STUDENT SUMMER INTERNSHIP TECHNICAL REPORT

Hydroxyapatite and Uranium Interaction in Moab Groundwater and Sediment

DOE-FIU SCIENCE & TECHNOLOGY
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Principal Investigators:

Olivia Bustillo (DOE Fellow Student)
Florida International University

Kenneth Williams Ph.D. (Mentor)
Lawrence Berkeley National Laboratory

Ravi Gudavalli Ph.D. (Mentor & Program Manager)
Florida International University

Leonel Lagos Ph.D., PMP® (Program Director)
Florida International University

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FIU Applied Research Center
FLORIDA INTERNATIONAL UNIVERSITY

EXECUTIVE SUMMARY

This research work has been supported by the DOE-FIU Science & Technology Workforce Development Initiative, an innovative program developed by the U.S. Department of Energy's Office of Legacy Management (DOE-LM) and Florida International University's Applied Research Center (FIU-ARC). During the summer of 2022, a DOE Fellow intern, Olivia Bustillo, spent 8 weeks doing a summer internship at Legacy Management's Grand Junction, CO office under the supervision and guidance of Ms. Jalena Dayvault and Dr. Kenneth Williams. The intern's project was initiated on July 15th 2022, and continued through August 26th 2022 with the objective of studying the interaction between hydroxyapatite and uranium within the Moab groundwater and sediment. The purpose of these experiments was to measure removal of uranium for a range of calcium, phosphate, and citrate concentrations to determine which recipe would be more effective for removal at the site.

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INTRODUCTION

Between 1956 and 1962, the Uranium Reduction Company operated a mill in Moab, UT that produced uranium concentrate. After Atlas Minerals Corporation (Atlas) bought the mill in 1962, they began selling the uranium concentrate to the U.S. Atomic Energy Commission through December 1970 for use in national defense programs. After this period, the uranium product was mainly used for commercial sales to nuclear power plants. While operating, the mill produced an average of 1,400 tons of ore a day. These productions created process-related wastes and tailings and although more than 90% of uranium was removed during processing, radium and other decay products remained in the tailings. Excess water in the tailings pile drained through underlying soils, resulting in contaminated groundwater. Between 1988 and 1995, decommissioning activities were conducted, processing buildings were demolished and were buried in the tailings pile. The tailings pile was estimated to contain 12 million cubic yards of mill tailings and other contaminated materials. Since DOE is responsible for cleaning up Uranium Mill Tailings Radiation Control Act (UMTRCA) Title I mill sites, DOE acquired ownership of the Moab site in 2001. Under this act, DOE is required to remediate the sites to Environmental Protection Agency (EPA) standards, including soils and groundwater. The groundwater and surface water at the site, that discharges into the Colorado river, is contaminated with ammonia, uranium, and other contaminants which poses a threat to the endangered fish species that inhabit the area. Due to this, the scope of the Moab Uranium Mill Tailings Remedial Action (UMTRA) Project include remediation of the groundwater at the site, focusing on ammonia and uranium. According to the Moab UMTRA Project information site, the interim action system that is currently in place involves extracting contaminated water and injecting freshwater into the system [1]. While this process has been effective at lowering the concentration of contaminants, a more long-term solution must be identified for implementation at the site. Scientists that work closely with the site are currently interested in utilizing a hydroxyapatite permeable reactive barrier for uranium remediation at the site, which was successfully implanted at the Old Rifle, CO site that also had a uranium contamination issue.

During the summer of 2022, DOE Fellow Olivia Bustillo, had an opportunity to participate in developing a plan for her second internship with the Office of Legacy Management through FIU's workforce development program. This plan included a laboratory experiment, designed by her with the support of her summer mentor Dr. Kenneth Williams, along with supplemental activities that would expose Bustillo to the work conducted by LM that relate to her interests, as well as allow her to learn more about how her research at FIU supports the goals within LM. The Fellow was stationed in Grand Junction, Colorado and performed site visits as necessary. In Grand Junction, Bustillo was primarily working in the Environmental Sciences Laboratory (ESL) on a project that relates to the ongoing remediation at the Moab, UT site. The experiments conducted in the ESL support the proof-of-principle hydroxyapatite (HA) study at the Moab, UT site for uranium (U) remediation that will occur later. The purpose of these experiments was to establish if the hydroxyapatite formulation used previously at the Old Rifle, CO site would be suitable for application at Moab, given a different groundwater and sediment chemistry. Also, to determine if the formula can be simplified by utilizing the pre-existing elements within the groundwater and sediment. Finally, evaluate whether pre-stimulating the sediments with organic carbon prior to the introduction of hydroxyapatite has a positive effect on uranium uptake time. To achieve the goal, experiments were conducted to measure the removal of uranium for a range of calcium, phosphate, and citrate concentrations to determine which recipe would be more effective for uranium removal at the site. It is important to note that if there are carbonates and bicarbonates in the system, uranium has a high tendency to interact with these constituents to create mobile species in the groundwater [2, 3, 4].

