PROJECT TECHNICAL PLAN

Project 2: Environmental Remediation Science & Technology

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INTRODUCTION

Nuclear weapons production and other defense-related activities at U.S. Department of Energy (DOE) sites have resulted in radionuclide and heavy metal contamination in the surface and subsurface environments in several locations nationwide. Florida International University (FIU) is conducting applied research in collaboration with Pacific Northwest National Laboratory (PNNL), Savannah River National Laboratory (SRNL) and Savannah River Ecology Laboratory (SREL) scientists to support environmental remediation efforts at Hanford Site and Savannah River Site (SRS), which are focused on cleanup technologies for contaminated soil and groundwater and the assessment of the fate and transport of contaminants in the environment. FIU is also teaming with scientists at Los Alamos National Laboratory (LANL) and the DOE Carlsbad Field Office (CBFO) to address contamination issues associated with the disposition and storage of large quantities of transuranic waste at the Waste Isolation Pilot Plant (WIPP), which originate from various DOE sites across the United States. The aim of FIU's research is to reduce the potential for contaminant mobility or toxicity in the surface and subsurface through the development and application of state-of-the-art scientific and environmental remediation technologies at DOE sites.

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As appropriate and within the parameters of the DOE-FIU Cooperative Agreement (CA), coordination at the proper level will occur with the sites and national laboratories involved in the project research efforts as well as with the points-of-contact at DOE HQ (e.g., HQ Project Leads, EM-3.2, CA Technical Monitor, COR, etc.).

During FIU Performance Year 7 (2016-2017), novel analytical methods and microscopy techniques will be used for characterization of various mineral and microbial samples prepared via laboratory-scale batch and column experiments. The data derived will provide relevant information for contaminant fate in natural systems and following remediation in the SRS F/H Area and the Hanford Site and for updating risk assessment models at WIPP. FIU will also develop a surface water model of the Tims Branch watershed at SRS to predict contaminant fate and transport during severe rainfall or storm conditions. Development of the Tims Branch hydrological model is supported by the application of geographic information systems (GIS) technology which serves as a foundation for management, storage, processing, analysis and visualization of spatiotemporal model configuration parameters and modeling results.

FIU's collaboration with scientists at the various DOE sites and national labs will ensure that the research conducted is synergistic with DOE-EM's environmental remediation goals and supports the resolution of critical science and engineering needs. The knowledge gained through this research will lead to a better understanding of the long-term behavior of contaminants in the subsurface and will be used to transform experimental and modeling innovations into practical applications deployed at the sites.

TECHNOLOGY NEEDS

Conventional site characterization methodologies provide limited understanding of the interactions between the hydrological cycle, contaminant mobilization and environmental impacts. This Project Technical Plan presents the use of laboratory-scale experiments to better understand and address fundamental questions regarding contaminant behavior in real sediment under natural conditions and during remediation, and the implementation of simplified systems that are representative of field-scale phenomena occurring at DOE sites. This project also uses conventional hydrologic and remediation analytical tools in combination with the latest scientific software (i.e., 2D and 3D numerical flow and transport models integrated with reaction kinetics and thermodynamic software) that are widely accepted by the EPA, USACE, and USGS, to provide an integrated solution for better understanding of the mobility and fate of contaminants in soil, surface water and groundwater at DOE sites.

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

The legacy waste from the development of atomic weapons at the Hanford Site has left significant radionuclide contamination in soil and groundwater. There is a need to further investigate the environmental fate of uranium and technetium under natural conditions and following remediation. For example, a significant residual mass of uranium still resides in the deep vadose zone (VZ) following release of over 200,000 kg of uranium from improper waste disposal and accidental spills (Szecsody et al. 2013). Further, approximately 703 Ci of ^{99}Tc have been released to the ground from historical releases, spills and leaks (Serne, Rapko and Pegg 2014).

Previous uranium releases have created plumes that threaten groundwater quality due to potential downward migration through the unsaturated VZ. The mobility of uranium in the groundwater at the Hanford Site is relatively high (K_d 0.11 – 4 L/kg at pH 8) due to the presence of carbonate and oxidizing conditions (Zachara et al. 2007). Remediation of deep vadose zone contamination located near the waste tanks in the 200 Area and in the saturated zone near the 300 Area by the Columbia River can potentially be completed via in situ methods by converting mobile, aqueous U-carbonate phases to lower solubility precipitates that are stable in the natural environment.

In situ methods to sequester radionuclides in the deep vadose zone will be more effective as contaminants cannot be effectively reached by traditional near-surface methods such as ex situ dredging. Further, the addition of liquid amendments may cause increased downward migration of contaminants. FIU has identified two technologies for in situ remediation of uranium that require further investigation at the laboratory-scale including ammonia (NH_3) gas injection for the 200 Area vadose zone and tripolyphosphate injection for the 300 Area saturated zone.

Ammonia gas injection is currently being considered for uranium remediation at the pilot scale in the 200 Area of the Hanford Site. Previous work has shown that the injection of NH_3 gas to the vadose zone is a viable method to decrease uranium mobility in the contaminated subsurface via pH manipulation and co-precipitation processes (Szecsody et al. 2012a, Zhong et al. 2015). Further, it is an attractive remediation technology because it will not require additional liquid input into the vadose zone that could initially increase uranium flux to the groundwater.

It is expected that under the alkaline conditions caused by injection of the weak base, mobile uranium species will be transformed to low solubility uranium precipitates and/or additionally coated by non-uranium precipitates that are stable in the natural environment (Szecsody et al., 2012). However, there is a need for a better understanding of the formation processes leading to co-precipitation of uranium and the stability of the U-bearing precipitates. This information is necessary to accurately predict the fate of uranium in post-treated vadose zone soil.

Pilot scale testing of tripolyphosphate injection for the formation of apatite and autunite minerals in the 300 Area subsurface was completed in 2009 (Vermeul et al. 2009). Although it was initially found to be an effective remediation technology, there was a rebound in aqueous uranium concentrations after several months. Therefore, there is a need to better understand the dissolution of autunite minerals especially through microbial pathways. Autunite and meta-autunite minerals, as $(X^m)_{2/m}[(UO_2)(PO_4)]_2 \cdot xH_2O$ where X is a monovalent or divalent cation, are an important group of uranyl minerals acting as a sink for dissolved U(VI) in soils. Even small quantities of phosphate present in groundwater can promote the formation of autunite group minerals that can persist over geologic periods (De Vivo et al. 1984).

The presence of soil bacteria can affect uranium mobility significantly. Bacteria may dissolve uranyl-phosphate minerals in an effort to obtain phosphorous, thus liberating uranium from the solid phase. In addition to the biological activity, the presence of bicarbonate ions enhances the release of U(VI) into the aqueous phase (Gudavalli et al., 2013). However, there is a need to better understand the mechanisms leading to uranium mobilization in the presence of microbes and bicarbonate.

The Columbia River, adjacent to the Hanford Site, exhibits large stage variations, causing fluctuations in the water table. These water table fluctuations and multiple rise-and-fall cycles in the river create an oxic-anoxic interface in this region. Previous assessments of Hanford sediment samples collected from this area noted a decline in cultivable aerobic bacteria and suggested the presence of facultative anaerobic bacteria (Lin et al., 2012; Marshall et al., 2008). Therefore, understanding the role of facultative anaerobic bacteria (e.g., Shewanella) native to this area as one of the factors affecting the stability of autunite solids is very important for designing a successful environmental remediation strategy. In Performance Year 6, FIU examined the effect *Shewanella* cells on the biodissolution of natual Ca-autunite solids; however, there is also a need to compare results with the biodissolution of Na-autunite minerals created in sediments after injections of polyphosphate amendments.

Bacteria in the subsurface are seldom found as solitary mobile organisms; rather, most microorganisms form interconnected immobile colonies known as biofilms. These biofilms are supported by extracellular polymers, which serve to strengthen bacterial attachment to solid surfaces as well as to provide structural integrity to the biofilm. Biofilm formation can produce various changes in the physical and electrical properties of a porous medium; these changes can be due to: clogging of pores (changes to porosity, permeability, and hydraulic conductivity), changes to overall shear strength and elastic moduli of media, production of proteinaceous extracellular appendages that facilitate electron transport and increase bulk electrical conductivity, alterations to pore fluid electrolyte concentrations, dissolution of minerals leading to increased surface roughness, and precipitation of magnetosomes (Atekwana and Slater 2009). There is a need for better detection of biofilms for implementation of any remediation technique. This may be possible via geophysical methods like spectral induced polarization (SIP).

Technetium (Tc) was previously produced at the site in large quantities as a fission product during the irradiation of ^{235}U-enriched fuel for plutonium genesis for nuclear weapons. It exhibits unique chemistry: under oxidizing conditions it is found as soluble pertechnetate (TcO_4^-), whereas under reducing conditions, it is found in the insoluble TcO_2 state. Nevertheless, in the presence of bicarbonates under reducing conditions, the existence of stable, aqueous Tc(IV) carbonate-hydroxo complexes has been recorded. Because Hanford groundwater and pore water are rich in bicarbonates, it is crucial to investigate the properties of Tc and its compounds (e.g. stability of Tc(IV)-carbonato complexes, extent of TcO_2 dissolution in carbonate solutions) under Hanford Site conditions to better understand and predict Tc fate and transport in the Hanford Site subsurface and for designing remedial strategies for this contaminant.

