YEAR-END TECHNICAL REPORT
September 29, 2021 to September 28, 2022

Long-Term Stewardship of Environmental Remedies: Contaminated Soils and Water and STEM Workforce Development

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FIU | Applied Research Center
FLORIDA INTERNATIONAL UNIVERSITY

Addendum:

This document represents one (1) of five (5) reports that comprise the Year End Reports for the period of September 29, 2021 to September 28, 2022 prepared by the Applied Research Center at Florida International University for the U.S. Department of Energy Office of Environmental Management (DOE-EM) under Cooperative Agreement No. DE-EM0005213.

The complete set of FIU's Year End Reports for this reporting period includes the following documents:

Project 1: Chemical Process Alternatives for Radioactive Waste
Document number: FIU-ARC-2021-800012997-04b-006

Project 2: Environmental Remediation Science and Technology
Document number: FIU-ARC-2021-800013918-04b-004

Project 3: Waste and D&D Engineering and Technology Development
Document number: FIU-ARC-2021-800013919-04b-005

Project 4: DOE-FIU Science & Technology Workforce Development Initiative
Document number: FIU-ARC-2021-800013920-04b-017

Project 5: Long-Term Stewardship of Environmental Remedies: Contaminated Soils and Water and STEM Workforce Development
Document number: FIU-ARC-2021-800013922-04b-004

Each document will be submitted to OSTI separately under the respective project title and document number as shown above. In addition, the documents are available at the DOE Research website for the Cooperative Agreement between the U.S. Department of Energy Office of Environmental Management and the Applied Research Center at Florida International University: https://doeresearch.fiu.edu

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PROJECT 5 EXECUTIVE SUMMARY

The Department of Energy (DOE) established Legacy Management (LM) in December of 2003, to manage its responsibilities associated with the legacy of the Cold War. DOE has taken major steps in satisfying environmental cleanup and LM ensures post-closure responsibilities are met for the protection of human health and the environment. LM coordinates closely with other Government organizations, including those within DOE, to ensure post-closure obligations are maintained when mission-related sites are closed and transferred to LM for long-term management. LM conducts post-closure site operations at approximately 98 sites in the United States and the territory of Puerto Rico and anticipates increasing to 128 sites by 2030. LM sites are generally described by the regulatory program and the types of environmental residual contamination remaining at the sites after remediation. Recognizing that LM sites are driven by their unique requirements such as operation and maintenance of remedial action systems, routine inspection and maintenance, and records related activities, Florida International University's Applied Research Center envisions developing a unique program to address LM's goals and preparing and securing the next generation workforce that will be required to accomplish these goals.

Florida International University (FIU), the largest Hispanic serving research-extensive institution in the continental United States, is one of the nation's leading producers of scientists and engineers from underrepresented groups. In 1995, DOE created a unique partnership with FIU to support environmental cleanup technology development, testing and deployment at DOE sites. This partnership spawned a research center at FIU dedicated to environmental research and development (R&D). The center, now known as the Applied Research Center, has tackled and helped solve problems at many DOE sites.

Since 1995, the Applied Research Center (ARC) at Florida International University (FIU) has provided critical support to the Department of Energy's Office of Environmental Management (DOE-EM) mission of accelerated risk reduction and cleanup of the environmental legacy of the nation's nuclear weapons program. ARC's applied research is performed under the DOE-FIU Cooperative Agreement. ARC's applied research, technology development; test & evaluation; and STEM workforce development covers four major areas of environmental cleanup operations: radioactive waste processing, facility decontamination and decommissioning, soil & groundwater remediation and modeling, and information technology (IT) development for environmental management. As discussed, and agreed among DOE EM and LM, FIU infrastructure and expertise developed under the Cooperative Agreement will be leveraged to initiate the pilot program for LM. To this end, the research & student training will be structured closely following the DOE Fellows program model.

To date, the DOE LM Fellows Program has inducted a total of four (4) minority FIU STEM students and engaged them in research topics investigating the use of apatite for uranium sequestration at the Old Rifle site, and the application of remote sensing technologies at LM sites.

The following DOE LM Fellows are supporting two research tasks developed under this project:

Task 1: Olivia Bustillo (graduate, M.S., environmental engineering)

Task 2: Shawn Cameron (graduate, M.S., mechanical engineering)

The following ARC researchers are supporting this project and mentoring the DOE-LM Fellows: Ravi Gudavalli (Ph.D., Env. Engineering, Mentor/Project Manager), Anthony Abrahao (M.S., Mechanical Engineering, Task 5.2, Mentor), Pieter Hazenberg (Ph.D., Hydrology and Quantitative Water Management, Task 5.2, Sr. Research Scientist), Leonel Lagos (Ph.D., PMP®, Mechanical Eng./Civil/Env. Engineering, PI, DOE Fellows Program Director), and Angelique Lawrence (M.S., Environmental Science, Technical support).

MAJOR ACCOMPLISHMENTS

Major accomplishments of this program to date include:

For Task 1:

- DOE Fellow Olivia Bustillo calculated atomic ratios of synthesized hydroxyapatite samples from EDS data and compared that with theoretic atomic ratios for confirmation, concluding Phase 1 of Task 1.
- FIU completed the experiments involving the incorporation and co-precipitation of uranium during the formation of apatite.
- FIU completed characterization of hydroxyapatite samples via energy-dispersive X-ray spectroscopy (EDS). Due to impurities present in the tape used to secure the samples, the analysis was repeated with a new tape and the mass percentage of elements present in the precipitate was obtained.
- FIU conducted scanning electron microscopy (SEM), X-Ray Diffraction (XRD) analysis of hydroxyapatite precipitates and noticed that the morphology for Scenario C is different from other scenarios.
- FIU completed the uranium incorporation and co-precipitation studies (Phase 2). A draft report was written and submitted as deliverable 2021-P5-D4, Draft Report on uranium incorporation and co-precipitation studies, on June 24, 2022.
- FIU completed step one of the Phase 3 experiment, which intends to imitate the application of hydroxyapatite technology once the hydroxyapatite has fully precipitated in the treatment zone and is interacting with the contaminated groundwater.

For Task 2:

- FIU conducted a literature review of various geophysical survey methods with the potential to map the subsurface in LM's disposal cells and drafted a summary report on the state-of-the-art geophysical sensors and their potential applications to LM disposal cells.
- FIU studied the application of void detection of concrete slabs and plans to incorporate this methodology for LM’s disposal cell sites.
- DOE Fellow Shawn Cameron drafted a study plan detailing the approach for Task 2.
- FIU processed historic weather data, temperature and precipitation for Rifle, CO and extended future data using representative concentration pathways (rcp) 4.5 and 8.5.
- FIU conducted a literature review of ground penetrating radar (GPR) technology and its capabilities and selected Noggin 250 GPR from Sensors and Software Incorporated for imaging and detecting subsurface erosions at the LM's Rifle disposal cell.
- FIU used the historical climate database from the Analysis of Record Calibration (AORC) to graph temperature and precipitation in a time-series format.
- DOE Fellow Shawn Cameron conducted a literature review to understand the Gazebo software to develop a path plan for the inspection platform for Rifle Site. He, along with

his mentors Mr. Anthony Abrahao and Dr. Pieter Hazenberg, visited Rifle Site on August 11, 2022, and Mexican Hat site on August 23, 2022, and participated in site visits.

For Task 3:

- Four (4) FIU students were competitively selected to become part of the STEM minority students selected for this program and officially inducted during the annual DOE Fellows Induction Ceremony hosted at FIU in November 2019, virtually in November 2020 and in November 2021.
- DOE Fellows finalized reports based on their internships conducted during summer 2021.
- Two DOE-LM Fellows participated in the undergraduate poster session (Eduardo Rojas) and the graduate poster session (Olivia Bustillo) of the annual DOE Fellows poster exhibition and competition and won 2nd and 3rd place respectively.
- FIU formally inducted Eduardo Rojas (Class of 2020) and Shawn Cameron (Class of 2021) into the DOE Fellows program.
- DOE Fellow Olivia Bustillo was awarded the DOE Fellow of the Year award (2021).
- DOE Fellow Olivia Bustillo attended the 2022 Waste Management Symposia held in Phoenix, Arizona from March 6-10 and presented her research in the form of an oral and poster presentation.
- Ms. Bustillo also had an opportunity to participate in the panel, *"Graduating Students and New Engineers - Wants and Needs - Are Companies Even Listening?"*, where she discussed the shift in the workplace culture due to Gen Z becoming the majority within the workforce.
- Ms. Bustillo and Drs. Lagos and Gudavalli also had an opportunity to meet with LM Director (Mr. Carmelo Melendez) and Technical Director for Long Term Stewardship (Dr. David Shafer).
- DOE Fellow Olivia Bustillo participated in an 8-week summer internship (2022) at Grand Junction, CO under the mentorship of Dr. Kenneth Williams and Ms. Jalena Dayvault.
- DOE Fellow Olivia Bustillo attended the DOE-LM All Hands meeting in St. Louis, Missouri and participated 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.
- Ms. Bustillo participated in the IAEA (International Atomic Energy Agency) meeting at Grand Junction. This meeting was attended by government representatives from Uzbekistan, Kyrgyzstan, and Tajikistan as well as DOE staff from across the country.
- DOE Fellows Oliva Bustillo and Shawn Cameron presented their 2022 summer research accomplishments to LM Senior management and staff.
- The DOE LM Fellows also participated in the Annual FIU Research Review held on 9/27/22 - 9/28/22 with DOE-HQ and site POCs and presented their research accomplishments.

TASK 1: USE OF APATITE FOR URANIUM SEQUESTRATION AT OLD RIFLE SITE

Task 1: Introduction

The Department of Energy Office of Legacy Management (DOE-LM) is charged with managing former DOE defense sites that have undergone cleanup but still have continuing post-closure management requirements. Although the goal of LM is to transition facilities/lands of these sites to beneficial use, site-specific factors often limit release for unrestricted use. These factors include: groundwater that is still being treated or which could not be effectively treated to regulatory standards, contaminants in the unsaturated zone that are inaccessible, and the presence of on-site disposal cells and landfills. The Old Rifle Site, CO is a former operating mill, which once processed uranium (U) ore from 1942 to 1958. The site was obtained by the State of Colorado in 1988, after which ownership was transferred to the City of Rifle in 2000. The site is currently being reused by housing an operations and maintenance facility, as well as conducting biogeochemical research on constituents of concern. Surface remediation of the site began in early 1992 and was completed in October 1996. Although the facility has since been demolished and the uranium mill tailings moved to a disposal cell, the alluvial aquifer below remains contaminated with uranium, vanadium, and selenium. This contamination occurred via seepage from the previous mill tailing piles and the raffinate pond at the site. It was predicted that the uranium remaining in the subsurface under the capped waste piles would be flushed by natural groundwater flow. However, the uranium has persisted at elevated concentrations in groundwater, much longer than predicted. This has been determined by analyzing groundwater samples twice a year, from 1998 to 2015. Uranium as a contaminant poses severe potential health hazards to humans and the environment. When unmonitored in the environment, uranium has the potential to affect the quality of surface water, groundwater, and food supplies. This is a toxic chemical that can lead to acute health effects such as kidney damage and various forms of cancer.

Several studies have proven that injection of apatite into groundwater is able to sequester uranium. Apatite, or hydroxyapatite (HA), has been used as a means to sequester uranium in areas where contaminant levels exceed the amount permitted, such as the maximum contaminant level (MCL). Apatite is a versatile tool regarding the immobilization of uranium, as it can potentially be used both ex-situ (as a sorbent for pump and treat systems) and in-situ (as a permeable reactive barrier or source area treatment). The DOE's Old Rifle Site in Colorado, which was once a uranium mill processing facility that operated throughout the late 1970's, has implemented a hydroxyapatite permeable reactive barrier (PRB) to remediate uranium. Although the facility has since been demolished and the uranium mill tailings have been moved to a disposal cell, the site is still contaminated with low levels of uranium. Using apatite to remediate uranium has proved effective at this site as well as the Hanford, WA site (Rigali et al. 2018). DOE-LM has implemented an in-situ HA PRB to remediate uranium at the Old Rifle site in Colorado (Szecsody et al. 2016). While this process has proven to be effective, a better understanding of the uranium removal mechanisms behind the interaction is required. Since uranium has a high tendency to create highly mobile uranium-carbonate species due to the interaction with carbonates and bicarbonates, it is important to understand the stability of uranium sequestration via hydroxyapatite (Gudavalli et al. 2018) (Gudavalli et al. 2013a, b).

FIU, in collaboration with DOE-LM, is investigating the use of apatite injection for sequestering uranium in groundwater. Specifically, FIU will study the mechanism of U removal from groundwater using apatite as well as the environmental factors that influence the stability of U removal. Part of this investigation includes characterizing the Old Rifle Site soil. The data obtained in this study will help fill the knowledge gaps with respect to the mechanisms involved in the removal of U and the stability of U removal and assist DOE-LM in remediating uranium at other sites where uranium is present in groundwater.

Task 1: Objectives

The purpose of this study is to identify the mechanisms of uranium removal by apatite and the stability of uranium removal under various environmental conditions (such as temperature, ORP, etc.). The specific objectives of this research include the following:

- Determine the mechanism of uranium removal from groundwater by apatite.
- Study the environmental factors that influence the stability of U removal over time.

A three-phase approach has been designed to identify the mechanisms of uranium removal. The first phase focuses on studying the synthesis, formation kinetics, and characterization of apatite by mixing calcium (Ca), citrate ($C_6H_8O_7$) and phosphate (PO_4^-) solutions. Phases two and three studies the interaction of uranium with apatite during and after formation of apatite. The mechanisms behind the interaction of uranium and apatite could include adsorption/sequestration of uranium onto apatite, precipitation of U-phosphate surface phases, phosphate precipitates coating uranium surface phases, or surface complexation. This year, the research completed phase one characterization and then focused on the second and third phase of the experiment, including the incorporation and co-precipitation of uranium onto hydroxyapatite as well as the sorption and desorption of uranium from hydroxyapatite. Hydroxyapatite takes approximately 3.5 - 5.3 weeks to fully form so the samples were allotted 6 weeks to reach equilibrium in all experiments. (Szecsody et al. 2017).

Phase two, the incorporation and co-precipitation experiment, will imitate the real-life conditions when applying this technology as a permeable reactive barrier. It studies the interaction of hydroxyapatite and uranium when aqueous HA is first injected and is in the process of precipitating. The purpose of this experiment is to study the incorporation and co-precipitation of uranium during the formation of HA.

Phase three focuses on studying the sorption and desorption of hydroxyapatite onto uranium. This step intends to imitate the application of this technology once the hydroxyapatite has fully precipitated in the treatment zone and is interacting with the contaminated groundwater.

