PROJECT TECHNICAL PLAN

Project 2: Rapid Deployment of Engineered Solutions to Environmental Problems

For the period September17, 2013 to May17, 2014

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INTRODUCTION

Uranium is one of the two most common radionuclides in the groundwater at 91 waste sites at 18 U.S. Department of Energy (DOE) facilities within the United States. Activities related to the nuclear energy and weapons production at the Hanford Site have resulted in widespread uranium contamination in the subsurface environment due to the unintended release of 202,703 kg of U to the ground surface. As the U waste infiltrated the vadose zone soil, it created a potential source for groundwater contamination and risk to receptors through water uptake from contaminated wells or discharges to surface water. Despite extensive remediation efforts initiated in the early 1990s, persistent uranium groundwater plumes identified in multiple locations around the site have persisted for many years. There is a growing concern that elevated uranium concentrations could enter the Columbia River along the shoreline contaminating sediment and aquatic biota. The protection of water resources from contaminated groundwater resulting from operations at the Hanford Site is a key element of the overall Hanford cleanup program.

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Uranium (VI) is a main contaminant of concern at the Hanford Site. It is present in vadose zone sediment as uranyl carbonates (liebigite and rutherfordine), co-precipitated with carbonates or hydrous silicates (uranophane $[Ca(UO_2)_2(SiO_3OH)_2{*}5H_2O]$ and Na-boltwoodite $[Na(UO_2)(SiO_4){*}1.5H_2O]$ (Zachara et al., 2007; Um et al., 2009). In addition, uranium is present as mobile aqueous and adsorbed phases (Szecsody et al., 2012). Slow downward migration of U creates a risk of higher U concentrations reaching the groundwater. Environmental factors, such as pore water ion composition, have tremendous effect on both uranium and its mineral phases. Additional research is necessary to understand the effect of these factors on the behavior of U(VI) in vadose zone sediments.

During FIU Year 3, two subtasks related to the Hanford Site were carried out in Project 2: Subtask 1.1 has involved a series of batch experiments to evaluate the removal of U(VI) and the effect of various concentration ratios of silicon and aluminum, in the presence of several bicarbonate, Ca concentrations and the addition of Mg into the solution mixture. For this subtask, FIU-ARC completed studies on the formation of Si-Al minerals in the presence of bicarbonate ions, 5 mM of aluminum, 5-10 mM of Ca and a mixture of 5 mM Ca and 5 mM Mg. These studies included experiments to evaluate for U(VI) removal as well as mineralogical and morphological characterization of U(VI)-bearing precipitates primarily by means of SEM/EDS, Raman spectroscopy and XRD methods to investigate the evolution of the precipitate with increasing aging time in the solution. This research is still on-going. Subtask 1.2 evaluated microbial-uranium interactions comprising of autunite mineral biodissolution studies in the presence of bicarbonate ions using a less tolerant to U(VI) strain *Arthrobacter* G968. FIU-ARC completed a series of autunite dissolution experiments using mixed reactors and reactors with inserts inoculated with the G968 strain and initiated atomic force microscopy (AFM) characterization of the G968 cell surface after exposure to U(VI) in the bicarbonate-bearing solutions.

During FIU Year 4, Project 2 will include two tasks. Each task will comprise of two subtasks conducted in close collaboration with Hanford and SRS site scientists. FIU ARC will continue to provide research support on uranium contamination and remediation at the Hanford Site with two subtasks under Task 1: Subtask 1.1, research on sequestering uranium at the 200 Area by *in situ* subsurface pH manipulation using NH_3 gas; and Subtask 1.2, experimentation on microbial-uranium interactions and the dissolution of autunite mineral with the less U(VI) tolerant strain, *Arthrobacter* G968, in the presence of bicarbonate ions.

The study under Subtask 1.1 evaluates the mechanisms and effectiveness of NH_3 injection in the vadose zone, which has significant uncertainties under Hanford VZ site-specific conditions. The injection of a NH_3 gaseous mixture causes the formation of NH_4OH and a subsequent increase in pH. This manipulation can significantly alter the pore water chemistry and promote the dissolution of silica, aluminum, calcium and other cations and anions from soil minerals to porewater. The concentration of anions and cations then is decreased over time due to the formation of various aluminosilicates and calcium/ magnesium carbonates. The subsequent decrease in pH to natural conditions would lead to co-precipitation of U(VI) with mobilized Si and/or incorporation into precipitates (Szecsody et al. 2010; Szecsody et al. (2012). These chemical reactions can potentially control the mobility of uranyl cations in soil systems since co-precipitated contaminants are less available for migration. This study will evaluate the solubility of uranium-bearing precipitates created after NH_3 gas injection and continue mineralogical and morphological characterization of U(VI)-bearing precipitates.

