

# PROJECT TECHNICAL PLAN

## Project 2: Environmental Remediation Science & Technology

*Performance Period: August 29, 2015 to August 28, 2016*

**Date submitted:**

October 5, 2015

**Principal Investigator:**

Leonel E. Lagos, Ph.D., PMP®  
Applied Research Center  
Florida International University  
10555 West Flagler Street, EC2100  
Miami, FL 33174

**Submitted to:**

U.S. Department of Energy  
Program Services Division, ME-643.1  
1000 Independence Avenue, SW  
Washington, D.C. 20585

*Cooperative Agreement DE-EM0000598*



**Applied Research Center**  
FLORIDA INTERNATIONAL UNIVERSITY



---

## INTRODUCTION

---

***Special Note:*** In an attempt to streamline the projects of this DOE-FIU Cooperative Agreement under their relevant research areas, the projects formerly executed in FIU Year 5 as Projects 2 & 3 (i.e., *Rapid Deployment of Engineered Solutions to Environmental Problems*; and *Environmental Remediation Technologies (EM-12)*) have now been combined under one project entitled, *Project 2: Environmental Remediation Science & Technology*.

**DOE EM HQ Contacts:**

John DeGregory, EM-13 FIU Project Liaison  
Kurt Gerdes (EM-12), Office Director for Soil and Groundwater Remediation  
Albes Gaona (EM-13), Project Liaison and Sustainable Remediation Task Lead  
Paul Beam (EM-12), FIU Backup  
Skip Chamberlain (EM-12), PNNL Lead  
Justin Marble (EM-12)  
Karen Skubal (EM-12)  
Bob Seifert (EM-11), Office Director

**DOE Site Contacts:**

Miles Denham (SRNL)  
Carol Eddy-Dilek (SRNL)  
Brian Looney (SRNL)

Kevin Kostelnik (SRNL)  
John Seaman (SREL)  
Patrick Jackson (SRS)  
Brady Lee (PNNL)  
Hope Lee (PNNL)  
Jim Szecsody (PNNL)  
Dawn Wellman (PNNL)  
Don Reed (LANL)

**ARC Program Contact:**

Leonel E. Lagos, PhD, PMP®  
Principal Investigator, Director of Research  
(305) 348-1810, E-mail: lagosl@fiu.edu

Applied Research Center  
Florida International University  
10555 W. Flagler St., Suite 2100  
Miami, FL 33174

Nuclear weapons production and other defense-related activities at the Hanford and Savannah River Sites have resulted in uranium contamination in the subsurface environment. The U.S. Department of Energy (DOE) faces the most monumental environmental restoration task in history: cleaning up contamination caused by the manufacturing of nuclear weapons in a network of 113 installations around the country. The number of environmental challenges is tremendous and the associated cost of cleanup will be enormous. The goal of the remediation efforts at Hanford and SRS, therefore, is rapid deployment of engineering solutions to assist with environmental cleanup of the contaminated soil and groundwater, seeking to reduce the potential for radionuclide mobility in the subsurface. During 2015-2020, FIU will work closely with Richland, Savannah River and DOE-HQ personnel to advance the knowledge and application of state-of-the-art environmental remediation technologies at DOE sites. The focus will be on providing technical solutions and needed knowledge through experimental studies and technology development and testing. FIU personnel will work closely with site engineers and

scientists in planning and executing work that addresses critical science and technology needs at Hanford, SRS, and LANL. The knowledge gained through these experimental studies will be used to transform experimental innovations into the practical applications deployed at the Hanford and Savannah River Sites as well as Los Alamos National Lab.

---

## TECHNOLOGY NEEDS

---

Conventional hydrologic and remediation methodologies provide limited understanding of the interactions between the hydrological cycle, contaminant mobilization and environmental impacts. This project uses conventional hydrologic and remediation analytical tools (accepted by the EPA, USACE, and USGS) in combination with latest scientific software (2D and 3D numerical flow and transport models integrated with reaction kinetics and thermodynamic software) to provide an integrated solution for understanding the mobility and the impacts of contaminants within soil and groundwater at DOE sites. In addition, state of the practice tools for analysis of sustainable and green remediation alternatives are needed to address long-term sustainability in terms of reduced environmental and energy footprints of the remedial actions.

### **Task 1: Remediation Research and Technical Support for the Hanford Site**

The reprocessing of irradiated fuel at the Hanford Site to obtain plutonium for atomic weapon production has left a legacy of radioactive waste that contains nearly 550,000 curies of radioactivity and 150 million kg (165,000 tons) of metals and hazardous chemicals. A significant portion of these materials reside within the vadose zone (VZ). This contamination created plumes that threaten groundwater quality due to potential downward migration through the unsaturated VZ. Sequestration of radionuclides such as uranium in the vadose zone is also more cost effective than groundwater remediation.

One technology under consideration to control U(VI) mobility in the Hanford vadose zone is a manipulation of sediment pH via ammonia gas injection to create alkaline conditions in the uranium-contaminated sediment. This technology allows the transformation of mobile uranium species to lower solubility precipitates and/or additionally coated by low-solubility precipitates that are stable in the natural environment (Szecsody et al., 2012). However, there is a need for a better understanding of the stability of the U-bearing precipitates created in the sediment as a result of ammonia gas remedial actions. This information would help to accurately predict the mobility of U(VI) in the post-treated vadose zone soil. Traditionally, solubility measurements are conducted in batch experiments measuring the amount of solute that can be dissolved in a solvent until the system reaches equilibrium (Giammar et al., 2002; Rai et al., 2005; Gorman-Lewis et al., 2008). This method is better suited to measure solubility of solids with respect to the groundwater saturated conditions. However, for the unsaturated vadose zone conditions, this approach might not accurately quantify the solubility of the solid phases. Evaluation of the literature suggests that the isopiestic method can closely mimic the mineral deliquescence process, which refers to the formation of an aqueous solution by the absorption of water by hygroscopic salt minerals (Carroll et al., 2005). Thus, isopiestic measurements may be the most appropriate way to quantify mineral solubility for the unsaturated vadose zone conditions. This method is considered very accurate, helping to make more realistic predictions of contaminant fate and transport in vadose zone environments. Experimental deliquescence data are limited for mixed salts (Gruskiewicz et al., 2007) and especially scarce for uranium-bearing multicomponent mixtures. The research objectives seek to characterize uranium solid phases in the multicomponent precipitates and determine their deliquescence behavior at various

temperatures. In addition, the solubility of uranium-bearing precipitates needs to be evaluated in flow-through experiments to allow for prediction of expected uranium and other elements released from solids. Studies will also need to identify the uranium phases formed by means of XRD and SEM-EDS that will be necessary for solids stability studies. This will grant insight into the long-term viability of the proposed remediation method in the vadose zone.

Another technology need for the ammonia remediation method is to investigate the potential biological and physical mechanisms associated with the fate of ammonia after injection into the unsaturated subsurface. The current mobility of uranium in the groundwater at the Hanford Site is relatively high ( $K_d$  0.11 – 4 L/kg at pH 8) (Zachara et al., 2007). Therefore, remediation methods including ammonia gas injection are under consideration to decrease the mobility of uranium within the vadose zone to decrease the overall flux of uranium into the groundwater. Ammonia gas injection is to be used at the Hanford Site to increase the pH of the vadose zone porewater. Based on this pH increase, silicate minerals that are expected to partially dissolve include kaolinite, montmorillonite and muscovite, exhibiting the greatest dissolution in laboratory-scale experiments with relevant Hanford sediments (Szecsody et al., 2012). Then, as the system returns to a neutral pH, different aluminosilicate minerals precipitate including ancinite, sodalite, brucite or goethite. The pH fluctuations and co-precipitation processes are expected to remove a significant fraction of uranium as both uranyl precipitates and co-precipitates with minerals.

Data on ammonia solubility and speciation in pure water at different pH and temperature is known. Existing literature suggests that the amount of ammonia in the soil solutions required to increase pH depends on the soil cation exchange capacity (CEC) and sediment and pore water buffering capacity.  $\text{NH}_3$  can be adsorbed to the various minerals in sediments including zeolite (1.03 – 9.33 mmol/g), alumina (3.01 mmol/g), and silica gel (3.01 mmol/g) (Guo et al., 2007; Helminen et al., 2000). However, pH effects will also impact the dissolution of these minerals. Gaseous  $\text{NH}_3$ , when in contact with soil moisture, dissolves and reacts to form  $\text{NH}_4^+$  and  $\text{OH}^-$  ions, leading to its weak base effects. The volatility of ammonia increases while the weak basic properties decrease with increasing pH due to changes in its aqueous speciation. Further, sediments and porewater saturated with carbonate, which is typical for the Hanford Site, require more ammonia due to the existing soil buffering capacity. However, Zhong et al. noted that there is a lack of understanding of the geochemical reactions caused by ammonia addition to the subsurface as well as the transport of ammonia in porous media (Zhong et al., 2015). Specifically, ammonia partitioning in these complex systems with porewater and groundwater solutions and sediment/mineral suspensions requires additional experimentation. Further, the partitioning of uranium between the liquid and solid phases in these systems in the presence of ammonia is not fully understood.

Tripolyphosphate injections are one of the methods to decrease the concentration of soluble uranium in contaminated plumes at the Hanford Site. The introduction of sodium tripolyphosphate amendments into uranium bearing porous media results in the formation of uranyl phosphate minerals (autunite) of general formula  $\{\text{X}_{1-2}[(\text{UO}_2)(\text{PO}_4)]_{2-1} \cdot n\text{H}_2\text{O}\}$ , where X, is a monovalent or divalent cation. The stability of the uranyl phosphate minerals in the subsurface is a critical factor, since it will determine the long-term effectiveness of the sodium tripolyphosphate injection as a remediation strategy. The presence of bacteria can affect uranium

mobility significantly since bacteria may dissolve uranyl-phosphate minerals, thus liberating uranium in the aqueous phase, in an effort to obtain phosphorous, a vital nutrient for their metabolism. In addition to the biological activity, bicarbonate presence in the aqueous phase seems to enhance the release of U(VI) in the aqueous phase. Our previous experiments with *Arthrobacter oxydans* G975 strain illustrated a bio-enhanced release of U(VI) from natural Ca-autunite in the presence of various concentrations of bicarbonate. In addition, *Arthrobacter* G968, a strain which exhibits low tolerance of U(VI), was able to bio-enhance the release of U(VI) from natural Ca-autunite at almost the same capacity as strain G975. The Columbia River at the site exhibits large stage variations, causing large water table fluctuations. These water table fluctuations and multiple rise-and-fall cycles in the river created an oxic-anoxic interface in this region. Previous assessments noted the decline in cultivable aerobic bacteria in subsurface sediments and suggested the presence of facultative anaerobic bacteria in Hanford sediment samples collected from this area (Lin et al., 2012). Therefore, understanding the role of aerobic, facultative (e.g., *Shewanella*) and anaerobic bacteria as one of the factors affecting the outcome of environmental remediation is very important. There is also a need to evaluate the biodissolution of Ca- and Na- autunite minerals and investigate the effect of Ca and bicarbonate ions on the microbial reduction of soluble U(VI). The study will also initiate an investigation on the effect of designed bacterial consortium or/and cultures enriched from 200 Area sediment core samples to explore the effect of bicarbonate on autunite dissolution and U(VI) bioreduction to U(IV).