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

The chronic leaching of SRS F/H Area soil may have impacted its morphological and physico-chemical characteristics, which in turn may have affected the soil's interaction with radionuclides. There is a need for data to compare background soil with acid-impacted soil from the area for properties such as ion exchange capacity, surface area and porosity. To this end, different profiles of acid-impacted soil are going to be created and characterized in the lab and their retention properties are going to be evaluated.

Humic substances (HS) are complex heterogeneous organic mixtures of polydispersed materials formed by biochemical and chemical reactions during the decay and transformation of plant and microbial remains. Humic substances account for 50-80% of the organic carbon in the soil or sediment and are known for their excellent binding capacity for metals, while being insoluble or partially soluble. This makes HS a strong candidate for remediation efforts to reduce the mobility of uranium (VI) in the subsurface. Humic acid, which carries a large number of functional groups, provides an important function in ion exchange and as a metal complexing ligand with a high complexation capacity being able to affect the mobility of actinides in natural systems. Different types of humic substances such as unrefined humic acid, modified humic acid and commercial humic acid will be used in this research to study the sorption of humic acid on the sediment at different pH and its effect on uranium removal.

Task 3: Surface Water Modeling of Tims Branch

Hydrological models are simplified representations of the natural hydrological cycle. They are mainly used as a tool to understand hydrological processes and to predict the hydrological behavior of a natural system under various conditions. The best hydrology models are those that can describe a specific natural system and produce results close to reality with the lowest level of model complexity and the least amount of input parameters. Today, hydrological models are being widely used as a tool for environment and water resources management. In addition, surface hydrology is one of the key components in solute transport mechanisms. Therefore, developing a hydrological model that can simulate surface hydrology and estimate the flow components is essential in contaminant fate and transport modeling, particularly in an area such as SRS in SC where both the surface water and groundwater have been contaminated from discharges associated with anthropogenic events at SRS process and laboratory facilities. This task will focus on developing a numerical model to simulate surface water flow velocity and depth over time in Tims Branch at Savannah River Site. The model will provide SRS scientists with a tool to estimate hydrological responses in Tims Branch under various extreme climate scenarios.

GIS technology will be continuously utilized throughout the project to support the hydrological model development. An ArcGIS geodatabase has been developed by ARC researchers for the Savannah River Site and the Tims Branch watershed as a foundation for management, storage, processing, analysis and visualization of environmental and hydrological parameters, and potentially building GIS-based water resources applications. The geodatabase possesses a spatial relational database management system (RDBMS) schema and relationship structure primarily based on the ArcHydro data model that is specific to hydrologic systems. This makes it a significant tool for conducting contaminant flow and transport analyses that require large amounts of high-quality spatial and temporal data in order to ensure reliability and validity of modeling results. ArcGIS tools significantly reduce the time needed for data preparation and improve overall efficiency by automating and batch processing model-specific geospatial and timeseries data via the development and implementation of process flow models. Utilization of the ArcGIS platform will continue to provide ARC researchers with a basis for management and geoprocessing of model configuration parameters, documenting process workflows, conducting geospatial analyses and visualization of model results. In addition, the SRS hydrologic geodatabase infrastructure enables linkage with other hydrologic modeling tools and applications to model hydrologic systems, and is scalable and replicable for implementation at other DOE sites.

Task 5: Remediation Research and Technical Support for WIPP

The U.S. Department of Energy’s Waste Isolation Pilot Plant (WIPP) is the world’s first deep geologic repository for disposal of transuranic waste (TRU). The facility is not currently operating following an airborne release from a waste drum failure due to an exothermic reaction in February 2014. This was due to incompatibility of mixed waste in the drum as received from LANL (organic adsorbent mixed with nitrate salt waste). It is due to re-open and begin accepting TRU waste again later this year.

There is currently a need to update the sorption parameters for the actinides to relevant WIPP minerals and geologic media. These parameters will be used to update the long-term risk assessment models for the site. The trivalent oxidation state is expected to dominate for both americium and plutonium with an estimate of 100% and 50% of the radionuclides, respectively, existing in the +3 oxidation state under WIPP-relevant conditions. Furthermore, the +4 and +6 oxidation states will be significant as well with approximately 50% of uranium and plutonium in the +4 oxidation state and 50% of uranium in the +6 oxidation state.

Previous Probabilistic Performance Assessment (PA) modeling indicates that human intrusion by inadvertently drilling into a pressurized brine pocket and/or the repository itself provides the most likely pathway to significant release of radionuclides from the system (U.S. DOE 1996). These releases may occur by five mechanisms: (1) cuttings, (2) cavings, (3) spallings, (4) direct brine releases, and (5) long-term brine releases. The most likely release pathway after human intrusion is through horizontal transport in the permeable layers of the Rustler formation located above the Salado formation.

Within the Rustler formation, the Culebra dolomite member is the most transmissive geologic layer, and therefore, the most susceptible release pathway (Meigs et al. 1997, Perkins, Lucero and Brown 1999). Because Culebra dolomite is the most likely long-term release pathway, it has been the focus of multiple reports investigating actinide partitioning. However, the fate of actinides and lanthanides in this system is still not well understood due to earlier experiments being conducted above solubility limits and under a limited range of conditions. It is important to develop sorption data for the trivalent actinides and lanthanides without experimental artifacts that is representative of the WIPP system.

FIU PERFORMANCE YEAR 7 PROJECT EXECUTION PLAN

The FIU Performance Year 7 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 Performance Year 7 Project Work Scope

Task No	Task
Task 1: Remediation Research and Technical Support for the Hanford Site	
Subtask 1.1	Remediation Research with Ammonia Gas for Uranium
Subtask 1.2	Investigation on Microbial-Meta-Autunite Interactions - Effect of Bicarbonate and Calcium Ions
Subtask 1.3	Investigation of Electrical Geophysical Response to Microbial Activity in the Saturated and Unsaturated Environments
Subtask 1.4	Contaminant Fate and Transport Under Reducing Conditions
Task 2: Remediation Research and Technical Support for Savannah River Site	
Subtask 2.1	Investigation on the Properties of Acid-Contaminated Sediment and its Effect on Contaminant Mobility
Subtask 2.2	The Synergistic Effect of Humic Acid and Colloidal Silica on the Removal of Uranium (VI)
Subtask 2.3	Humic Acid Batch Sorption and Column Experiments with SRS Soil
Task 3: Surface Water Modeling of Tims Branch	
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 Watershed
Task 5: Remediation Research and Technical Support for WIPP	

PROJECT TASKS

This project will be conducted in close collaboration between FIU, PNNL, SRNL, SREL, LANL and CBFO scientists in order to plan and execute research at the Hanford Site, SRS and the WIPP site 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 laboratory-scale studies which utilize novel analytical methods and microscopy techniques for characterization of various mineral and microbial samples. Tasks also include the implementation of hydrological models which help to predict the behavior and fate of existing and potential contaminants in the surface and subsurface. The following details the scope of work for the tasks under this project for FIU Performance Year 7.

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

Background

Remediation of radionuclides in the Hanford Site is a significant technical challenge due to the complex conditions in the subsurface. For example, the deep vadose zone creates unique remediation challenges since contaminants reside at depths, which are difficult to reach with near-surface remediation techniques. Further, the presence of carbonates and oxidizing conditions significantly increases the mobility of many contaminants including uranium and technetium. Uranium is currently the most prominent contaminant at the Hanford Site in terms of mass.

FIU ARC will collaborate and maintain communication with PNNL researchers, Jim Szecsody, Nik Qafoku, Timothy Johnson, Brady Lee and Hope Lee, to provide research support on uranium and technetium fate and remediation technologies at the Hanford Site with four subtasks under Task 1.

Subtask 1.1, *Remediation Research with Ammonia Gas for Uranium,* will include research on sequestering uranium at the 200 Area by *in situ* subsurface pH manipulation using NH_3 gas. This potential remediation technology is expected to transform mobile uranium species to lower solubility precipitates that are stable in the natural environment. Ammonia gas injection will raise the pH of the vadose zone pore waters leading to dissolution of silica-containing minerals such as quartz, montmorillonite, muscovite and kaolinite (Wan et al. 2004a, Wan et al. 2004b, Szecsody et al. 2013, Szecsody et al. 2012b). This will initially result in an increase in dissolved Si^{4+} and Al^{3+} as well as small increases in Na^+, K^+, $Fe^{2+/3+}$, Cl^-, F^- and SO_4^{2-} (Szecsody et al. 2013, Szecsody et al. 2012b). Subsequently, as the ammonia evaporates and the system returns to a neutral pH, U is expected to be immobilized as part of a complex co-precipitation process with cations dissolved from natural minerals in the first phase. There are two phenomena that are expected to decrease the mobility of U: 1) U (co)precipitation as solubility of Si, Al and similar ions decreases, and 2) Coating of U (co)precipitates with non-U, low-solubility precipitates. Some of the low solubility precipitates that are expected to form include cancrinite, sodalite, hydrobiotite, brucite and goethite (Bickmore et al. 2001, Zhao et al. 2004, Qafoku et al. 2004, Qafoku and Icenhower 2008).