Research under Subtask 1.2 will focus on the effect of bicarbonate on the autunite mineral microbial dissolution and U(VI) biouptake by less tolerant to U(VI) *Arthrobacter* G968. Experiments will explore *A.* G968 strains on autunite biodissolution and U(VI) biouptake, make a comparison between G975 and G968 strains, continue to inspect bacterial surfaces exposed to uranium in the presence of aqueous bicarbonate via atomic-force microscopy (AFM), and evaluate for cells viability via fluorescence-based assay.

Remediation research and technical support for the Savannah River Site will be conducted under Task 2 and include two (2) technical subtasks. The subtask 2.1 will focus on groundwater remediation with silica (Si) injection and investigate if any synergy between humid acid (HA) and silica would influence the behavior of uranium. The subtask 2.2 will focus on monitoring of U(VI) bioreduction after the ARCADIS demonstration at the F-H area to inject a molasses-based reagent into the subsurface.

> The activities described in the Continuation Application for FIU Year 4 were planned for a period of performance from May 18, 2013 to May 17, 2014. However, two no cost extensions were executed by DOE-EM for FIU Year 3, which extended the end of the FIU Year 3 period of performance to September 16, 2013. Therefore, the period of performance for the FIU Year 4 activities described in this Project Technical Plan is shortened to 8 months, September 17, 2013 to May 17, 2014. The

scope of some tasks has been affected/reduced due to the shortened period of performance and will be re-evaluated as FIU approaches the May 2014 timeframe. The affected scope may transfer to FIU Year 5.

The affected tasks from the CA for this project include the following:

- Subtask 1.1: Sequestering Uranium at the Hanford 200 Area Vadose Zone by In Situ Subsurface pH Manipulation Using NH3 Gas - Isopiestic testing will cover pH 10.8-11 conditions conducted at various temperatures from 5oC to 50^{o}C. Changes in the pH will be accounted for during FIU Year 5. In addition, plans for the characterization studies of U-bearing precipitates by the sequential liquid extractions to evaluate changes in U leaching will be delayed until FIU Year 5.
- Subtask 2.1: FIU's Support for Groundwater Remediation at SRS F/H Area - Experiments will be extended to find out the effect of silica solutions on the U removal using the same experimental matrix as for the study on the colloidal silica. In addition, experiments will explore the effect of the higher HA concentrations ranging from 10 to 50 ppm.
- Subtask 2.2: Monitoring of U(VI) Bioreduction after ARCADIS Demonstration at F-Area Based on discussions with Miles Denham, SRS should be able to get either one groundwater sample or mineral trap diffusion sample. We think that analyses of the diffusion mineral trap samples will greater supplement our on-going microcosm studies if we initiate them in FIU Year 4 and then continue in FIU Year 5. Aquifer materials of the trap samples preserved using nitrogen gas will be analyzed for mineralogy via SEM/EDS and XRD. The analysis of groundwater samples will be initiated during FIU Year 5.

OVERVIEW OF WORK ACCOMPLISHED DURING FY12 (FIU Year 3)

- Completed testing on the formation of U(VI)-bearing precipitates using various Si:Al ratios in the presence of bicarbonate (November 2012). Completed a progress report on the morphological changes of U-bearing precipitates over time via SEM/EDS (January 2013).
- Completed the AFM assessment on bacteria exposed to U (VI) in bicarbonate-bearing solutions and developed a progress report on this research (April 2013).
- Prepared a manuscript entitled, "The effects of aqueous bicarbonate and calcium ions on uranium biosorption by *Arthrobacter* G975 strain," that was submitted to the *Chemical Geology* journal and accepted for publication on August 17, 2012.
- Prepared a manuscript entitled, "Effect of bicarbonate on the dissolution of sodium meta-autunite," and submitted it to the Environmental Chemistry (June 2013). Under revision after peer review.
- Finalized a journal manuscript entitled "Comparison of the kinetic rate law parameters for the dissolution of natural and synthetic autunite in the presence of bicarbonate ions" and submitted it to the Chemical Geology (February 2013). Manuscript was accepted and published on June 2013.

- The doctoral dissertation manuscript of Ravi Gudavalli based on research associated with this project was approved by the FIU Graduate School for graduation in the Fall 2012 semester.
- Presented results of research at the WM2013 Conference (February 2013).
    - Investigation on Microbial Dissolution of Uranium (VI) from Autunite Mineral (13421), Paola Sepulveda (DOE Fellow), Yelena Katsenovich, Leonel Lagos. (Oral presentation).
    - U(VI) sequestration in the presence of bicarbonate and calcium ions via subsurface pH manipulation using ammonia gas injection (Student Poster), Claudia Cardona (DOE Fellow), Yelena Katsenovich, Leonel E. Lagos.
    - Analysis of morphological changes of U-bearing precipitates over time by SEM/EDS (Student Poster), Robert Lapierre (DOE Fellow).