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

The F/H Area Seepage Basins located in the center of SRS received approximately 1.8 billion gallons of acidic waste solutions (pH from 3.2 to 5.5) contaminated with a variety of radionuclides and dissolved metals. DOE has made great efforts over many years to clean up the site and remediate the groundwater, but uranium concentrations still remain 10-1000 times higher than the maximum contaminant level (MCL = 0.13  $\mu\text{M}$  or 20.271 pCi/L). The acidic nature of the basin waste solutions caused the mobilization of metals and radionuclides, resulting in contaminated groundwater plumes. Uranium, strontium, technetium and iodine are some of the key contaminants of concern associated with the F-Area groundwater plume.

As an alternative to sodium hydroxide, a solution with high carbonate alkalinity was used later to overcome soil acidity effects of minerals surfaces. However, bicarbonate complexation reactions with uranium often result in the formation of very stable and mobile aqueous species. As a result, there is increased interest for the identification of alternative alkaline solutions that can amend the pH and not exhibit significant limitations.

This task investigates whether a base solution of dissolved silica can be used to replace the carbonate base and evaluates the potential use of sodium silicate for radionuclide removal from the aqueous phase. This research also investigates the mechanisms of the reaction through complexation with silica-bearing solid phases or co-precipitation with Si. Another technology need for the remediation of the F/H Area from uranium is to study applications of humic substances. Humic substances (HS) are ubiquitous in the environment and are found in soils, groundwater and fresh water. HS consist of complex organic molecules formed by the decomposition of plant and animal tissue by microorganisms.

SRNL has been testing unrefined, low cost humic substances using a product known as Huma-K as an amendment that can be injected into contaminant plumes to enhance sorption of uranium at low pH conditions typical for the SRS conditions. The advantage of using an unrefined humic substance is that it is inexpensive and can be used for full scale deployment of remediation technologies. Huma-K is sold by Land and Sea Organics located in Modest, California, as a source of humic substances to increase soil fertility. It contains more than 86% of humic substances that were extracted from leonardite, which is a low ranking coal.

Another line of research is focusing on the evaluation of microcosms mimicking the enhanced anaerobic reductive precipitation (EARP) remediation method previously tested at SRS F/H Area. The addition of the molasses substrate solution to groundwater produces anaerobic conditions conducive to the reductive precipitation of uranium due to the significantly decreased solubility of its +4 oxidation state. The SRS soil features very low alkalinity and previous assessments by FIU suggested that acidic conditions might hinder the formation of any iron-sulfide precipitates. There is a need for geochemical modeling studies to determine the range of environmental conditions in which the formation of siderite and pyrite solid phases would occur. This would extend knowledge and improve understanding on the applicability of this technology.

### **Task 3: Surface Water Modeling of Tims Branch**

This task will conduct work related to water, sediment, mercury and tin in Tims Branch, a site impacted by 60 years of anthropogenic events associated with discharges from process and laboratory facilities at SRS. Tims Branch provides a unique opportunity to study complex systems science in a full-scale ecosystem that experienced controlled step changes in boundary conditions. The task will develop and test a full ecosystem model for a relatively well defined system in which all of the local mercury inputs were effectively eliminated via two remediation actions (2000 and 2007). The research will directly support the interpretation of historical data on the trends in contaminant concentrations in Tims Branch biota and support planning and execution of future biota sampling in this important ecosystem.

GIS technology will be extensively utilized to support the hydrological model development, not only for data storage and integration, but also for pre- and post-processing of model-specific data. DOE sites have accumulated years of data and millions of spatial and temporal records related to the hydrological cycle, contaminant transport, and parameters of remediation technologies. In addition, numerical models produce gigabytes of computed spatial and temporal data for each computation node. Advances in ArcGIS software through the development of geodatabase technology, coupled with the development of data models such as ArcHydro which possesses a spatial relational database management system (RDBMS) schema and relationship structure specific to hydrologic systems, provides modelers with tools and applications to assist in the management, storage, processing, analysis and visualization of flow and contaminant transport data. The geodatabase can serve as a tool for contaminant flow and transport analyses which require large amounts of high-quality spatial and temporal data in order to ensure reliability and validity of modeling results. In addition, the coupling of this type of geodatabase structure with a numerical model such as MIKE SHE/11 can serve as an efficient tool that significantly reduces the time needed for data preparation (Castle, E., 2003). ArcGIS tools can be used to automate and simplify the process of calling stored GIS and timeseries data. Gogu et al.

(2001) stresses the benefits of putting large volumes of data into a structured, coherent and logical computer-supported system to ensure validity and availability for concurrent use by multiple users and provide a foundation for building GIS-based water resources applications. The hydrologic geodatabase developed in this project possesses a structure that enables linkage with scalable hydrologic modeling tools, applications to model hydrologic systems, and in this case, enables the testing of the potential impacts of extreme weather on the SRS watersheds.

#### **Task 4: Sustainability Plan for the A/M Area Groundwater Remediation System**

DOE sites are developing sustainability programs, projects and initiatives in order to help meet the goals as set out in individual Site Sustainability Plans (SSPs) and the overall U.S. DOE 2013 Strategic Sustainability Performance Plan. There are many benefits of implementing sustainable practices, including reducing costs as well as fostering better engagement and acceptance of improved remediation strategies and sustainable practices by regulators, the public, and other stakeholders. These benefits are in addition to the more obvious ones of reducing energy consumption, improving air and water quality, minimizing impact to the environment, reducing carbon footprints, and reducing waste generation.

#### **Task 5: Remediation Research and Technical Support for WIPP**

This task will focus on the laboratory experiments supporting research relevant to the geologic nuclear waste repositories. Specifically it will target the conditions of the Waste Isolation Pilot Plant (WIPP), which is a deep underground repository for the disposal of transuranic (TRU) radioactive waste developed by the DOE. The research will center on understanding the mechanisms controlling the fate and transport of radionuclides in a wide range of environments conditions pertinent to radionuclide waste-storage scenarios. Most experiments will be conducted under WIPP-relevant reducing conditions using aqueous solutions of varying ionic strength including WIPP simulated brine formulations or include organic ligands and iron. In addition, the project is intended to evaluate the potential microbial effect on the stability of actinides under the conditions of nuclear waste repositories in varying high-ionic strength matrices. These studies will gain a better understanding of the ecology at WIPP and the potential effects of environmental factors, including microbial activities on actinides stability in the waste systems.

---

## FIU YEAR 6 PROJECT EXECUTION PLAN

---

The FIU Year 6 tasks which are part of the main scope are identified in the table below. A detailed description is provided below for each project task

**Table 1. FIU Year 6 Project Work Scope**

Task No	Task
<b>Task 1: Remediation Research and Technical Support for the Hanford Site</b>	
Subtask 1.1	Sequestering uranium at the Hanford 200 Area vadose zone by in situ subsurface pH manipulation using NH <sub>3</sub> gas
Subtask 1.2	Investigation of microbial-meta-autunite interactions - effect of bicarbonate and calcium ions
Subtask 1.3	Evaluation of ammonia fate and biological contributions during and after ammonia injection for uranium treatment
<b>Task 2: Remediation Research and Technical Support for Savannah River Site</b>	
Subtask 2.1	FIU's support for groundwater remediation at SRS F/H Area
Subtask 2.2	Monitoring of U(VI) bioreduction after ARCADIS demonstration at the SRS F-Area
Subtask 2.3	Humic acid batch sorption experiments into the SRS soil
Subtask 2.4	The synergetic effect of HA and Si on the removal of U(VI)
Subtask 2.5	Investigation of the migration and distribution of natural organic matter injected into subsurface systems
<b>Task 3: Surface Water Modeling of Tims Branch</b>	
Subtask.3.1	Modeling of surface water and sediment transport in the Tims Branch ecosystem
Subtask 3.2	Application of GIS technologies for hydrological modeling support
Subtask 3.3	Biota, biofilm, water and sediment sampling in Tims Branch
<b>Task 4: Sustainability Plan for the A/M Area Groundwater Remediation System</b>	
Subtask 4.1	Sustainable Remediation Analysis of the M1 Air Stripper
Subtask 4.2	Sustainable Remediation Support to DOE EM Student Challenge
<b>Task 5: Remediation Research and Technical Support for WIPP</b>	

---

## PROJECT TASKS

---

This project will be conducted in close collaboration between FIU, Hanford Site, SRS, and LANL scientists in order to plan and execute research that supports the resolution of critical science and engineering needs, leading to a better understanding of the long-term behavior of contaminants in the subsurface. Research involves novel analytical methods and microscopy techniques for characterization of various mineral and microbial samples. Tasks include studies which predict the behavior and fate of radionuclides that can potentially contaminate the groundwater system in the Hanford Site 200 Area; laboratory batch and column experiments, which provide relevant data for modeling of the migration and distribution of natural organic

matter injected into subsurface systems in the SRS F/H Area; laboratory experiments investigating the behavior of the actinide elements in high ionic strength systems relevant to the Waste Isolation Pilot Plant; surface water modeling of Tims Branch at SRS supported by the application of GIS technology for storage and geoprocessing of spatial and temporal data; and support for the DOE EM student challenge. The following details the scope of work for the tasks under this project for FIU Year 6.

## **Task 1: Remediation Research and Technical Support for the Hanford Site**

---

Task 1 is a joint effort with the Pacific Northwest National Laboratory (PNNL). Three subtasks have been identified and will be developed during FIU Year 6.

### **Background**

Remediation of radionuclides in the Hanford Site vadose zone (VZ) is a significant technical challenge since contaminants reside at depths which are difficult to reach with near-surface remediation techniques. Past waste disposal practices have relied on the assumption that the thick VZ beneath the 200 Area would retain most radionuclides. It is recognized today that the vadose zone is a dynamic environmental system and the spread of contaminants through the VZ created plumes that provide an ongoing source of contamination for the underlying aquifer and the Columbia River. Uranium is one of the key contaminants of the Hanford Site VZ. Its mobility in the subsurface is affected by the soil compositions and presence of carbonates, which may complex with U(VI). The resulting uranyl-carbonate complexes are the predominant uranium (VI) aqueous species in Hanford's pore water, and due to their high mobility, are considered as a potential source of contamination for the underlying aquifer. Consequently, *in situ* remediation methods require sequestration of uranium in the subsurface to prevent further spreading of mobile uranium species.

FIU ARC will continue to provide research support on uranium contamination and remediation at the Hanford Site with three subtasks under Task 1. **Subtask 1.1**, "*Sequestering Uranium at the Hanford 200 Area Vadose Zone by In Situ Subsurface pH Manipulation Using NH<sub>3</sub> Gas*," will include research on sequestering uranium at the 200 Area by *in situ* subsurface pH manipulation using NH<sub>3</sub> gas. This technology allows the transformation of mobile uranium species to lower solubility precipitates that are stable in the natural environment (Szecsody et al., 2012). The research will continue isopiestic measurements initiated in FIU Year 5 using U-bearing precipitates. The isopiestic method is considered as one of the most accurate methods for the solubility determinations. In addition, U(VI) release will be evaluated via flow-through experiments. Experiments will be also continued for the characterization of uranium-bearing solid phases. For these studies, an access proposal was drafted and submitted to PNNL's Environmental Molecular Sciences Laboratory (EMSL), which features a radiochemistry annex to facilitate studying the chemistry of actinides such as uranium.