Geochemical changes within the subsurface during remediation are often temporary unless they are moving the system towards its natural equilibrium. However, the co-precipitation processes removing uranium from the aqueous phase are expected to occur as the system returns to equilibrium (or neutral pH). Therefore, as long as the solid phases are relatively insoluble, uranium will be immobilized.

Subtask 1.2, *Investigation of Microbial-Meta-Autunite Interactions - Effect of Bicarbonate and Calcium Ions.* Microbial activities in environmental systems are an important geochemical factor, playing an essential role in the fate and transport of subsurface contaminants. The effect of the microbes should be considered in the design of remedial actions. The Hanford vadose zone sediments have been shown to contain viable microorganisms that can influence the stability of uranium-bearing solid phases and the uranium mobility in the environment. This task 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 bacterial consortium 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 impact of subsurface facultative microorganisms or microbial consortia on 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, *Investigation of Electrical Geophysical Response to Microbial Activity in Saturated and Unsaturated Environments*, was initiated in FIU Performance Year 6 and is focused on the influence and corresponding electrical geophysical response of microbial activity on the geochemical factors affecting uranium sequestration. The microbial consortia provided by PNNL for these studies were derived from Hanford Site sediment samples. In particular, the Spectral Induced Polarization (SIP) response of microbe growth and biofilm formation and the corresponding changes in pore water properties such as conductivity, pH, and oxidation reduction potential will be studied. This task will focus on laboratory-scale experiments to show the possibilities of using SIP for remote sensing of microbial effects at larger scales.

Subtask 1.4, *Contaminant Fate and Transport Under Reducing Conditions,* investigates the fate and transport of Tc in conditions related to the Hanford Site in the presence of different levels of bicarbonates under reducing conditions. Technetium-99 (Tc-99) is one of the major contaminants of concern at the Hanford Site. When Tc is exposed to the atmosphere or any moderately oxidizing environment, it is found as pertechnetate (TcO_4^-) with valence state +7. Pertechnetate is highly soluble, does not sorb onto sediments and migrates at the same velocity as groundwater (Kaplan, Parker and Kutnyakov 1998), whereas under reducing conditions, technetium is found in the +4 valence state. Tc(IV) is expected to either sorb onto the sediments or precipitate as insoluble $TcO_2 \cdot nH_2O$ (Icenhower et al. 2008). Technetium migration is affected by the porewater and groundwater chemical composition and soil mineralogy. Hanford groundwater and porewater are rich in bicarbonates. The existence of stable Tc(IV) carbonate-hydroxo complexes, such as $Tc(CO_3)(OH)_3^-$ and $Tc(CO_3)(OH)_2$, in near-neutral or basic conditions has been suggested in literature (Eriksen Trygve et al. 1992, Paquette and Lawrence 1985, Alliot et al. 2009). Nevertheless, there is very limited data on the crystal structure and coordination of those complexes, as well as any interaction with soil components under reducing conditions and hence, their fate in the environment is not well understood.

This task will investigate the partitioning of Tc between the aqueous phase and actual Hanford soil in the presence of bicarbonates under reducing conditions. Furthermore, the potential re-mobilization of prior immobilized Tc(IV) as an effect of bicarbonate concentration will be investigated. Technetium under reducing conditions is expected to be in poorly soluble Tc(IV) forms. However, the presence of bicarbonates may affect its mobility significantly: in the anoxic pore water bicarbonate ions may form soluble Tc(IV)-carbonato-hydroxo complexes of Tc(IV) (Alliot et al. 2009).

Objectives

Subtask 1.1: The aim of this task is to understand the processes leading to removal of uranium from the aqueous phase during and following ammonia gas injection for remediation. This will include laboratory experiments and modeling (1) to measure diffusion of ammonia gas under unsaturated conditions, (2) to identify the processes leading to formation of precipitates in the presence and absence of minerals and sediments, and (3) to characterize the solid phase precipitates in terms of their specific phases and stability under natural conditions. In order to better understand the formation and stability of precipitates following ammonia gas injection, it will also be important to investigate the redox changes and the effects of various ions on precipitation processes (i.e. carbonate, Si, Al, Ca, Mg, Fe). This task will also attempt to determine if the formation of U precipitates occurs differently in solutions in the presence or absence of minerals and sediments.

Subtask 1.2: This task investigates the biodissolution of synthetic Na-autunite and natural Ca-autunite solids under oxygen restricted conditions and accounts for uranium release in the presence of bicarbonate ions. Uranyl ions are toxic for bacteria. However, in the presence of bicarbonate, bacteria are viable and can affect weathering of solid phases, which have been created as a result of remedial actions. This may lead to the release of uranium back to the environment. Two types of bacterial cultures will be used in this investigation: a pure culture of *Shewanella oneidensis* MR1, and microbial consortia enriched at PNNL from Hanford soil in the presence of autunite.

Subtask 1.3: The objective of this task is to investigate the influence and corresponding electrical geophysical response of microbial activity on uranium sequestration. This investigation will address whether the formation of biofilms has a direct contribution to the SIP (Spectral Induced Polarization) response within sediments. The microbial consortia for column inoculation to measure the geophysical signature has been provided by PNNL.

Subtask 1.4: The purpose of this task is to initiate an investigation of the fate and transport of Tc under reducing conditions in the presence of bicarbonate ions, which are abundant in the Hanford Site groundwater and pore water compositions.

Benefits

Subtask 1.1: Injection of reactive gases such as NH_3, to create alkaline conditions in the vadose zone, is an innovative technology that may be used to decrease uranium mobility in the subsurface. This task will improve understanding of the dissolution and secondary product formation of minerals during and after ammonia gas injection. It will also provide parameters to model the diffusion of ammonia gas in the vadose zone to help better design a remediation technique. In addition, it will produce a description of the processes leading to immobilization of uranium and an understanding of the stability of the solid phases formed during the remediation process. This will help to predict the long term effectiveness of the potential remediation technology.

Subtask 1.2: Hanford Site soil is rich in calcite resulting in the presence of significant levels of aqueous bicarbonate ions. These are the predominant species affecting the dissolution of uranium-bearing solids and facilitating uranium desorption reactions, thus increasing uranium mobility in soil and sediments. This task will investigate bacteria-U(VI) interactions using facultative microorganisms growing in oxygen-restricted conditions and examine the potential role of bacterial consortia enriched from sediment core samples collected from the 200 Area to influence U(VI) release from autunite minerals and U(VI) biotransformation in the presence of bicarbonate ions. Experimental results will provide a broader picture of how the natural subsurface microbial community can influence autunite stability and affect uranium release back to the aqueous phase and help acquire a more thorough understanding of the phenomena influencing uranium mobility in the complex natural environment.

Subtask 1.3: This subtask will help to identify methodologies for tracking the remediation process within the subsurface with minimal impacts to the vadose zone through geophysics. Electrical geophysical techniques are useful due to their non-invasive nature as well as their cost effectiveness, especially when compared to the traditional methods of drilling boreholes and taking samples manually. Geophysical measurement systems can be set up to work remotely and take continuous measurements through automation.

Subtask 1.4: There is limited data on Tc interaction with soil under reducing conditions and in the presence of bicarbonates, hence the contaminant’s fate in the environment is not well understood. Furthermore, immobilized Tc(IV) (through sorption on sediments or precipitation as Tc(IV)-oxide) may be extracted by carbonates and re-enter the aqueous phase in the form of the complexes mentioned above. There is currently no information on the re-solubilization of Tc(IV)-oxide due to the presence of carbonates. The proposed task will investigate the Tc(IV)-carbonate complexes as a potential mechanism for technetium migration in reducing geochemical environments. This task will generate new information on the chemistry of technetium under Hanford Site conditions and will contribute to the planning of remedial strategies pertaining to this contaminant.

Technical Approach

Task 1 is a joint effort with the Pacific Northwest National Laboratory. Four subtasks have been identified and will be developed during FIU Performance Year 7.

Subtask 1.1: Remediation Research with Ammonia Gas for Uranium

FIU’s research will focus on ammonia and uranium fate via batch experiments with synthetic pore waters and column experiments in relevant minerals and sediments. Batch and flow dissolution tests initiated during FIU Performance Year 6 will continue using both pure minerals and Hanford sediments in the presence of synthetic pore waters with variable bicarbonate concentrations.