Task 1: Methodology

Materials

This study utilized a mix of solutions containing sodium citrate, calcium chloride, phosphate, and uranium as appropriate. The phosphate solutions used in the experiment included tri-sodium phosphate, ammonium dihydrogen phosphate, disodium phosphate, and monosodium phosphate, based on previous studies (Szecsody et al. 2016). Figure 1 displays the composition ratios used throughout the experiments described in this report.

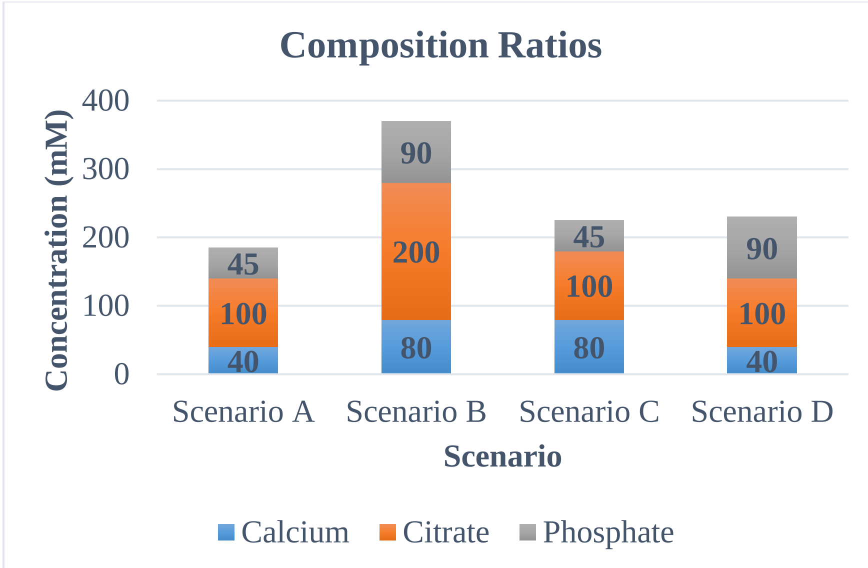

Figure 1. Composition of calcium, citrate and phosphate ratios.

Synthesis of Hydroxyapatite

Synthesis of hydroxyapatite consisted of creating stock solutions of calcium, phosphate, and citrate. Different Ca:Citrate:P ratio samples were created as seen in Figure 1, to determine the optimum ratio for maximum yield of hydroxyapatite. The samples were monitored for 6 weeks before being prepared for analysis. Throughout the 6 weeks, the pH was measured regularly and 200µL aliquots were collected at regular intervals. Aliquots were centrifuged at 2700 RPM for 30 minutes and supernatant was extracted to be analyzed via Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES) to measure aqueous concentrations of Ca and P. The precipitate that formed at the end of the six weeks can be seen in Figure 2. At the end of 6 weeks, remaining supernatant was removed and solid samples were washed three times with deionized water to remove impurities. Washing was achieved by mixing the precipitate with deionized water, followed by centrifuging, removing the supernatant and replacing it with fresh deionized water. Once washing was complete, the precipitate was placed in an oven at 30°C until dry. Dried solids were stored in small scintillation vials and solids were characterized via Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy (SEM-EDS) and X-ray Powder Diffraction (XRD) to confirm the elemental composition as hydroxyapatite. In between running the samples, they were stored in a desiccator for preservation.

Incorporation and Co-Precipitation studies

The incorporation and co-precipitation experiments consisted of creating stock solutions of calcium citrate, phosphate, and uranium. Similar to previous experiments, different Ca:Citrate:PO_4 ratios (Figure 1) were created in 40 mL triplicates to study the influence of varying stoichiometric ratios on the interaction investigated here. Specifically, Scenarios A, C, and D were used for this study. Scenario B was not included since it has the same stoichiometric ratio as Scenario A. The uranium concentration was kept constant at 250 ppb throughout all samples, based on background concentrations at the Old Rifle, CO site. The samples were monitored for 6 weeks before being prepared for analysis. Throughout the 6 weeks, the pH was measured regularly and 200 µL aliquots were collected at regular intervals. Aliquots were immediately diluted with 800 µL of 2% nitric acid to preserve the samples prior to analysis. To prepare the aliquots for analysis, they were centrifuged at 2700 RPM for 30 minutes and the supernatant was extracted to be analyzed via Inductively Coupled Plasma - Optical Emission Spectroscopy and Mass Spectroscopy (ICP-OES/MS) to measure aqueous concentrations of Ca, P, and U. The precipitate that formed at the beginning and end of the 6 weeks can be seen in Figure 3 - Figure 4. At the end of the 6 weeks, remaining supernatant was removed and solid samples were placed in an oven at 30°C until drying was complete (Figure 5). Once dry, the precipitate was analyzed via XRD and SEM-EDS for characterization. Dried solids were then stored in a desiccator for preservation.

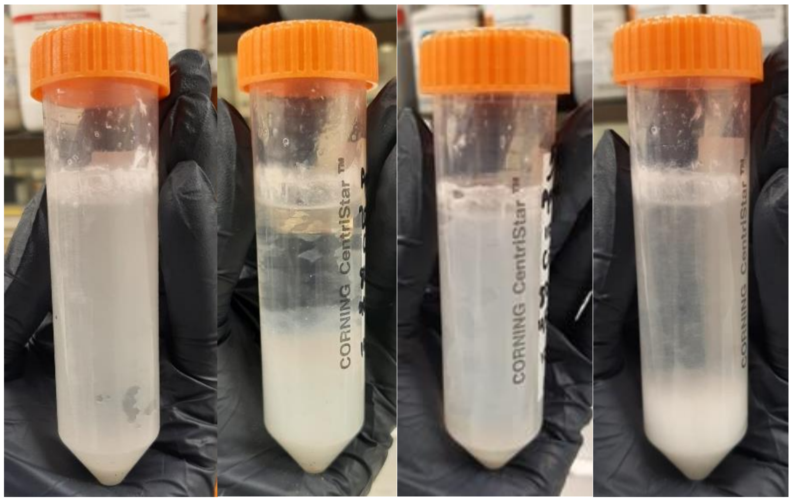

Figure 2. Precipitate formed in week 6 for Scenarios A, B, C, and D (left to right).

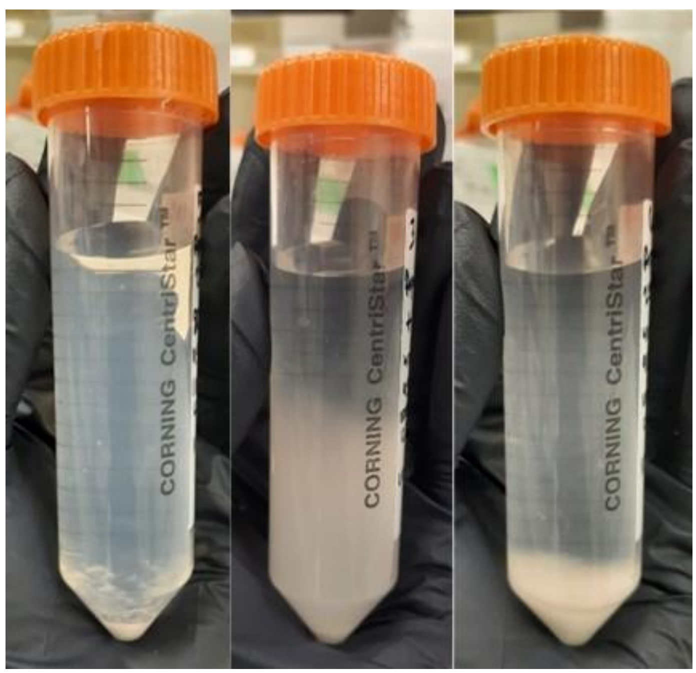

Figure 3. Amorphous precipitate formed in week 1 for Scenarios A, C, and D (left to right) with uranium.

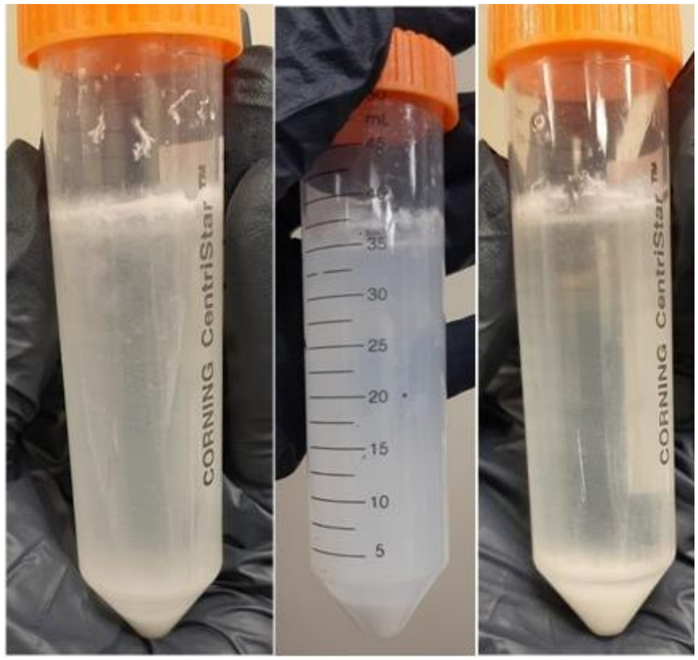

Figure 4. Crystalline precipitate formed in week 5 for Scenarios A, C, and D (left to right) with uranium.

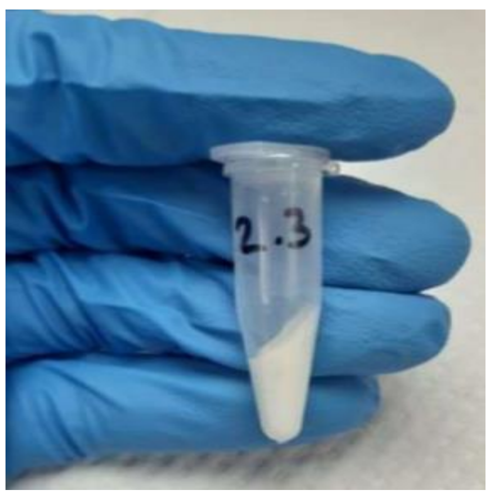

Figure 5. Dried HA precipitate formed during synthesis.

Sorption and Desorption Studies

Samples that were prepared for this experiment followed a similar procedure to the incorporation and co-precipitation studies, except the hydroxyapatite was initially synthesized without U. Calcium and phosphate solutions were combined in triplicates at the same varying stoichiometric ratios as used in the incorporation and co-precipitation studies, with a constant citrate concentration of 100 mM. The pHs of these samples were monitored, and aliquots were collected until the samples had been given sufficient time to equilibrate, i.e., 6 weeks. The aliquots collected will be analyzed on an ICP-OES to obtain the total calcium and phosphorus concentrations throughout the duration of the 6 weeks. The solids will then be prepared for characterization by XRD and SEM-EDS and compared to the results obtained from previous experiments. Once the samples have reached equilibrium, an equal amount of dry apatite from each scenario will be measured and brought into contact with 250 ppb of U, then additional time will be given until equilibrium is reached once again. This point will be determined by collecting aliquots and analyzing them on an ICP-MS to establish the uranium concentrations over time.

XRD analysis

A Bruker D2 PHASER XRD instrument (Figure 6) was used for characterization of the hydroxyapatite solids that formed throughout these experiments. Samples were individually packed flat on to a sample holder (Figure 7) and analyzed via XRD from a 2θ value of 5-90˚ with a 0.05° step size. Observed X-ray diffraction patterns were matched to the International Centre for Diffraction Data's power diffraction file database (PDF) with the pattern matching software DIFFRAC.EVA.V5.1 for analysis.

Figure 6. Bruker D2 PHASER XRD instrument.

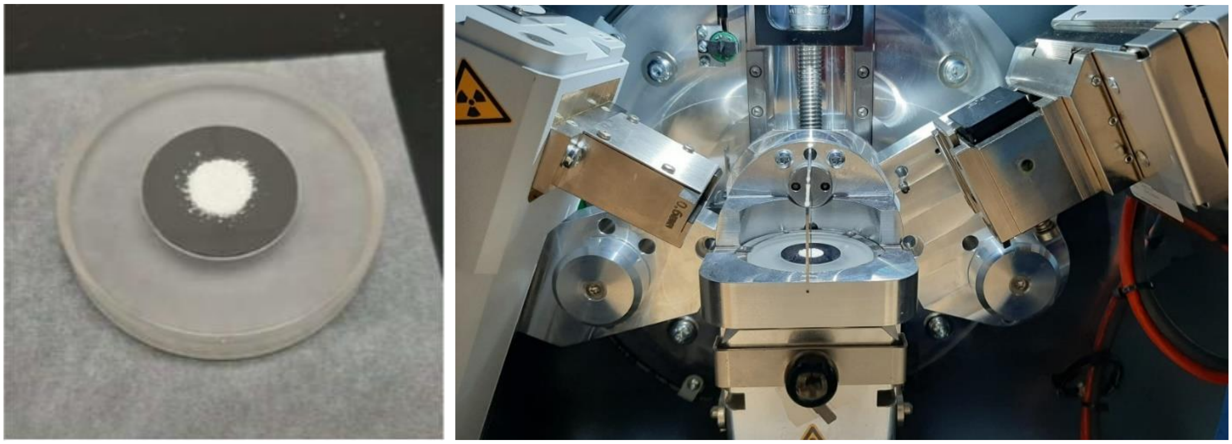

Figure 7. Hydroxyapatite powder on sample holder preprared for XRD analysis.

SEM-EDS analysis

Prior to being loaded into the instrument, the respective samples were mounted on metal studs layered with carbon tape and loaded into a six-stub holder to ensure that the samples were secured properly (Figure 8). The surface characterization was accomplished using a JEOL IT500HR Field

Emission Microscope equipped with the Bruker XFlash 6160 energy dispersive x-ray spectroscope with a 60 mm window SDD detector. EDS analysis was conducted at a 15 kV accelerating voltage with a 10 mm working distance to properly observe the surface characteristics. When conducting EDS analysis, at least three points from each sample were selected to detect the presence of elements. Due to the use of the carbon tape, carbon was deconvoluted when interpreting the data obtained from the EDS analysis. SEM analysis was initially conducted on raw hydroxyapatite samples, but was later sputter coated with gold using an SPI Module Sputter Coater and Vacuum Base with Pump 110v to obtain sharper, clearer images (Figure 9).