TECHNOLOGY NEEDS

One of the challenges facing the U.S. Department of Energy (DOE) environmental cleanup project is vadose zone contamination at the Hanford Site. The goal of this project is to prevent further groundwater degradation and restore its quality since contaminants residing in the vadose zone create a “source” for groundwater contaminations and risk for potential receptors. One of the elements of these efforts is the evaluation of various engineered treatment alternatives targeted to reduce the exposure associated with potential downward contaminant migration from the vadose zone to the groundwater. Application of these technologies can cause natural attenuation of contaminants in vadose zone environments and decrease the flux to groundwater (Wellman et al, 2012). Injection of reactive gases such as NH_3 in low moisture content vadose zone (VZ) sediments is an innovative technology to mitigate uranium contamination and effectively control the contaminants downward migration. The desired outcome of this research is more accurate predictions on the formation of U(VI)-bearing precipitates with the goal to potentially minimize contaminant migration in the deep vadose zone and to define the solubility behavior of uranium-bearing precipitates under Hanford Site simulated conditions.

Uranyl phosphate solids created in soil and groundwater as a result of remedial actions to control uranium mobility in the subsurface is a phosphorus-containing mineral. It can attract bacteria thriving under oligotrophic conditions to liberate phosphorus to meet their nutrients requirements. The destruction of the mineral structure causes U remobilization back into the environment. Increased microbial activity that influences meta-autunite stability is an important geochemical factor affecting the uranium release back to the environment and U(VI) mobility in the specific environmental conditions present at the Hanford Site’s subsurface. Previous experiments showed that compared to the tolerant to uranium toxicity *Arthrobacter* G975 strain, the less resistant to U(VI) G968 strain is able to bio-enhance the release of U(VI) from natural Ca-autunite at almost the same capacity in the presence of various concentrations of bicarbonate. Research on the mechanisms of bacteria-uranium interactions in the presence of bicarbonate will continue to determine the long-term effectiveness of tripolyphosphate injection remediation strategy.

The Savannah River Site (SRS) was one of the major DOE industrial complexes responsible for plutonium production during the Cold War. Between 1955 and 1988, the F/H Area Seepage Basins located in the center of SRS received approximately 1.8 billion gallons of acidic waste solutions (pH from 3.2 to 5.5) contaminated with a variety of radionuclides and dissolved metals.

The acidic nature of the basin waste solutions caused the mobilization of metals and radionuclides, resulting in contaminated groundwater plumes. The constituents of concern (COCs) associated with the F-Area groundwater plume are tritium, uranium-238, iodine-129, strontium-90, curium-244, americium-241, technetium-99, cadmium and aluminum. The COCs in the H-Area are tritium, strontium-90 and mercury. The pump-and-treat water treatment unit designed and built in 1997 to remove metals and radionuclides eventually became less effective, prompting research for new remedial alternatives. A base injection system using a sodium hydroxide solution directly into the F-Area groundwater started in 2004, replacing the expensive pump-and-treat unit. The injection of the base helped to decrease concentrations of Sr and U; however, concentrations of iodine was unaffected by this treatment. FIU will investigate the effect of silicate injections to groundwater resulting in a pH increase leading to uranium sequestration and evaluate if any synergy between U(VI) and humic acid will influence the behavior of U(VI).

In 2010, ARCADIS demonstrated the *in situ* addition of a carbohydrate substrate molasses to create anaerobic reactive zones for metal and radionuclide remediation via the Enhanced Anaerobic Reductive Precipitation (EARP) process. The addition of a carbon substrate to groundwater produces anaerobic conditions conducive to the reductive precipitation of uranium. The investigation will involve the analysis of groundwater and soil to verify the removal of U(VI) as well as mineralogical studies relating to the re-oxidation of a bioreduction zone. The effectiveness of the EARP process will be evaluated for the treatment of radionuclides and metals (U(VI), Fe, Mg, S, and Si) and the total organic carbon.

Objectives

The objective of Subtask 1.1 is to evaluate the stability of U-bearing precipitates created after NH_3 (5% NH3 in 95% nitrogen) pH manipulation in the synthetic solutions mimicking conditions found in the vadose zone at the Hanford Site 200 Area. The study will examine the solubility of formed uranium-bearing solid phases via isopiestic measurements and investigate the effect of environmental factors relevant to the Hanford vadose zone on the solubility of solid phases. Solubility experiments will be conducted under different pH ranging from 7 to 11, concentrations of bicarbonate ions ranging between 0-100 mM, and temperature. The experiments will also explore the effect of age of precipitate on its solubility. In addition, studies will analyze mineralogical and morphological characteristics of precipitates by means of XRD and SEM-EDS to confirm the identity of the solid phase before and after the solubility experiments. All solubility experiments will be conducted via the isopiestic method, which is considered as one of the most accurate methods for the solubility determinations.

Experiments on the detailed characterization of created uranium-bearing precipitates will continue. Studies will analyze mineralogical and morphological characteristics of precipitates by means of X-ray diffraction (XRD) and scanning electron microscope energy-dispersive spectroscopy (SEM-EDS) to identify U(VI)-containing solid phases and confirm the identity of the solid phase before and after solubility experiments.

