

FIU PROJECT 2 - TASK 1.1 - 2014 FACT SHEET

Sequestering Uranium at the Hanford 200 Area Vadose Zone by In Situ Subsurface pH Manipulation Using NH₃ Gas Injection

FIU's Applied Research Center (ARC) is supporting the U.S. Department of Energy's Hanford Site in developing a strategy to improve the efficiency of the uranium stabilization process through pH manipulation using NH₃ gas injection.

Characterization of vadose zone (VZ) soil at the 200 Area has identified a number of radiological and hazardous contaminants, including technetium and uranium. This work is focused on long-lived uranium contamination, which is one of the key contaminants of concern that needs to be reduced to below levels that can cause harm to human health and the environment. Injection of reactive gases such as NH₃, is an innovative remediation technology shown to mitigate uranium contamination in soil. The injection of NH₃ gas causes ammonia gas dissolution in soil moisture, with the formation of NH₄OH and a subsequent increase in pH. This manipulation will significantly alter the pore water chemistry and affect the dissolution of silica and aluminosilicate from soil minerals, followed by co-precipitation of U(VI) [as uranyl (UO₂²⁺)] and Al at higher pH conditions. The main objective of the project is to evaluate the role of major pore water constituents such as Al, Si, bicarbonate and Ca on the formation of precipitates after NH₃ injection and to examine the solubility of formed minerals under environmental conditions relevant to the Hanford vadose zone. The batch experiments include preparation of a series of vials on synthetic fluids imitating contaminated pore water. The concentrations of major constituents including silicate, aluminate, calcium and bicarbonate are in the range reported for the Hanford VZ.

Objectives

- Examine the effect of concentration ratios of *silicon to aluminum* on the removal process of U(VI) in the presence of various bicarbonate and calcium ion concentrations.
- Evaluate the role of major pore water constituents such as Al, Si, bicarbonate and Ca on the formation of precipitates.
- Analyze mineralogical and morphological characteristics of precipitates by means of XRD and SEM-EDS to identify uranium-bearing solid phases.
- Examine the solubility of uranium-bearing solid phases via isopiestic measurements and explore the effect of age of precipitate on its solubility.
- Examine the effect of temperature on the solubility of U(VI)-bearing precipitates.

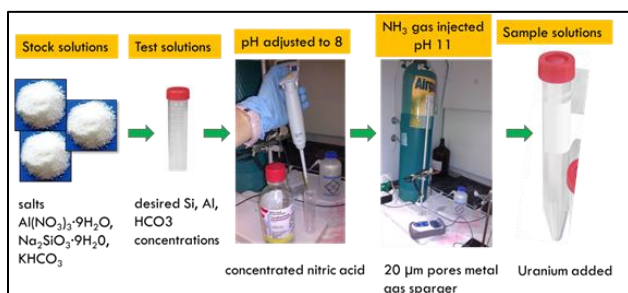


Figure 1. Experimental procedures.

Benefits

- Understanding the role of pore water constituents on the removal of U(VI) to predict the mineralogical changes and the formation of precipitates that would be created in the treated VZ soil.
- Yields information on the formation and solubility behavior of U(VI)-bearing precipitates under environmentally relevant Hanford Site VZ conditions.
- Evaluates the composition of U-bearing precipitates and relates them to the expected uranium species via solid phase characterization using XRD and SEM/EDS.

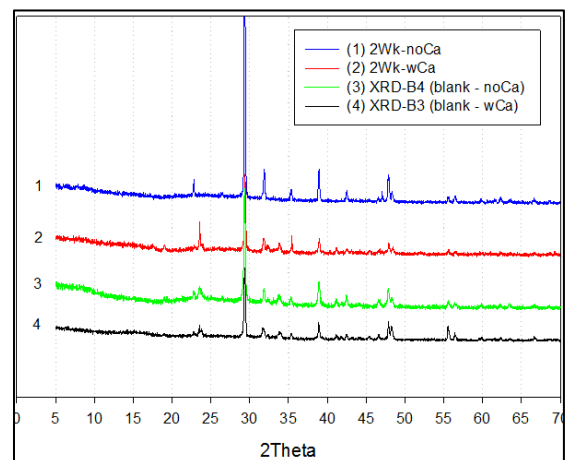


Figure 2. Comparison of the diffraction patterns of sample precipitates prepared with and without calcium and their corresponding U-free blanks.

FIU PROJECT 2 - TASK 1.2 - 2012 FACT SHEET

Investigation on Microbial-Meta-Autunite Interactions - Effect of Bicarbonate and Calcium

FIU's Applied Research Center (ARC) is supporting the U.S. Department of Energy's Hanford Site in developing a strategy to improve the efficiency of the uranium stabilization process through polyphosphate injection technology.