The data obtained will help fill the knowledge gaps on the mechanisms involved in the removal of U, the stability of the removal and assist DOE-LM in remediating uranium in sites where U is present.

RESEARCH DESCRIPTION

Materials and Method

Groundwater and sediment from the UPD22 injection well at the Moab, UT site were used in this study. It is estimated that the Moab groundwater contains uranium at a level of about 2000 ppb, according to the Moab UMTRA Project 2021 Groundwater Program Report [5]. Five (5) sets of triplicate samples were created to include the following amendments: (1) Original formulation for hydroxyapatite used in Old Rifle, CO proof-of-principle study. (2) Only calcium citrate. (3) Only sodium phosphate. (4) Initially stimulate sediments with organic carbon to establish if this influences uranium uptake. (5) Control set with only Moab sediment and groundwater. The samples can be seen in week one and week five in Figure 1 - Figure 2. From these figures, it can be seen that samples from amendment 1, 2, and 4 transitioned from a clear color to black within the water and within the soil for amendment 1 and 4. Since the Moab groundwater is primarily brackish water, it has a high ionic strength. The organic carbon within amendments 1, 2, and 4, in conjunction with the brackish water, leads to stimulation of iron and sulfur, possibly resulting in an iron sulfide precipitate. The concentrations for the five sets of samples described above are shown in Table 1.

Figure 1. Samples from Scenarios 1 Through 5 Investigated in Week 1 (left to right).

Figure 2. Samples from Scenarios 1 Through 5 Investigated in Week 5 (left to right).

Table 1. Concentrations of Reagents Used for Each Set of Samples.

	Amendment Concentration (mmol/L)				
Chemical (formula)	**1**	**2**	**3**	**4**	**5**
Trisodium citrate dihydrate ($C_6H_5Na_3O_72H_2O$)	100	100	x	x	x
Calcium chloride dihydrate ($CaCl_2H_2O$)	40	40	x	x	x
Disodium phosphate (Na_2HPO_4)	32.4	x	32.4	x	x
Monosodium phosphate (NaH_2PO_4)	5.6	x	5.6	x	x
Diammonium phosphate ($(NH_4)_2HPO4)$)	2	x	2	x	x
Sodium Acetate ($C_2H_3NaO_2$)	x	x	x	30	x

Throughout the duration of these experiments, the pH was measured (Figure 3) and 1 ml aliquots were collected daily and stored in the fridge. Prior to being stored, 200 µl of the aliquots was immediately taken and diluted 50 times with 5% nitric acid, which was then stored in the fridge until analysis. The diluted samples were analyzed on ICP-MS on a weekly basis to obtain calcium, uranium, and iron concentrations.

Figure 3. Measuring pH of Sample 5B.

After analyzing the first set of data from ICP-MS, it was revealed that the uranium concentrations in the third scenario were almost at zero within the first two days. This was unexpected since the water is estimated to have high levels of uranium. To ensure that these results could be replicated, another set of triplicates (scenario 3.1) of this scenario was created.

RESULTS AND ANALYSIS

The results from the data reveal that the original formulation of hydroxyapatite, as well as the phosphate-only amendment, reduce uranium significantly. The calcium citrate amendment appears to increase the uranium levels, which could be due to uranium being released from the sediment. The results also show that sodium acetate amendment did not have much of an effect on uranium concentrations and acts very similar to the control set. Scenario 3.1, which replicates scenario 3, showed the same significant decrease of uranium within the first day as scenario 3. This indicated that these results are consistent and reproducible. These changes in uranium concentrations over the duration of the experiment can be seen in Figure 3. The pH was monitored throughout the experiment (Figure 4) and stays between 8.5 and 6.5 for all the scenarios investigated. The calcium concentrations for scenarios 1 & 2 decreased over a period of time due to the formation of hydroxyapatite (Figure 5). In scenarios 3, 4 and 5 slight (20-100 mg/L) calcium leaching from sediment was observed.