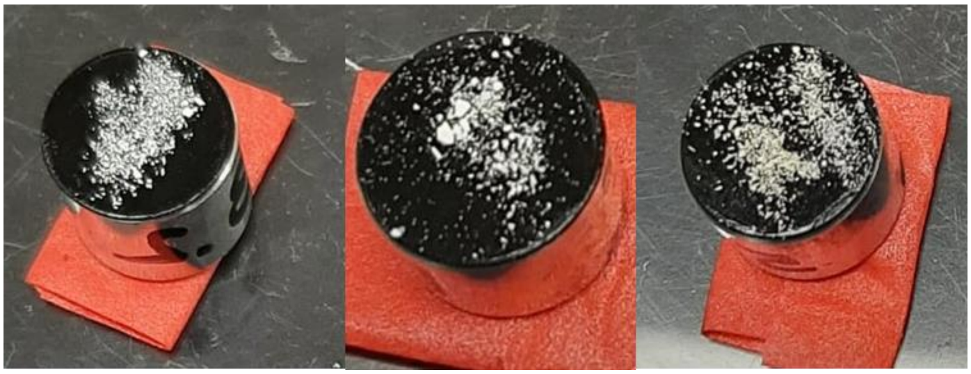

Figure 8. Dried HA precipitate prepared for SEM analysis.

Figure 9. Instrument used to gold coat samples.

ICP-OES/MS analysis

Aqueous samples were analyzed via iCAP RQ Quadrupole (Thermo Fisher) inductively coupled plasma - mass spectrometry (ICP-MS) and Optima 7300 DV (Perkin Elmer) inductively coupled plasma - optical emission spectrometry (ICP-OES) on a weekly basis to measure aqueous concentrations of Ca, P, and U over time. Prior to analysis, the aliquots were further diluted to ensure the concentrations of Ca, P, and U would be within the range of the calibration curve. The ranges included 0.5 - 20 ppm for P, 0.5 - 20 ppm for Ca, and 0.1 - 100 ppb for U. Before analyzing the samples, the standards were run through the instrument to create the calibration curve. The dilution factors for each scenario varied between 200 - 400 times depending on the sample. Diluted samples were placed in the sample racks for analysis. Once the raw data was obtained from the instrument, these values were multiplied by the respective dilution factor to acquire the actual concentration of Ca, P, or U from each sample.

Task 1: Results and Discussions

Hydroxyapatite Synthesis and Characterization Studies:

Hydroxyapatite was synthesized at varying stoichiometric ratios to investigate the effect of elemental composition on apatite formation. 200 µL aliquots collected at regular intervals during the six-week synthesis of hydroxyapatite were analyzed via ICP-OES on a weekly basis to determine change in total Ca and P over time to establish apatite formation kinetics. Aliquots were immediately diluted with 800 µL of 2% HNO_3 prior to analysis. Based on the initial concentrations used to synthesize apatite, dilution factors were chosen to reduce the amount of Ca and P in the samples to values that were within range of the calibration curve previously created. The range of the calibration includes 0.5-10 ppm for Ca and 0.5-20 ppm for P. As time passed, it was assumed that these concentrations would decrease as precipitation occurred and HA began forming. These dilution factors were adjusted on a weekly basis for each scenario, if required, based on the previous weeks' analysis as seen in Table 1. The data acquired has been processed to show the change in concentrations of total Ca and P over time, as seen in Figure 10 - Figure 11. The concentration of Ca rapidly decreased within the first three days and then stabilized, indicating the reaction was initiated within that period. Change in phosphorus concentrations was similar to the Ca trend observed, decreasing rapidly within the first three days followed by stabilization.

Table 1: Dilution Factors Used During Analysis for Each Scenario

	Week 1	Week 2	Week 3	Week 4
Scen A	400	300	300	200
Scen B	400	400	300	300
Scen C	400	400	400	400
Scen D	400	300	300	200

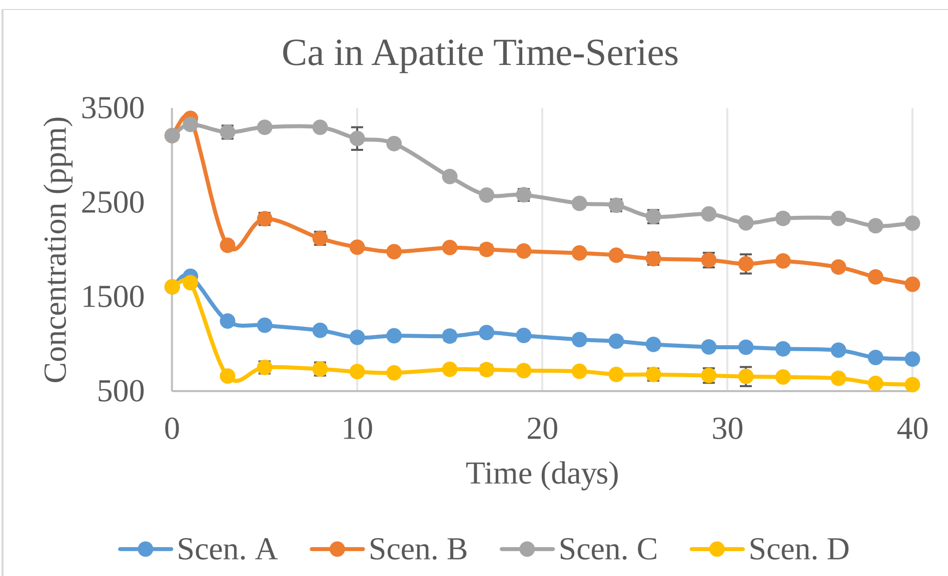

Figure 10. Change in calcium concentration during apatite formation.

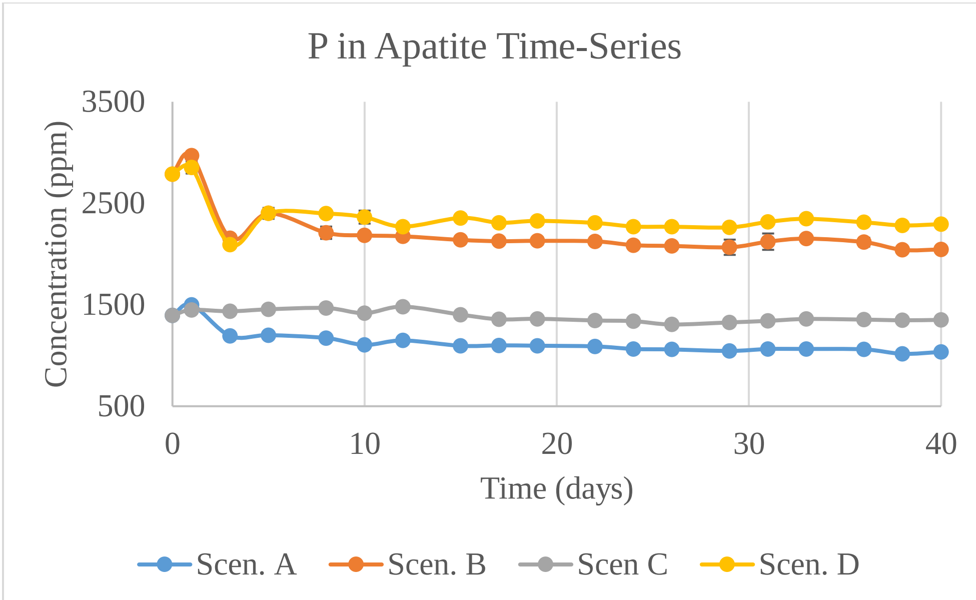

Figure 11. Change in phosphorus concentrations during apatite formation.

Elemental analysis was conducted to characterize the dry precipitate at the end of the experiment. EDS analysis of the washed solid precipitate identified all elements present and the mass percentage of each, as seen in Table 2. The prominent elements identified via EDS included oxygen, calcium, and phosphorus with trace amounts of sodium found, as shown in Figure 12. Sodium (Na) is present since Na was included in three of the salts used to synthesize HA. Using the mass percentage, the atomic ratio was calculated for each scenario and compared to the theoretical estimated value. The calculations that were performed to obtain the atomic ratio values are displayed under Table 2, which demonstrates an example computation. An example calculation for scenario D can be seen in Table 3. The calculated atomic ratio for each scenario was comparable to the theoretical value, verifying that the precipitate formed was hydroxyapatite in all scenarios, as shown in Table 4 below.

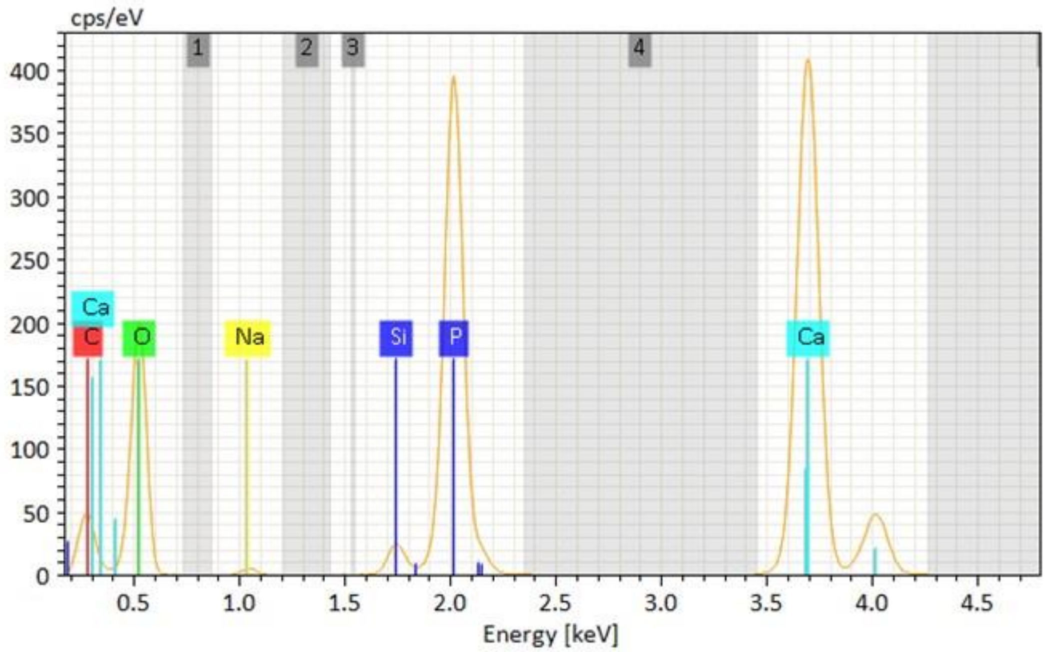

Figure 12. EDS spectrum for Scenario D, representative of all scenarios.

Table 2. Average Mass Composition (%) from EDS Analysis

Element	Scenario A	Scenario B	Scenario C	Scenario D
Oxygen	36.969	36.530	21.559	36.577
Phosphorus	15.629	15.331	3.902	15.314
Calcium	41.831	41.548	41.215	41.690
Sodium	0.250	0.380	0.143	0.409

$$Molar\ Quantity = \frac{Average\ Mass\ \%}{Molecular\ Weight}$$

$$Atomic\ Ratio = \frac{Molar\ Quantity\ (Element\ of\ Interest)}{Molar\ Quantity\ (Lowest\ Value)}$$

Table 3. Atomic Ratio Calculations for Scenario D

	Average Mass %	Molecular weight (g/mol)	Molar Quantity	Atomic Ratio
Oxygen	37.88	16.00	2.37	4.45
Phosphorus	16.48	30.97	0.53	1.00
Calcium	40.50	40.08	1.01	1.90

Table 4. Calculated vs Theoretical Atomic Ratio

Atomic Ratio					
Element	**Theoretical**	**Scenario A**	**Scenario B**	**Scenario C**	**Scenario D**
Ca	4.33	4.35	4.51	4.71	4.45
P	1	1	1	1	1
O	1.67	1.81	1.93	2.11	1.9

SEM analysis was conducted by coating the samples in gold to prevent any charging of the surface to acquire high-resolution images of the synthesized HA. The resulting images showed a porous structure for Scenarios A, B, and D, while Scenario C displayed a flake-like structure. The images obtained from this analysis can be seen in Figure 13 - Figure 16. These images will be used for comparison in the experiments which introduce uranium.

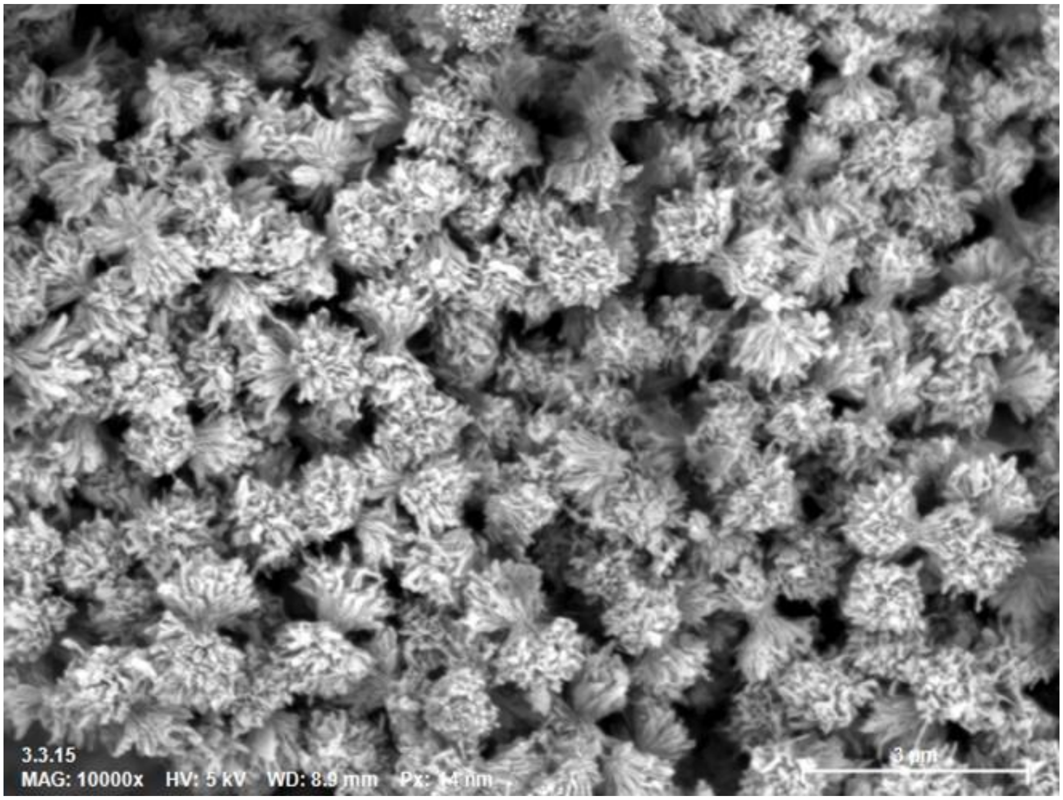

Figure 13. SEM Image for Scenario A.