Specifically, the experiments to quantify the partitioning of U and mineral dissolution following treatment with NaOH and NH_4OH will be expanded by addressing the following variables as part of FIU Performance Year 7: solid to liquid ratios, initial uranium concentrations and bicarbonate concentrations. Data will also be generated following treatment with ammonia gas which will enable a comparison of redox changes due to gas (NH_3 gas) versus liquid (NH_4OH) treatments. Kinetics experiments will also be included during FIU Performance Year 7 to complement the equilibrium data collected during Year 6. Experiments will be also conducted with low Si/Al ratios to supplement data previously obtained in mineral-free systems using synthetic solutions mimicking Hanford pore water conditions. In addition, solid phases will be characterized via flow-through and sequential extraction experiments at lower Si concentrations. This work directly complements ongoing experiments at PNNL.

During FIU Performance Year 7, the scope of work will include the following studies conducted in collaboration with PNNL's Jim Szecsody and Nik Qafoku.

- Equilibrium and kinetic batch experiments will investigate uranium partitioning and co-precipitation, and ammonia fate and mineral dissolution upon base addition. Samples will include either a simple NaCl or synthetic porewater developed with our PNNL collaborators. The following conditions will be considered:
    - Samples will be adjusted with either NaOH (aqu), NH_4OH (aqu) or NH_3 (gas) to compare treatment options. The effects of Na^+ versus NH_4^+/NH_3 ions on mineral solubility and uranium fate will be investigated with the two aqueous solutions. The NH_4OH(aqu) versus NH_3(g) will then be used to compare redox conditions. It is expected that gas injection will remove significant amounts of aqueous carbonate and oxygen while aqueous addition (as NH_4OH) should remain relatively oxidizing. Variable bicarbonate and uranium concentrations will also be used to investigate their effect on uranium speciation and precipitation. The solid phase will consist of clean sediments from the Hanford 200 Area and pure minerals relevant to the site (quartz, montmorillonite, illite, kaolinite, calcite and muscovite).
    - Experiments will also be conducted at low Si/Al ratios and variable HCO_3^-/Ca/Mg/Fe to determine the minimum concentration of Si in the system that causes coagulation reactions with U after ammonia gas applications. Experiments will be conducted in the presence and absence of solid minerals and sediments to elucidate the mechanisms leading to precipitation. Previous research shown that uranium is likely to adsorb on specific surfaces of minerals; however, it still unknown if the minerals act as a catalyst for precipitation.
    - Following basic treatments, solid materials will be investigated with additional batch desorption/dissolution, flow-through, sequential extraction and microscopy experiments to define the potential of uranium and mineral dissolution after ammonia gas injection. Conventional characterization techniques will be used, including but not limited to TEM, SEM-EDS, XRD, and FTIR. A proposal is currently being written for submission to EMSL facilities to allow access to additional characterization techniques.
- The short term (months to two years) geochemical fate of NH_3 will also be investigated via 1-D column experiments with 200 Area sediments prepared with variable initial water content. NH_3 (gas) will then be allowed to diffuse into the columns both horizontally and vertically to investigate the rates of diffusion and the effects of buoyancy on the migration of ammonia over time. Multiple 10 ft long PVC columns with a ½" diameter will be prepared

for each set of conditions to be sacrificed and sectioned at variable times to be able to measure pH, conductivity and NH_3 in pore water. The information obtained from these experiments will be used later to simulate NH_3 diffusion to support the upcoming NH_3 gas injection tests at the pilot scale to be conducted by PNNL.

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

Previous research by FIU has suggested that in the presence of bicarbonate, uranyl-carbonate complexes formed in the solution do not strongly interact with the negatively charged bacterial surface, which in turn can mitigate U(VI) toxicity on cells and keep them active and viable during the mineral dissolution process. Experiments on microbial dissolution of Ca-autunite are ongoing and will continue in FIU Performance Year 7; however, the microbial dissolution of Na-autunite by anaerobic bacteria in the presence of bicarbonate ions still needs to be evaluated to compare the effect of Ca ions on the biodissolution of autunite and uranium reduction from U(VI) to U(IV). In addition, FIU will investigate the effect of the microbial consortia enriched by PNNL on the biodissolution of autunite to compare results with the pure *Shewanella oneidensis* MR1 strain. The same microbial consortia will be used to investigate the influence of microbial activity on the corresponding electrical geophysical response in sediments conducted via Subtask 1.3.

Subtask 1.3: Investigation of Electrical Geophysical Response to Microbial Activity in the Saturated and Unsaturated Environments

FIU will work with PNNL to investigate the influence and corresponding electrical geophysical response of microbial activity on vadose zone uranium sequestration with the objective of addressing the following:

- Does the formation of biofilm have a direct contribution to the spectral induced polarization (SIP) response within vadose zone sediment and is that distinguishable from the indirect effects of microbial action such as dissolution of minerals and changes in pH?
- What influence might microbial activity have on the pore water pH level? Is that influence detectable in the SIP magnitude response and distinguishable from abiotic processes in the pore water?
- What influence might microbial activity have on the dissolution and subsequent re-precipitation of silicate minerals? 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 and uranium sequestration?

General test methods will include one-dimensional columns. Six columns filled with Hanford sediment and a layer of autunite were set up during FIU Performance Year 6 and saturated with synthetic groundwater. In Year 7, columns will be inoculated with microbes and monitored over time using geochemical, microbiological, and SIP analyses. Differences in the column test analysis results will be used to quantitatively assess the questions above. Initial experiments will not use ammonia injection and will instead study the effect of microbes under saturated conditions. The following matrix will be used for column experiments:

1	2	3	4	5	6
SGW *	SGW‡	SGW* + Glucose	SGW‡ + Glucose	SGW* + Glucose + Inoculum	SGW‡ + Glucose + Inoculum

* No HCO_3, ‡3 mM HCO_3

As research progresses, FIU will shift from saturated to unsaturated columns in order to more accurately model the conditions within the vadose zone during FIU Performance Year 7. In the following year (FIU Performance Year 8), FIU will consider injecting ammonia gas injections into the columns to complement the research efforts underway at PNNL on the use of ammonia gas as a remediation strategy.

This research will also investigate the bacterial community transformation in soil before and after ammonia addition. The evaluation of the bacterial community will require molecular biology tools and will be conducted as part of a DOE Fellow student internship at PNNL during summer 2017.

Subtask 1.4: Contaminant Fate and Transport Under Reducing Conditions

During FIU Performance Year 7, FIU will initiate an investigation by performing sorption experiments of Tc-bearing solutions on Hanford Site soil in different bicarbonate concentrations under reducing conditions. More specifically, the first set of experiments will focus on investigating the retention of Tc(IV)-carbonate complexes by Hanford soil under reducing conditions.

FIU will complete a set of experiments that pertain to the soil-aqueous phase partitioning of Tc(IV)-carbonate complexes. Initially, Hanford soil suspensions at different Tc-bicarbonate concentrations at pH 7.5 will be prepared and introduced into the anaerobic glovebox and bicarbonate-free samples will serve as controls. The reducing conditions in the glovebox will be adjusted by purging the glove box with N_2, and oxygen concentrations will be recorded by the oxygen analyzer inside the glove box. Periodically, aliquots from the supernatant will be isolated and Tc concentrations will be measured by means of liquid scintillation counting (LSC). Total iron concentrations (which can be traced back to the soil's composition) will be measured by means of ICP-OES and ferrous iron will be determined spectrophotometrically. Moreover, experiments focusing on the potential re-mobilization of prior immobilized Tc(IV) on Hanford soil will include soil suspensions in a pertechnetate solution, introduced in the glovebox and reducing conditions will be applied. The concentration of soluble Tc(VII) will be monitored in order to ensure reduction of Tc(VII) to Tc(IV). Subsequently, bicarbonate solutions will be introduced and the system will be equilibrated on a shaker under reducing conditions in order to study the re-mobilization of Tc(IV) in the aqueous phase as a function of bicarbonate concentration and time. Discrimination between Tc(VII) and Tc(IV) in the aqueous phase will be performed by a solvent extraction technique. Tc-bearing solid phases will be characterized by means of SEM-EDS at the Florida Center for Analytical Electron Microscopy (FIU Modesto Maidique Campus). In the following years, FIU will continue the investigation on technetium fate and transport in the presence of other ligands (e.g. nitrates) and other contaminants (e.g., uranium, chromium) under reducing conditions.

Task 2: Remediation Research and Technical Support for SRS

Background

Approximately 1.8 billion gallons of acidic waste containing radionuclides and dissolved heavy metals were disposed of in SRS F/H Area seepage basins, which led to the unintentional creation of highly contaminated groundwater plumes consisting of radionuclides and chemicals with an acidic pH of 3 to 5.5. The acidity of the plumes contributes to the mobility of several constituents of concern (COC) such as tritium, uranium-238, iodine-129, and strontium-90 for the F-Area plume and tritium, strontium-90 and mercury for the H-Area plume. Task 2 research is focused on uranium (VI), which is a key contaminant of concern in the F-Area groundwater plume.