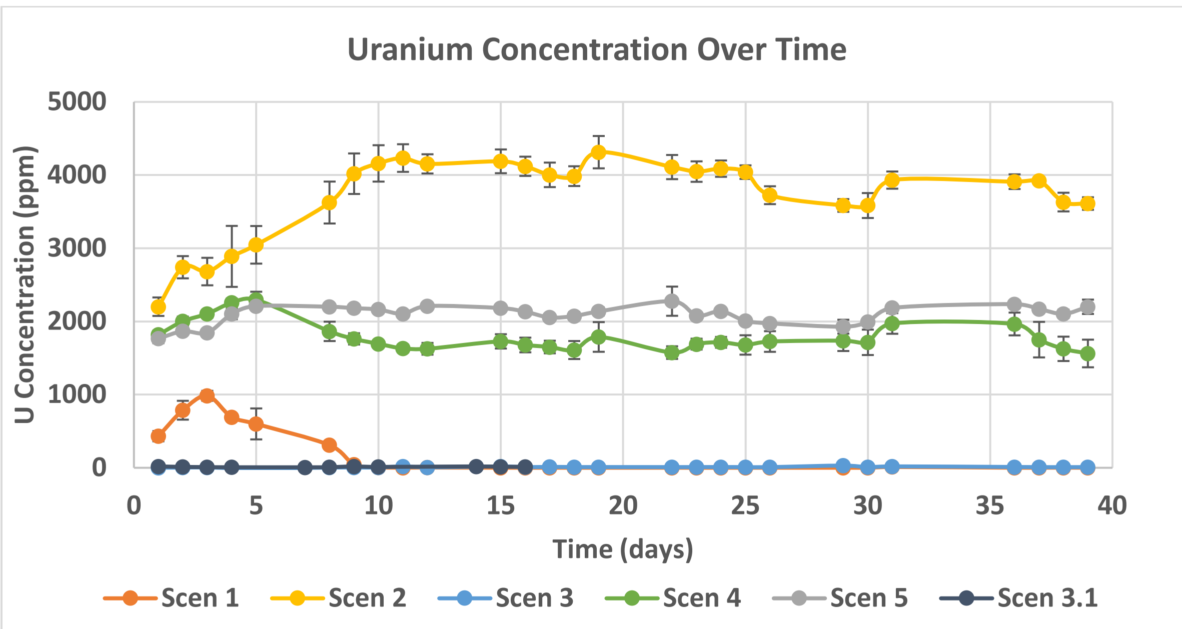

Figure 4. Uranium Concentration Over Time for All Scenarios.

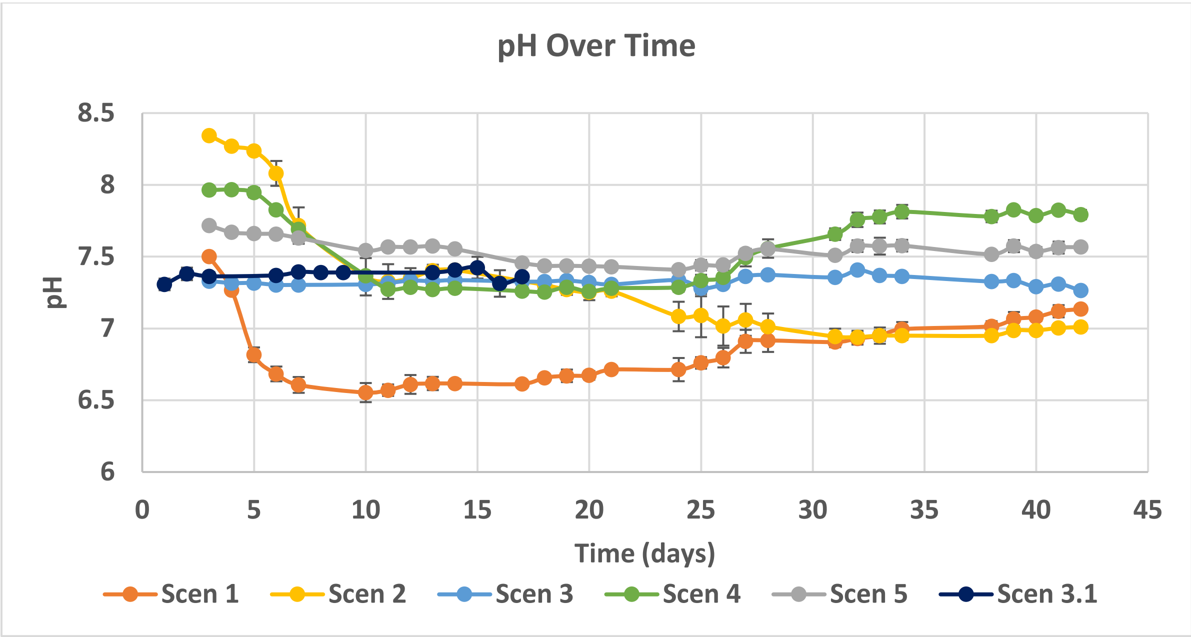

Figure 5. pH Over Time for All Scenarios.