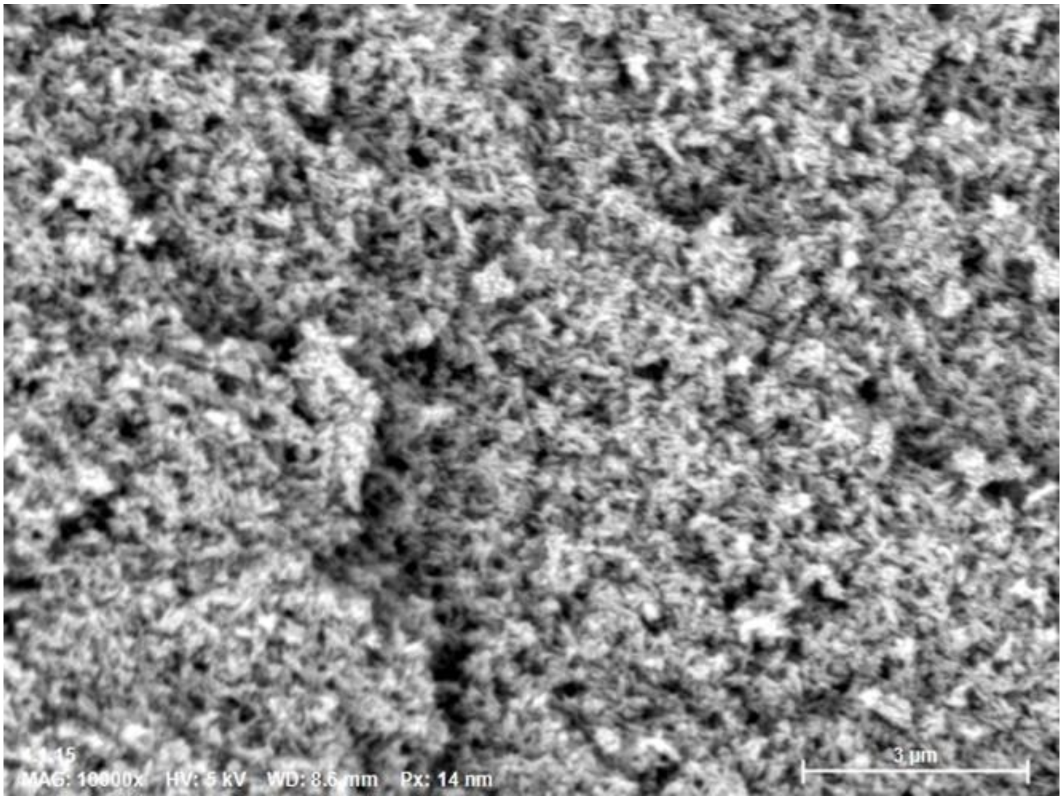

Figure 14. SEM Image for Scenario B.

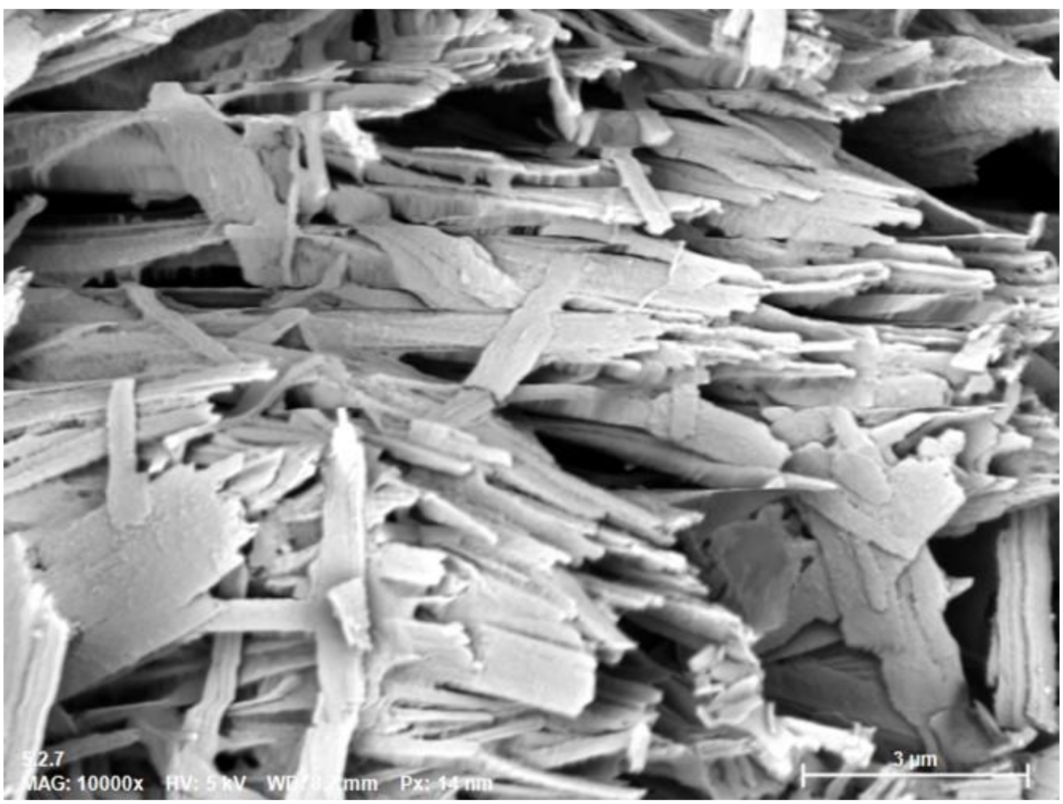

Figure 15. SEM Image for Scenario C.

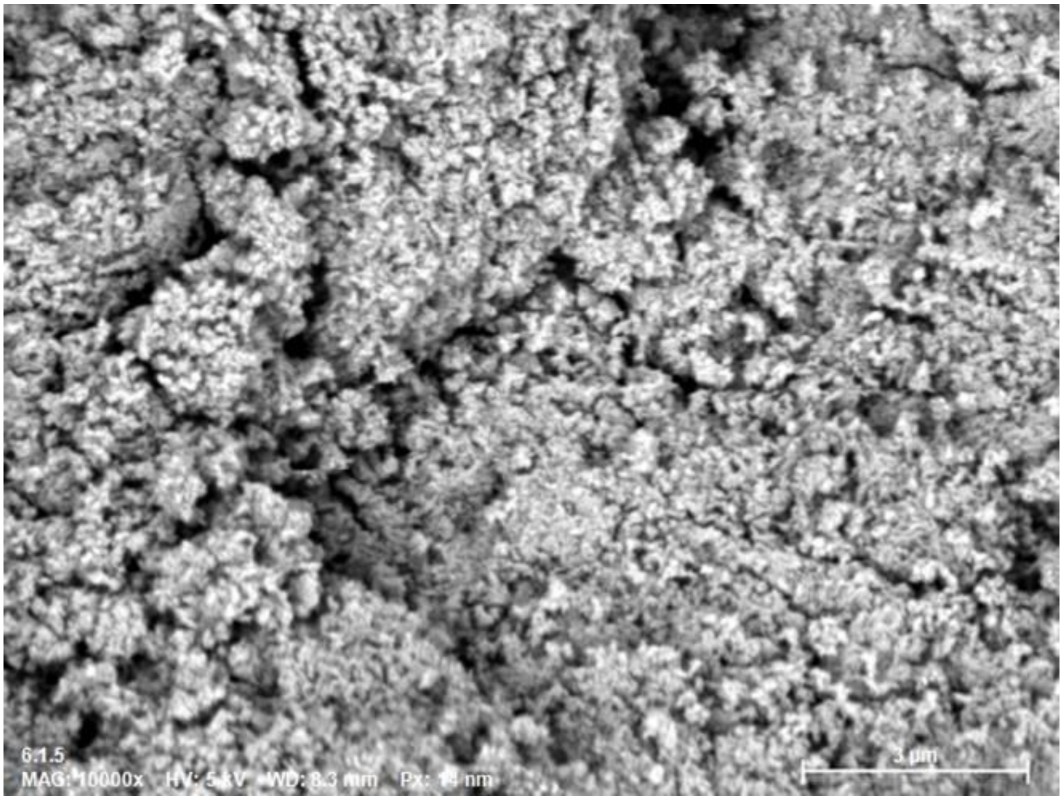

Figure 16. SEM Image for Scenario D.

XRD analysis revealed peaks that matched extremely well to hydroxyapatite in all scenarios, except Scenario C, as shown below in Figure 17 - Figure 20.

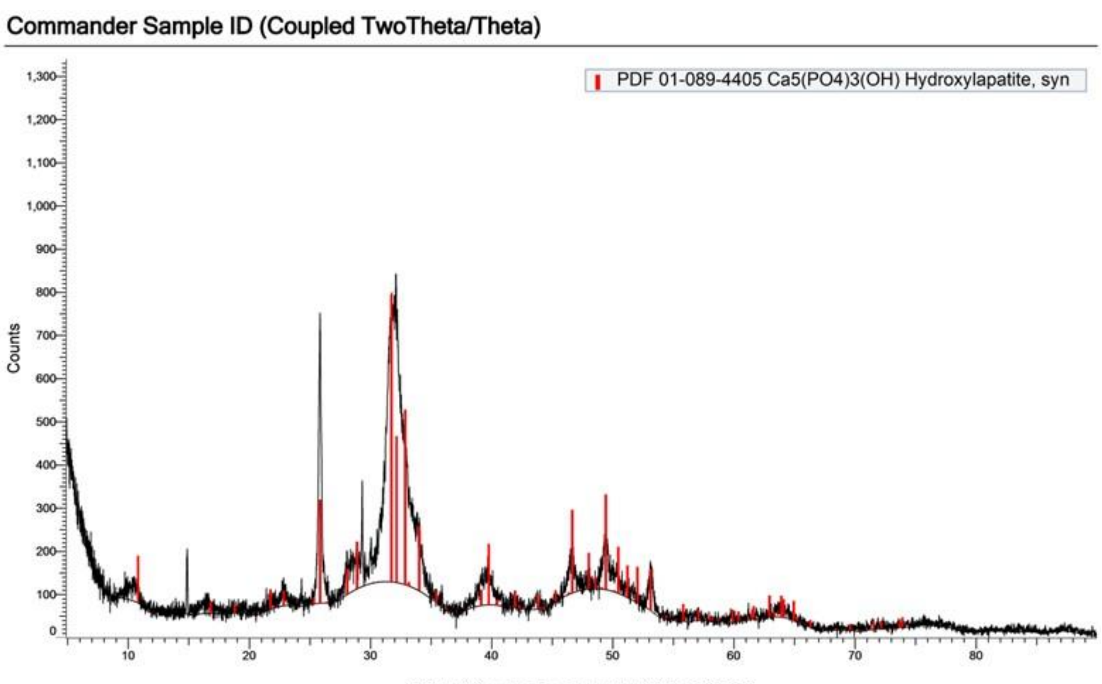

Figure 17. Matched XRD pattern for Scenario A without uranium.

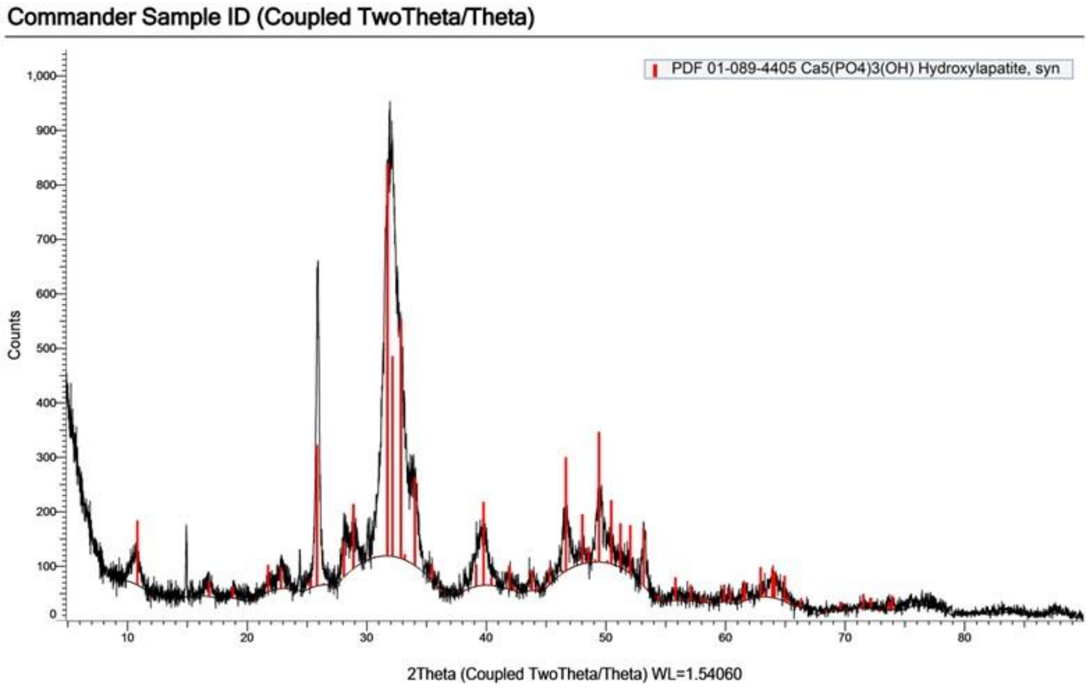

Figure 18. Matched XRD pattern for Scenario B without uranium.

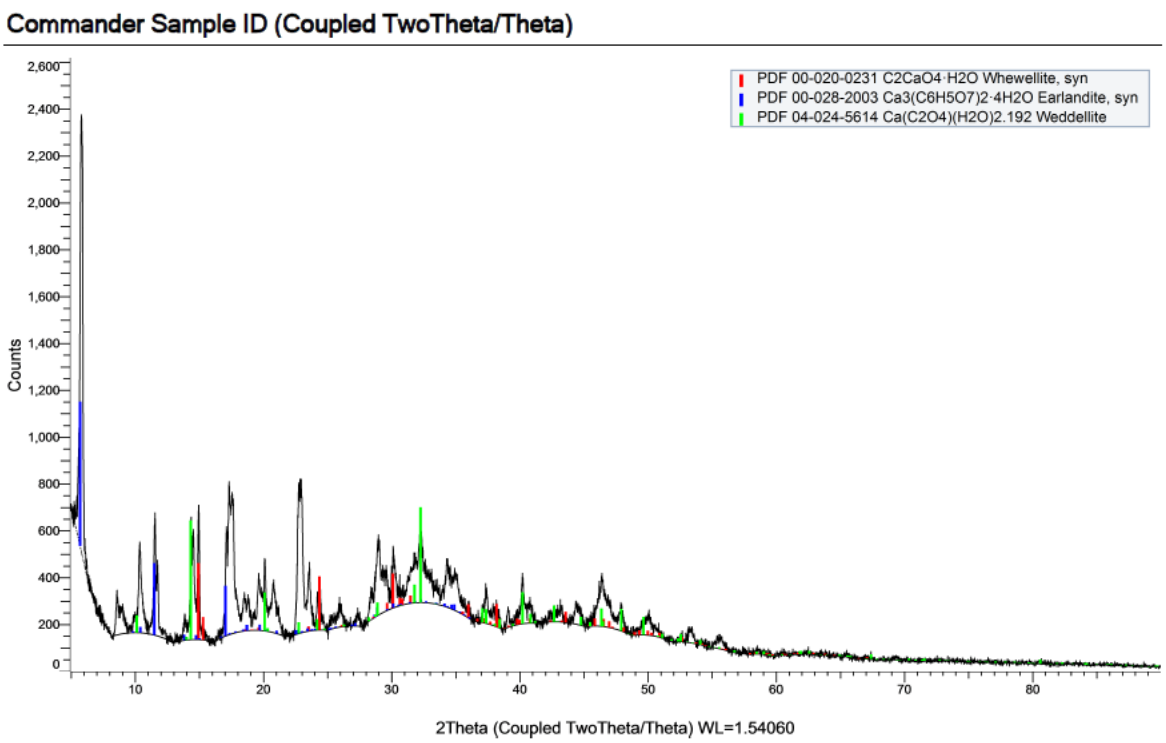

Figure 19. Matched XRD pattern for Scenario C without uranium.