The study under **Subtask 1.2**, "*Investigation of Microbial-Meta-Autunite Interactions - Effect of Bicarbonate and Calcium Ions*," will examine the effect of bicarbonate ions on the microbial dissolution of Na-autunite mineral by facultative microorganisms *Shewanella oneidensis* MR1. In addition, the study will examine the effect of a designed bacterial consortium or/and microbial culture enriched from core samples collected from the 200 Area on the autunite minerals bio -

dissolution process and reduction of released U(VI) in the presence of bicarbonate ions. The role of subsurface facultative microorganisms or microbial consortium to impact the stability of the autunite mineral created in sediments as a result of tripolyphosphate injections to sequester uranium (VI) in the subsurface has not been a consideration in the past.

**Subtask 1.3**, “*Evaluation of Ammonia Fate and Biological Contributions During and After Ammonia Injection for Uranium Treatment*,” will focus on the potential biological and physical mechanisms associated with the fate of ammonia after injection into the unsaturated subsurface. This task evaluates factors controlling ammonia gas partitioning with liquid and sediments and quantifies the relative rate of these processes. A new Subtask 1.3.3 will be initiated in FIU Year 6, focusing on the influence and corresponding electrical geophysical response of microbial activity on the vadose zone uranium sequestration process using gas phase ammonia injections.

To perform Task 1, FIU will be in continuous communication with the PNNL researchers, including Jim Szecsody, Nik Qafoku, Timothy Johnson, Brady Lee and Hope Lee.

## Objective

There are several objectives for the proposed experiments under Task 1.

The objectives of **Subtask 1.1** are to: (i) investigate the deliquescence behavior of U-bearing solids prepared with 2 ppm of U(VI) and compare experimental data with results obtained using U-free multicomponent solids; and (ii) evaluate the release of U(VI) from precipitate via flow-through experiments. This task also identifies uranium-bearing solid phases formed after the treatment and evaluates the effect of carbonate on the uranyl phases detected. Carbonate ( $\text{CO}_3^{2-}$ ) was selected because it is a major constituent in the porewater composition forming strong complexes with the uranyl ions.

Natural systems are complex and their behavior is dictated by the synergistic and/or antagonistic effect of both biotic and physico-chemical factors. The objective of **Subtask 1.2** is to investigate the dissolution of uranyl-phosphate minerals by facultative bacteria in bicarbonate amended media. More specifically, the research will focus on the biodissolution of Ca-autunite and Na-autunite by *Shewanella oneidensis* under anoxic and oxygen-restricted conditions and evaluate the role of bicarbonate and  $\text{Ca}^{2+}$  ions on this phenomenon. It is expected that under anoxic conditions, facultative microbial species will likely possess the ability to reduce U(VI) to U(IV) depending on the electron donors present. Moreover, the formation of aqueous uranium species and/or secondary minerals is expected to differ after the dissolution of natural Ca-autunite and synthetic Na-autunite, which will be taken into consideration during the biodissolution process. In addition, this study will initiate an assessment of the effect of a designed bacterial consortium and/or cultures enriched from sediment core samples collected from the 200 Area to explore the effect of bicarbonate on autunite dissolution and U(VI) biotransformation to U(IV).

The objective of **Subtask 1.3** is to investigate the mechanisms associated with the fate of ammonia and uranium in the Hanford vadose zone after ammonia gas injection into the unsaturated subsurface. FIU experiments will focus on ammonia and uranium partitioning between the gaseous, aqueous and solid phases in bicarbonate-amended solutions and synthetic porewaters in the presence of pure minerals and sediments. Initial experiments for Subtask 1.3.1

will investigate if uranium and mineral sorption/dissolution/precipitation processes are solely a pH effect or if the presence of ammonia has an additional impact. The microbiological transformations in soil after ammonia gas injections and geochemical reactions will also be investigated using molecular biology and geophysics techniques to identify and quantify factors controlling the relative rate of these processes through Subtasks 1.3.2-1.3.3. The geophysical measurements may lead to a realistic method of tracking remediation and microbial processes in the subsurface.

## **Benefits**

**Subtask 1.1:** Injection of reactive gases, such as  $\text{NH}_3$ , to create alkaline conditions in the vadose zone, is an innovative technology used to decrease uranium mobility in the subsurface contaminated with radionuclides. This task will investigate the deliquescence behavior of U(VI)-bearing precipitates created as a result of ammonia gas injection into the synthetic groundwater solutions mimicking 200-Area pore water and measure the release of U(VI) from precipitates in the flow-through experiments. This study will also evaluate formed minerals and examine their mineralogical and morphological characteristics.

**Subtask 1.2:** Aqueous carbonate ions present in the soil and groundwater are the predominant aqueous species affecting the dissolution of uranium-bearing solids and facilitating uranium desorption reactions from soil and sediments, thus increasing uranium mobility in soil and sediments. This task will also investigate bacteria-U(VI) interactions using facultative microorganisms growing in oxic-anoxic conditions and examine the potential role of bacterial cultures enriched from sediment core samples collected from the 200 Area or a designed bacterial consortium containing Gram-positive and Gram-negative bacteria to influence U(VI) release from autunite minerals and U(VI) biotransformation in the presence of bicarbonate ions. The technical plan is designed to provide a spherical overview of all the different factors that affect uranium mobility in this complex natural system, such as physico-chemical, biotic and mineralogical factors, and subsequently provide a more thorough understanding of the phenomenon

**Subtask 1.3:** The research outlined in the subtask will help to understand the science behind the expected ammonia gas injection technology and its capacity to decrease uranium mobility in the vadose zone. It will identify the fate of ammonia in the subsurface (i.e. sorption to sediments, volatilization to the gas phase, solubilization to porewaters) and the controlling factors leading to a decrease in uranium mobility in the subsurface (including: pH effects, ammonia effects, mineral dissolution and precipitation, microbial effects and uranium speciation/precipitation/dissolution changes) in Subtasks 1.3.1 and 1.3.2. This increased understanding of the controlling mechanisms of the remediation technology will aid in the prediction of future success. Further, Subtask 1.3.3 will help to identify methodologies for tracking the remediation process within the subsurface with minimal impacts to the vadose zone through geophysics.

## **Technical Approach**

Plans for FIU Year 6 include the following subtasks:

### **Subtask 1.1: Sequestering Uranium at the Hanford 200 Area Vadose Zone by In Situ Subsurface pH Manipulation Using NH<sub>3</sub> Gas**

Remediation of the vadose zone is the most difficult soil and groundwater challenge remaining at Hanford. A contaminated vadose zone is out of reach using traditional surface methods and may continue to threaten groundwater quality. The focus of this task is to evaluate the stability of U-bearing precipitates created after NH<sub>3</sub> pH manipulation in the synthetic solutions mimicking conditions found in the vadose zone at the Hanford Site 200 Area.

The study will be conducted via the isopiestic method and investigate the effect of temperature and solids composition relevant to the Hanford vadose zone on the deliquescence behavior of multicomponent solids containing U(VI). This year, the isopiestic experiments will be conducted at 25°C.

Experiments will be conducted to evaluate the activity of water for various multicomponent precipitates and the occurrence of solid-liquid transitions for multicomponent precipitates that contain Na-Si-Al-Ca-U-HCO<sub>3</sub> ions at various ratios and U(VI). The concentration of U(VI) will be kept constant at 2 ppm for all samples. This concentration is similar to what was used in the earlier study conducted to investigate the effect of Si and Al concentration ratios on the removal of U(VI) in alkaline conditions by NH<sub>3</sub>. The concentration of sodium silicate (100 mM) and aluminum (5 mM) will be unchanged for all samples. Four samples will be prepared with 3 mM bicarbonate and amended with 0 mM, 5 mM, 10 mM and 15 mM of calcium chloride. Another four samples will be prepared with 50 mM of bicarbonate and amended with the same concentrations of calcium chloride as the 3 mM bicarbonate samples. An additional two samples will be prepared with 100 mM sodium silicate to be able to compare osmotic coefficients values for sodium silicate with the literature data. All samples will be dried and placed in the isopiestic chamber along with CaCl<sub>2</sub> and NaCl standards. During the experiments, data will be collected on water activities and osmotic coefficients using the gravimetric isopiestic method until the relative humidity (or water activity) reaches sufficiently high levels for the mixture of initially dry precipitates to deliquesce, forming highly concentrated brine solutions. These results will help to understand the relationship between deliquescence, relative humidity (or water activity) and temperature for multicomponent uranium-bearing precipitates.

Additional experiments will be conducted via continuous flow reactors (CFR) to measure the release of U(VI) from U(VI)-bearing multicomponent precipitates created in conditions mimicking ammonia gas applications for the Hanford Site vadose zone. Uranium release will be measured via continuous injection of the Hanford Site synthetic groundwater through a single-pass flow-through (SPTF) apparatus. An electronic peristaltic cartridge pump will control the flow rate of a liquid solution. Effluents from each precipitate sample will be collected continuously and sample aliquots will be retained for both pH measurements and to analyze all of the major elements in the precipitates by inductively coupled plasma (ICP-OES). The mass of the uranium will be calculated and correlated with the major constituents (Si, Ca, Al, and bicarbonate concentrations) each time that samples are collected. After completing the CFR experiment, precipitate samples will be analyzed using X-ray diffraction (XRD) and scanned electron microscope (SEM) to determine the mineralogical and morphological changes in the precipitate samples. The CFR experiment will be conducted at the same temperature as the isopiestic experiments (25°C).

### ***Subtask 1.1.1: Characterization of the uranium-bearing phases***

The continuing effort to effectively characterize the uranium-bearing solid phases produced by the application of the ammonia gas injection method to a laboratory scale synthetic pore water solution will be supported by modifying sample preparation and analysis methods based on the input of specialists in the field. Among the changes being made is the vacuum filtration and washing of solid samples in an attempt to prevent the precipitation of soluble uranium phases with the evaporation of left over liquids from the supernatant. These changes were in response to the tentative identification of a solid sodium uranyl carbonate phase, which should be soluble in our aqueous system. It is anticipated that the modified sample preparation will limit the formation of these soluble phases, which are not believed to be representative of the system being mimicked in our experiments. The preparation of these samples will be followed by the routine analysis using methods including kinetic phosphorescence analyzer (KPA) and scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS) for the supernatant and precipitate phases, respectively.

In addition to the sample preparation modifications, the research team is pursuing the assistance of PNNL's Environmental Molecular Sciences Laboratory (EMSL) for access to their instrumentation dedicated to studying radiological samples. Specifically, samples will be prepared according to the new methods prior to being sent to EMSL for study using electron microprobe analyzer (EMPA), focused ion beam (FIB) imaging and milling, and transmission electron microscope (TEM) imaging with selective area electron diffraction (SAED). It is anticipated that EMPA will be able to provide quantitative elemental composition information that will allow a chemical formula for the uranium-rich region to be approximated. The combination of FIB with TEM's electron diffraction capabilities will allow for an area of interest to be sectioned out and isolated for diffraction analysis, potentially allowing for the determination of the structure and identity of the uranium phase. The use of the EMSL facilities is contingent on the acceptance of a formal research proposal, which was submitted in August 2015 to EMSL for review.