The goals of experimental activities under subtask 1.2 are to investigate the bacteria interactions with uranium using as an example a less U(VI)-tolerant strain and to study the potential role of bicarbonate, which is an integral complexing ligand for U(VI) and a major ion in the pore water composition. In our previous assessments of several strains, previously isolated from Hanford soil, *Arthrobacter* G968 was identified as a less-tolerant strain to U toxicity compared to

Arthrobacter G975. G975 showed stronger abilities to tolerate higher concentrations of U(VI), almost triple the value compared to the G968. The main objectives of this task are (i) make a comparison between G975 and G968 strains on U(VI) release from the autunite mineral; (ii) inspect bacterial surfaces after exposure to U(VI) in the bicarbonate-bearing synthetic groundwater solution via atomic-force microscopy (AFM) and investigate for cell viability; and (iii) determine the difference between microbial effect on uranium release from synthetic and natural autunite. The dissolution experiments and microscopic analysis were initiated in FIU Year 3 and evaluation of results will be continued throughout Year 4.

The objectives of the proposed experimental work for subtask 2.1 are (i) to evaluate whether a base solution of dissolved silica can be used to replace the previously used carbonate base, (ii) evaluate if silica solutions have enough alkalinity to restore the pH of the treatment zone, (iii) to investigate the hypothesis that some uranium in the current treatment zone is bound to silica and (iv) study if any synergy between humid acid (HA) and silica will influence the behavior of uranium.

The objective of subtask 2.2 is to monitor the U(VI) bioreduction after the ARCADIS demonstration at the F-Area the in situ addition of a carbohydrate substrate to create reactive zones for metal and radionuclide remediation via the EARP process. Without this monitoring, the technology cannot be adequately evaluated. The proposed investigation will involve the analysis of groundwater and soil from the bioreduction site to verify the continued sequestration of U(VI) as well as mineralogical studies relating to re-oxidation of a bioreduction zone.

Benefits

Deep vadose zone contamination of radionuclides requires *in-situ* stabilization to convert aqueous U-carbonates mobile phases to lower solubility precipitates that are stable in the natural environment. Injection of reactive gases, such as NH_3, to create alkaline conditions in the vadose zone is an innovative technology used to decrease uranium mobility in subsurfaces contaminated with radionuclides. This task investigates the mechanisms and effectiveness of NH_3 gas injection on the removal of uranium (VI) in the synthetic groundwater solutions mimicking 200-Area pore water. Clearly, an understanding of the role of pore water constituencies on the removal of U(VI) is needed to predict the mineralogical changes and the formation of precipitates that would be created in the treated vadose zone soil. Ammonia is a highly soluble gas and its injection in the vadose zone causes the formation of NH_4OH followed by a subsequent increase in pH. Changes in pore-water pH can profoundly affect the dissolution of soil minerals such as calcite, feldspar, iron oxides, and quartz residing in the vadose zone. These reactions potentially induce the release of cations such as Si, Al, Ca, Mg, Na, and K from soil minerals to pore water. The subsequent decrease in pH to natural conditions would lead to precipitation of calcium and magnesium carbonates and aluminosilicates along with mobilized silica that can possibly coat sequestered contaminants in a process called co-precipitation. These chemical reactions can potentially control the mobility of uranyl cations in soil systems since co-precipitated contaminants are less available for migration. This study will evaluate the solubility of formed minerals and examine their mineralogical and morphological characteristics to confirm the identity of the solid phase before and after solubility experiments.

Aqueous carbonate ions present in the soil and ground water are the predominant aqueous species affecting the dissolution of uranium-bearing solids and facilitating uranium desorption reactions from soil and sediments, thus increasing uranium mobility in soil and sediments. This task will also investigate bacteria-U(VI) interactions under oxidizing conditions and study the potential role of bicarbonate to influence U(VI) release from autunite minerals and reduce uranium adsorption by bacterial cells. In the presence of bicarbonate cells exhibit higher viability in response to uranium toxicity. Active uranium- resistant bacteria can decrease the long-term stability of uranyl-bearing precipitates created in soil as a result of remedial actions. The research will promote the understanding of the effect of these factors on the behavior of U(VI) in groundwater and sediments to support remedial actions implemented in the 300 and 200 Areas.

The proposed FIU research for the F/H area at SRS will investigate whether dissolved sodium silicate solutions have enough alkalinity to replace the carbonate base being used to correct the acidic nature of the contaminated sediments. This investigation will also evaluate if U(VI) in the treatment zone is bound to silica. The other aspect of this task is to study if any synergetic interactions between humic acid and silica will influence 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. In addition, humic acids (HA) are important ligands, significantly affecting the mobility behaviour of actinides in the environment. The study will be conducted using batch and column experiments and evaluate surface morphology and compositions of sediments. Experiments will be extended to investigate whether contaminates remain sequestered after the ARCADIS demonstration at the F-Area. This is particularly important since the remediation strategy chosen by ARCADIS relies on changing the geochemical conditions in a direction that is opposite of their natural evolution.