During FIU Performance Year 6, FIU completed the following two subtasks:

1) "FIU's support for groundwater remediation at SRS F/H Area" which evaluated whether sodium silicate solutions have sufficient alkalinity to restore the natural pH of the groundwater, and included batch sorption and desorption kinetic experiments, soil characterization studies, and speciation modeling. Sequential extraction experiments were used for the identification of the soil phase to which U(VI) is bound. The research also evaluated the effect of ionic strength as well as Ca and Mg concentrations on the removal of uranium, and determined zero retention for strontium and rhenium (a chemical analog of technetium). The research was successful by confirming that dissolved sodium silicate solutions at a concentration of 70 mg/L have enough alkalinity to replace the carbonate base being used to correct the acidic nature of the contaminated sediments. The studies also presented evidence that, under circumneutral conditions, goethite contributes to a stronger binding of U(VI).
2) "Monitoring of U(VI) bioreduction after ARCADIS demonstration at the SRS F-Area" which was based on the molasses injections in the F/H Area wells to create anaerobic conditions in the subsurface. The sample analysis and speciation modeling completed did not suggest the formation of reduced iron phases such as siderite or pyrite.

During FIU Performance Year 7, the scope of work under Task 2 will include three (3) technical subtasks conducted in collaboration with scientists at the Savannah River Site to support groundwater remediation at SRS F/H Area. These subtasks will focus on the evaluation of remediation techniques for contaminated groundwater, as well as on the role of different environmental factors on the fate and transport of the contaminants of concern. This task involves expansion of FIU's research in the SRS F/H Area to investigate the possible synergy between colloidal silica and humic acid that may have an effect on the removal of uranium from contaminated groundwater. The research also evaluates the effects of different environmental variables such as pH and uranium concentrations on the process. Another study will include batch and column sorption experiments with humic acid, which simulate the creation of a sorbed humate treatment zone in the acidic groundwater contaminated with uranium. This data will be used for the modeling of the migration and distribution of natural organic matter injected into subsurface systems. Furthermore, the properties of sediments contaminated by acid will be investigated as well as their sorption characteristics in the range of concentrations for single and multiple contaminants to be able to compare with clean background sediments. This investigation will be extended to evaluate the mobility of U(VI) and other contaminants of concern such as Tc in acid-affected sediments.

Objective

This scope of Task 2 assists in evaluating the mobility of actinides in natural systems in search of new remedial alternatives.

Subtask 2.1, *"Investigation on the Properties of Acid-Contaminated Sediment and its Effect on Contaminant Mobility,"* The objective of subtask 2.1 is to identify the morphological and physico-chemical characteristics of sediments that are affected by chronic acid leaching (compared to clean background soil) and correlate the selected properties with the sorptive characteristics of the sediments for SRS contaminants of concern.

Subtask 2.2, *"The Synergistic Effect of Humic Acid and Colloidal Silica on the Removal of Uranium (VI),"* The objective of subtask 2.2 is to study the synergetic interactions between HA and colloidal silica on uranium removal at varying uranium concentrations in the system. Previous studies have focused on the influence of varying HA concentration on uranium removal at constant U(VI) concentration. However, it is important to study the effect of varying uranium concentration in the presence of HA and colloidal silica at variable pH.

Subtask 2.3, *"Humic Acid Batch Sorption and Column Experiments with 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. Specifically, this study which is conducted via batch experiments, will evaluate the removal of uranium by Huma-K by varying parameters such as pH, time, and concentration of uranium. Another objective of this study is to investigate the sorption behavior of humic acid versus pH via flow-through column experiments and study the effect of sorbed HA on uranium mobility through porous media.

Benefits

Subtask 2.1: The identification of the physico-chemical characteristics that are affected due to exposure to acid and their role in radionuclide sorption by the soil will help to achieve a better understanding of the mobility of the contaminants of concern. For example, properties such as porosity and surface area may increase as a result of acid leaching and affect radionuclide retention.

Subtask 2.2: The investigation under this subtask will evaluate the synergy between colloidal Si and humic acid on the removal of U(VI) via batch reactors at varying uranium concentrations and analyze post-reaction sediments for surface morphology and composition. This study will also assist in evaluating the mobility of actinides in natural systems in the presence of colloidal silica and humic acid to understand the potential for colloid-facilitated transport of uranium in the SRS subsurface.

Subtask 2.3: This study will demonstrate whether or not Huma-K injection is a promising in-situ remediation method for the removal of uranium from the aqueous phase and determine appropriate conditions for optimal removal. Also, the study of the removal of uranium by Huma-K at different pH values will help to determine if Huma-K can also be implemented at other DOE sites, which do not have acidic conditions. In addition, FIU will investigate the sorption behavior of modified humic acid for groundwater remediation versus pH and study the effect of sorbed humic on uranium removal from the aqueous phase in the flow-through and batch experiments mimicking SRS field application conditions. This subtask will also provide coupling between flow and transport of the contaminant in the subsurface to simulate the response of the system after the injection of humate. These studies will determine approaches to deploy humate technology under varying site conditions since the results from the laboratory experiments can be correlated with the injection tests previously conducted in the field.

Technical Approach

The scope of work under Task 2 includes three (3) technical subtasks which will be conducted in collaboration with SRNL scientists, Drs. Miles Denham and Brian Looney, at the Savannah River Site.

Subask 2.1: Investigation on the Properties of Acid-Contaminated Sediment and its Effect on Contaminant Mobility

This task involves expansion of FIU's research in the SRS F/H Area to compare properties of acid-contaminated and background sediments that may affect the mobility of uranium in contaminated groundwater. One of the parameters of investigation is the sorption characteristics of different contaminants in a single or multi-contaminant system. The research will evaluate the mobility of uranium in acid-contaminated soil to compare results with clean sediments.

During FIU Performance Year 7**,** research will be initiated on the characterization of acid-contaminated sediments using clean and acidified soils to investigate their interaction with uranium (VI). More specifically, sediment from the SRS F/H Area will be loaded in columns and will be conditioned by passing through acidified deionized water (pH 2.5 adjusted with HNO_3). The concentrations of Si and Al in the leachate will be monitored (which can be traced back to kaolinite present in the soil) and different profiles of the acid-impacted soil samples, based on the kaolinite removal, will be produced. These samples will be dried in a conventional oven and characterized for changes in morphology and major elements by means of Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS), and changes in surface area and porosity by means of Brunauer-Emmett-Teller Surface Area Measurement (BET). The determination of ion exchange capacity will be considered and the most appropriate method to achieve this will be determined. Finally, batch sorption experiments will be conducted with the acid-impacted soil samples using U(VI)-bearing SRS synthetic groundwater. Sorption efficiency of these samples will be compared to the equivalent sorption capacity of background soil under acidic or circumneutral conditions.

Subtask 2.2: The Synergistic Effect of Humic Acid and Colloidal Silica on the Removal of Uranium (VI)

This subtask will research the synergetic interactions between humic acid and colloidal silica to determine their influence on the behavior of uranium. Humic substances are a major component of soil organic matter and are known for their ability to influence the behavior and fate of heavy metals. Humic substances are ubiquitous organic macromolecules with variable compositions formed by the decomposition of biomass. Studies have shown that humic acids (HA) function as important ion-exchange and metal-complexing ligands carrying a large number of functional groups with high complexing capacity that can greatly affect the mobility of actinides in natural systems. This task extends FIU's research conducted in Performance Year 6 in order to investigate if U(VI) is bound to colloidal silica and if any synergy exists between humic acid (HA) and colloidal Si that would influence the removal of uranium. FIU previously conducted experiments to study the effect of synergetic interactions between humic acid and colloidal silica on uranium removal while varying the concentration of humic acid between 10 - 50 ppm.

During FIU Performance Year 7, FIU will explore the effect of synergetic interactions between HA and colloidal silica on uranium removal by varying uranium concentrations in the solution. Batch synthetic groundwater samples will be prepared to mimic the contaminated groundwater at SRS, with pH adjusted in the range from 3 to 8. The following binary, ternary and quaternary systems will be evaluated at each pH condition in the presence of HA at different uranium concentrations ranging between 10 - 50 ppm for the removal of U(VI) from the aqueous solutions:

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

Post-treatment sediment samples will be dried and characterized via SEM-EDS to reveal surface topography and determine if there is any correlation between elements across the surface.

Subtask 2.3: Humic Acid Batch Sorption and Column Experiments with SRS Soil

This subtask combines two research topics that focus on the mobility of uranium in the presence of Huma-K (an agricultural amendment composed largely of humic acid) and other agricultural amendments (commercially sold generic humate customized for groundwater remediation) provided by SRNL via batch and column experiments. In order to understand and predict uranium mobility, U(VI) adsorption/desorption experiments will be performed using background (clean) F-Area aquifer sediments. The migration and distribution of humate and its effect on U(VI) mobility will be studied via column experiments.

The interaction of uranium with sediment in the presence or absence of humic acid involve complex mechanisms that are not yet well understood. The interaction of U(VI) with humic acid can affect the adsorption of U on sediment, therefore altering its mobility. To better understand the complex environment created by the addition of Huma-K, a comprehensive investigation is needed to address some key factors that control the adsorption of Huma-K on Savannah River Site sediments and the removal of U using Huma-K-coated sediments.