Prior to starting the proposed EMSL analysis, a set of optimization and pre-screening experiments will be completed. This will ensure that any samples selected and prepared for shipping to the EMSL facility will be relevant and capable of providing the type of data being sought. Planned experiments will feature a full-factorial design with two factors at three discrete levels, for a total of nine. The supernatant phases produced will be analyzed by KPA for uranium content; the results of which will be used as optimization criteria. Additionally, precipitate samples will be analyzed by SEM/EDS for the uranium rich phases anticipated based on prior experiments. The presence of these hot spots will be required of any samples being selected for further analysis.

### **Subtask 1.2: Investigation of Microbial-Meta-Autunite Interactions - Effect of Bicarbonate and Calcium Ions**

FIU research on microbial dissolution of autunite will continue to investigate the effect of facultative bacteria (*Shewanella oneidensis* MR-1) on the dissolution of uranyl phosphate minerals. *Shewanella* sp. is a gram-negative, facultative bacterium capable of using a broad variety of electron acceptors, including U(VI). The representative bacterial strain was obtained

from PNNL after performing aerobic and anaerobic enrichments, along with molecular characterization of the microbial community.

Experiments will be conducted using inoculated and control samples containing a specific amount of Na-autunite and bicarbonate amended medium. Sampling will be taken at specific time intervals over the period of 2-3 months. Aqueous concentrations of U and P will be determined using kinetic phosphorescence analyzer (KPA) and inductively coupled plasma - optical emission spectroscopy (ICP-OES). Samples will be filtered through a 0.20  $\mu\text{m}$  nylon syringe filter and diluted and acidified with 0.016 M nitric acid containing 10 ppm of yttrium as internal standards to correct for instrumental drift and mass bias of the ICP-OES. Biological analyses will be performed at specific time intervals in an attempt to correlate dissolution with microbiological ability. More specifically, the growth and potential toxicity of uranium on *Shewanella oneidensis* will be evaluated by means of cells lysis and total protein determination. At specific time intervals, bacterial suspensions will be isolated and after centrifugation and cell lysis by boiling, the total protein content will be determined calorimetrically (bicinchoninic acid assay). With the aid of protein standards and known bacterial suspensions, the protein content is correlated to the number of cells, and in this way, bacterial growth is monitored in the presence of different uranium and bicarbonate concentrations. Furthermore, live and dead assay by means of fluorescence microscopy will be used in order to obtain a clear picture of the ratio of live and dead cells under the different physico-chemical conditions. Finally, scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) analysis will be performed to examine changes over time in mineral surface composition. In addition, speciation modeling will be used to predict different uranium species in the aqueous phase, as well as the formation of secondary minerals. Experimental results will be compared to the data obtained for Ca-autunite bio-dissolution experiments using *Shewanella oneidensis* MR-1 to evaluate for the microbial dissolution of Na and Ca autunite in bicarbonate-amended solutions. In addition, FIU will initiate experiments using a designed consortium of Gram-positive and Gram-negative bacteria and/or and use cultures enriched by PNNL from sediment core samples to examine their effect on autunite dissolution and U(VI) reduction in the presence of bicarbonate ions. The research will also evaluate how modifications in media composition such as uranium and bicarbonate concentrations affect changes in the microbial community. This line of research will be extended to the next year. Microbial cultures for this research will be obtained from PNNL.

### **Subtask 1.3: Evaluation of Ammonia Fate and Biological Contributions During and After Ammonia Injection for Uranium Treatment**

#### ***Subtask 1.3.1: Investigation of $\text{NH}_3$ partitioning in bicarbonate-bearing media***

In order to understand the equilibrium and kinetics of partitioning of  $\text{NH}_3$  and U(VI) in these systems, saturated batch experiments will be used to investigate  $\text{NH}_3$  and U partitioning within the solid and aqueous phases. Hanford sediments and pure minerals including quartz, smectite (i.e. montmorillonite), illite, kaolinite and calcite will be included in the experiments. The pure minerals were chosen based on Table 2 and include the major components of the bulk and clay-sized fraction as well as kaolinite because it is a common mineral at multiple DOE sites and calcite because it is a reactive mineral. Unsaturated batch experiments and saturated flow cell reactors will be within the scope as well to ensure that the complexities of the vadose zone are fully understood. In addition to the experiments described below, speciation modeling will also be conducted for comparison with experimental results.

- Initial batch experiments will consider equilibrium U(VI) adsorption to the solid phase [pure mineral or Hanford soil] and mineral dissolution at initial ionic strength similar to Hanford groundwater [using NaCl or NaNO<sub>3</sub> or NaClO<sub>4</sub>] at pH 7.5. After batch suspensions have equilibrated, the pH will be adjusted to 11.5 – 12.5 with either NaOH or NH<sub>4</sub>OH (at variable molar strengths) to investigate U partitioning and mineral dissolution. If necessary, the final ionic strength will be adjusted so that each sample is at similar final ionic strength. Further investigations of aqueous speciation are also within this scope. The goal of these experiments is to discriminate between effects solely related to the pH fluctuation and effects of ammonia ions.
- The above experiments will be repeated with NH<sub>4</sub>OH and data describing the kinetic sorption (at pH 7.5)/desorption (at pH 12.5) for U(VI) and sorption for NH<sub>3</sub> at pH 12.5 will be gathered. Further monitoring of the experiments will be continued to monitor precipitation as the system re-equilibrates with air. Monitoring of pH, conductivity, NH<sub>3</sub>, U and major cations will be completed. These simplified experiments will describe the kinetics of U(VI) partitioning and mineral dissolution caused by ammonia injection via simple systems.
- Further experiments will investigate NH<sub>3</sub> and U partitioning in aqueous solutions with batch experiments at variable pH (7.5-12.5), variable bicarbonate (beginning with 0 and 3 mM HCO<sub>3</sub><sup>-</sup>), constant total ionic strength (adjusted by NaCl, NaClO<sub>4</sub> or NaNO<sub>3</sub> electrolyte), ammonia (0 – 2.5 M), uranium (500 ppb) and solids (25 g/L, pure minerals and Hanford soil). The objective is to elucidate the kinetics in batch simple systems under a range of conditions relevant to the Hanford vadose zone.

**Table 2. Major Minerals in the 200 Area (Serne et al., 2008)**

<b>Mineral</b>	<b>Bulk Fraction</b>	<b>Clay-sized Fraction</b>
Quartz	30-80	5-10
Feldspar	10-30	<5
Smectite	ND	30-35
Illite	ND	15-40
Chlorite	ND	15-20
Kaolinite	ND	ND-10
Calcite	ND-5	15-20

***Subtask 1.3.2: Bacterial community transformations before and after NH<sub>3</sub> additions***

- Investigate the bacteria community transformation in soil before and after ammonia addition. The evaluation of the bacterial community will require molecular biology tools. These experiments will be conducted at PNNL during students' summer internships.

***Subtask 1.3.3: The influence of microbial activity on the corresponding electrical geophysical response after ammonia injections in the vadose zone***

- FIU will work with PNNL to investigate the influence and corresponding electrical geophysical response of microbial activity on vadose zone uranium sequestration using gas phase ammonia injections. The first objective is to address the following through a literature review:

- What influence might microbial activity have on the pore water pH level after ammonia injection? Is that influence detectable in the spectral induced polarization (SIP) magnitude response and distinguishable from the SIP magnitude response caused by ammonia partitioning into the pore water?
- What influence might microbial activity have on the dissolution and subsequent re-precipitation of silicate minerals after ammonia injection? Is that influence detectable in the SIP phase response, and distinguishable from the SIP phase response caused by dissolution/precipitation in a sterile environment?
- Depending on the outcome of the previous questions, is it possible to use SIP at the field scale to determine the influence of microbial activity on the performance of gas phase ammonia uranium sequestration?
- Following a literature review of the field, initial experiments utilizing 1-D laboratory columns will be set up at the Applied Research Center. However, initial experiments will be completed at PNNL during student summer internships under the supervision of Jim Szecsody and Timothy Johnson.
- FIU will support one or more students at PNNL for the execution of this scope with supervision.

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

---

### **Background**

During the cold war period from 1955 until 1988, SRS was involved in the production of plutonium and irradiated fuel, which created a large amount of radioactive and hazardous acidic waste. Approximately 1.8 billion gallons of acidic waste solutions (pH from 3.2 to 5.5) contaminated with a variety of radionuclides and dissolved metals were discharged into F/H Area's unlined seepage basins located in the center of SRS. The acidic nature of the basin waste solutions caused the mobilization of metals and radionuclides, resulting in contaminated groundwater plumes. The constituents of concern (COCs) associated with the F-Area groundwater plume are tritium, uranium-238, iodine-129, and strontium-90. The COCs in the H-Area are tritium, strontium-90 and mercury. The pump-and-treat water treatment unit designed and built in 1997 to remove metals and radionuclides eventually became less effective, prompting research for new remedial alternatives. Humic substances (HS) are ubiquitous organic macromolecules that account for 50 - 80% of the organic carbon in the soil or sediment, which have variable composition formed by the microbial decomposition of biomass. HS are known for their excellent binding capacity for metals, making HS a strong candidate for remediation efforts to reduce the mobility of uranium (VI) in the subsurface. Three main fractions of HS are identified based on their solubility in dilute acids and bases. Humic acids (HA) represent a fraction which is soluble in base but insoluble at pH<2; fulvic acids (FA) are a fraction that is soluble under all pH conditions, and humins are insoluble under all pH conditions. Studies showed that HA can function as an important ion-exchange and metal-complexing ligand carrying a large number of functional groups with high complexing capacity that can greatly affect the mobility behavior of actinides in natural systems.

This task also involves expansion of FIU's research related to the SRS F/H area environmental issues and investigates whether any synergy exists between colloidal silica and humic acid that may affect the removal of uranium from contaminated groundwater. These experiments also suggest if the sodium silica solutions have sufficient alkalinity to restore the pH of the treatment zone and whether silica solutions can be injected into the subsurface without clogging the aquifer permeability. Other studies will include column experiments, which simulate the creation of a humate treatment zone where acidic groundwater contaminated with uranium has been introduced.

## Objective

There are several objectives of the proposed experimental work for this task. **Subtask 2.1**, "*FIU's support for groundwater remediation at SRS F/H Area*," will: (i) determine the optimal concentration of sodium silicate for the restoration of the pH of the treatment zone in a multi-contaminant system, (ii) assess the efficiency of the proposed remediation technology on the immobilization of contaminants of concern, (iii) investigate the stability of the sequestered contaminants after sodium silicate application, (iv) examine the role of soil's properties in the formation and behavior of colloidal silicate particles and precipitates, and (v) examine transport properties of sodium silica and silica particles through soil porous media.

The objective of **Subtask 2.2**, "*Monitoring of U(VI) bioreduction after ARCADIS demonstration at the SRS F-Area*," is to conduct thermodynamic speciation modeling for the conditions pertaining to the low alkaline SRS acidic soil augmented with molasses and sulfate to suggest the possibility of siderite and pyrite minerals formation.