FIU YEAR 4 PROJECT 2 EXECUTION PLAN

Plans for FIU Year 4 include following subtasks:

Task 1: Sequestering Uranium at the Hanford 200 Area Vadose Zone by *In Situ* Subsurface pH Manipulation Using NH3 Gas

Subtask 1.1: Sequestering Uranium at the Hanford 200 Area Vadose Zone by *In Situ* Subsurface pH Manipulation Using NH_3 Gas

In the environment, solubility influences the behaviors and fate of many contaminates and to a great extent determines its mobility in the subsurface. The isopiestic method, which is considered as one of the most accurate methods for the solubility determinations, will be applied to measure the solubility of precipitates created after ammonia gas injections to sequester uranium in the vadose zone. Precipitates will be prepared using varied Si concentrations (1, 50 and 100 mM) to study different molar ratios of Si:Al (1, 10 and 20) at concentrations of bicarbonate ranging from 0 to 100 mM. The procedures for sample preparations will follow methods described in the 2011 and 2012 Year End Reports. Experimental solutions for the isopiestic measurements will be prepared by weight using 15-mL nickel cups before placing them in an aluminum block kept at a constant temperature in a sealed chamber equilibrated to a constant pressure by pumping air out to reach about 4.5 kPa. The initial experiments will be conducted at a constant temperature of 23^oC and pH of 10.8-11, until the system reaches equilibrium. Later experiments will be extended to test solubility in a wide range of temperatures ranging from 5^oC to 50^oC and pHs from 7 to 11. The basic features of the isopiestic method include isothermal equilibration through a common vapor phase of samples of known mass and known initial concentration. All of the solutions at equal vapor pressure or isopiestic equilibrium have the same solvent activities. By equilibration of the samples with a standard of known solvent activities under the conditions of the experiment as a function of molality, the solvent activity of other solutions can be determined (Rard, 1985). The apparatus to conduct the experiments consists of a vacuum desiccator, or closed chamber kept at a constant temperature. The apparatus is also equipped with a high accuracy pressure transducer with a range of 0-30 psia (Omega Engineering, Inc.) that will provide an accurate measuring of water vapor pressure and allow for monitoring as the system approaches equilibrium. The system reaches equilibrium when the solutions in the samples have the same molality. This method allows for the determination of the molality of the solutions, the molecular weight of the solute and water activity.

Experiments to evaluate the mineralogy of the precipitates will continue. The concentrations of major constituents including silicate and aluminate in the Si/Al molar ratio will be varied from 1-50 and bicarbonate ion concentrations will range between 0-100 mM. Characterization studies of precipitates prepared with 200 ppm of U(VI) identified very small peaks for ceikaite, $Na_4(UO_2)(CO_3)_3$, which is the most soluble and mobile uranyl carbonate phase. The formation of this phase is probably due to the high sodium content in the sample, associated with the sodium silicate initially used in the sample preparations. Experiments will be conducted to explore several methods of sample preparation to minimize this interference. The increase in U(VI) concentration to 500 or 1000 ppm will be considered to increase the atomic percentage of U(VI)) in the precipitate samples for more accurate phase identification. Precipitates with U(VI) will be dried and further characterized in detail by SEM/EDS and XRD analysis to identify U-bearing phases and determine morphological features of formed precipitates. In addition, these samples will be characterized by the sequential liquid extractions to evaluate changes in U leaching in FIU Year 5. Several sequential liquid extractions of increasing strength will be used to characterize U mobility when the harder to extract phases are less mobile (Szecsody et al., 2012). The procedure of sequential extractions is described in Szecsody et al., 2012. These results will supplement the solubility experiments conducted via the isopiestic method.

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

During FIU Year 4, experimental work will be conducted to investigate the bacterial interactions of a less U(VI)-tolerant strain under oxidizing conditions and study the potential role of bicarbonate, which is an integral complexing ligand for U(VI) and a major ion in groundwater compositions. This task will focus on bacterial-U(VI) interactions under oxidizing conditions and examine the ability of less tolerant-to-U(VI) oligotrophic microbial species, such as *Arthrobacter* G968 that have previously been isolated from Hanford Site soil, to influence the dissolution of natural and synthetic autunite. Our previous results suggest that indigenous microorganisms in subsurface environments can affect the liberation of U(VI) even while not in direct contact with the mineral. The dissolution mechanisms include complexation reactions due to the secretion of protons and various ligands, physico-chemical interactions between the uranyl cation and the bacterial cell wall polymers, and bacterial attachment to the surface of the mineral particles, which produce unique physiochemical conditions that catalyze chemical reactions to release P and U(VI) from the mineral structure. These can decrease the long-term stability of uranyl-bearing precipitates created in soil as a result of remedial actions.