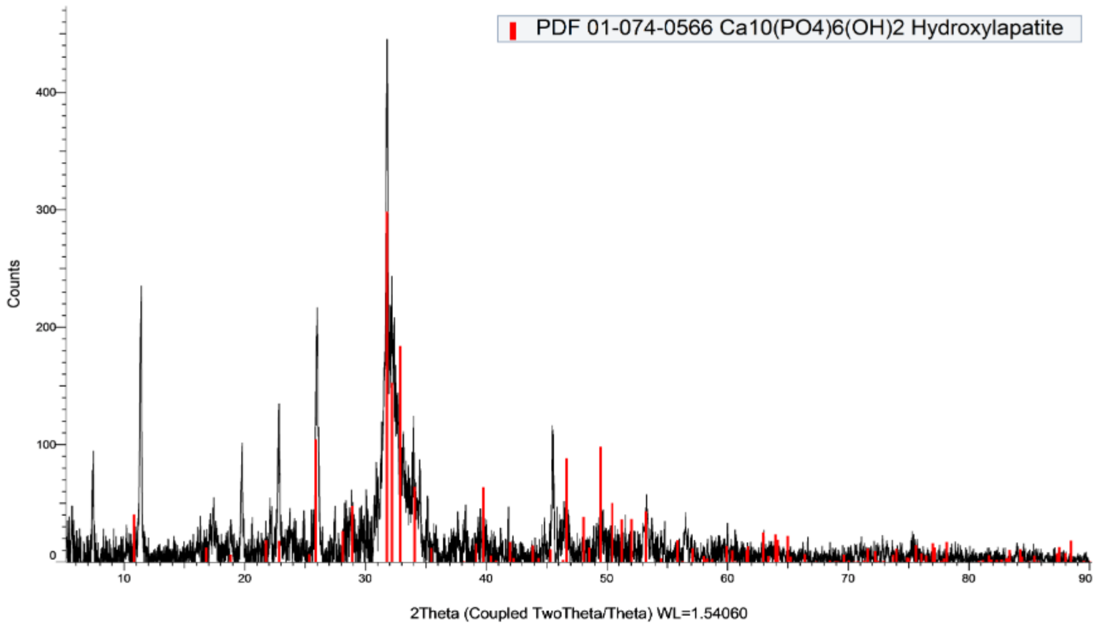

Figure 20: Matched XRD pattern for Scenario D without uranium.

Incorporation and Co-Precipitation Studies:

Aqueous samples were analyzed via ICP-OES to measure concentration for total Ca and P, and via ICP-MS for total U concentration over time and to establish formation kinetics. The change in concentration of Ca and P obtained from ICP-OES analysis can be seen in Figure 21 and Figure 22. Since HA is composed of Ca and P, their concentration is expected to decrease as the precipitate forms. P concentrations show a rapid decrease within the first week for Scenarios A and D, with a more gradual decrease in Scenario C. A similar trend was seen for Ca in Scenarios A and D, decreasing rapidly within the first week followed by stabilization. The phosphorus concentration for Scenario C showed a very gradual decrease throughout the experiment. The change in concentration of U obtained from ICP-MS analysis can be seen in Figure 23. Uranium concentration for Scenarios A and D showed a significant decrease within the first five days and then stabilized throughout the remainder of this experiment. Scenario C displayed a slight decrease in U concentration in the first three days of the experiment and continued to gradually decrease until equilibrium was reached.

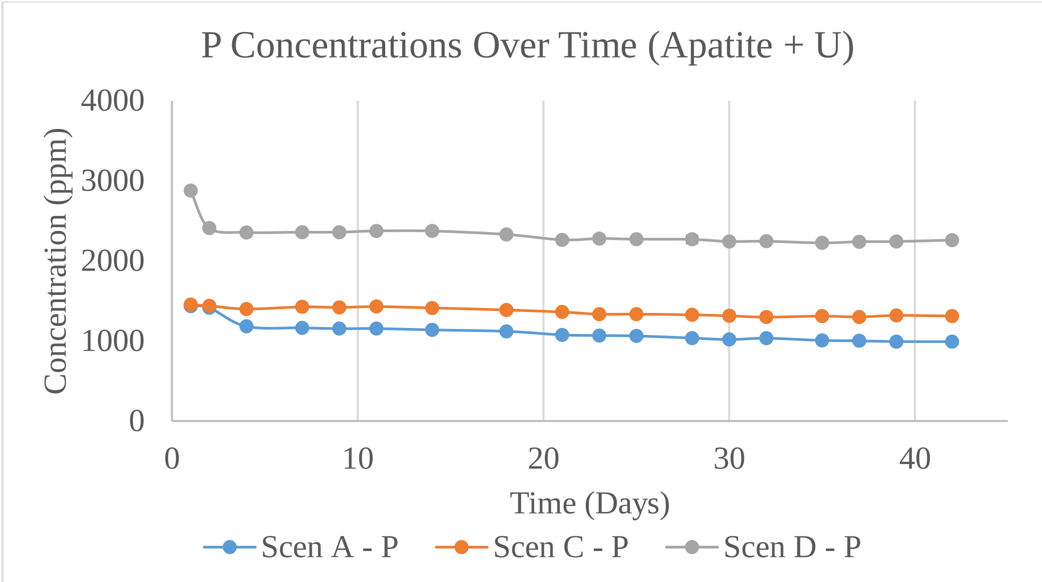

Figure 21. Change in phosphorus concentration during HA formation in the presence of uranium.

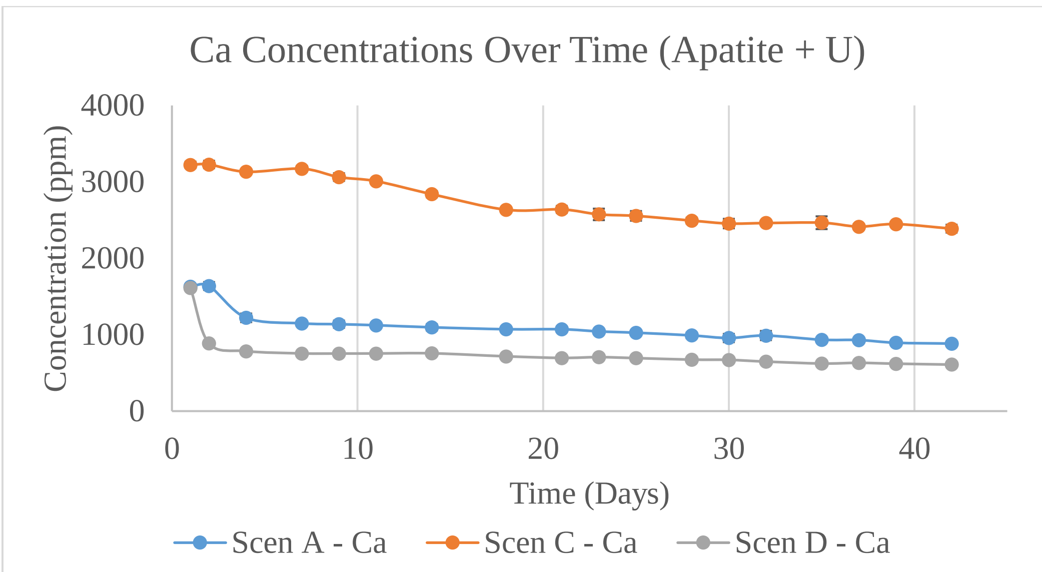

Figure 22. Change in calcium concentration during HA formation in the presence of uranium.

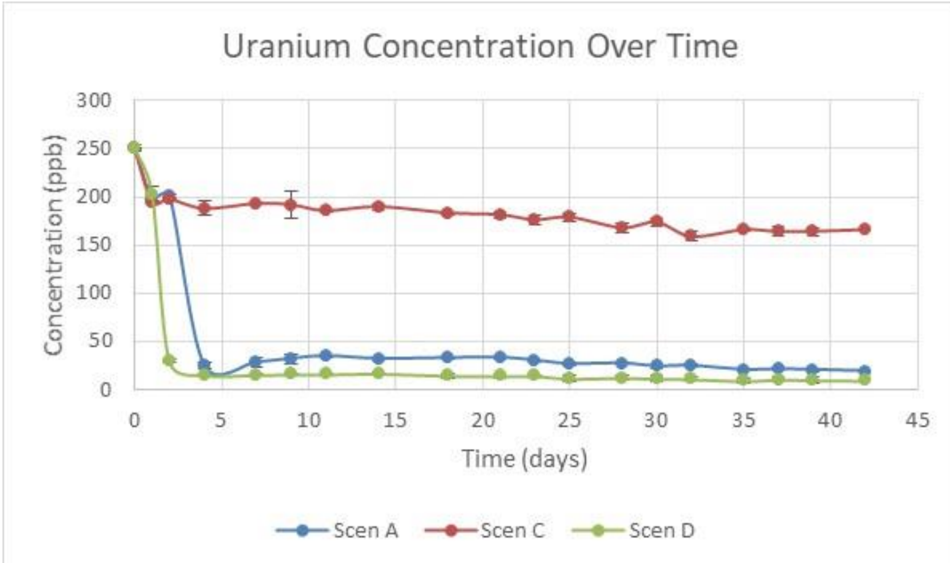

Figure 23. Change in uranium concentration over time during apatite formation.

The data obtained from ICP-OES for the previous experiment, which did not contain uranium in the samples, was overlain with the results from the current experiment discussed above for comparison. As seen in Figure 24 and Figure 25, the concentrations from both experiments followed a very similar trend for Ca and P in all scenarios.

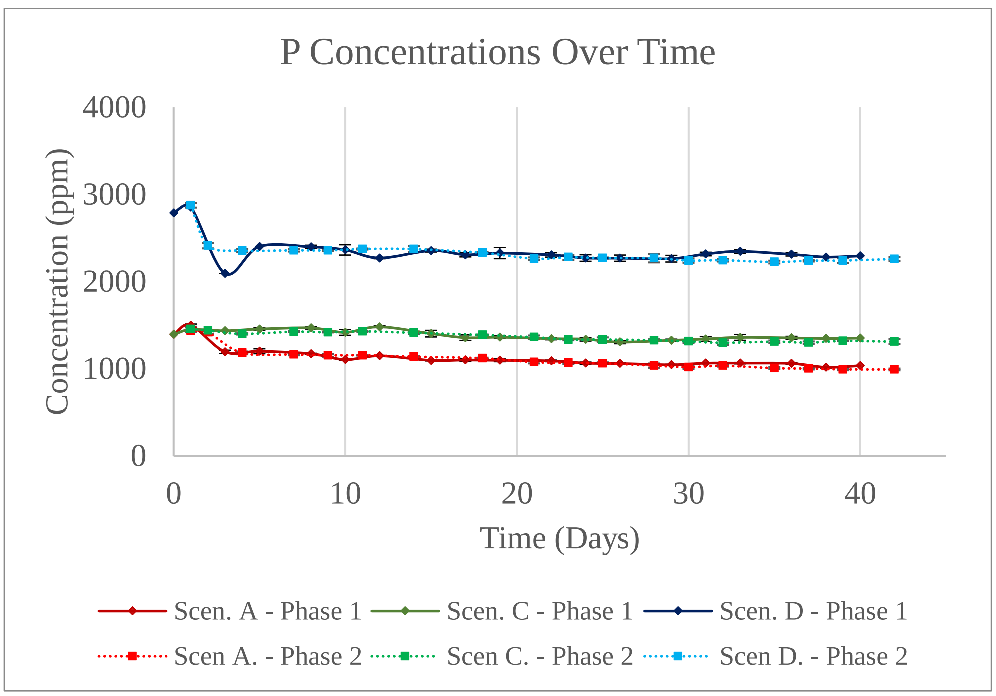

Figure 24. Comparison of phosphorus concentrations over time.

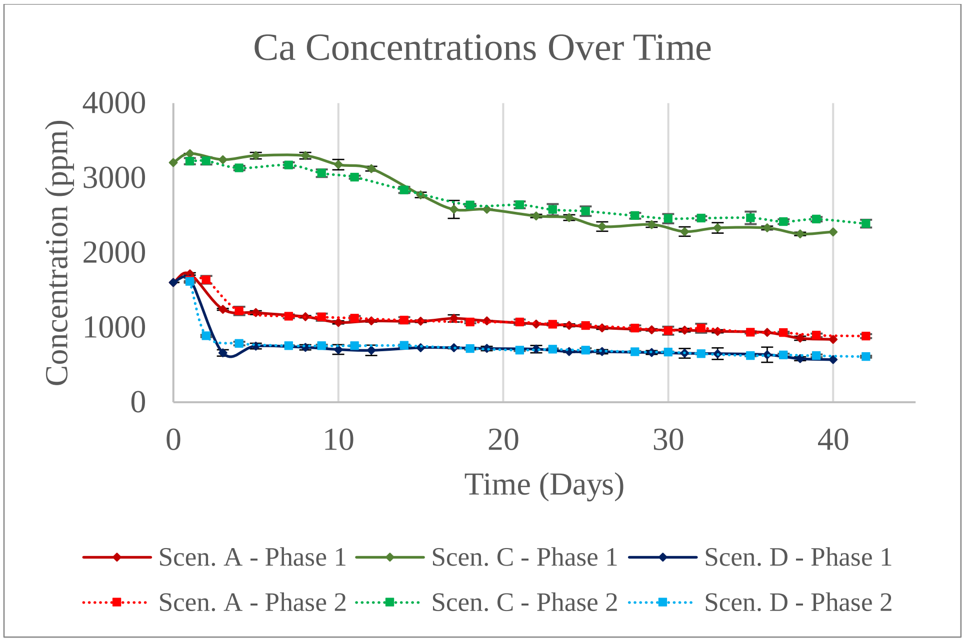

Figure 25. Comparison of calcium concentrations over time.

