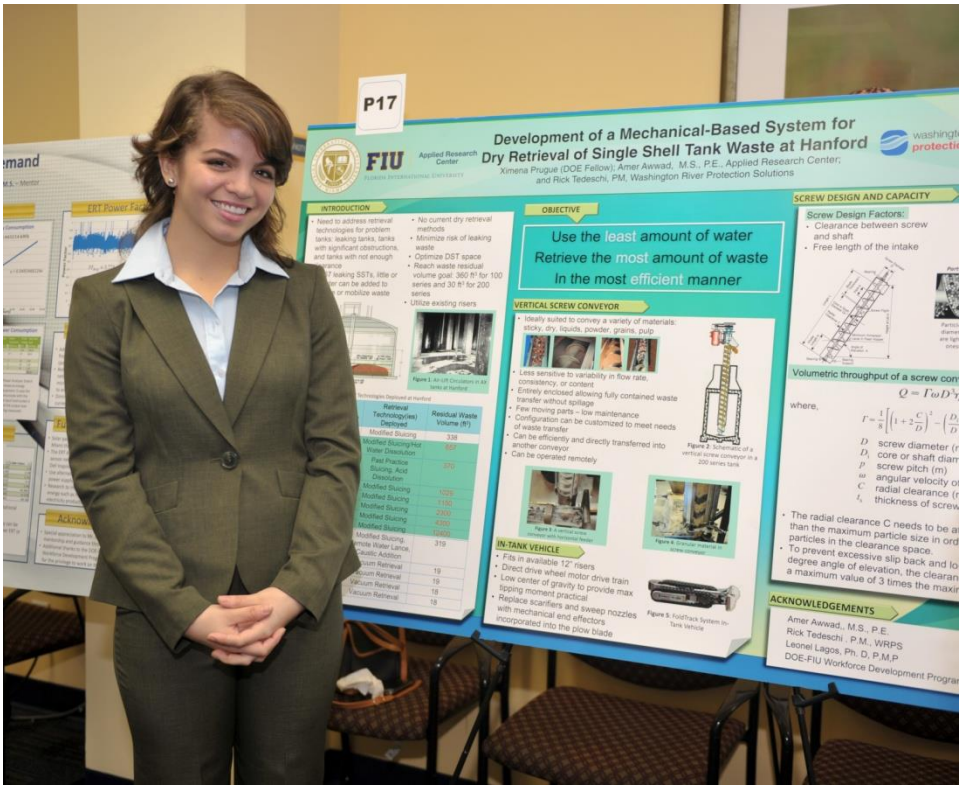


Figure 5-1. DOE Fellow Ximena Prugue presenting her research work at the 2012 Poster Exhibition and Competition

Figure 5-2. DOE Fellow Lucas Nascimento presenting his research work at the 2012 Poster Exhibition and Competition

- The Nuclear Decommissioning Report from the United Kingdom, in its September/October issue, published an article titled "DOE Fellows training the future workforce of scientists and engineers for DOE-EM", where the partnership between Florida International University and DOE is featured as a successful program in which FIU minorities students are specially mentored and trained to join the DOE workforce. Besides explaining the objectives of the program, the article emphasizes the accomplishments of the program and the challenges faced by the DOE Fellows as well.

- On November 13, 2012, Florida International University's (FIU's) Applied Research Center (ARC) conducted the sixth (6th) annual DOE Fellows Induction Ceremony. This year, Ms. Alice Williams (Associate Principal Deputy Assistant Secretary for the U.S. Department of Energy Office of Environmental Management) was one of the keynote speakers for the ceremony. Ms. Williams welcomed the FIU students to the DOE Fellows program and noted the impressive level of knowledge and skills they already possess.

  Other distinguished guests included Ms. Rosa Elmetti (DOE EM International Program) and Mr. Lee Brady (DOE EM D&D and Facility Engineering), both DOE Fellow alumni Class of 2008 who have successfully secured employment with DOE EM. FIU was represented by Dr. Elizabeth Bejar (Vice Provost for Academic Affairs), Dr. E. George Simms (Director of Pre-Collegiate Programs and Grants), Dr. John Proni and Dr. Ines Triay (ARC Executive Directors), and Dr. Leonel E. Lagos (DOE Fellows Program Director), Dr. Kevin Cooper (Indian River State College – Nuclear Education and Training Center), as well as FIU faculty, staff, and students.