During FIU Performance Year 7, FIU will initiate an investigation of the removal of uranium by Huma-K and SRS sediments. This study will evaluate the effect of time (kinetics), pH, and initial uranium concentrations, as well as extend the investigation of U(VI) desorption via the following batch experimental matrix:

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

This study will be conducted in the following manner:

For the kinetics experiment, an initial uranium concentration will be allowed to equilibrate with SRS sediment and SRS sediment coated with Huma-K for different time periods at pH 4 and 7.

To study the removal of uranium by SRS sediments, a sorption experiment will be performed where uranium with different concentrations will be brought in contact with 1 gram of SRS soil at pH 4 and 7. Samples will be vortex mixed, placed on a platform shaker for three days, and centrifuged. The supernatant will be analyzed by a kinetic phosphorescence analyzer (KPA).

To study the removal of uranium by SRS sediments coated with Huma-K, initally, 20mL of Huma-K solution with known pH (4 and 7) will be brought in contact with 1gram of SRS soil for five days. After five days, samples will be centrifuged, and the supernatant will be replaced by a uranium solution with different concentrations at pH 4 and 7. Samples will be analyzed in the same manner as the sorption experiments for background sediments.

For the desorption of uranium previously adsorbed, a batch desorption experiment will be conducted at pH 4 and 7, where initially a known concentration of uranium will be sorbed to SRS sediment and SRS sediment coated with Huma-K at pH 4 and 7. After five days of rotation, samples will be centrifuged, the residual uranium concentration in the supernatant will be determined and the supernatant will be replaced with deionized water at different pH values (4 and 7). Samples will be rotated and centrifuged in the same exact way as previously described. The desorbed uranium concentration in the aqueous phase will be determined by as determined KPA analysis.

Furthermore, the use of a new modified humic acid as a potential remediation method is going to be explored and compared with Huma-K in order to determine which one is more suitable for the removal of uranium and under what environmental conditions the removal is optimal. This humic acid was modified by Perminova's group where alkoxysilyl-moieties were incorporated into the humic acid structure, which is supposed to enhance the sorption affinity of humic acid towards hydroxylated surfaces. For this study, detailed characterization of the modified humic acid is going to be performed by means of scanning electron microscopy with energy dispersive x-ray spectroscopy (EDS) analysis, fourier transform infrared (FTIR) spectroscopy, and potentiometric titrations. Also, the uranium removal at pH 4 and 7 is going to be conducted with SRS sediments coated with modified humic acid. All these results will be compared with the results from the Huma-K experiments in order to determine which product is better for the removal of uranium from contaminated groundwater.

The migration and distribution of natural organic matter injected into subsurface systems will also be explored via column studies. This research aims to understand the sorption of humic acid under varied pH levels and to study the effect of HA on uranium mobility through porous media via flow-through column experiments for the range of environmental conditions at DOE sites. For each of the column tests, a series of effluent samples will be collected at the column exit and then 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 U(VI) and HA.

During FIU Performance Year 7, FIU will continue to work in coordination with SRS and DOE Office of Soil and Groundwater personnel to conduct column studies to investigate the effect of HA on uranium mobility through porous media. Previously, FIU tested a commercially available unrefined HA known as Huma-K; in FIU Performance Year 7, FIU will focus on other commercially available humate products to be able to compare results with the data obtained for Huma-K. This comparison will lead to recommendations for the remediation strategy at the SRS F/H Area. Sorption of uranium to sediment in the presence of HA depends on various components such as HA concentration, soil minerals and experimental conditions (e.g., pH, etc.). This task will investigate the influence of humic acid on the sorption of U(VI) onto sediments collected from the F/H Area in a column experimental set-up. In addition, FIU will estimate the U transport parameters to better predict the mobility of uranium in the presence of various humate products.

Task 3: Surface Water Modeling of Tims Branch

Background

This task involves the development of a hydrological model to be used as a tool for predicting the fate and transport of sediment and contaminants in Tims Branch at SRS. This site has been impacted by anthropogenic events associated with nuclear weapons research resulting in contaminant discharges from process and laboratory facilities. Tims Branch is a second order stream in the A/M Area of SRS. In 2000 and 2007, innovative mercury (Hg) removal systems (i.e., a wetland treatment system and an air stripping system) were implemented in the northern and eastern headwaters of Tims Branch with concomitant discharge of inorganic tin (as small micro particles and nanoparticles) initiated in 2007 as a step function with high quality records on the quantity and timing of the release. These treatments effectively eliminated mercury inputs to Tims Branch. Sampling of the biota in Tims Branch (2006 and 2010) documented that fish Hg concentrations 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 fish concentrations.

Tims Branch provides a unique opportunity to study complex systems science in a full-scale ecosystem that experienced controlled step changes in boundary conditions. This task is therefore aimed at developing and testing a full pollutant transport model for a relatively well defined system. The principal objectives are to apply geographical information systems (GIS) and flow and contaminant transport modeling tools to the Tims Branch system to examine the response of the system to historical discharges and environmental management remediation actions. The research under this task 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, particularly considering the effect of extreme hydrological events on stream flow and the transport of sediment and contaminants. In addition, this research fosters collaboration between the students and scientists at FIU and the scientists at the Savannah River National Laboratory and the Savannah River Ecology Laboratory. 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.

During FIU Performance Year 7, 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.

Objectives

The principal objective of this task is to develop a hydrological model to predict stream flow and the fate and transport of sediment and contaminants in the Tims Branch watershed, and to monitor the system's response to extreme hydrological events. During FIU Performance Year 6, FIU conducted research in collaboration with SRNL and SREL scientists focused on preliminary development of a surface water model of the Tims Branch watershed and the application of geographical information systems (GIS) tools for management, processing and visualization of spatiotemporal model configuration data.

In FIU Performance Year 7, research will continue on the development of a hydrological model to simulate stream flow, and sediment and contaminant transport in Tims Branch, which takes into consideration intercompartmental transfers, stormflow impacts and downstream transport of contaminants such as tin, mercury and uranium. Initial studies will focus on modeling of surface water hydrology and stream flow. The research will support understanding the response of the Tims Branch ecosystem to innovative EM developed treatment technologies that have eliminated anthropogenic mercury and other contaminant (e.g., uranium) sources from the watershed. The sampling and analysis activities identified under this task will be dependent on the availability of SRNL/SREL funds to provide support to FIU for site-required permitting and oversight activities as well as sample preparation and analysis costs.

Benefits

In general, hydrological models are the standard tools used for investigating surface/subsurface flow behavior. They provide insights for water resource management and decision making, and evaluate the water quality, erosion, deposition, and transport. The MIKE SHE/MIKE 11 model being developed for Tims Branch can be used as a tool to better understand the effect of extreme weather on flow in Tims Branch. The results of the hydrology model will be used to assess the fate and transport of remedial by-products, such as tin dioxide or other existing solutes (uranium, plutonium), that may have direct or indirect impact on the environment in SRS. The outcome of such a model can determine spatial and temporal distribution of suspended particles or contaminants in the area when storms or heavy rainfalls occur

The MIKE SHE/MIKE 11 hydrological modeling package being used has a 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

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 Performance 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 Performance Year 6, FIU completed Phase 1 with a revised model domain and implementation of the MIKE SHE overland flow, evapotranspiration, unsaturated and saturated flow modules. The preliminary stage of Phase 2 was also initiated which involved delineation of the stream network using ArcGIS and MIKE 11 tools. Details of the work scope planned for FIU Performance Year 7 (highlighted in red in Figure 1) are provided below.