Polyphosphate injected to sequester uranium undergoes hydrolysis in aqueous solutions to orthophosphate forms, which serve as readily available nutrients for the various micro-organisms that thrive under these specific conditions and may even lead to an increase in their growth. The presence of rapidly adapting bacterial populations in sediment could strongly influence the migration/dissolution of uranium by dissolution and desorption due to the secretion of protons and various ligands. Therefore, understanding the role of bacteria in phosphate remediation technology and the interactions between meta-autunite and the microbes is very important. Of particular concern, however, is the long-term stability of the sequestered uranium in the subsurface that may undergo subsequent remobilization. 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 is designed to 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.

Objectives

- Examine the ability of oligotrophic microbial species to influence the dissolution pathways of U (VI) present in the groundwater as stable meta-autunite.
- Investigate the bacteria interactions with uranium using a less U (VI)-tolerant strain and study the potential role of bicarbonate, which is an integral complexing ligand for U (VI) and a major ion in the pore water composition.
- 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.
- Determine the difference between microbial effect on uranium release from synthetic and natural autunite.
- Evaluate for bacterial viability in the presence of bicarbonate ions via a fluorescence microscopy Dead/Live assay.

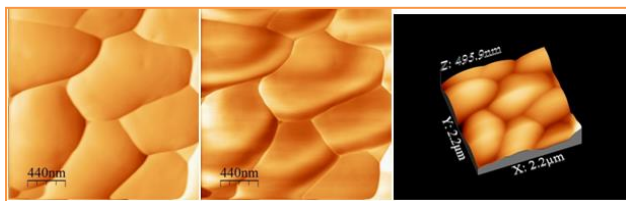


Figure 1. G968 control sample (scan size 2.2 x 2.2 μm^2) illustrating smooth bacterial surface with no uranium and no bicarbonate present. The deflection image on the left, friction image in the middle and 3D topographic image (Z range 440 nm) on the right

Benefits

- Evaluates the role of bacteria in the bio-enhanced release of U(VI) from autunite in the presence of various concentrations of bicarbonate up to 10 mM, even while not in direct contact with the mineral.
- Evaluates the effect of bicarbonate on the bacterial viability in the presence of toxic U^{6+} ions.
- Yields insights on bacterial-U(VI) interactions under oxidizing conditions and the ability of less tolerant-to-U(VI) oligotrophic microbial species, such as *Arthrobacter* G968 to influence the dissolution of natural and synthetic autunite in the presence of bicarbonate.

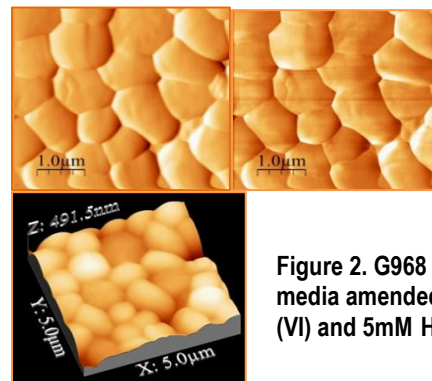


Figure 2. G968 cultured in media amended with 10ppm U (VI) and 5mM HCO_3 .

The deflection image on the left, friction image (V) in the middle and topographic image (Z range 1.0 μm) on the right. These images illustrates lower levels of precipitate due to the presence of bicarbonate.

FIU PROJECT 2 – 2014 FACT SHEET

Rapid Deployment of Engineered Solutions for Environmental Problems at Hanford - FIU's Support for Uranium Remediation at the Hanford Site

FIU's Applied Research Center (ARC) is supporting the U.S. Department of Energy's Hanford Site in developing a strategy to improve the efficiency of uranium stabilization process through polyphosphate injection technology.

Uranium has been recognized as one of the most widespread groundwater contaminants at the U.S. Department of Energy's (DOE) Hanford site, Washington State. In oxidized groundwater conditions that are typically present at the Hanford site, soluble uranyl ion (UO_2^{2+}) creates strong complexes with carbonate and $Ca_2UO_2(CO_3)_3^0$ and $UO_2(CO_3)_2^{2-}$ are the predominant U(VI) aqueous species. The concentration of uranium exceeds the maximum contaminant level for drinking water of 30 $\mu\text{g/L}$ required by EPA. Injections of a soluble sodium tripolyphosphate amendment into the uranium contaminated groundwater and soil have been shown to effectively sequester uranium through the formation of insoluble uranyl phosphate minerals. However, the effect of carbonate complexation on uranyl phosphate dissolution is needed to be evaluated.

Results of this research will be incorporated into the systems-based model of 300A for DOE RL and is being used to support CHPRC in the design of the remediation approach.