Ms. Williams, Ms. Elmetti and Mr. Brady had the opportunity to participate in morning tours of the ARC research laboratories and listen to DOE Fellows presenting their research work. Presentations were given by Dr. Lagos and DOE Fellows Lilian Marrero and Jaime Mudrich. Dr. Lagos presented an update on the DOE-FIU Cooperative Agreement, the DOE Fellows program, the D&D KM-IT web-based knowledge management system, and the newly developed DOE-FIU Cooperative Agreement website dedicated to the DOE-EM research being conducted at ARC. Lilian Marrero presented her EM research and thesis on "Improvements in the Suspended Sediment Interactions Module of An Integrated Flow and Mercury Transport Model for East Fork Poplar Creek Watershed, Oak Ridge, Tennessee" and Jaime Mudrich presented his EM research and thesis on "Development of a LBM-Based Multiphase Simulation Tool to Model Pulsed-Air Tank Mixing." Tours of the ARC facilities included visits to the radiological and composites laboratories as well as technology demonstrations in the multifunction assessment facility (i.e., high bay) of some of the more large-scale DOE projects. Technologies showcased included the experimental design and setup of wireless sensors for in situ decommissioning and evaluation of the sensor network energy demand; evaluation of pipeline unplugging instrumentation and technologies for Hanford (e.g., a peristaltic crawler for pipeline unplugging); and experiments related to soil & groundwater research for Hanford's uranium contamination. In addition, the distinguished guests and FIU faculty had the opportunity to interact with the DOE Fellows during a poster exhibition following the induction ceremony.

During this year's Induction Ceremony, 13 new FIU minority students were inducted as DOE Fellows.

- Nicole Anderson (Graduate, Civil Engineering)
- Jennifer Arniella (Undergraduate, Mechanical Engineering)
- Francisco Bolanos (Undergraduate, Mechanical Engineering)
- Dania Castillo (Undergraduate, Civil Engineering)
- Dayron Chigin (Undergraduate, Electrical Engineering)
- Robert Lapierre (Graduate, Chemistry)
- Joel McGill (Graduate, Civil Engineering)
- Lucas Nascimento (Undergraduate, Electrical Engineering)
- Raul Ordonez (Undergraduate, Electrical Engineering)
- Valentina Padilla (Undergraduate, Environmental Engineering)
- Mariela Silva (Graduate, Engineering Management)
- Gabriela Vazquez (Undergraduate, Mechanical Engineering)
- Revathy Venkataraman (Graduate, Information Technology)

In addition, awards were presented to the DOE Fellows that won the DOE Fellows Poster Exhibition and Competition held on October 17, 2012. First place went to Mr. Jaime Mudrich for his poster titled, "PaRAllel Thermal-Hydraulics Simulations using Advanced Mesoscopic Methods." Second place went to Ms. Elicek Delgado-Cepero for her poster titled "Battery-less Wireless Sensors for Structural Health Monitoring for In Situ Decommissioning Tasks." Third place went to Ms. Ximena Prugue for her poster titled

"Development of a Mechanical-Based System for Dry Retrieval of Single Shell Tank Waste at Hanford."

- For the fourth year, the DOE Fellow of the Year Award and the Mentor of the Year Award were presented in the ceremony. DOE Fellows were requested to nominate their ARC mentors and ARC mentors were requested to nominate the DOE Fellows. An ARC committee was established to review and select the winners from the submitted nominations. The 2012 Mentor of the Year Award went to research engineer Mr. Jose Varona and the 2012 DOE Fellow of the Year Award was given to Ms. Lillian Marrero (DOE Fellows Class of 2011).
- A new award for the Alumni DOE Fellow of the Year was also presented at the ceremony to honor and recognize the professional achievements of former DOE Fellows. The 2012 Alumni DOE Fellow of the Year was presented to Ms. Rosa Elmetti (DOE Fellows Class of 2008). In addition, a second new award was presented to Ms. Patty Cepero for her superior efforts in successfully coordinating and organizing the DOE Fellows' Induction Ceremony.