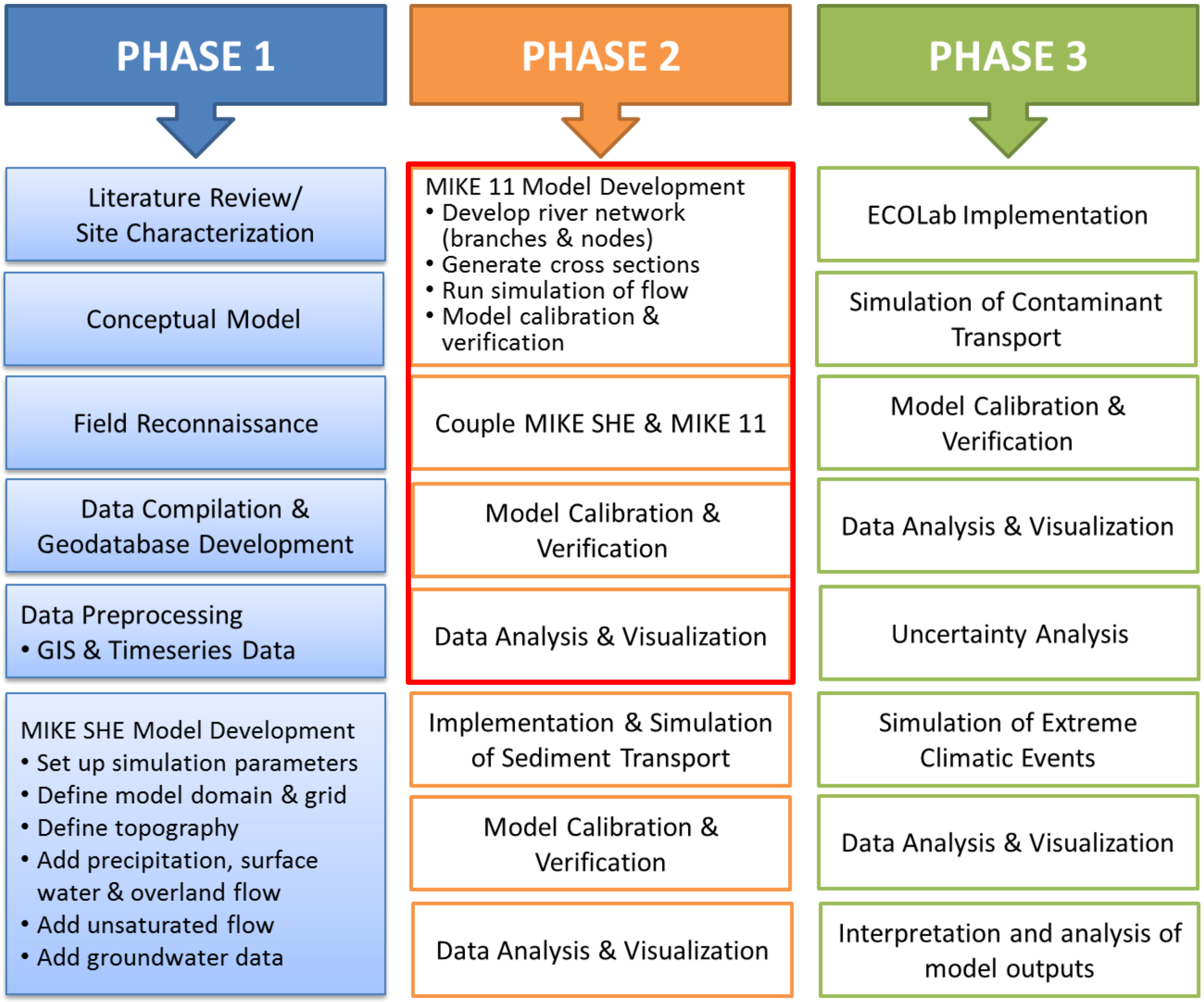

Figure 1. Hydrological modeling phases and detailed future plans.

Subtask 3.1: Modeling of Surface Water and Sediment Transport in the Tims Branch Ecosystem

The overall objective of this subtask is to develop an integrated surface water, infiltration loss, and contaminant transport model to investigate the fate and transport of contaminants such as mercury and tin in Tims Branch at SRS. Surface hydrology 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. In addition to the application of the MIKE SHE/MIKE 11 integrated modeling system, alternative distributed models will be implemented to achieve the stated objectives. The use of the distributed model will complement and expand the capabilities of the existing MIKE models. During FIU's Performance Year 7, the MIKE SHE/MIKE 11 modeling system will be fully developed. The main surface water modeling tasks include the following:

- Rainfall frequency analysis and scenario design
  - ➢ Extreme hydrological event analysis to determine hyetograph for Tr = 2, 5, 10, 25, 50, 100 and 200 years

  - Design storm for each extreme event based on the Soil Conservation Service (SCS)
  - Generation of the 24-hour hyetographs for each return period
- MIKE SHE model refinement
  - Element size modification
  - Calibration
  - Sensitivity analysis
  - Scenario analysis
- Completion of MIKE 11 stream flow model development for A-014 outfall
  - Calibration
  - Sensitivity analysis
  - Scenario analysis
- Coupling of MIKE SHE and MIKE 11 hydrological models
  - Calibration and validation of the coupled modeling system
  - Sensitivity analysis
  - Scenario analysis
  - Depth and velocity calculation for each climate scenario
  - Comparison of model results and runtime performance assessment.
- Estimation of Evapotranspiration (ET) to generate ET time series
- Implementation of an alternative distributed hydrologic, flow and transport model
- Data analysis and visualization

Daily precipitation time series data from existing rain gauge stations in the Tims Branch and neighboring watersheds will be used to perform a frequency analysis of extreme events. The results of the frequency analysis will determine the 24-hour maximum rainfall amounts corresponding to Tr = 2, 5, 10, 25, 50, 100 and 200 year events. By analyzing the rainfall data and the shape of SCS non-dimensional design storms for different areas of the United States, the option that can be best adapted to the study area will be determined. This will allow 24-hour hyetographs to be generated for each of the selected return periods.

This rainfall information will be incorporated into the surface water model to simulate spatiotemporal distribution of flow depth and velocity in Tims Branch for each extreme hydrologic scenario. These results will provide better understanding of the hydrological changes in Tims Branch during extreme weather. The hydrological outputs derived from the models will be used to develop the contaminant transport model, as hydrology plays an important role in transporting contaminants in surface water and groundwater. Note that the Tims Branch ecosystem represents an important applied science opportunity as a result of significant past research by SRNL and SREL. Recent innovative cleanup technologies developed by DOE EM have eliminated anthropogenic mercury sources from Tims Branch watershed; however, a known quantity of relatively inert tin oxide tracer was introduced to the ecosystem. DOE EM has highlighted the need to track this tin and to learn from its behavior in the Tims Branch system.

In order to optimize the model performance and capability, and to increase the spatial resolution of model results, various element sizes will be tested to establish the minimum element size that can be implemented without increasing simulation runtime. Simulations of hydrological processes may occasionally become time consuming if the element size is too small. Coarser element size may limit the model's ability to capture the details of flow on the surface. Therefore finding the right element size that is fine enough to detail the spatial flow distribution within the acceptable simulation runtime is important in model performance and results.

Physically based hydrological models such as MIKE SHE/MIKE 11 are mathematical representations of real time components of the hydrological cycle. They require extensive amounts of data such as topography, water depth, river network, etc. Some of the required data such as water depth, rainfall and evapotranspiration (ET) are in the form of time series and are publically available through state or federal agencies. Time series of ET, however, may not be available for most of the SRS area. Rather, it can be estimated using various methods such as Penman-Monteith or Priestley-Taylor. In order to increase model accuracy, times series of ET in the SRS area during the period of time that coincides with rainfall and discharge time series will be estimated.

In support of FIU's hydrological modeling effort, a flow and transport distributed model developed by FIU researchers will be implemented in parallel for comparative data analysis in order to substantiate this research work for scientific publication in peer reviewed journals, and to help further develop the hydrological modeling skills of FIU's graduate students. This FIU flow and transport model is based on an unstructured mesh finite-volume method that can be adapted to complex terrain and uses higher resolution and accuracy on the areas that are more sensitive to the pollutants flow and transport. This model also takes advantage of Graphic Processing Unit high performance computing and can run more than 100 times faster than comparable non-parallelized models, which can be a significant advantage when trying to simulate high resolution flow and transport or long term events.

Subtask 3.2: Application of GIS Technologies for Hydrological Modeling Support

Application of GIS technology is a key component in hydrological modeling that helps to prepare data, display results and conduct further spatial analyses. During FIU Performance Year 7, the ArcGIS geodatabase that was developed by ARC researchers for the Savannah River Site and the Tims Branch watershed to store, manage, and process environmental and hydrological parameters required for preliminary development of the existing MIKE SHE and MIKE 11 models, will be updated with recent Tims Branch watershed/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. FIU researchers will continue to apply GIS modeling tools to maximize efficiency by automating and batch processing model-specific geospatial and timeseries data via the implementation of process flow models.

GIS tools will also be used for delineation of the stream network and generation of cross-sections and profiles of the major and minor tributaries of Tims Branch. Advanced geospatial analyses will also be conducted for the Tims Branch watershed. This will include the examination of time series land use and land cover maps of the Tims Branch watershed to evaluate if there is any impact of land use/land cover change on the watershed hydrology. In addition, topographical changes as a result of the implementation of man-made structures along the A-014 outfall tributary will be examined to determine any hydrological impacts on the Tims Branch watershed. Utilization of the ArcGIS platform will continue to provide ARC researchers with a basis for management and geoprocessing of model configuration parameters, documenting process workflows, conducting geospatial analyses and for visualization of model results.

FIU graduate and undergraduate students will be mentored and trained on how to update and query the existing geodatabase within the ArcGIS environment, perform geoprocessing tasks, conduct geospatial analyses and generate maps and graphs for reporting and visualization of model results.