**Subtask 2.3**, "*Humic acid batch sorption experiments into the SRS soil*," will determine if the low cost unrefined humate solution known as Huma-K, which contains humic/fulvic acids of different molecular weight, can be used to facilitate uranium adsorption in order to control its mobility in acidic groundwater. The study also evaluates environmental factors that could possibly enhance desorption process of HumaK previously sorbed to SRS sediments, and investigates to what extent HumaK can get desorbed. In addition, the study initiates experiments addressing the removal behavior of uranium using Huma-K and SRS sediments. The purpose of this study is to evaluate the removal effectiveness of uranium for the following experimental conditions:

- Savannah River Site sediments + Uranium
- Savannah River Site sediments + Uranium + Huma-K
- Sediments coated with Huma-K + Uranium
- Uranium + Huma-K

In addition, **Subtask 2.4**, "*The synergetic effect of HA and Si on the removal of U(VI)*," will investigate synergetic interactions between humic acid (HA) and colloidal silica that may influence the removal of uranium in the presence of SRS sediments. Specifically, research will evaluate the effect of 30 ppm of HA and compare results with previously obtained data on the addition of 10 and 50 ppm of HA.

The objectives of the proposed research under **Subtask 2.5**, *“Investigation of the migration and distribution of natural organic matter injected into subsurface systems,”* are to understand the sorption of humic acid versus pH and study the effect of HA on uranium mobility through porous media via flow-through column experiments. For each of the column tests, a series of samples will be collected at the column exit and will be measured to determine the breakthrough curves as a function of pH. Analytical methods will be applied to determine the sorption parameters and the interactions between metal and HA.

## **Benefits**

**Subtask 2.1:** The proposed FIU research for the F/H Area at SRS will investigate whether dissolved sodium silicate solutions, an environmentally benign reagent, can replace the carbonate base used so far to correct the acidic nature of the contaminated sediments. Furthermore, it will evaluate the extent that silica, through polymerization and/or coagulation reactions at low pH values, can co-precipitate uranium and other contaminants present in the groundwater, as well as the role of other factors, such as the presence of iron, in this process. The presence of iron oxide, for example, could accelerate Si polymerization and/or coagulation reactions, leading to a more extensive co-precipitation of radionuclides with Si gel. This research project will also attempt to provide a better understanding in the formation of Si colloidal particles and subsequently, the colloidal transport/immobilization of contaminants through soil porous media.

**Subtask 2.2:** ARCADIS EARP molasses injection technology, applied in the F/H Area, relies on changing the geochemical conditions in a direction that is opposite of their natural evolution. In addition to experiments conducted in FIU Year 5, speciation modeling will be done to suggest the possibility of siderite or pyrite solid phase formation and recommend the applicability of this technology for the low alkaline conditions of SRS.

**Subtask 2.3:** This study will use desorption experiments to evaluate whether the sorption of HumaK onto SRS sediments is a reversible process. It will also help to understand the binding mechanism of HumaK onto SRS sediments. Furthermore, experiments will provide information on the stability of this remediation method and advise if this technology is a feasible method to remove uranium from acidic groundwater typical at SRS.

**Subtask 2.4:** The investigation under this subtask will evaluate via batch reactors the synergy between colloidal Si and humic acid on the removal of U(VI) from the treatment zone and analyze post- reacted sediments for surface morphology and composition.

**Subtask 2.5:** Under this subtask the sorption behavior of Huma-K versus pH will be evaluated in the flow-through experiments mimicking SRS field application conditions. This subtask will provide coupling between flow and transport of the contaminant in the subsurface and will investigate the spatial and temporal changes within the subsurface to simulate the response of the system after injection of humate.

## **Technical Approach**

The scope of work under this task will include five technical subtasks conducted in collaboration with scientists at the Savannah River Site. These subtasks will focus on evaluation of silica- and humate-based techniques for remediation of uranium-contaminated groundwater.

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

During FIU Year 5, the experimental procedures were focused on determining the amount of sodium silicate that would restore the pH in circumneutral conditions and would achieve uranium removal from the aqueous phase. In an effort to mimic the real SRS conditions in the lab, co-contaminants, such as Sr(II) and Tc(VII) (through its surrogate  $\text{Re}^{7+}$ ) will be included in the experiments and the efficiency of sodium silicate concentration used so far to remove uranium from the solution mixture and restore pH to the neutral conditions will be re-assessed. The suggested remediation technology could be effective in the removal of Sr(II) along with U(VI), due to the role that positively charged cations play in the de-stabilization of negatively charged silica colloidal particles leading to their consequent precipitation. On the other hand, the amendment with sodium silicate is not expected to affect the negatively charged perhenate ions, based on an electrostatic interactions hypothesis. Nevertheless, it is important to study the efficiency of the remediation method proposed in a multi-contaminant system. Furthermore, the conditions under which insoluble calcium uranate ( $\text{CaUO}_4$ ) is formed will be explored. Another critical factor to be investigated is the stability of the sequestered contaminants after any treatment. To this end, batch liquid extractions will be performed to measure uranium concentrations in aqueous and adsorbed phases. These experiments will use SRS synthetic groundwater with pH adjusted to the SRS groundwater range (pH 3-5). Furthermore, uranium extractions using more aggressive liquids will be considered in an effort to further elucidate the stability of the solid formations.

In our previous experiments, significant amounts of iron and aluminum were detected in the aqueous phase. Both these elements can be traced back to the soil composition, as SRS synthetic groundwater does not contain any of them. Cations, due to their positive charge, are known for their capacity to destabilize the negatively charged silica particles, resulting in colloidal precipitation that frequently encompasses metal cations present in the aqueous phase. The contribution of Fe and Al cations to the formation and behavior of silica amorphous particles is going to be explored with batch experiments that, instead of SRS soil, will include mixture of pure quartz and kaolinite (absence of Fe), as well as pure quartz (absence of both Al and Fe).

Finally, the transport properties of colloidal particles and dissolved silica through soil porous media will be investigated. Continuous flow experiments will assist in comprehension of the mobility and wash out of colloidal particles, as well as solid forms of interest.

Analysis of U(VI) is going to be performed with kinetic phosphorescence analyzer (KPA), while the rest of the contaminants, as well as Si, are going to be analyzed with inductively coupled plasma – optical emission spectroscopy (ICP-OES). Any filter samples that retain any colloidal formations are going to be dried in a conventional oven and will be analyzed through scanning electron microscopy – energy dispersion microscopy (SEM-EDS) in order to further elucidate the nature of the colloidal formations.

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

FIU will conduct thermodynamic speciation modeling using data obtained in microcosm experiments prepared with SRS sediments, augmenting the solution mixture with molasses and sulfate. The microcosm experiments were completed in May 2015. The thermodynamic

modeling for the conditions pertaining to the low alkaline SRS acidic soil augmented with molasses and sulfate would predict the possibility of siderite and pyrite mineral formation. The results of the modeling can also indicate the applicability of this technology for the low alkaline conditions. In addition, FIU will keep a placeholder for this subtask in the event the site would need support or technical assistance for diffusion trap sample analysis.

### **Subtask 2.3: Humic acid batch sorption experiments into the SRS soil**

This study will determine if the low cost unrefined humate solution known as Huma-K, which contains humic/fulvic acids of different molecular weight, can be used to facilitate uranium adsorption to control the mobility of uranium in acidic groundwater. In Year 6, FIU will extend batch experiments to investigate the kinetics of the humic substances desorption process. Desorption experiments will help to understand the mechanisms that govern the interactions of humic substances in HumaK and SRS sediments. The study will be conducted by first adsorbing a known concentration of HumaK at low pH (pH = 4) onto a SRS soil sample of known weight (1g). In the previous experiments, it was found that at pH 4 there was a precipitation of humate. This amount of precipitated humate will be taken into account during desorption studies to distinguish between desorption and re-dissolution processes. The supernatant will be removed and then replaced by DI water with pH adjusted to the same level (pH = 4). At predetermined time intervals, samples will be withdrawn and centrifuged. The concentration of the supernatant will be measured by UV-vis spectrophotometer. The amount of the remaining adsorbed Huma-K will be calculated from the difference between the initial concentration of adsorbed Huma-K and the Huma-K concentration remained in the supernatant from desorption. The concentration that was sorbed will be determined by using UV-vis spectrophotometer. Similar experiments will be conducted to investigate the Huma-K desorption kinetics and the effect of environmental conditions such as pH (from 4 to 8) and presence of  $\text{NaNO}_3^-$  salt on the Huma-K desorption from sediments. The experimental design for the desorption experiments will include the replacement of the supernatant solution after the adsorption process is completed by DI water with pH values adjusted to the same conditions as sorption. The effect of sodium nitrate on the desorption process will be investigated via replacement of the supernatant solution by DI water containing  $\text{NaNO}_3^-$ , which is a typical anion in the SRS groundwater. Since  $\text{NO}_3^-$  is an anion, it can be electrostatically attracted to the positive charged sites of the sediments, so the surface may become neutral or negatively charged, and this could diminish the sorption of HumaK because it could block the binding sites where HumaK could bind. Also, an attempt will be made to initiate experiments on the kinetics of uranium removal in the presence of HumaK at pH 4. The concentration of U(VI) will be analyzed with kinetic phosphorescence analyzer (KPA). This study will be continued in the following year to investigate the effect of different environmental factors that could diminish the uranium removal process using HumaK.

### **Subtask 2.4: The synergistic effect of humic acid and colloidal silica on the removal of uranium (VI) in the conditions pertaining to F/H Area of SRS**

Previous studies suggested that the retention of U(VI) via sorption in the presence of HA is a complex process that mainly depends on the types of soil minerals, HA concentrations and the experimental conditions. This task will investigate if there are any synergistic interactions between U(VI) ions, humic acid and colloidal silica under oxidized conditions and study the influence of HA and Si on the sorption of U(VI) onto sediments collected from the F/H Area.

Experiments will also study the effects of different environmental variables such as pH ranging between 3 and 8, presence of U(VI) and concentrations of HA and colloidal Si on the removal behavior of U(VI) in the multi-component batch systems.

The synthetic groundwater will be formulated based on the concentration of elements found in the contaminated groundwater with pH adjusted in the range from 3 to 8. The following binary, ternary and quaternary systems will be evaluated at each pH conditions in the presence and absence of HA on the removal of U(VI) from the aqueous solutions:

- Si (3.5 mM) + U(VI) (0.5 ppm)
- Si (3.5 mM) + U(VI) (0.5 ppm) + HA (30 ppm)
- U(VI) (0.5 ppm) + HA (30 ppm)
- Sediments + Si (3.5 mM) + U(VI) (0.5 ppm)
- Sediments + Si (3.5 mM) + U(VI) (0.5 ppm) + HA (30 ppm)
- Sediments + U(VI) (0.5 ppm) + HA
- Sediments + U(VI) (0.5 ppm)

Fumed colloidal silica, silicon (IV) oxide 99%, will be used as a source of silica and humic acid sodium salt (50-60% as humic acid) as a source of HA. Some previously conducted experiments with 10 ppm of HA will be repeated to maximize the accuracy of the results. The sediments' surface composition will be analyzed via scanning electron microscopy and energy-dispersive-spectrometry (SEM-EDS). The quantitative measurements of the surface composition will show the distribution of elements throughout the sample. The distribution of carbon might suggest if HA polymerized and precipitated on the surface or between sediment particles. The SEM-EDS analysis will also reveal surface topography and provide information of any correlation between elements across the surface.