The precipitate was also prepared for XRD analysis and ran through the instrument. The resulting peaks were then matched to identify the mineral(s) present in the samples. The peaks matched extremely well to hydroxyapatite in all scenarios, except Scenario C, as shown below in Figure 26 through Figure 28. Due to the difference seen in Scenario C's XRD pattern, the other triplicates from this scenario were run on XRD to ensure that this was not an anomaly found in the single triplicate that was analyzed. A similar pattern for each of the triplicates was obtained through this analysis.

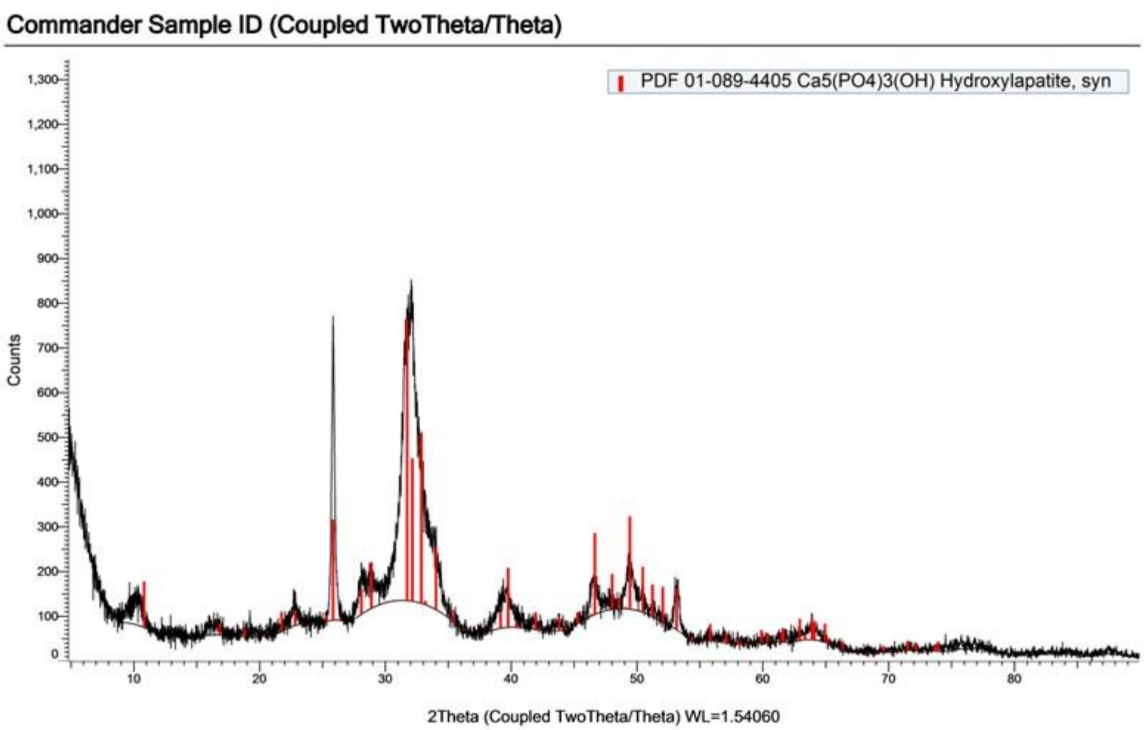

Figure 26. Matched XRD pattern for Scenario A with uranium.

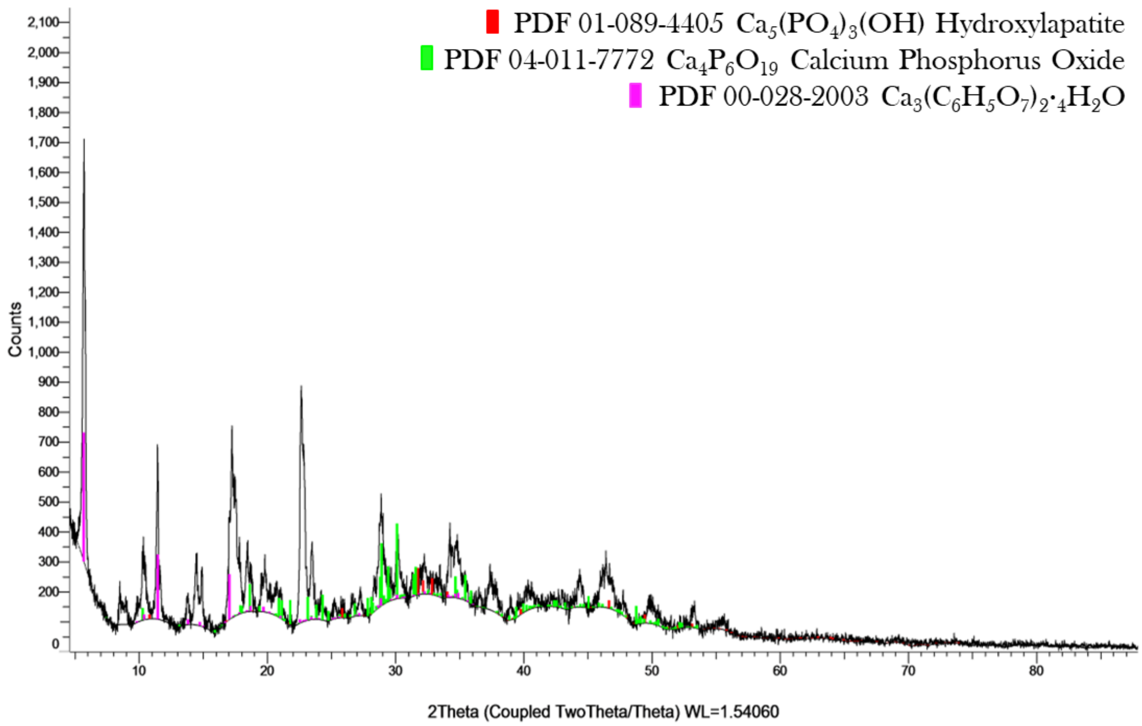

Figure 27. Matched XRD pattern for Scenario C with uranium.

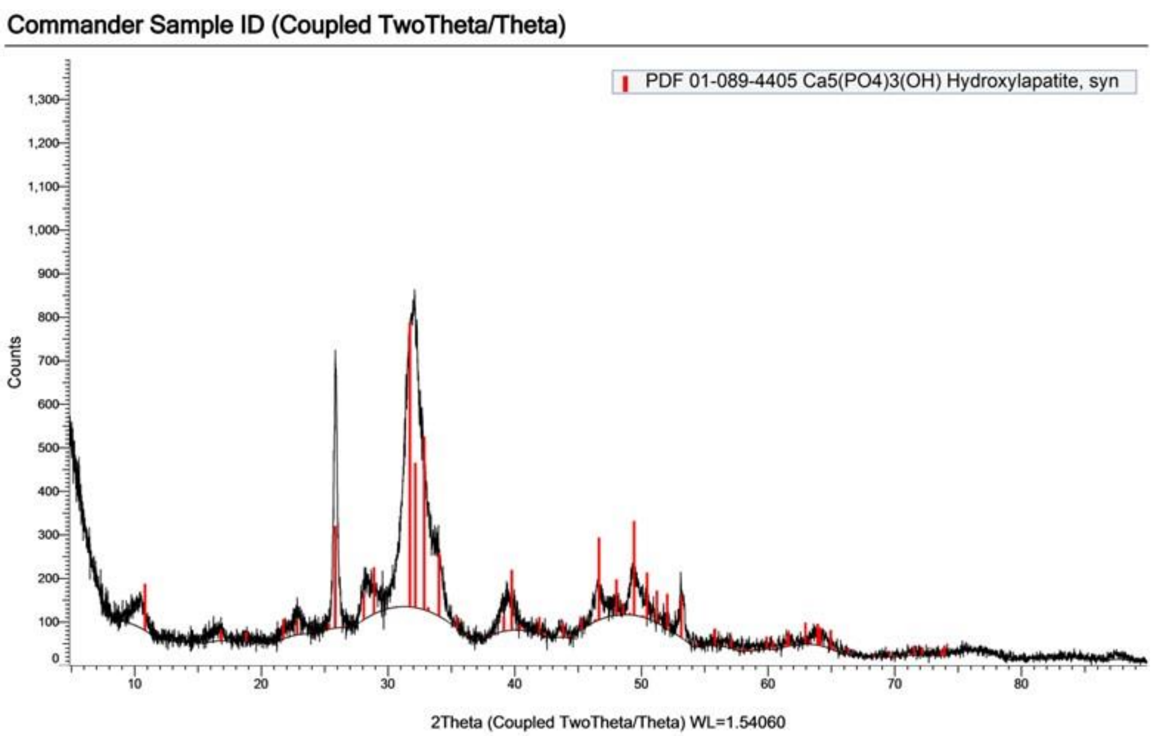

Figure 28. Matched XRD pattern for Scenario D with uranium.

The solid samples are currently being analyzed on SEM-EDS instrumentation to obtain results.

Sorption and Desorption Studies

Hydroxyapatite was synthesized for Scenarios A, C, and D and samples were monitored for 6 weeks. All of the aliquots collected during the six-week monitoring period were diluted 200-400 times with 2% HNO_3 and analyzed via ICP-OES to obtain the total calcium and phosphorus concentrations, as shown in Figure 29 and Figure 30. The dilution factor changes since the concentrations are expected to decrease as the experiment continues, as Ca and P are used to form the solid hydroxyapatite.

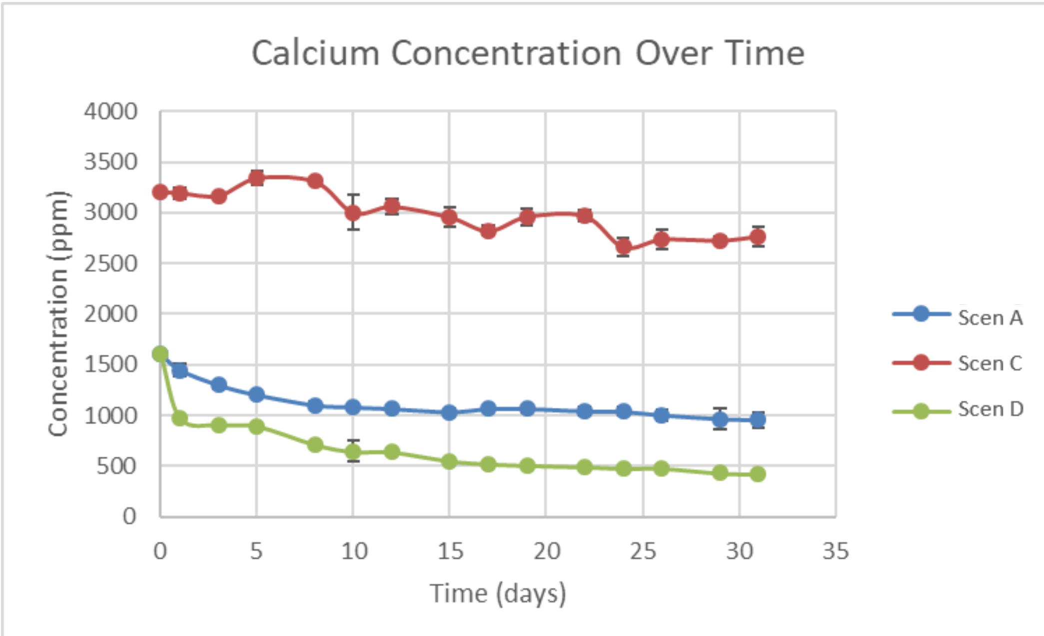

Figure 29. Change in calcium concentration over time.

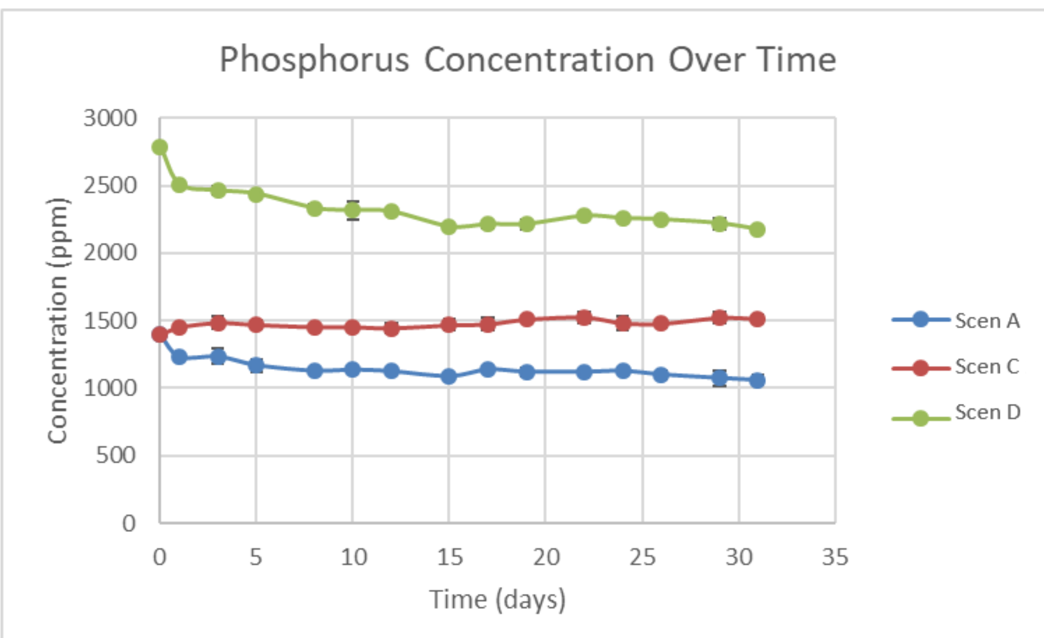

Figure 30. Change in phosphorus concentration over time.

Task 1: Conclusions

Based on results from Phase 1 experiments, synthesis and characterization of hydroxyapatite, mixing calcium citrate with a combination of phosphate salts resulted in formation of hydroxyapatite. At all stoichiometric ratios investigated, the characterization of the resulting precipitate indicated successful hydroxyapatite formation except Scenario C, which continuously displayed anomalies throughout characterization. From EDS analysis, phosphorus and oxygen levels are lower for Scenario C when compared to all other scenarios. Also, XRD revealed that the precipitate formed in this scenario was not purely hydroxyapatite, as other minerals were formed concurrently. ICP-OES analysis for Scenario C also showed that phosphorus was not used up as it should be if forming hydroxyapatite, further supporting that hydroxyapatite was not precipitated as it was in the other scenarios. Subsequent experiments will only include Scenarios A, C, and D to study the uranium-hydroxyapatite interaction at a constant citrate level. This concludes the Phase one of this study.