This research provides a more comprehensive understanding into important microbiological processes affecting autunite stability within subsurface bicarbonate-bearing environments. The main objectives of the research are to:

- Investigate the effect of bicarbonate on the microbial dissolution of the autunite mineral and U(VI) adsorption by *Arthrobacter* G968;
- Make a comparison between G975 and G968 strains;
- Inspect the bacterial surfaces in the presence of bicarbonate and uranium in the solution using atomic-force microscopy (AFM);
- Determine the difference between microbial dissolution of synthetic autunite versus natural autunite;
- Determine the change in viability of cells exposed to U(VI) in the presence of bicarbonate via fluorescent microscope using Live/Dead stain.

The study planned for FIU Year 4 will examine the bacterial interactions with uranium of a less U(VI)-tolerant strain under oxidizing conditions to find the differences between the microbial effect on U(VI) release from synthetic and natural autunite.

Previous abiotic experiments conducted to investigate the effect of aqueous bicarbonate on the uranium rate of release from natural Ca-autunite and synthetic Na-autunite showed a higher stability of Na-autunite. The biodissolution experiments will be extended to investigate the U release from the synthetic Na-autunite in the low-phosphorous culture growth media augmented with various concentrations of bicarbonate and inoculated with G968 strains. Post-experimental assessment of bacteria and mineral will apply SEM-EDS to characterize the solid phase's surface morphology during U(VI) release. In addition, this task will evaluate the uranium (VI) bioaccumulation by G968 in synthetic groundwater with varying bicarbonate concentrations and determine the viability of the G968 strain to U(VI) exposure in bicarbonate-amended media via fluorescent microscope using Live/Dead stain. U(VI) precipitates adsorbed on the bacterial surfaces may interfere with cell metabolism and nutrient transport across the cell wall; so, it may be necessary to evaluate the effect of bicarbonate on the *Arthrobacter* G968 cells viability.

The analysis of the uranium concentration will be carried out by the KPA-11 (Chemcheck Instruments, Richland, WA). Aqueous concentrations of sodium and phosphorus in the samples will be determined by means of Optima 7300 ICP-OES (Perkin Elmer). Atomic force microscopy will be used to monitor changes at the nanoscale level in the G968 cell surface topography and adhesion before and after the cells are exposed to various concentrations of uranium and bicarbonate ions. The presence of cells on the mineral surface during dissolution of autunite and changes on the cell surface composition during bacterial uptake of U(VI) will be detected by using a SEM-Energy-Dispersive-Spectrometry (SEM-EDS) Noran System Six Model 200.

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

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

Between 1955 and 1988, the F/H Area Seepage Basins located in the center of SRS received approximately 1.8 billion gallons of acidic waste solutions (pH from 3.2 to 5.5) contaminated with a variety of radionuclides and dissolved metals. The acidic nature of the basin waste solutions caused the mobilization of metals and radionuclides, resulting in contaminated groundwater plumes. The constituents of concern (COCs) associated with the F-Area groundwater plume are tritium, uranium-238, iodine-129, and strontium-90. The COCs in the H-Area are tritium, strontium-90 and mercury. The pump-and-treat water treatment unit designed and built in 1997 to remove metals and radionuclides eventually became less effective, prompting research for new remedial alternatives. A system injecting a sodium hydroxide solution directly into the F-Area groundwater at gates of a funnel-and-gate started in 2004, replacing the expensive pump-and-treat unit. The purpose was to create a treatment zone in which the acidic nature of the contaminated sediments is corrected, thereby promoting adsorption of cationic contaminants. A solution with high carbonate alkalinity was initially used to overcome the surface acidity of plume influenced minerals. The enhanced mobility of uranium in high carbonate solutions was not a concern because so little uranium was adsorbed at the plume pH of 3.2. However, re-injection of a base solution is periodically required to restore the pH of the treatment zone. Use of a high carbonate solution raises the issue of re-mobilization of uranium sorbed within the treatment zone. Monitoring data indicate that injection of the base helps to decrease concentrations of Sr and U; however, concentrations of iodine were unaffected by this treatment.

Interestingly, re-injection of the high carbonate base appears to re-mobilize some uranium, but not at concentrations that exceed drinking water standards. SRNL has hypothesized that the uranium that enters the elevated pH treatment zone may be sequestered by interaction with silica coatings on kaolinite. Silica would be anticipated to remain after incongruent dissolution of the kaolinite by the acidic plume. In fact, silica replacing the clay matrix has been observed by optical microscopy. Uranium bound to silica may resist re-mobilization by the carbonate solution.

Two issues drive the proposed FIU research. The first is whether a base solution of dissolved silica can be used to replace the carbonate base. This requires knowledge if a $pH \leq 10$ silica solution has sufficient alkalinity to restore the pH of the treatment zone, whether silica solutions can be injected into the subsurface without clogging the aquifer permeability. The first step of this investigation is to find out the effect of silica solutions or colloidal Si on uranium removal. The investigation will also evaluate the hypothesis that some uranium in the treatment zone is bound to silica.