Task Objectives

- Quantify the effect of carbonate complexation on autunite minerals and investigate factors such as temperature (5-60°C) and pH (6-11) on the dissolution kinetics.
- Characterize synthetic autunite mineral created by the direct precipitation method by using scanning electron microscopy (SEM), X-ray diffraction (XRD) analyses, and N_2 -adsorption BET method to determine the surface area of autunite solids.
- Conduct dissolution experiments in a single-pass flow-through (SPFT) apparatus using carbonate as a buffer solution.

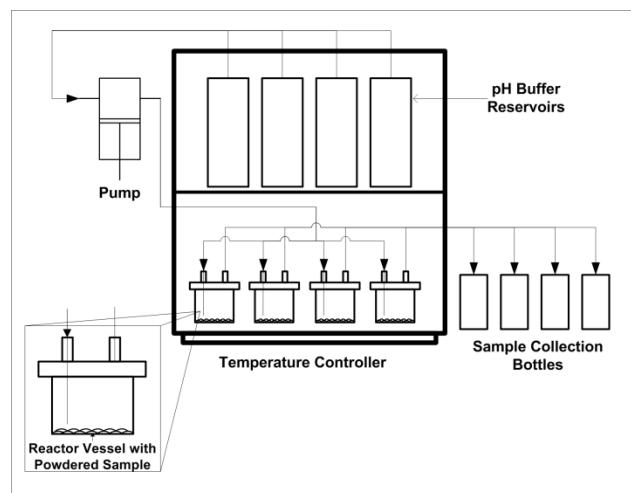


Figure 1 Schematic of single-pass flow-through experiments

Task Benefits

- Understanding the impact of low and high bicarbonate concentration on the release of uranium from autunite to predict long-term fate and transport of uranium.
- Quantifies kinetic rate law parameters of autunite dissolution in the presence of carbonate ligand under strictly controlled conditions.
- Provides critical data need to be able to predict how long sodium autunite will persist in the 300A under the dynamic bicarbonate concentrations that change seasonally as a result of river fluctuations
- Ability to develop an effective solution for immobilization of uranium and predicting its fate and transport in the subsurface.

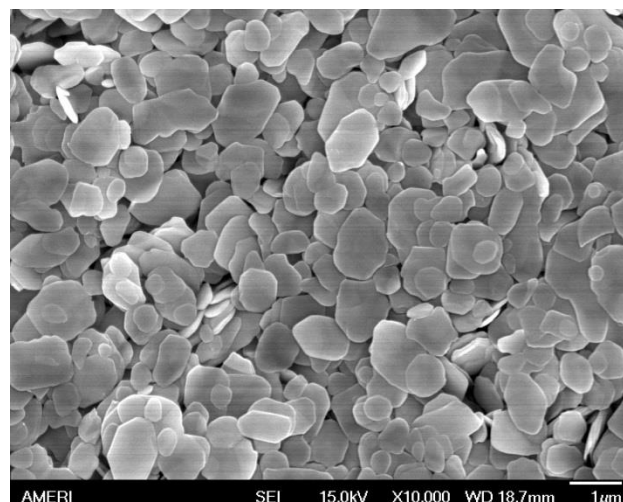


Figure 2 Image of post-reacted Na-autunite minerals

FIU PROJECT 2 - 2014 FACT SHEET

Rapid Deployment of Engineered Solutions to Environmental Problems at Hanford

FIU's Applied Research Center (ARC) is supporting the U.S. Department of Energy's Hanford Site in developing a strategy to improve the efficiency of the uranium stabilization in the subsurface.

The investigation targets uranium (U) contamination in the vadose zone (VZ) of the 200 Area that may affect potential discharges to the Columbia River via groundwater migration. Injection of reactive gases such as NH₃ is an innovative technology that targets U contamination in the VZ to reduce the potential for radionuclides mobility in subsurface. The alkaline conditions can greatly enhance the solubility of most Al- and Si-containing minerals by many orders of magnitude. The following decrease in pH will cause uranium co-precipitation during the crystallization of minerals. Stability of these U precipitates need to be studied to better understand the mobility of U(VI). Microbial activities in many environmental systems are additional layers of complexity that affect U(VI) mobility in the subsurface. In nature, a variety of bacteria may enhance the mobility of heavy metals or radionuclides by dissolution and desorption due to the secretion of protons and various ligands. This project investigates the bacterial effect on U(VI) release from the Calcium autunite mineral to provide understanding of the important microbiological processes affecting autunite stability and uranium mobility within subsurface bicarbonate-bearing environments. Make comparison between strains G975 and G968 on the dissolution of U(VI) from autunite.

Objectives

- Evaluate the stability of U-bearing precipitates created after NH₃ injection to manipulate pH in the vadose zone at the 200 area of the Hanford Site.
- Examine the solubility of uranium bearing solid phases via isopiestic measurements and evaluate the effect of environmental factors such as temperature.
- Examine the mineralogical and morphological characteristics of precipitates before and after solubility experiments via XRD and SEM-EDS.
- Investigate the bacterial interactions with uranium using strain less tolerant to U(VI) and study the potential role of bicarbonate on the interactions.
- Make comparison between strains G975 and G968 on U(VI) release from autunite mineral and inspect bacterial surface after exposure to U(VI) via AFM and investigate cell viability via fluorescent microscope using live/dead stain.