Phase two investigated the change in chemical composition and the structure of the various stoichiometric ratios for each scenario. Experimental data showed that hydroxyapatite was successfully synthesized for Scenarios A and D while Scenario C displayed anomalies throughout the analyses conducted, as it did in Phase 1 studies. This could be the reason the uranium concentration did not decrease in Scenario C as it did in the other two scenarios, which purely formed hydroxyapatite. From ICP-OES analysis, it was found that hydroxyapatite reaction was initiated within the first week after synthesis. ICP-MS analysis revealed that uranium concentrations also decreased significantly within the first week, indicating that incorporation and co-precipitation could be a key mechanism involved in removing uranium from the groundwater via hydroxyapatite. Scanning electron microscopy equipped with energy dispersive X-ray spectroscopy (SEM-EDS) analysis will be conducted in the future to further support the results found here. These results, and those that will be obtained from Phase three will be compared to results from previous experiments.

The data obtained through these experiments will help fill the knowledge gaps with respect to the mechanisms involved in the removal of U and the stability of the removal and assist DOE-LM in remediating uranium at the site where uranium is present. Furthermore, FIU will study the sorption and desorption mechanism of U removal from groundwater using apatite as well as the environmental factors that influence the stability of that removal, including temperature and oxidation-reduction potential (ORP).

Task 1: References

Rigali, Mark, et al. “Performance of an In Situ Hydroxyapatite Permeable Reactive Barrier at the Old Rifle Uranium Processing Mill Site.” 2018.

Gudavalli, Ravi, et al. “Comparison of the kinetic rate law parameters for the dissolution of natural and synthetic autunite in the presence of aqueous bicarbonate ions.” 2013.

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Gudavalli, Ravi, et al. “Quantification of kinetic rate law parameters for the dissolution of natural autunite in the presence of aqueous bicarbonate ions at high concentrations.” 2018.

Szecsody, JE, et al. “Use of a Ca-Citrate-Phosphate Solution to Form Hydroxyapatite for Uranium Stabilization of Old Rifle Sediments: Laboratory Proof of Principle Studies.” Mar 2016.

Szecsody, JE, et al. “Influence of Ca-Citrate-Phosphate Mixtures on Rifle Sediment Treatment for Uranium Remediation.” Aug 2017.

TASK 2: CLIMATE RESILIENCY STUDIES FOR LONG-TERM SURVEILLANCE OF DOE-LM SITES

Task 2: Introduction

By fulfilling the Department of Energy's (DOE) post-closure responsibilities, The Office of Legacy Management (LM) protects human health and the environment through effective and efficient long-term surveillance and maintenance of disposal cells located across the United States. Among the many disposal cells that LM overseas, the disposal cell in Rifle, Colorado is being studied to ensure the integrity of the cell continues to prevent the release of contaminants.

The Rifle, Colorado disposal cell site, which is a Uranium Mill Tailings Radiation Control Act (UMTRCA) Title I disposal site, is licensed to the Department of Energy (DOE) and managed by the Office of Legacy Management (LM). The UMTRCA is a federal law that provides procedural disposal, long-term management, and control of uranium mill tailings to minimize or eliminate hazardous material exposure to the population. Under this law, which was passed in 1978 by Congress, the DOE has decontaminated 22 inactive uranium-ore processing sites. These radioactive materials have been encapsulated and approved for storage in the U.S. Nuclear Regulatory Commission (NRC) disposal cells. The Rifle disposal cell site, which was included under NRC general license to the DOE in 1998, undergoes routine inspection which includes assessment of the condition of the site's visible features, noting any changes in the condition of the cell that will go against the Long-Term Surveillance Plan (LTSP), and evaluating the need for any maintenance, inspection, and monitoring.

The disposal cell is located on 205 acres of land in Estes Gulch, roughly 6 miles north of the city of Rifle, Colorado. The 205-acre site, formerly Bureau of Land Management (BLM) land, was transferred to the DOE in August 1991 for use as the Rifle disposal cell. Of the 205 acres of land, the disposal cell comprises 71 acres of the transferred land. The disposal cell has a multicomponent triangular shape that measures nearly 3,000 feet on three sides. The multi-component design of the cell contains 3.7 million cubic yards of radioactive materials from the relocated tailings of two former processing sites. Thus, the disposal cell is comprised of a total of 2,738 curies of radium-226. The components of the cell determine the specific task to either reduce the flux escaping from the cell, protect against erosion, or provide overall protection against drying and water infiltration.

Florida International University (FIU), in collaboration with the U.S. Department of Energy's Office of Legacy Management (DOE-LM), plans to investigate an effective way to monitor the long-term effects of climate on the disposal cell's subsurface. Due to natural environmental causes, there is a potential for subsurface delineation of water pockets. Without causing any damage to the multi-layer design, geophysical survey sensors are a potential technology that uses non-evasive ground-based physical sensing to collect information about the Earth's subsurface. The research obtained on the state-of-the-art geophysical survey sensors will depict a method for mapping the subsurface of the disposal cells for potential groundwater and buried delineation. Additionally, FIU plans to investigate the effects of climate change on environmental remedies employed at DOE-LM sites. Considering the specific environmental characteristics of the LM sites, targeted monitoring methods and technologies will be explored to address Legacy Management's climate resiliency goals for the long-term monitoring of disposal cells.

Task 2: Objectives

The main goals of this task are to evaluate the viability of (a) using traditional geophysical technologies for cost-effective site characterization and monitoring of existing subsurface conditions of LM's disposal cells, and (b) leveraging long-term historical weather data to correlate stressors in sites' hydrology that potentially lead to sudden changes of the subsurface. Investigations will pursue the following objectives:

- Evaluate commercially available geophysical systems and state-of-the-art sensors, such as ground penetrating radar, electrical resistivity imaging (ERI), and electromagnetic/magnetic surveys.
- Compile precipitation and temperature data and parse the historical impact of this climate forcing on the hydrology of DOE-LM sites across the US.

During FIU Year 2, this study focused on evaluating the possibility of using state-of-the-art geophysical survey sensors as a cost-effective method for site mapping and monitoring the conditions of LM's disposal cells. The use of geophysical survey sensors is a way to steadily collect information that is associated with the features of the Earth's subsurface. The sensors use the collected data to map the subsurface features in a non-destructive manner. This study also includes the long-term climate analysis that potentially impacts the disposal cell's hydrology and its sudden changes within the subsurface.

Task 2: Methodology

Materials

This study utilizes several publicly available databases to compile historical and future climate variables of the disposal cell located in Rifle, Colorado. The historical and future climate variables will inform LM of the weather conditions that the disposal cell experienced and will experience in the upcoming years.

Literature Review on Different Types of Geophysical Survey Sensors

A literature review of the different types of geophysical survey methods was performed, ([2], [3], [4], [5], [6], and [8]), the authors summarized the characteristics of each method that will be used to assemble a sensor selection decision matrix, filtering out the best survey method to inspect the disposal cell subsurface.

Figure 31 depicts the different geophysical surveying technologies that can be used for ground-based physical sensing to produce detailed underground images or mappings. Subsurface mappings can show any delineation in the earth's underground such as any voids, groundwater, underground irregularities, and much more. Each proposed method uses a different mapping technique to accomplish the subsurface data collection, requiring specific equipment and tools that are factored into the decision matrix compilation.

Problem: Deciding on which Geophysical Method to Pursue	Ground Penetrating Radar	Electrical Resistivity Imaging	Seismic Refraction
Requirements/Criteria			
Equipments	Display Unit Data Transfer USB slot Optional External GPS Cart Frame Cell Battery GPR Sensor	Resistivity/IP/SO Meter Switching Apparatus Electrode Cables Stainless Steel Stakes Power Source	Measurement tape Trigger cable ABEM Terraloc MK8 Sledgehammer Battery Striker plate Geophones
Depth Range	Up to 100 ft(30 meters)	10 to 30 meters (Lower Resolution but deeper Investigation)	15 to 20 meters
Data Format	2D or 3D Subsurface Images	2D or 3D Subsurface Images	Numerical Data
Capabilities(But not Limited too)	Cavity Detection Hydrogeology Detects Metal/Non-Metal Voids Undergroud irregularities	Sinkhole/Void Locating Mapping of Depth to Bedrock Groundwater Landfill delineation	Limited to mapping bedrock depths and rippabilities

Figure 31. Decision matrix for geophysical survey methods.

Geophysical Survey Sensor Evaluation

A literature review was conducted of the geophysical survey methods, commercially available sensors, and their application programming interface (API) ([9] and [10]). The authors describe the sensor's API which helps define a set of protocols for building and integrating application software providing direct access to surveyed data. Most sensors output sectional images from the scanned area; however, FIU plans to create 2D/3D maps delineating subsurface structures in a disposal cell to integrate into existing digital surface models of the terrain, which would require an adequate vendor's API.

Communication with a particular ground-penetrating radar (GPR) manufacturer that would detect subsurface erosions at the cell was accomplished. One potential candidate is the NOGGIN® GRP series from Sensors and Software Incorporated. As illustrated in Figure 32, the series comes in four different frequencies and configurations accordingly to other terrain specifications. The company provides an open application programming interface (API) to interface their GPRs, crucial for integrating the sensor into a mobile platform. The goal is to develop and deploy an autonomous ground robot that creates 3D maps from the disposal cell's subsurface and terrain delineations without disturbing the cell coverage.

Figure 32. NOGGIN® GPR series.

FIU's next objective for the GPR series was to understand the applications of detecting buried objects and underground voids that the ground penetrating radar is capable of. The application for void detection is important for LM's disposal cells and the continuous monitoring of the cell's structure. Figure 33 - Figure 35 are examples of a survey inspection done by the company Sensors & Software Inc. In this case, they used the ground penetrating radar to identify potential voids of a concrete slab. The raw data from Figure 34 was processed into depth slices that can be viewed in Figure 35. The depth slices that are 40 cm under the surface are shown to have high amplitude reflections, which can be the possibility of voids in the subsurface.

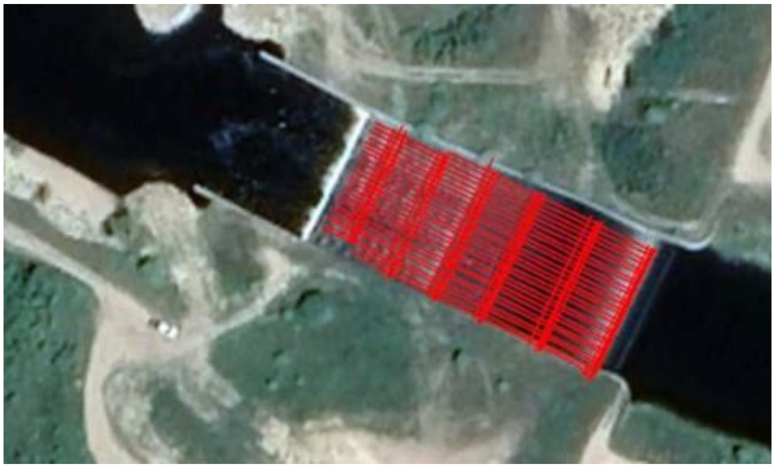

Figure 33. Google Earth image of the survey path (Image from Sensors & Software Inc.).

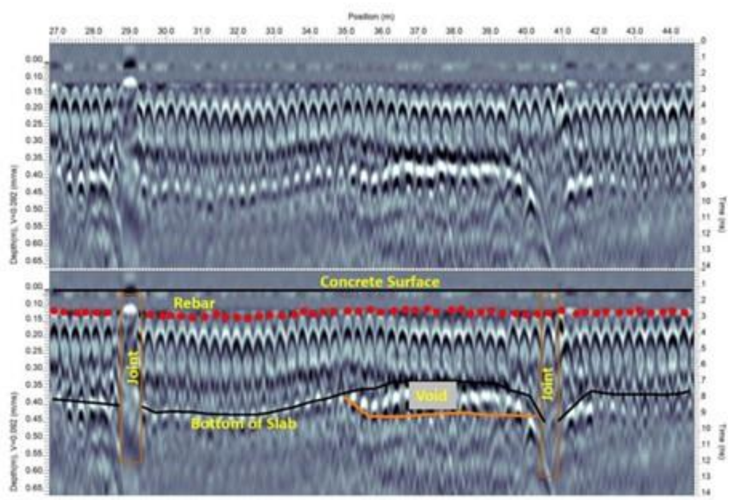

Figure 34. Raw Data of the Interpreted Voids (Image from Sensors & Software Inc.).

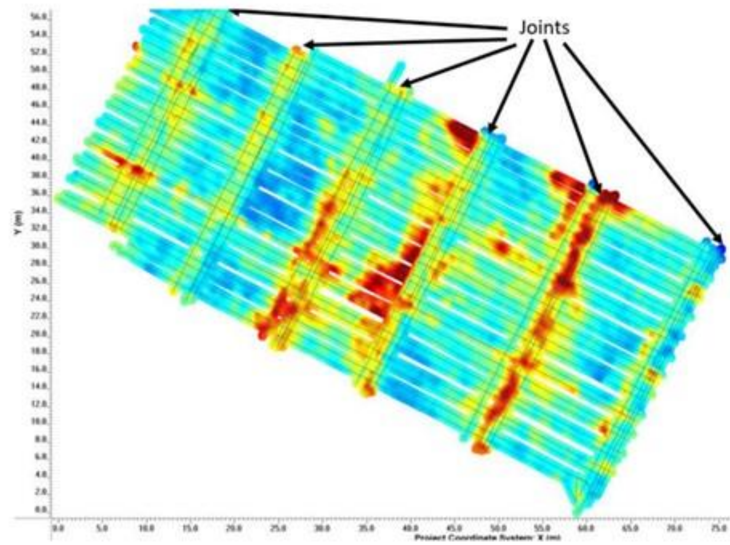

Figure 35. Depth Slice of the Surveyed Path (Image from Sensors & Software Inc.).

Based on this application of void detection of concrete slabs, FIU plans to incorporate the same methodology for LM's disposal cells. This will help monitor the cell's subsurface and detect any current or future voids that may occur. The DOE-LM Fellow continued to research the applications that the ground penetrating radar is capable of that could potentially help monitor LM's disposal cells.