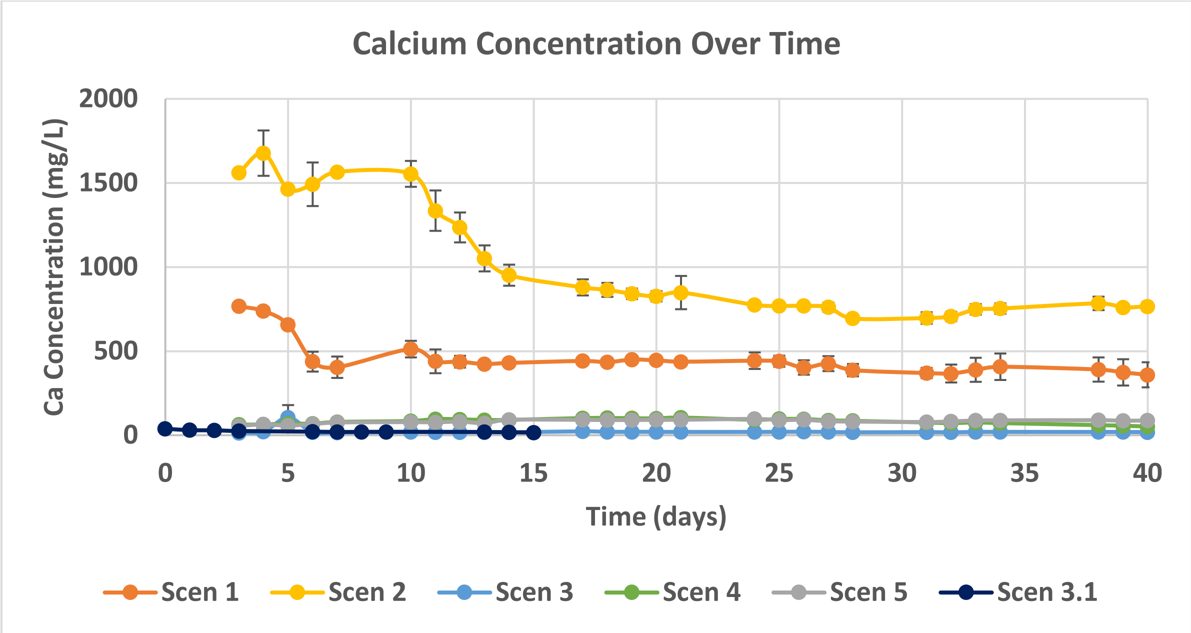

Figure 6. Calcium Concentration Over Time for All Scenarios.