#### **Subtask 2.5: Investigation of the migration and distribution of natural organic matter injected into subsurface systems**

FIU will continue to work in coordination with SRS and DOE Office of Soil and Groundwater personnel to conduct column experiments that will simulate humic acid (HA) flow through porous media and evaluate its effect on uranium contamination. HA organic molecules become less mobile as the pH of the solution is reduced due to the flushing by SRS groundwater, which is acidic in nature. Column experiments to study the sorption/desorption of humic acid and its effect on the uranium mobility using SRS soil collected from the F/H area will be continued to completion at FIU-ARC. The data from these experiments will then be used to perform modeling of the migration and distribution of HA injected in the subsurface. For each of the column tests, a series of samples will be collected at the column exit. These samples will be analyzed and concentrations will be plotted as effluent breakthrough curves. Obtained data will be used to determine the transport parameters of HA and HA in combination with U(VI), which would impact the sorption/ desorption behavior of radionuclides.

## **Task 3: Surface Water Modeling of Tims Branch**

---

### **Background**

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

Tims Branch is a second order stream in the A/M Area of SRS. In 2000 and 2007, innovative mercury removal systems were initiated in the northern and eastern headwaters of Tims Branch; a wetland treatment system and an air stripping system, respectively. These treatments effectively eliminated mercury inputs to Tims Branch. The air stripping treatment system resulted in the controlled discharge of low-levels of inorganic tin oxide particles into the ecosystem. Sampling of the biota in Tims Branch (2006 and 2010) documented that mercury concentrations in fish have decreased significantly (more than 70% in the contaminated reach) since 2007. Additional sampling will be required to document the sustainability of the observed decreases and to document the ultimate performance of the system in reducing mercury concentrations in fish. Results from this study are key to evaluating the effectiveness of wetland treatment and tin (II)-based mercury treatment at the SRS site, and are also relevant to evaluating the potential of using water treatment and novel remediation technologies in other mercury-contaminated stream systems.

This research will directly support interpretation of historical data on the trends in contaminant concentrations in Tims Branch biota, and support planning and execution of future biota sampling in this important ecosystem. A secondary objective of the research is to support DOE-supported student interns (DOE Fellows) and foster collaboration among the Savannah River National Laboratory, Florida International University and the Savannah River Ecology Laboratory scientists.

### **Objectives**

The overall objectives of this task are:

- Development of an integrated hydrological model of the Tims Branch watershed.
- Development of a GIS-based data management system (geodatabase) and the use of GIS tools for processing and visualization of spatial and temporal data to support hydrological model development.
- Sample and data collection for development of an eco-hydrological database to support the modeling efforts. Student support for sample and data collection during student internships will help to foster collaboration with SRNL/SREL

Model development includes extensive data preparation, preliminary simulation, calibration, validation, and visualization. During FIU Year 5, preliminary development of a hydrological model of the Tims Branch watershed was initiated, supported by the application of GIS tools for preparation of model-specific data parameters. The work scope for FIU Year 6 to Year 10 will therefore include:

- Completing the incorporation of the MIKE SHE model configuration parameters required for simulation of the spatiotemporal distribution of overland flow (OL), evapotranspiration (ET), and flow in the unsaturated and saturated zones (UZ/SZ) of the Tims Branch watershed.
- Running the OL/ET/UZ/SZ modules simultaneously within the MIKE SHE model domain for prediction of the water balance of the Tims Branch watershed.
- Developing a 1-D model of the Tims Branch stream network using MIKE 11 to simulate flow depth and velocity over time in Tims Branch.
- Coupling the MIKE SHE watershed model and the MIKE 11 river model to simulate flow in the Tims Branch watershed.
- Integrating the coupled MIKESHE/MIKE 11 flow model with ECO Lab to simulate sediment/contaminant transport in the Tims Branch watershed. Modeling the sediment/contaminant transport is dependent on the results of the surface flow simulation; therefore the transport model will be developed after the surface water model is fully developed.
- Calibrating the models to evaluate and refine parameter values by comparing simulated and observed values in an attempt to develop a model that represents the watershed. Different statistical evaluation methods will be employed to ensure the accuracy of the calibration results. This calibration and validation exercise helps to improve the predictive capability and reliability of the model. The main steps used for model calibration include: identification of calibration parameters, sensitivity analysis and numerical optimization.
- Performing model uncertainty and sensitivity analyses.
- Performing simulations of extreme storm events to: (a) understand the potential impact on flow depth and velocity in Tims Branch, (b) determine the potential for contaminant transport due to the resuspension and remobilization of sediment during such extreme events, and (c) identify areas where sediment/contaminants might further be deposited.

These tasks will be further supported by *in situ* data collection and sampling of sediment, biota, and biofilm in Tims Branch watershed and analysis of the collected samples to quantify tin, mercury, and uranium concentrations.

## Benefits

Conventional hydrologic and remediation analytical tools (accepted by EPA, USACE, and USGS) in combination with latest scientific software (2D/3D numerical flow and transport models integrated with reaction kinetics and thermodynamic software) provides an integrated solution for understanding mobility and impacts of contaminants at DOE sites. The model being developed can be used as a tool to provide a better understanding of the effect of extreme weather on flow in Tims Branch. This modeling effort also provides state-of-the-practice tools

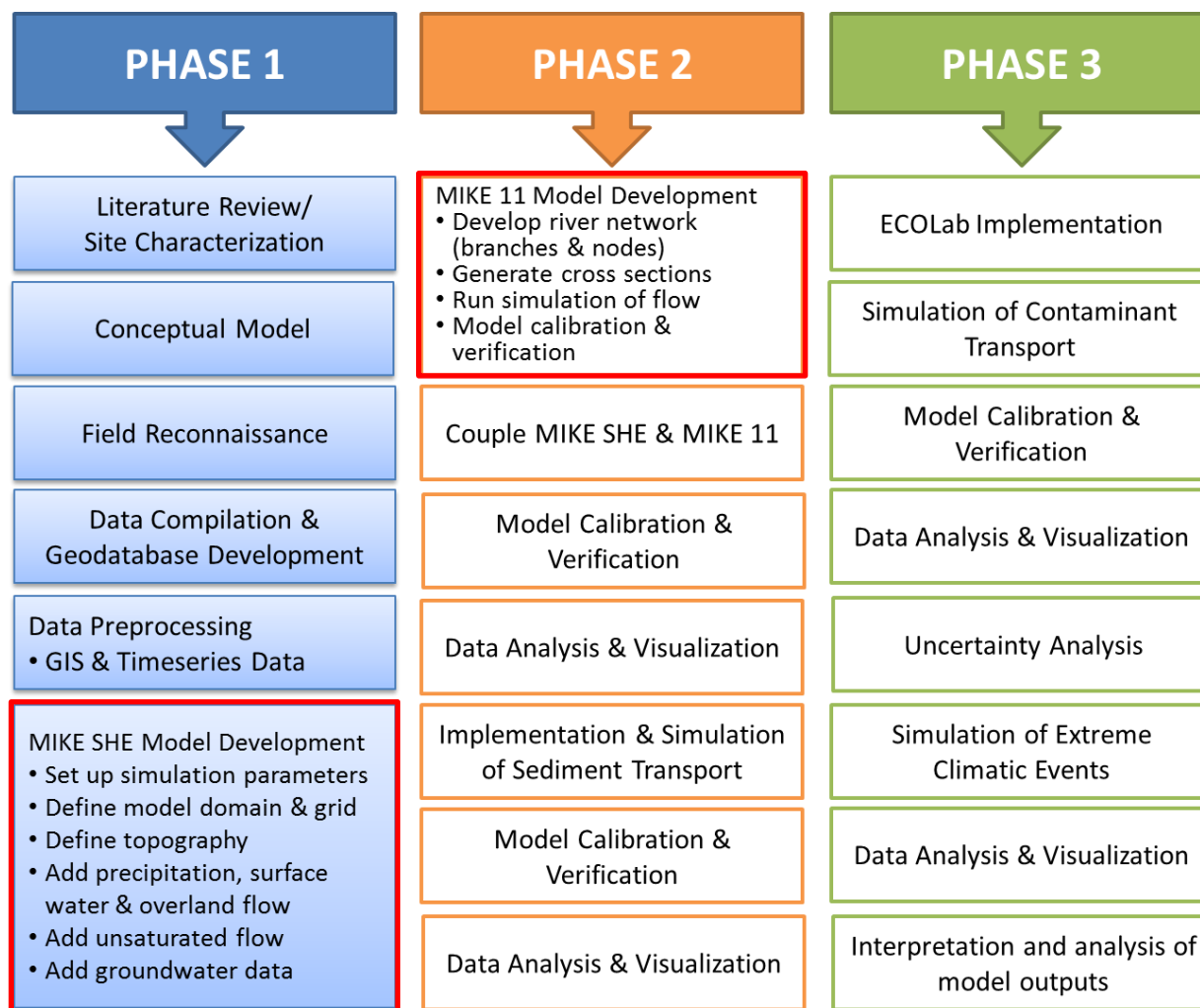
for analysis of green and sustainable remediation alternatives needed to address long term sustainability in terms of reduced environmental and energy footprints of remedial actions.

The MIKE SHE/MIKE 11 hydrological modeling package being used has a geographic information systems (GIS) user interface built into its system that can directly use spatial GIS databases (geodatabases) for model inputs. The use of GIS data is significant not just for the spatial representation of hydrologic features, but particularly because of its integration with timeseries data attributes such as flow rates and directions, contaminant concentrations, water levels, precipitation, etc. Availability of data in this format shortens the time for model-specific data preparation and ultimately model development. The geodatabase provides an advanced spatial data structure needed to address the management, processing, and analysis of large GIS and timeseries datasets derived from multiple sources that are used for numerical model calibration, uncertainty analysis, and simulation of flow and contaminant fate and transport during extreme climatic events. The geodatabase developed is based on the ArcHydro and ArcGIS Base Map data models with modifications made for project-specific input parameters. The significance of this approach was to ensure its replicability for potential application at other DOE sites. Application of GIS tools will also aid in the pre-processing and analysis of hydrological model data; automation of repetitive geoprocessing tasks; and production of maps for visualization of the surface water hydrology of the Tims Branch watershed.

Performing simulations of extreme storm events provides DOE-EM/SRS with information that can assist in: (a) understanding the potential impact on flow depth and velocity in Tims Branch, (b) determining the potential for contaminant transport due to the resuspension and remobilization of sediment during such extreme events, and (c) identifying areas where sediment/contaminants might further be deposited.

### **Technical Approach**

**During FIU Year 6**, FIU will continue to support SRS and DOE Office of Soil and Groundwater remediation goals by conducting a targeted study of contaminants and the recovery of Tims Branch, which may include biota and biofilm sampling, and flow and contaminant transport modeling of Tims Branch to examine the response of the ecosystem to innovative EM-developed remediation treatment technologies that have eliminated anthropogenic mercury sources from this watershed.