Figure 5-3. DOE Fellow (Jose Matos) Explaining his DOE-EM Research to DOE Representatives

Figure 5-4. DOE Fellows Class of 2012 with DOE and FIU Representatives

- The Fellows completed the presentations of their summer internship experience as part of the DOE Fellows weekly meeting. Table below shows the presentation schedule for fall 2012:

DOE Fellow	DOE Site/National Lab/Contractor	Location	Presentation Date
Jaime Mudrich Eric Inclan	Oak Ridge National Laboratory	Oak Ridge, TN	09/07/12
Ximena Prugue	Washington River Protection Solutions, Hanford Site	Richland, WA	09/12/12
Heidi Henderson	Oak Ridge Reservation	Oak Ridge, TN	09/19/12
Lillian Marrero	Sullivan International Consulting	Chicago, IL	09/26/12
Janty Ghazi	DOE-HQ EM-23 (Tank Farm Program)	Washington, DC	10/03/12
Revathy	Y-12 Security Complex, Oak	Oak Ridge, TN	10/10/12

Venkataraman	Ridge		
	DOE Fellows Poster Exhibition/Competition		**10/17/12**
Josh Midence	Savannah River National Lab	Aiken, SC	10/24/12
Claudia Cardona	DOE-HQ EM-12 (Soil/Groundwater)	Washington, DC	10/31/12
Elicek Delgado	Sullivan International Consulting	Chicago, IL	11/0712
	DOE Fellows Induction Ceremony		**11/13/12**
Robert Lapierre	Pacific Northwest National Lab	Richland, WA	11/21/12
Gabriela Vasquez	ARC Research	Miami	11/28/12
Lucas Nacimiento	ARC Research	Miami	12/05/12
Dania Castillo	ARC Research	Miami	12/12/12

- A professional paper entitled, "Training and Mentoring the Next Generation of Scientists and Engineers to Secure Continuity and Successes of the US DOE's Environmental Remediation Efforts" was accepted by the Waste Management 2013 Symposia. In addition, DOE Fellows and other students completed preparation of brief abstracts on their research, including work performed at ARC and during their summer internships, for submittal to the conference and presentation during the student poster session. Titles of student poster are shown on the table below.

DOE Fellow/Student	Abstract Title
Jennifer Arniella	High-Level Waste Pipeline Unplugging Technologies: Asynchronous Pulsing System
Francisco Bolanos	Computer Simulations of Multiphase Flow Systems Applied to Transfer of High-Level Waste
Claudia Cardona	The Effect of Ca Ions on the Removal of U(VI) at the Hanford Site Area
Dania Castillo	Computational Simulation and Evolution of High-Level Waste Pipeline Plugs at Hanford
Elicek Delgado-Cepero	Battery-less Wireless Sensors for Structural Health Monitoring for In-Situ Decommissioning of DOE Facilities
Janty Ghazi	Hydrogen in Pipes and Ancillary Vessels in Waste Treatment Plant at the Hanford Site

Heidi Henderson	Storm Water Management Model Analysis of the Oak Ridge Storm Water Collection System Up To Outfall 211
Robert Lapierre	Single Pass Flow-Through Testing of Metals for Hanford 200 Area Vadose Zone
Lilian Marrero	Improvements and Modifications of an Integrated Flow and Mercury Transport Model for East Fork Poplar Creek, Oak Ridge, Tennessee
Jose Matos	Development of Improved Bodies for a Peristaltic Crawler for Unplugging of Hanford Waste Transfer Pipelines
Joel McGill	Degradation of Grout: Compressive Strength Comparative Analysis
Joshua Midence	Saltstone Processing of Low-Level Waste at Savannah River Site
Jaime Mudrich	A Lattice Boltzmann Method for the Analysis of Gas Behavior in Hanford Tanks
Lucas Nascimento	Acoustic Pulse Reflectometry For Identifying Pipeline Properties At Hanford Site
Raul Ordonez	Sensor Network Energy Demand for In-situ Decommissioning Applications at Savannah River Site
Justin Phillips	Mobile Device Applications using Cloud Computing on Service Oriented Architecture
Ximena Prugue	Development of a Mechanical based System for Dry Retrieval of Single-Shell Tank Waste at Hanford
Mariela Silva	SharePoint Based Secured Collaboration System for DOE-EM project management
Gabriela Vazquez	Improved Third Generation Peristaltic Crawler for Removal of High-Level Waste Plugs in Hanford Site Pipelines
Revathy Venkataraman	D&D Technology Services Development using Windows Communication Foundation on Cloud

- DOE Fellows continued to assist EFCOG in developing Lessons Learned and Best Practices documents. A total of 7 the Best Practices and Lessons Learned documents are final, one is with DOE for review and approval, and one is awaiting review by site personnel. The new best practice (SRS R and P -Reactor Disassembly Basin *In Situ* Decommissioning) has been drafted by a DOE Fellow and is under FIU review.