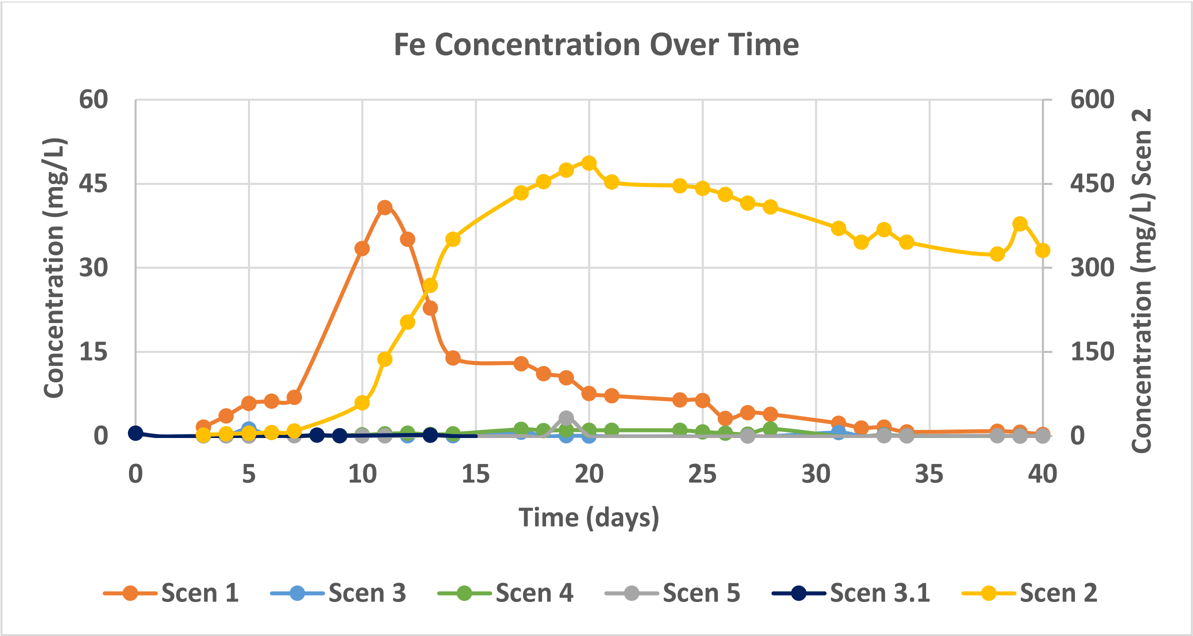

Figure 7. Iron Concentration Over Time for All Scenarios.

CONCLUSION

The experiments conducted this summer studied the effect of the original hydroxyapatite recipe used at the Old Rifle, CO site, along with various alterations of this recipe, on the uranium concentrations in groundwater at the Moab, UT site. Using Moab groundwater and sediment, these experiments provided information on how uranium would behave when introduced to the varying amendments. These experiments revealed that two of the amendments, the original formulation and the phosphate-only recipe, would significantly reduce uranium within the first week. The phosphate-only recipe shown to reduce the uranium concentration from about 2000 ppb to about 2 ppb within a few hours from initial mixing. To ensure that these results were reproducible, another set of phosphate-only samples were prepared. These samples produced the same dramatic decrease in uranium concentrations on day one. This indicates that there is sufficient calcium within the Moab groundwater and sediment to form hydroxyapatite, without needing to inject the calcium-citrate amendment into the subsurface. While the original formulation also showed a promising decrease in uranium levels, it took more time to see this reduction. This could be due to the inclusion of calcium-citrate in the amendment, interfering with the rapid formation of hydroxyapatite since microorganisms in the solution require time to consume the citrate in order to allow the calcium to freely interact with phosphate. It should be noted that the calcium-citrate amendment resulted in an increase in uranium concentrations, which could be attributed to uranium leaching from the sediment. This also indicates that there is not sufficient phosphate in the Moab groundwater and sediment to form hydroxyapatite. The sodium acetate amendment had no significant effect on the uranium concentration, and closely followed the trends of the control samples. The control samples fluctuated minimally throughout the duration of the experiment. From these results, the use of the phosphate-only amendment is recommended for use at the Moab site to reduce uranium concentrations since it produced rapid, considerable results with half of the supplies required for an injection at the site.

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APPENDIX

During the summer, DOE Fellow was involved in several activities outside of the experimental work, including participating in the DOE-LM All-Hands training in St. Louis, Missouri, the International Atomic Energy Association (IAEA) Coordination Group for Uranium Legacy Sites (CGULS) workshop in Grand Junction, CO, a tracer test at the Moab site, and participating in a disposal cell inspection in Rifle, CO. Along with this, she was able to participate in several internal meetings within LM to gain insight on the work that is required to meet their goals that are in line with LM's mission. Additionally, she collected groundwater from the UPD22 injection well from the Moab, UT site that was used in her experiments. The All-Hands training was a week-long event consisting of various leadership trainings, a tour of the Weldon Spring, MO site, and a variety of team building exercises. Throughout this meeting, Ms. Bustillo was able to gain a wealth of information that she can apply to her own career and future leadership positions. During this meeting, she had the opportunity to meet and learn about the roles that each team within LM holds, and how they all collaborate in order to successfully execute their mission. She was also able to participate in the tracer test that was conducted at the Moab, UT site, which was a precursor to the hydroxyapatite injection that will occur later this year. During the tracer test, she was able to review the data from her summer experiments with her internship mentor, Dr. Kenneth Williams. Along with this, Ms. Bustillo took part in the IAEA meeting in Grand Junction. During this meeting, government representatives from Uzbekistan, Kyrgyzstan, and Tajikistan came to the Grand Junction, CO office, as well as DOE staff from across the country, to share information about long-term stewardship. This meeting was a great opportunity for Ms. Bustillo to continue learning about the importance of long-term stewardship and the collaboration required across different entities to accomplish their related goals.