The second issue is to investigate if any synergy between humid acid (HA) and silica will influence the behavior of uranium. Humic substances are ubiquitous organic macromolecules with variable composition formed by the decomposition of biomass. Studies showed that HA function as an important ion-exchange and metal-complexing ligand carrying a large number of functional groups with high complexing capacity that can greatly affect the mobility behavior of actinides in natural systems. Previous studies suggested that the retention of U(VI) via sorption in the presence of HA is a complex process of the system components and depends on the soil minerals, HA concentration and the experimental conditions. This task will investigate if there are any synergistic interactions between U(VI) ions, humic acid and silica under oxidized conditions and study the influence of HA and Si on the sorption of U(VI) onto sediments collected from the F/H Area. Experiments will also study the effects of different environmental variables such as pH, presence of U(VI) and concentrations of HA and Si on the removal behavior of U(VI) in the multi-component batch systems. The concentration of Ca will be kept constant at the level of a few ppm similar to the study area groundwater conditions.

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

- Si (3.5mM) +U(VI) (0.5ppm) (no sediments and HA).
- Si (3.5mM) +U(VI) (0.5ppm) + HA (10ppm), (no sediments)
- U(VI) (0.5ppm) + HA (10ppm) (no Si and sediments).
- Sediments+ Si (3.5mM) +U(VI) (0.5ppm) (no HA)
- Sediments+ Si (3.5mM) +U(VI) (0.5ppm) + HA
- Sediments +U(VI) (0.5ppm) + HA, (no Si)
- Sediments+ U(VI) (0.5ppm), (no Si and HA)

Literature data suggests using the solid/liquid ratio in the range of 3g/L to 5g/L. The batch experiments will be done using commercial colloidal silica. Separate experiments will be conducted in the presence of a high pH sodium silicate solutions used as a base. In addition, sodium silicate solutions will be used as a base to investigate silica abilities to increase the system's pH. An attempt will be made to combine both substances in the base solution (HA and sodium silicate) to create the alkalinity needed for the complexation reaction between silica and U(VI). In those experiments, the concentration of HA used will be 10 ppm.

The sediments' surface composition will be analyzed via scanning electron microscopy and energy-dispersive-spectrometry (SEM-EDS). The quantitative measurements of the surface composition will show the distribution of elements throughout the sample. The distribution of carbon might suggest if HA polymerized and precipitated on the surface or between sediment particles. The SEM-EDS analysis will also reveal surface topography and provide information of any correlation between elements across the surface.

The next experimental step will evaluate HA migration to obtain the transport parameters. The column experiments will be conducted using sediments collected in the F/H Area. Initially, Br tracer tests will be used to evaluate the transport parameters and then determine if transport of HA and Si through the soil column is retarded. Prior batch experiments will help to determine the column's dimensions and height of the sediment layer.

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

In 2010, ARCADIS demonstrated the *in situ* injections of a carbohydrate substrate, molasses, to create reactive zones for metal and radionuclide remediation via the Enhanced Anaerobic Reductive Precipitation (EARP) process. The addition of the molasses substrate solution to groundwater produces anaerobic conditions conducive to the reductive precipitation of uranium. An important aspect of any *in situ* remediation of metal and radionuclide contamination is the longevity of contaminant immobilization. Regulators and stakeholders will approve leaving contaminants in the subsurface only if they are assured that contaminants will remain sequestered for long periods of time. This is particularly true when the remediation strategy relies on changing the geochemical conditions in a direction that is opposite of their natural evolution. Bioreduction of metals/radionuclides in an aerobic aquifer is an example of this. To demonstrate effectiveness of bioreduction, monitoring must be done on the re-oxidation of the artificially reduced zone and the effects on the contaminants. The funding for ARCADIS was not sufficient for this monitoring. Without this monitoring the technology cannot be adequately evaluated. The proposed investigation will involve the analysis of groundwater and soil from the bioreduction site to verify the continued sequestration of U(VI) as well as mineralogical studies relating to possible re-oxidation of minerals from the bioreduction zone.

Several experimental sets are planned for this subtask. One of them is a set of microcosm studies prepared with SRS sediments, augmenting the solution mixture with molasses. SRS sediments contain iron and these experiments will determine whether forms of reduced iron such as siderite and pyrite would arise in the reducing zone. These experiments will also explain the types of reactions that might occur in the anaerobic aquifer.

In addition, changes in the groundwater water chemistry from the ARCADIS treated site will be evaluated via water samples analysis. During a summer internship at SRNL, a DOE Fellow conducted analysis on old well data from ARCADIS monthly reports to determine which wells should be sampled. Tentatively, 7 groundwater sampling events will occur with a total of 56 samples collected for analysis of field parameters at the site and then for anions by means of ion chromatograph at SRNL. The samples will then be acidified and shipped to FIU for U(VI) analysis via KPA instruments, dissolved metals such as Fe, Mg, Mn, S, and Si via ICP-OES and total organic carbon (TOC) by means of a Shimadzu TOC analyzer.