**Figure 1. Hydrological modeling phases and detailed future plans.**

Figure 1 provides an outline of the modeling work scope for simulation of the fate and transport of tin in the Tims Branch watershed. During FIU Year 5, FIU completed several components of Phase 1 which included a literature review and site characterization; development of a conceptual model of the Tims Branch watershed; creation of a geodatabase to store and manage the data being used for hydrological model development; the use of GIS tools to preprocess hydrological model data; and preliminary development of the MIKE SHE hydrological model. Preliminary model development has included the simulation of overland flow, which is one of the main components of the MIKE SHE modeling system in hydrological analysis due to the fact that a significant amount of water flows as overland flow/surface runoff that joins streams and waterbodies. Knowledge of the temporal and spatial distribution of overland flow helps to understand flow as a function of climate and catchment characteristics in the land phase of the hydrological cycle. Accurate prediction of overland flow helps to understand the surface water responses to changes in vegetation, climate variability and topography of a watershed. In this study emphasis was placed on understanding the characteristics of overland flow as a function of climate and catchment characteristics and other hydrological processes including evapotranspiration, infiltration and unsaturated and groundwater flow. During FIU Year 6, FIU

will complete Phase 1 and begin the preliminary stages of Phase 2. Further details of the FIU Year 6 work scope (highlighted in red in Figure 1) is provided below.

### **Subtask 3.1: Modeling of surface water and sediment transport in the Tims Branch ecosystem**

Surface water and sediment transport models will be applied to the Tims Branch ecosystem. Supplementary models will also be applied to match and predict the behavior of mercury, tin, and other elements (e.g., uranium) in this ecosystem. Note that the Tims Branch ecosystem represents an important applied science opportunity as a result of significant past research by SREL and SRNL. This collaborative effort is specifically focused on improving the conceptual and quantitative modeling of a real-world ecosystem that was impacted by DOE operations for 50 years and which is now recovering. Recently, innovative EM-developed treatment technologies have eliminated anthropogenic mercury sources from this watershed and introduced a known quantity of relatively inert tin oxide tracer.

The hydrological model being developed will be used as a tool to simulate flow and the potential for contaminant (mercury, tin and uranium) transport in Tims Branch during extreme storm events. This will provide valuable insight during the monitoring phase following the implementation of the applied remediation technology to remove the mercury contamination in Tims Branch. The work scope to be performed in FIU Year 6 includes:

- Extension of the model domain to incorporate the entire Tims Branch watershed (*as opposed to just the portion that lies within the SRS boundary that was previously used based on available data provided*).
- Refinement of the MIKE SHE model developed in FIU Year 5 to simulate overland flow with configuration parameters that have been modified according to the revised model domain (Tims Branch watershed).
- Input of MIKE SHE model configuration parameters required for simulation of evapotranspiration and flow in the saturated and unsaturated zones.
- Preliminary data preparation and model setup for development of the Tims Branch stream network required for simulation of channel flow using MIKE 11.

Preliminary simulations will be conducted with completed MIKE SHE components only (as identified above) and will not include stream flow. Completion of the MIKE 11 set-up, coupling of MIKE SHE and MIKE 11, model calibration and verification, incorporation of ECO Lab, simulation of extreme climate events and other relevant scenarios will be conducted in FIU Year 7 and beyond. Calibration and validation will be performed after coupling to ensure model capability to simulate surface water flow in the entire domain. Sensitivity analyses will be implemented to examine the model responses to changes in various parameters. Uncertainty analysis will be carried out to determine the reliability of developed model predictions based on input parameters and *in situ* data measurement.

### **Subtask 3.2: Application of GIS technologies for hydrological modeling support**

A geodatabase was developed by FIU to support the hydrological modeling work being performed at SRS by serving as a centralized data storage and management system, which stores

data required by or derived from the GIS-based water resources applications. The existing geodatabase will be updated with recent SRS site monitoring data available from various sources including SRNL, USGS, NRCS STATSGO or SSURGO soil databases, and the U.S. EPA MRLC or NALC land cover databases. GIS modeling tools will also be applied to perform associated geoprocessing of downloaded or model-derived data. Training will be provided to FIU graduate and/or undergraduate students on how to update and query the existing geodatabase within the ArcGIS environment, perform geoprocessing tasks and generate maps and graphs for reporting purposes.

The work scope to be performed in FIU Year 6 includes:

- Download and pre-processing of model-specific geospatial and timeseries configuration parameters to fill in data gaps needed for the revised Tims Branch watershed model domain using GIS tools.
- Update of GIS maps of Tims Branch hydrology, geology, land use, vegetation cover, topography, etc. for revised model domain.
- Development of a report on the methodology for development of the GIS-based data management system (geodatabase) and the use of GIS tools for processing and visualization of spatial and temporal data used in hydrological model development.
- Geospatial analysis of timeseries data to depict for example land use and topographic changes in the Tims Branch watershed over time.

### **Subtask 3.3: Biota, biofilm, water and sediment sampling in Tims Branch**

The sampling and analysis activities identified under this task will require identification of sufficient funds for SRNL/SREL to support site-required permitting and oversight activities and sample preparation and analysis costs. The task includes sampling fish and other biota, water and sediment in Tims Branch to assess the ecosystem response (cleanup progress) to applied remediation technologies; analysis of total mercury and tin in tissue, biofilm and sediment; and possible speciation analysis on sediment for mercury, tin and other elements (e.g., uranium). This would provide a key peg-point documenting the impacts of the innovative stannous chloride air stripping technology for mercury in outfalls and has the potential to show that fish concentrations have been reduced below FDA guideline levels. The sampling will be initiated by FIU students during their summer 2016 internship at SRNL/SREL and continued if necessary throughout the year by FIU students and/or ARC researchers. Samples will be primarily analyzed by SRNL/SREL. Sediment samples requiring the use of scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDS) technology for determination of surface morphology at the nanoscale level and elemental composition will be shipped to FIU for analysis.

Student support will be provided during FIU Year 6 for:

- Biofilm sampling in Tims Branch (SRNL).
- Water and sediment sampling in Steed Pond to be analyzed for tin believed to be present at the nanoscale level (SRNL). ARC to assist with SEM analysis of the sediment samples from Steed Pond for tin.

- Water and sediment sampling in Tims Branch to be analyzed for uranium. Data parameters would be used for model simulation using the hydrological model currently being developed by FIU for Tims Branch. Sample analysis will be carried out by SREL.
- Re-establishing the Steed Pond/Tims Branch sampling station where measurements were previously taken by SREL using a YSI water monitoring unit and an ISCO sampler. Updated equipment (as determined by FIU/SREL) will be deployed by an FIU student/staff member and periodically calibrated for estimation of stream flow and turbidity. Routine monitoring will then continue throughout the year by either a student or FIU-ARC researcher with support from SREL personnel.

## **Task 4: Sustainability Plan for the A/M Area Groundwater Remediation System**

---

### **Background**

The research and analysis under this task is being performed in support of DOE EM-13 (Office of D&D and Facilities Engineering) under the direction of Mr. Albes Gaona, program lead for DOE's Sustainable Remediation Program.

Sustainable remediation analyses require the collection and analysis of historical site remediation system design and performance including electrical energy usage, contaminant recovery per well, optimized air stripper operation, and more. During 2014-2015, extensive analysis of contaminant recovery per well was performed and published in reports and publications. FIU searched through SRS annual reports to locate per well recovery of TCE and PCE from the start of operations until December 2012 (the end of current data supplied to FIU to date). FIU plotted the monthly mass of TCE and PCE recovered from wells RWM 1-12 from 1987 to 2012. FIU has also analyzed the equipment, processes, hydraulic containment of contamination, and is developing a set of actions for the existing infrastructure of the groundwater remediation system that will reduce the environmental burden of the A/M Area groundwater remediation system. Below is a description of the task plan for the sustainable remediation analysis of the SRS A/M Area groundwater remediation system which will follow from FIU Year 5 research. The analysis and a report will be completed by December 18, 2015 that will complete this analysis.

### **Technical Approach**

#### **Subtask 4.1: Sustainable Remediation Analysis of the M1 Air Stripper**

During FIU Year 6, FIU will work with SRNL and DOE EM-13 to complete an engineering analysis of the M1 air stripper's components and operation, and make recommendations for greener and more sustainable alternatives. FIU is proposing to develop a set of actions for the existing infrastructure of the groundwater remediation system that will reduce the environmental burden of the A/M Area groundwater remediation system while potentially reducing the duration of operation for the treatment system.

The analysis of the M1 Air Stripper will focus on the M1 air stripper: its mechanical systems, volume flow rate of water and contaminant concentration, performance of the packing material, and the blower motor.

The existing environmental burden associated with operating the A/M Area groundwater remediation system will be determined. This baseline will serve as the basis for identifying opportunities and evaluating options. The following information has been compiled to establish the baseline: historical trends of groundwater pumping, line pressure, contaminant concentration, water level and mass recovery for individual recovery wells, air/water ratio, flow rates and influent concentration operating time for the air stripper. Additional systems and activities, such as system control and monitoring, will be reviewed to complete the baseline picture.

Recovery wells in the A/M Area groundwater remediation system have been operated with constant speed pumps since the system began operation. The constant speed pumps produce line pressures that range from 35 – 95 psig. In some cases, the pumps may be producing excess pressure that is not required and as a result are continuously consuming energy that is not necessary for operation. The piping diagram and operating pressure throughout the system will be studied to identify wells which may be able to operate using a smaller pump while still maintaining the same flow rate.

The A1 air stripper has operated at a constant air/water ratio since it began operation. The air/water ratio was set to treat the prevailing influent contaminant concentrations existing at start-up. Contaminant concentrations have decreased significantly over the last 27 years of operation and, as a result, the air/water ratio can likely be decreased. The water flow rate is set by the hydraulic containment objective and is not considered to be an option for improvement. The air flow rate, however, is based on the influent contaminant concentration. It is believed that the air flow rate can be reduced and still meet the discharge limits at the outfall receiving effluent from the A1 air stripper. Reducing the air flow rate would significantly reduce the energy demand since the A1 air stripper operates constantly. Current influent concentrations will be used with published design guidelines for air strippers to determine the minimum air flow rate that would meet treatment specifications. A new blower will be recommended based on the outcome of the air stripper analysis.

The following steps are proposed:

- Analysis of available data of air mass flow rates and contaminant removal efficiency. Determine the overall system efficiency and provide recommendations for the optimal air flow rates which will provide the lowest overall cost of operation.
- Analysis of the contaminant concentration from all recovery wells feeding the M1 air stripper and the current packing material and recommend component and process changes to improve the efficiency, lower the electrical energy usage and lessen the environmental footprint of the stripper operation.
- Development of an engineering analysis with input from SRNL and the SRS remediation contractor for improvement to the M1 air stripper.
- Analysis of a renewable energy system to power the M1 air stripper to include solar and/or wind. This would include costs for components properly sized and for installation.

#### **Subtask 4.2: Sustainable Remediation Support to DOE EM Student Challenge**

During FIU Year 6, FIU will use the lessons learned and sustainability expertise gained during FIU Year 5 under this project to provide guidance and support to the new Task 11 (DOE EM

Student Challenge) under Project 4 (FIU-DOE Science and Technology Workforce Development Program). The DOE EM Student Challenge is described fully in the Project 4 PTP. The DOE EM Student Challenge is the natural extension to the previous sustainable remediation analysis of SRS's A/M Area Groundwater Remediation System. It is expected that sustainability principles will be an integral part of the Challenge teams' technical solutions to the problem set being studied.