Subtask 3.3: Biota, Biofilm, Water and Sediment Sampling in Tims Branch

For application of the hydrological model being developed for Tims Branch, a rigorous calibration and validation exercise is necessary to increase confidence in its ability to estimate flow velocity and contaminant transport. The main challenges in hydrological modeling, however, are finding observed/measured data for the model calibration and validation process. It is therefore often necessary to collect additional field data to support model validation. During FIU Performance Year 6, field sampling and data collection in Tims Branch was initiated by ARC researchers and FIU students (DOE Fellows) with support from SREL. This effort included sampling of water and sediment in Tims Branch, and measurement of stream cross-section profiles and field environmental conditions such as flow velocity, suspended particle concentration and other water quality parameters. *In situ* field data will be used for model validation and to assess the Tims Branch ecosystem response (cleanup progress) to implemented remediation technologies. The collected samples will be analyzed for mercury, tin and other elements (e.g., uranium). During FIU Performance Year 7, seasonal sampling and *in situ* data collection will continue as necessary by FIU students and/or ARC researchers with support from SRNL/SREL scientists based on their availability of funding. Seasonal sampling and data collection is essential to the contaminant transport model specially when simulating the spatiotemporal distribution of contaminant concentration during and after an extreme rainfall event. FIU’s proposed sampling and *in situ* data collection for Performance Year 7 includes the following activities:

- Measurement of flow velocity in at least two locations upstream and downstream of Tims Branch.
- Measurement of flow velocity along A-014 outfall tributary at the same locations where data was collected during the fieldwork conducted in August 2016.
- Collection of water quality timeseries data including turbidity, temperature, and pH in the water column along the A-014 tributary and the main Tims Branch stream.
- Sediment core sampling and thickness measurement at locations along the A-014 tributary and the main Tims Branch stream.
- Laboratory analysis of contaminant (e.g., mercury, tin and uranium) concentration.

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

The work under this task was performed in support of SRNL and DOE EM-4.11 (Office of Infrastructure and D&D) under the direction of Mr. Albes Gaona, program lead for DOE's Sustainable Remediation Program. This task was completed during FIU Performance Year 6 and will not be continued for FIU Performance Year 7.

Task 5: Remediation Research and Technical Support for WIPP

Background

The current PA for the WIPP recommends a K_d range of 20 – 400 mL/g for Pu(III) and Am(III) for WIPP conditions (Brush and Storz 1996). However, reliable measurements have not been reported for actinide and lanthanide sorption to dolomite minerals. Previous experiments reported issues with oversaturation with respect to actinide and lanthanide solubility and often did not cover the range of conditions expected for the WIPP (Brush and Storz 1996, Brady, Papenguth and Kelly 1999, Perkins et al. 1999). For example, the experiments cited for the PA from Brush and Storz (1996) were conducted in relevant brines but they did not report pH for Am(III) and data is limited for Nd(III). The partitioning coefficient reported for Pu(III) and Am(III) were 260 and 2005 mL/g, respectively (Brush and Storz 1996). Further, previous researchers have reported a range of K_d values from 200 – 10^6 mL/g for sorption of Am(III) and Pu(III) to calcite and dolomite minerals (Shanbhag and Morse 1982, Higgo and Rees 1986, Dosch 1979, Brush and Storz 1996, Perkins et al. 1999, Lucero, Heath and Brown 1998).

FIU ARC will collaborate with research scientists Donald Reed and Timothy Dittrich in support of Los Alamos National Laboratory's field office located at the Carlsbad Environmental Monitoring and Research Center (CEMRC) in Carlsbad, New Mexico.

Objective

The objective is to update the experimental sorption data for actinides using the actinide or an oxidation state analog via mini-columns and batch experiments across a range of ionic strengths in the presence of relevant WIPP minerals and ligands. FIU Performance Year 7 will focus on understanding sorption of the trivalent oxidation state to dolomite minerals in the presence of relevant ligands including but not limited to oxalic acid, citric acid and natural organic matter.

Benefits

These experiments are expected to significantly reduce the uncertainty in the partitioning coefficients for the trivalent actinides in the presence of dolomite under WIPP relevant conditions. These experiments may allow the DOE to increase the K_d parameters for the trivalent actinides as the current PA models assume a K_d range of 20 – 400 mL/g as compared to the reported range of 200 – 10^6 mL/g. This could lead to a significant cost savings in engineered barriers and environmental monitoring as an increase in the K_d value will predict a decrease in mobility of the actinides at the WIPP and, likely, a decrease in the need for additional barriers and monitoring.

Technical Approach

During FIU Performance Year 7, mini-column and kinetic batch sorption experiments begun in Year 6 will be continued with Nd(III), as an analog for the actinide(III) oxidation state, and dolomite to refine the procedures for experiments with radioactive elements. Ionic strength will be varied from 0.01 – 5.0 M with NaCl to ensure investigation of conditions relevant to brines from both the near field and far field which may be transported through the dolomite formation. Relevant ligands will also be considered in batch and mini column experiments. Experiments will also begin with Am(III) to confirm the use of Nd(III) as an analog for the trivalent oxidation state. A proposal is in progress to begin handling Am at the FIU ARC facilities. However, if regulatory issues arise with respect to handling at FIU ARC, Am experiments may be conducted at LANL CEMRC facilities. Further, these experiments are directly applicable to ongoing work at LANL CEMRC with more complex brines and will allow for important comparisons between the systems.

PROJECT MILESTONES

Milestone No.	Milestone Description	Completion Criteria	Due Date
2016-P2-M1	Submit three draft papers to Waste Management 2017 Symposium	Acceptance notification by WM17 reviewers	11/4/2016
2016-P2-M2	Submit abstract to ACS Spring Conference (Subtask 1.1)	Submission of memo by Project Manager	11/30/2016
2016-P2-M3	Complete development of MIKE 11 stream flow model for A-014 outfall (Subtask 3.1)	Submission of memo by Project Manager	12/08/2016
2016-P2-M4	Complete the creation of acid-impacted soil samples through conditioning of SRS F/H Area soil with acidified water in columns (Subtask 2.1)	Submission of memo by Project Manager	12/15/2016
2016-P2-M5	Complete training on LSC analytical technique and trial-and-error experiments for separations and determination of Tc(IV) and Tc(VII) (Subtask 1.4)	Submission of memo by Project Manager	1/27/2017
2016-P2-M6	Complete batch experiments of uranium removal by Huma-K sorbed on SRS sediments (Subtask 2.3)	Submission of memo by Project Manager	2/15/2017
2016-P2-M7	Complete a set of column experiments using modified humic acid (Subtask 2.3)	Submission of memo by Project Manager	2/28/2017
2016-P2-M8	Complete calibration of MIKE SHE and MIKE 11 models (Subtask 3.1)	Submission of memo by Project Manager	3/01/2017
2016-P2-M9	Complete batch experiments on the biodissolution of Na-autunite (Subtask 1.2)	Submission of memo by Project Manager	3/20/2017
2016-P2-M10	Complete coupling of MIKE SHE and MIKE 11 models (Subtask 3.1)	Submission of memo by Project Manager	5/05/2017

DELIVERABLES

Client Deliverables	Responsibility	Acceptance Criteria	Due Date
Draft Project Technical Plan	Project Manager	Acknowledgement of receipt via E-mail two weeks after submission	9/30/2016
Technical report on the results of columns monitoring using geochemical and SIP analyses (Subtask 1.3)	Project Manager	Acknowledgement of receipt via E-mail two weeks after submission	1/30/2017
Technical report on the Investigation on the Properties of Acid-Contaminated Sediment and its Effect on Contaminant Mobility (Subtask 2.1)	Project Manager	Acknowledgement of receipt via E-mail two weeks after submission	2/13/2017
Technical report on the synergy between colloidal Si and HA on the removal of U(VI) (Subtask 2.2)	Project Manager	Acknowledgement of receipt via E-mail two weeks after submission	3/31/2017
Technical report on the Investigation of the Removal of Uranium by Huma-K Sorbed on SRS Sediments via Batch Experiments (Subtask 2.3)	Project Manager	Acknowledgement of receipt via E-mail two weeks after submission	4/03/2017
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	4/7/2017**
Technical report on the effect of ionic strength on the sorption of neodymium to dolomite (Task 5)	Project Manager	Acknowledgement of receipt via E-mail two weeks after submission	5/12/2017
Technical report on the surface water modeling of Tims Branch (Task 3)	Project Manager	Acknowledgement of receipt via E-mail two weeks after submission	6/15/2017
Monthly Progress Report	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	9/29/2017**
Draft Year End Report	Project Manager	Acknowledgement of receipt via E-mail two weeks after submission	10/13/2017

**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/LANL/CBFO 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, LANL	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, LANL	30 working days after completion of performance period	E-mail	Project Manager
Papers and presentations	DOE EM, PNNL, SRNL, SREL, LANL	As developed for conferences (e.g., WM17)	E-mail	Project Manager
Milestone completion E-mail	DOE EM, PNNL, SRNL, SREL, LANL	At completion of milestone	E-mail	Task Manager
Coordination of project activities	DOE EM, PNNL, SRNL, SREL, LANL	As needed to discuss issues and reach consensus	Phone, E-mails	Project 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 Performance Year 7. 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. Any field and laboratory work performed by FIU at the DOE sites will be conducted in accordance with the sites' required security and health and safety protocols.

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