Benefits

- Provides information on the mechanisms and effectiveness of NH₃ injection on the removal of U(VI) and the role of pore water constituents that will help predict the mineralogical changes and formation of precipitates.
- Yields information on the formation and solubility behavior of U(VI)-bearing precipitates under environmentally relevant Hanford Site VZ conditions.
- Evaluates the role of bacteria in the bio-enhanced release of U(VI) from autunite even while not in direct contact with the mineral.
- Determines biosorption parameters of the process that can be used for further modeling purposes to predict the effect of Ca and HCO₃⁻ ions on U(VI) mobility in aerobic bacteria-bearing systems.

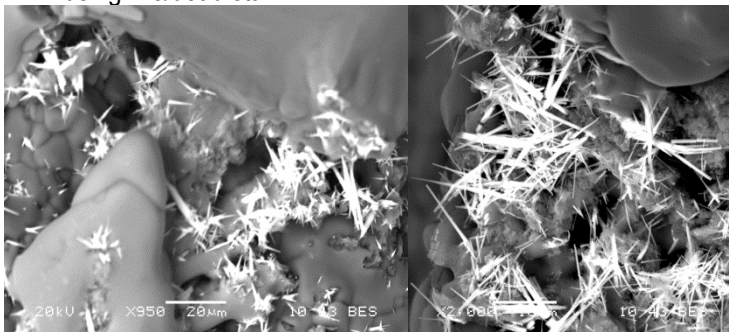


Figure 1. Backscatter SEM images of samples prepared with (L) and without (R) calcium showing the U-rich crystal-like forms

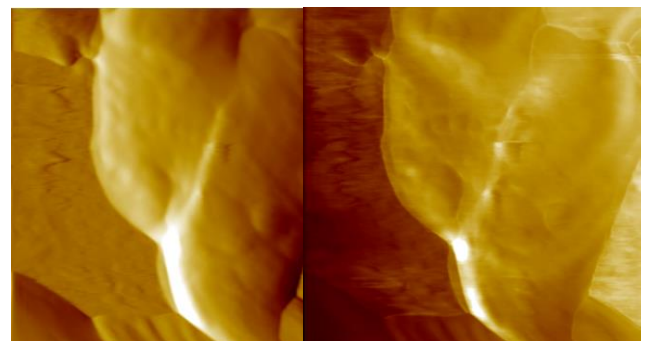


Figure 2. G968 strain exposed to U, Deflection image on the left and friction on the right. Image illustrates two bacterial cells adhered to each other to further examine roughness.

FIU PROJECT 2 - TASK 2 - 2014 FACT SHEET

Rapid Deployment of Engineered Solutions for Environmental Problems at SRS

FIU's Applied Research Center (ARC) is supporting the U.S. Department of Energy's Savannah River Site in remediating uranium in F/H area seepage basins.

The F/H area seepage basins received approximately 1.8 billion gallons of acidic (pH 3.2-5.5) waste solutions contaminated with 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 major constituent of concern is uranium (U). The pump-and-treat treatment system designed and built in 1997 became less effective prompting research for new remediation alternatives. This project investigates the effect of silicate injections to groundwater resulting in a pH increase leading to U(VI) sequestration and evaluates if any synergy between U(VI) and humic acid will influence the behavior of U(VI). ARCADIS technology demonstrated the in situ addition of carbohydrate substrate molasses to create anaerobic reactive zones for metal and radionuclide remediation via the Enhanced Anaerobic Reductive Precipitation (EARP) process. The investigation involves 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 is being evaluated for the treatment of radionuclides and metals (U(VI), Fe, Mg, S, and Si) and the total organic carbon.

Objectives

- Evaluate whether a base solution of dissolved silica can replace the previously used carbonate base and if silica solutions have enough alkalinity to restore the pH of the treatment zone.
- Investigate the hypothesis that some uranium in the current treatment zone is bound to silica and study if any synergy between humic acid (HA) and silica influences the behavior of uranium.
- 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.
- Analyze groundwater and soil samples 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

- Provides information on whether dissolved sodium silicate solutions have enough alkalinity to replace the carbonate base being used to correct the acidic nature of the contaminated sediments.
- Investigates the effect of silica solutions or colloidal Si on the uranium removal and proves the hypothesis that some uranium in the treatment zone is bound to silica.
- Provides insight of synergetic interactions between humic acid and silica that influences the behavior of uranium.
- Microcosm studies determines whether solid phases of reduced iron such as siderite and pyrite would arise in the reducing zone and explain the types of reaction that might occur in the anaerobic aquifer.