## **Task 5: Remediation Research and Technical Support for WIPP**

---

### **Background**

The following task is in support of the Los Alamos National Laboratory's field office in Carlsbad, New Mexico, and in collaboration with research scientist Donald Reed (LANL). This research center has been tasked with conducting experiments in the laboratory to better understand the science behind deep geologic repositories for the disposal of nuclear waste. The majority of their work is conducted in high ionic strength systems relevant to the Waste Isolation Pilot Plant (WIPP), located nearby. WIPP is currently the only licensed repository for the disposal of defense waste in the world.

However, the facility is not currently operating following an airborne release from a waste drum which failed to contain waste following an exothermic reaction of the waste. This was due to incompatibility of mixed waste received from LANL (organic adsorbent mixed with nitrate salt waste). Although off-site releases of  $^{239/240}\text{Pu}$  and  $^{241}\text{Am}$  were detected slightly above background, they were still below levels deemed unsafe to the public. FIU-ARC is now initiating a new task to support basic research efforts requested to update risk assessments for the WIPP site.

### **Objective**

The objective of this task is to support LANL researchers in the basic science research required to address concerns in risk assessment models for the re-opening of the WIPP site for acceptance of defense waste.

### **Benefits**

The benefits of this research will be further elaborated once the technical focus of experiments has been discussed further with research scientist Donald Reed at LANL.

### **Technical Approach**

FIU is working closely with Donald Reed at LANL to refine the scope of work for this task in order to provide environmental remediation research via laboratory experiments. Potential areas of research under discussion include: (1) solubility of the actinides at high temperature (30, 60, and 90°C) in the presence of ligands, (2)  $K_d$  coefficients for actinides under WIPP relevant conditions using batch and/or column experiments, and (3) investigate microbial interactions with actinides in high ionic strength systems.

## PROJECT MILESTONES

Milestone No.	Milestone Description	Completion Criteria	Due Date
2015-P2-M1	Submit draft papers to Waste Management 2016 Symposium	Acceptance notification by WM16 reviewers	11/6/2015
2015-P2-M2	Complete refinement of MIKE SHE model configuration parameters for the simulation of overland flow using revised model domain (Subtask 3.1)	Submission of memo by Project Manager	12/30/2015
2015-P2-M3	Complete input of MIKE SHE model configuration parameters for simulation of evapotranspiration (Subtask 3.1)	Submission of memo by Project Manager	2/29/2016
2015-P2-M5	Complete input of MIKE SHE model configuration parameters for simulation of unsaturated flow (Subtask 3.1)	Submission of memo by Project Manager	3/31/2016
2015-P2-M6	Complete input of MIKE SHE model configuration parameters for simulation of flow in the saturated zone (Subtask 3.1)	Submission of memo by Project Manager	6/30/2016

## DELIVERABLES

Client Deliverables	Responsibility	Acceptance Criteria	Due Date
Draft Project Technical Plan	Project Manager	Acknowledgement of receipt via E-mail two weeks after submission	10/05/2015
Draft sustainable remediation report for the M1 air stripper	Project Manager	Acknowledgement of receipt via E-mail two weeks after submission	12/18/2015
Progress report on the experimental results on autunite mineral biodissolution (Subtask 1.2)	Project Manager	Acknowledgement of receipt via E-mail two weeks after submission	2/15/2016
Presentation overview to DOE HQ/Site POCs of the project progress and accomplishments (Mid-Year Review)	Project Manager	Presentation to DOE HQ and Site POCs	2/29/2016**

Literature Review of Geophysical Resistivity Measurements and Microbial Communities (Subtask 1.3.3)	Project Manager	Acknowledgement of receipt via E-mail two weeks after submission	3/18/2016
Progress report on batch experiments on sodium silicate application in multi-contaminant systems (Subtask 2.1)	Project Manager	Acknowledgement of receipt via E-mail two weeks after submission	4/11/2016
Progress report on the synergy between colloidal Si and HA on the removal of U(VI) (Subtask 2.4)	Project Manager	Acknowledgement of receipt via E-mail two weeks after submission	4/21/2016
Progress Report for Subtask 3.1: Modeling of surface water and sediment transport in the Tims Branch ecosystem	Project Manager	Acknowledgement of receipt via E-mail two weeks after submission	4/29/2016
Progress Report for Subtask 3.2: Application of GIS technologies for hydrological modeling support	Project Manager	Acknowledgement of receipt via E-mail two weeks after submission	4/29/2016
Progress report on column experiments to investigate uranium mobility in the presence of HA (Subtask 2.5)	Project Manager	Acknowledgement of receipt via E-mail two weeks after submission	5/20/2016
Progress report on batch experiments for ammonia injection task (Subtask 1.3.1)	Project Manager	Acknowledgement of receipt via E-mail two weeks after submission	6/22/2016
Monthly Progress Reports	Project Manager	Acknowledgement of receipt via E-mail two weeks after submission	Monthly
Quarterly Progress Reports	Project Manager	Acknowledgement of receipt via E-mail two weeks after submission	Quarterly
Presentation overview to DOE HQ/Site POCs of the project progress and accomplishments (Year End Review)	Project Manager	Presentation to DOE HQ and Site POCs	8/31/2016**
Draft Year End Report	Project Manager	Acknowledgement of receipt via E-mail two weeks after submission	10/14/2016

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

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

---

## COMMUNICATION PLAN, ISSUES, REGULATORY POLICES AND HEALTH AND SAFETY

---

### Communication Plan

---

The communication with the clients and relevant experts at DOE-EM/PNNL/SRNL/SREL is a critical component of the project. The mode of communication will be e-mails, telephone/conference calls and meetings at the site. Though site-specific contact persons have been identified, constant communication will be maintained with client stakeholders at DOE HQ and the DOE sites and highlights of project accomplishments provided to ensure all parties involved are aware of the project progress.

Information Item	Client Stakeholder	Schedule	Communication Method	Responsible Stakeholder
Status Update Teleconferences	DOE EM, PNNL, SRNL, SREL	Monthly	Phone	Project Manager
EM-HQ Status Update Phone Call	DOE EM	Bi-Weekly	Phone	Principal Investigator
Quarterly Report	DOE EM	End of Q1, Q2, Q3, Q4	E-mail	Project Manager
Draft Year End Report	DOE EM, PNNL, SRNL, SREL	30 working days after completion of performance period	E-mail	Project Manager
Papers and presentations	DOE EM, PNNL, SRNL, SREL	As developed for conferences (e.g., WM16)	E-mail	Project Manager
Milestone completion E-mail	DOE EM, PNNL, SRNL, SREL	At completion of milestone	E-mail	Task Manager

### Anticipated Issues

---

Project 2 receives significant support from DOE Fellows. It is anticipated that DOE Fellows will be supporting research related to this project (undergraduate and graduate) during FIU Year 6. It is anticipated that research under this task may be used by students as the basis for a thesis or dissertation towards a graduate degree and would be impacted by a re-direction of the project task scope. FIU will communicate closely with DOE HQ and site contacts throughout the performance of the research tasks in order to accurately forecast the duration of the research tasks and minimize the potential negative impact of scope redirection on the graduate studies of any students working on that task.

## **Regulatory Policies and Health and Safety**

---

All laboratory experiments and pertinent FIU on-site task activities will be performed in accordance with FIU-ARC's Project-Specific Health and Safety Plan (PSHASP). Standard health and safety issues normally associated with field activities and laboratory experiments will not directly apply to project work related to computer-based modeling and information technology development. Much of the environmental and GIS data used for hydrological model development will require security clearance from SRNL. As such, cyber security measures will be established to ensure that data integrity is maintained. In addition to the FIU-ARC firewalls and the built-in software and hardware security protocols, all computers used in this project must adhere to FIU's University Technology Services (UTS) Security and IT Policies which are outlined in detail at <http://it.fiu.edu/security/index.shtml> and <http://security.fiu.edu/Pages/policies.aspx>. Security measures such as password protection will also be implemented in addition to an effective security strategy for sharing the database via the internet with other project stakeholders such as DOE or DOE site contractors.

## References

---

Carroll, Alai M, Craig L, Gdowski G, Hailey P, Nguyen AQ, Rard J, Staggs K, Sutton M, Wolery T, 2005. Chemical Environment at Waste Package Surfaces in a High-Level Radioactive Waste Repository. Lawrence Livermore National Laboratory, report UCRL-TR-212566.

Castle, E. (2003). Geodatabases in Design: A Floodplain Analysis of Little Kitten Creek. Thesis. Brigham Young University.

Giammar DE, and JG Hering, 2002. Equilibrium and Kinetic Aspects of Soddyite Dissolution and Secondary Phase Precipitation in Aqueous Suspension." *Geochimica Et Cosmochimica Acta*. 66,18 p.3235-3245.

Gogu, R. (2001). GIS-based hydrogeological databases and groundwater modelling. *Hydrogeology Journal*, 9:555–569. DOI 10.1007/s10040-001-0167-3.

Gruszkiewicz MS, Palmer DA, Springer RD, Wang P, Anderko A, 2007. Phase Behavior of Aqueous Na–K–Mg–Ca–Cl–NO<sub>3</sub> Mixtures: Isopiestic Measurements and Thermodynamic Modeling. *J Solution Chem*, 36, p. 723–765

Guo, X., L. Zeng, X. Li and H.-S. Park (2007). "Removal of ammonium from RO permeate of anaerobically digested wastewater by natural zeolite." *Separation Science and Technology* 42(14): 3169-3185.

Helminen, J., J. Helenius, E. Paatero and I. Turunen (2000). "Comparison of sorbents and isotherm models for NH<sub>3</sub>-gas separation by adsorption." *Aiche Journal* 46(8): 1541-1555.

Lin, X., Kennedy, D., Peacock, A., McKinley, J., Resch, C.T., Fredrickson, J., Konopka, A. 2012. Distribution of Microbial Biomass and Potential for Anaerobic Respiration in Hanford Site 300 Area Subsurface Sediment. *Applied and Environmental Microbiology*, 78(3), 759-767.

Szecsody, J. E., M. J. Truex, M. J. Zhong, T. C. Johnson, N. P. Qafoku, M. D. Williams, W. J. Greenwood, E. L. Wallin, J. D. Bargar and D. K. Faurie (2012). "Geochemical and Geophysical Changes during Ammonia Gas Treatment of Vadose Zone Sediments for Uranium Remediation." *Vadose Zone Journal*: 1-13

Zachara, J. M., C. Brown, J. Christensen, J. A. Davis, E. Dresel, C. Liu, S. Kelly, J. Mckinley, J. Serne and W. Um (2007). "A site-wide perspective on uranium geochemistry at the Hanford Site."

Zhong, L., J. E. Szecsody, M. J. Truex, M. D. Williams and Y. Liu (2015). "Ammonia gas transport and reactions in unsaturated sediments: Implications for use as an amendment to immobilize inorganic contaminants." *Journal of Hazardous Materials* 289: 118-129.