Doc	BP/LL	Title	POC	Status as of 12/31/2012
1	BP	Explosive Demolition of Buildings 337, 337B, and the 309 Stack at the Hanford's 300 Area	Daniel Beckworth, Bob Smith, and Thomas Kisenwether	FINAL
2	BP	Open Air Demolition of Asbestos Gunite by Using a Track Mounted Wet Cutting Saw	Rob Vellinger	FINAL
3	BP	185-3K Cooling Tower Demolition	Bill Austin	FINAL
4	BP	Historical Hazard Identification Process for D&D	Paul Corrado	FINAL
5	LL	Closure of the Reactor Maintenance, Assembly, and Disassembly Facility and the Pluto Disassembly Facility at the Nevada National Security Site	Annette Primrose	Sent to DOE HQ for final review.
6	LL	Unanticipated High Dose During the Removal of Wire Flux Monitor Cabling from the HWCTR Reactor Vessel	Bill Austin	FINAL
7	LL	SPRU Lesson Learned	Brad Smith	Awaiting review by site personnel.
8	BP	Structural Code Guidance for D&D Activities at DOE Facilities	Kirk Dooley	FINAL
9	BP	Electrical Code Guidance for D&D Activities at DOE Facilities	Kirk Dooley	FINAL
10	BP	SRS R and P -Reactor Disassembly Basin In Situ Decommissioning	Bill Austin	Under review at FIU

Milestones and Deliverables

Milestone 2012-P5-M4 was completed and the summer interns' reports were sent to DOE by the due date. Also, milestone 2012-P5-M5 was completed, and a list of recruited DOE Fellows, class of 2012 was sent to DOE personnel.

Milestone 2012-P5-M6, Conduct Induction Ceremony – Class of 2012, was completed on November 13, 2012, and milestone 2012-P5-M7, submittal of student abstracts to the Waste Management Symposium, was completed on 12/28/12.

FIU Year 3 Milestones and Deliverables for Project 5

Milestone/ Deliverable	Description	Due Date	Status	OSTI
2012-P5-M1	Selection of new DOE Fellows - Spring 2012	05/30/12	Complete	
Deliverable	Draft Project Technical Plan sent to DOE	06/18/12	Complete	
Deliverable	List of 2012 Student Summer Interns and their research assignment	06/29/12	Complete	
2012-P5-M2	Waste Management Symposium 2013 abstract submitted	8/17/2012	Complete	OSTI[7]
2012-P5-M3	DOE Fellows Complete Summer Internships	08/31/12	Complete	
2012-P5-M4	Summer Internships Reports Completed	10/05/12	Complete	
Deliverable	Deliver Summer 2012 Interns reports to DOE	10/19/12	Complete	OSTI
2012-P5-M5	Selection of new DOE Fellows – Fall 2012	10/30/12	Complete	
Deliverable	List of identified/recruited DOE Fellow (Class of 2012)	10/31/12	Complete	
2012-P5-M6	Conduct Induction Ceremony – Class of 2012	11/13/12	Complete	
2012-P5-M7	Waste Management Symposium 2013	12/31/2012	Complete	OSTI
Deliverable	Draft Year End Report	06/28/13	On Target	OSTI

Work Plan for Next Quarter

- Coordinate travel for DOE Fellows to attend Waste Management 2013 Symposium.
- Present professional paper to Waste Management 2013 Symposium.
- DOE Fellows to develop posters and present at student poster session to Waste Management 2013 Symposium.
- Begin Spring 2013 campaign to recruit DOE Fellows into the program.
- Begin coordination of internship placements for summer 2013 at DOE sites, national laboratories, DOE-HQ, and DOE contractors.

[7] Announcement of published journal or conference paper will be submitted to OSTI