To understand the mechanisms of mineral growth and precipitation *in situ*, diffusion mineral trap samples will be collected in place for a longer period of time. Collected samples filled with aquifer materials and preserved using nitrogen gas will be analyzed for mineralogy via SEM/EDS and XRD. The results will be compared to the soil analysis of a molasses- untreated zone to identify some differences that could be attributed to the changes in the redox conditions. The mineralogical results will be compared to the microcosm samples.

To perform this subtask, FIU will be in continuous communication with our SRNL contacts, Miles Denham and Brian Looney.

Project Milestones

Milestone No.	Milestone Description	Completion Criteria	Due Date
2013-P2-M1	Complete experimental plan on solubility measurements via isopiestic method	E-mail notification to DOE	1/30/14
2013-P2-M2	Completion of experimental plan including modifications for new samples prepared to minimize nitratine formation	E-mail notification to DOE	2/14/14
2013-P2-M3	Completion of testing of Dead/Live bacteria	E-mail notification to DOE	1/20/2014
2013-P2-M4	Completion of batch experiments using colloidal silica, humate, sediments and U(VI)	E-mail notification to DOE	2/5/14
2013-P2-M5	Completion of microcosm studies prepared with SRS sediments,	E-mail notification to DOE	1/31/2014

Deliverables

Client Deliverables	Responsibility	Acceptance Criteria	Due Date
Draft Project Technical Plan	Project Manager	Acknowledgement of receipt via E-mail two weeks after submission	10/17/2013
Subtask 1.1 Progress report on literature review and experimental plan on solubility measurements via isopiestic method	Project Manager	Acknowledgement of receipt via E-mail two weeks after submission	2/25/2014
Subtask 1.1.Progress report on characterization of new samples prepared to minimize nitratine formation	Project Manager	Acknowledgement of receipt via E-mail two weeks after submission	4/11/2014

Subtask 1.2 Progress report on bacterial growth in the present of 5-20ppm of U(VI) in bicarbonate-bearing solutions and AFM assessment on bacteria exposed to U(VI).	Project Manager	Acknowledgement of receipt via E-mail two weeks after submission	4/30/2014
Subtask 2.1 Progress report on the results of batch experiments using colloidal silica, humate, sediments and U(VI)	Project Manager	Acknowledgement of receipt via E-mail two weeks after submission	03/15/2014
Subtask 2.2 Progress report on microcosm studies prepared with SRS sediments, & Groundwater analysis	Project Manager	Acknowledgement of receipt via E-mail two weeks after submission	02/07/2014
Draft Year End Report	Project Manager	Acknowledgement of receipt via E-mail two weeks after submission	6/30/2014
Quarterly status and progress summary reports	Project Manager	Acknowledgement of receipt via E-mail two weeks after submission	Quarterly

Communication Plan

The project has some elements that require significant information and/or action from the site in order to proceed with the proposed scope. Therefore, the communication with the clients and relevant experts at Hanford, SRS and DOE-HQ 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 Hanford Site to ensure all parties involved are aware of the project progress.

Information Item	Client Stakeholder	When?	Communication Method	Responsible Stakeholder
Status Update Teleconferences	DOE-HQ and PNNL (Dr. Dawn Wellman) SRNL (Dr.	Monthly	Phone	Project Manager

	Miles Denham)			
EM-HQ Status Update Phone Call	DOE EM Technical Coordinator	Bi-Weekly	Phone	Principal Investigator/Project Manager
Quarterly Status	DOE EM-32 Hanford, SRNL	End of Q1, Q2, Q3, Q4	E-mail	Project Manager
Draft Year End Report	DOE EM-32 Hanford, SRNL	30 working days after completion of performance period	E-mail	Project Manager
Milestone completion E-mails	DOE EM-32 Hanford, SRNL	At completion of milestone	E-mail	Task Manager

Anticipated Issues

Due to annual weather conditions in South Florida, there is the potential for hurricane damage to the FIU-ARC research facilities. In 2005, FIU was closed down for two weeks as repairs were made to roads and electrical power in the area. Post hurricane repair and construction on the roof of the Engineering Campus building where FIU-ARC resides took 8 additional months. The function of the fume hoods within all major laboratories were shut down for 3-8 months as these repairs progressed and this caused a major delay in analytical experiments due to the need to schedule and share existing functional hoods in other parts of the University. Post hurricane repair following significant storm events of this nature have the potential to cause delays in research activity. Contingency plans will be developed to minimize any potential impacts on the overall task schedule.

Regulatory Policies and Safety Concerns

This project involves research conducted in facilities at the Applied Research Center which are designed specifically for R&D studies. Most of the experiments proposed under the Project 2 will be carried out at FIU's Radiological Laboratory under controlled radiological conditions and in accordance with FIU's radiological license. All radioactive wastes generated during the experiments will be disposed of according to local, state, and federal regulations. All necessary health and safety precautions will be followed in accordance with the project's PSEHASP. All student employees will complete online safety courses as well as a briefing for the safety in the laboratory in which they are performing research. No undergraduate student will perform research in a laboratory without direct oversight of faculty, staff, or a qualified graduate student.

References

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