Geophysical survey sensors make it possible to map the conditions of the earth's subsurface in a non-evasive manner. These types of sensors collect data that is related to the earth's features and then visualize the data in some sort of contour plot or graph. The sensors that were evaluated are the ground penetrating radar, electrical resistivity imaging, seismic refraction, and electromagnetic survey. Each sensor has different conditions for surveying the region of the layer. These conditions or requirements such as the equipment, data collection, and plotting are much different between each sensor but the capability for subsurface detection is accurate. The scope of this report is to essentially select one of these geophysical sensors for mapping and monitoring the conditions of LM's disposal cells for future integration onto a robotic platform.

Geophysical Survey Sensor Selection

Given the potential that the ground penetrating radar presents, FIU focused on this technology and its capabilities for the subsurface detection of LM's disposal cells. FIU conducted a literature review of the technology ([11]), which highlights the significance of the radar's wavelengths for target detection, resolution, and the maximum depth of penetration. Efforts to understand the wavelength and its dependency on the frequency of the radar's antenna provide a practical preliminary estimate for selecting an appropriate antenna in MHz, which would in turn increase the accuracy of the site survey.

The main activity is to then finalize the selection of a candidate ground-penetrating radar (GPR) suitable for imaging and detecting subsurface erosions at LM's Rifle disposal cell. The selection was based on subsurface erosions discovered in 2017 at the Mexican Hat Disposal Cell in Utah.

As illustrated in Figure 36, the erosion only manifested on the surface as slight depressions where the rock cover had subsided into the voids.

Figure 36. Erosion issues at the Mexican Hat Disposal Cell in Utah.

Potential causes are construction issues, including dispersive clays in the interbed layers between the radon barrier and the overlying rock cover. However, LM does suspect climate change is a contributing cause. Despite the Southwest USA's terrible drought, climate change trends project that precipitation events will be more intense, as in recent meteorological records from LM's sites. The rock cover essentially plays little role in slowing runoff during short intense rainfall events.

Considering that other LM sites may have similar features, the selected sensor is a Noggin 250 GPR from Sensors and Software Incorporated, depicted in Figure 37. The 250 MHz frequency model is commonly used for underground mapping and underground storage tanks; thus, this sensor can delineate shallow voids similar to those at Mexican Hat. Along with the GPR, the NIC-500N, a network interface controller, will allow full integration into FIU's autonomous robotic ground platform.

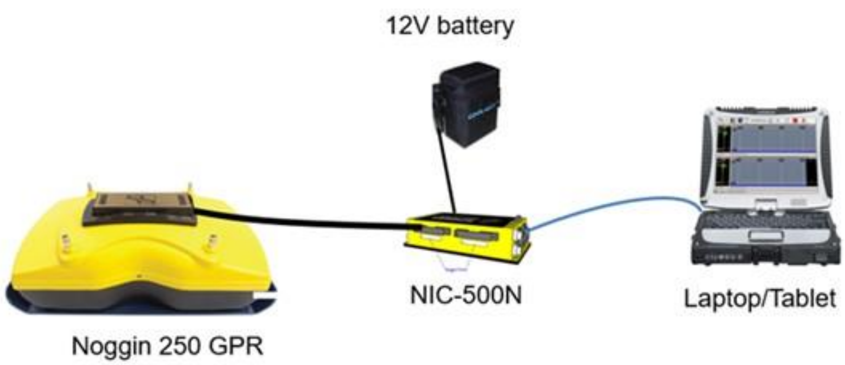

Figure 37. Noggin 250 Ground Penetrating Radar.

<u>DOE-LM Rifle Disposal Cell Inspection</u>

The Fellow performed a thorough site inspection among LM staff and state officials to capture any areas of concern. Figure 38 shows pictures during the annual site inspection. The site visit was instrumental in understanding terrain conditions, logistics, and deployment challenges crucial in designing FIU's Ground Penetrating Radar robotic platform.

Figure 38. LM's annual inspection for the Rifle Disposal Cell.

In addition, participating in the pre-inspection safety briefing, post-inspection de-brief, group questions, and team comments enriched the Fellow's academic education by exposing him to methods and operational procedures employed by LM during site inspections, as well as inspectors' expectations.

Climate Trend Analysis

Studying historical weather trends for the disposal cell located in the city of Rifle, Colorado helped to better understand if the accumulation of water in the disposal cell is coherent with the weather conditions of its surroundings. Based on different circumstances, numerous organizations continuously record climate data every minute, hour, day, month, or year. These climate variables can be publicly accessible through their online database or repository. The National Oceanic and Atmosphere Administration (NOAA) Analysis of Record for Calibration (AORC), and Lawrence Berkeley National Laboratory's (LBNL) climate model were used as the available resources to compile historical and future time series plots.

Task 2: Results and Discussions

Climate Analysis provided by the National Oceanic and Atmospheric Administration (NOAA):

Figure 39 shows the averages of each year from 1930 to 2008 of the maximum temperature, minimum temperature, and precipitation throughout the years. The trend line is implemented to view the behavior of the weather conditions over the years. Any increase or decrease in the overall data can be interpreted by the trend line and its equation. The regression coefficient shows how well the data best fits the model, so the sporadic events of the data can be evaluated. Each graph can be seen to have low regression coefficients as a result of spikes in the data. The data starts to become erratic after 1978 for the maximum and minimum temperature graphs. The precipitation graph has spikes throughout the data which also explains the low regression coefficient. These phenomena will be looked at and compared with other weather stations and their values to evaluate the consistency of the region's weather conditions.

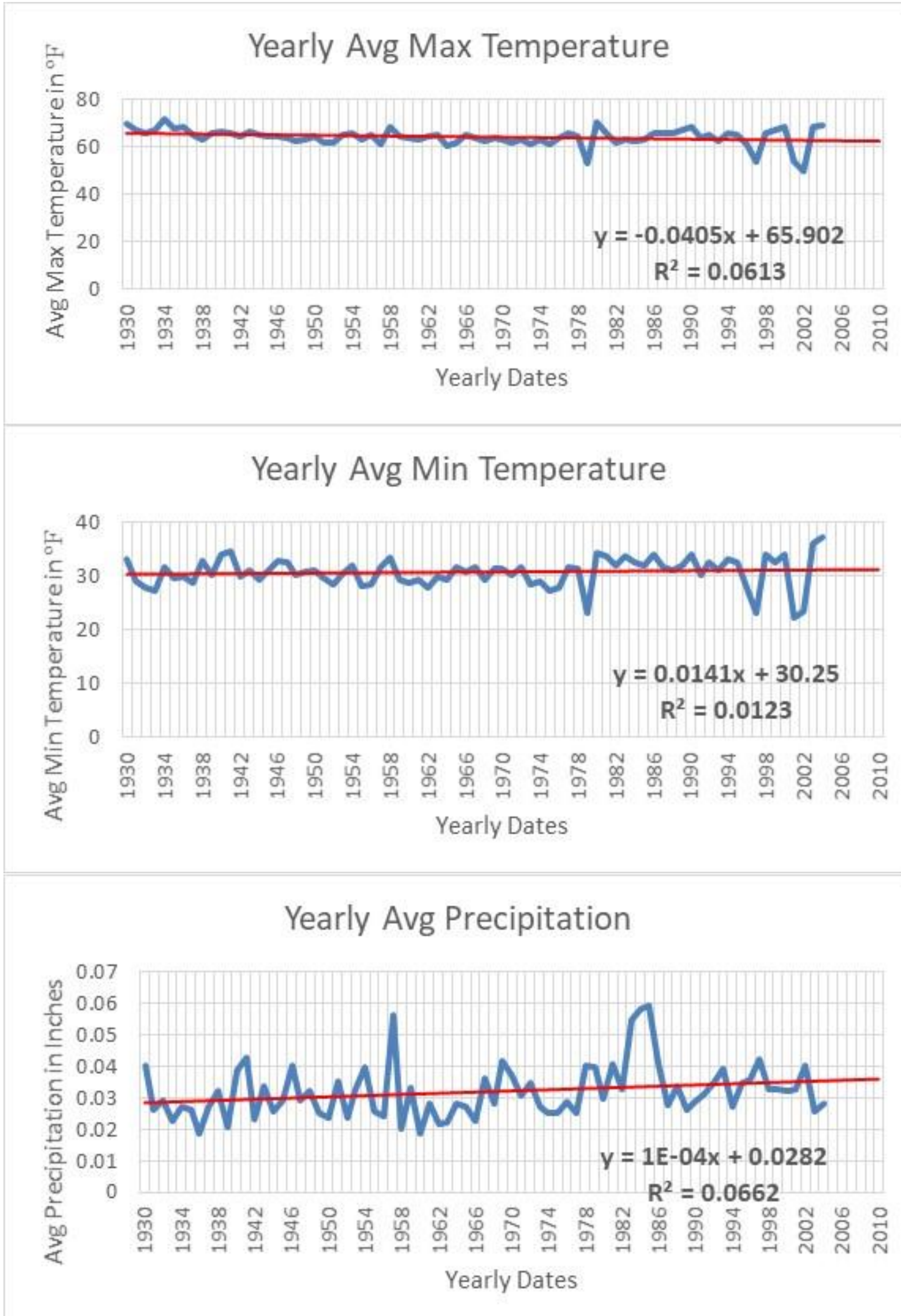

Figure 39. Rifle's historical weather trends.

The raw historical daily precipitation and maximum temperature data for the Rifle site that the Lawrence Berkley National Laboratory has through their GitHub was processed. The daily values are imported and converted into their yearly averages using Python. Figure 40, Figure 41, and Figure 42 show the process of first importing the .csv file, which includes the historical daily mean and standard deviation. Using Python and the tool ".resample()", the file can be converted to average monthly and yearly values given that the date column is in a DateTime format. The process described and depicted below is what was done with the precipitation values, but the same principles also apply for the maximum temperature, RCP 4.5, and RCP 8.5.

```
RFL_CO_historical_pr=pd.read_csv('RFL_CO_historical_pr.csv')
print(RFL_CO_historical_pr)

       Unnamed: 0      mean       std        date
0               0  0.142458  0.247443  1950-01-01
1               1  0.972290  2.177500  1950-01-02
2               2  2.270195  6.352240  1950-01-03
3               3  2.042946  3.410490  1950-01-04
4               4  1.577984  3.171629  1950-01-05
...           ...       ...       ...         ...
20449       20449  0.293046  0.775327  2005-12-27
20450       20450  0.929537  1.770608  2005-12-28
20451       20451  0.566302  0.859090  2005-12-29
20452       20452  0.123515  0.216802  2005-12-30
20453       20453  0.498472  1.213128  2005-12-31

[20454 rows x 4 columns]
```

Figure 40. Python script for importing CSV files.

```
# Daily To Monthly Precipitation
RFL_CO_historical_pr.date=pd.to_datetime(RFL_CO_historical_pr.date)
RFL_CO_historical_pr1 = RFL_CO_historical_pr.resample('M',on='date').mean()
print(RFL_CO_historical_pr1)

            Unnamed: 0      mean       std
date
1950-01-31        15.0  1.545136  3.348645
1950-02-28        44.5  1.317495  2.586516
1950-03-31        74.0  1.267010  2.516628
1950-04-30       104.5  1.148277  2.056432
1950-05-31       135.0  1.103079  2.210685
...                ...       ...       ...
2005-08-31     20316.0  1.676969  3.321615
2005-09-30     20346.5  1.381414  3.194016
2005-10-31     20377.0  1.092153  2.609316
2005-11-30     20407.5  1.175668  2.538296
2005-12-31     20438.0  1.323479  2.553730

[672 rows x 3 columns]
```

Figure 41. Python script for converting daily to average monthly precipitation data.

```
### Daily To Yearly Precipitation
RFL_CO_historical_pr.date=pd.to_datetime(RFL_CO_historical_pr.date)
RFL_CO_historical_pr2 = RFL_CO_historical_pr.resample('Y',on='date').mean()
print(RFL_CO_historical_pr2)

            Unnamed: 0      mean       std
date
1950-12-31       182.0  1.272178  2.535122
1951-12-31       547.0  1.236831  2.465740
1952-12-31       912.5  1.237237  2.448885
1953-12-31      1278.0  1.260947  2.592467
1954-12-31      1643.0  1.402204  2.807568
1955-12-31      2008.0  1.288390  2.665607
1956-12-31      2373.5  1.276827  2.624459
1957-12-31      2739.0  1.284627  2.622068
1958-12-31      3104.0  1.305256  2.640028
1959-12-31      3469.0  1.293231  2.581643
1960-12-31      3834.5  1.369449  2.887412
1961-12-31      4200.0  1.254040  2.621509
1962-12-31      4565.0  1.317120  2.700134
1963-12-31      4930.0  1.303609  2.743627
1964-12-31      5295.5  1.316623  2.730194
1965-12-31      5661.0  1.208277  2.430073
1966-12-31      6026.0  1.231885  2.502456
```

Figure 42. Python script for converting daily to average yearly precipitation data.

Figure 43 and Figure 44 depict the average historic precipitation and the historic maximum temperature that range from 1950 to 2005. The future predictions or the representative concentration pathways (RCP) 4.5 and 8.5 are shown on the same plot as the historic maximum temperature and precipitation. The RCP predictions for the years 2006 to 2099 are future scenarios that show how the normal and the highest daily human emission usage in W/m^2 will affect the earth's climate, and the model will predict the future climate based on these scenarios.

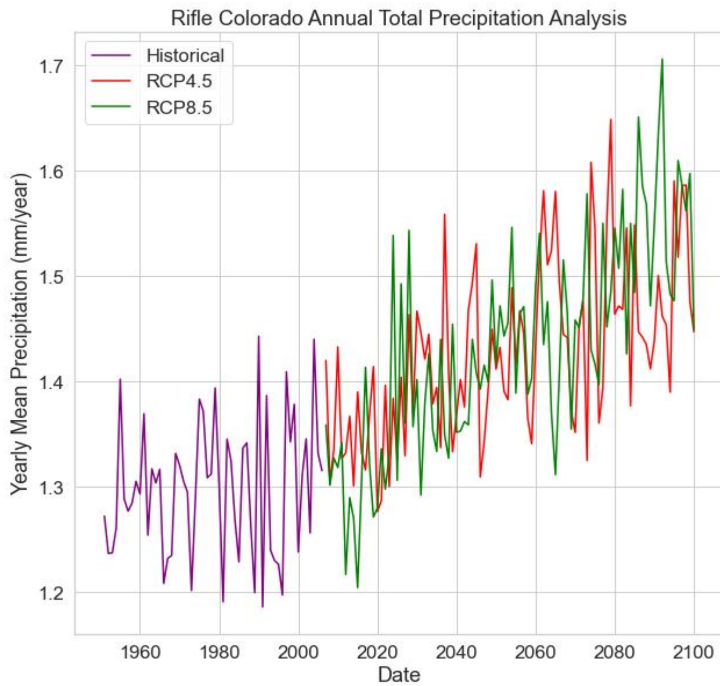

Figure 43. Average Rifle, Colorado annual total precipitation.

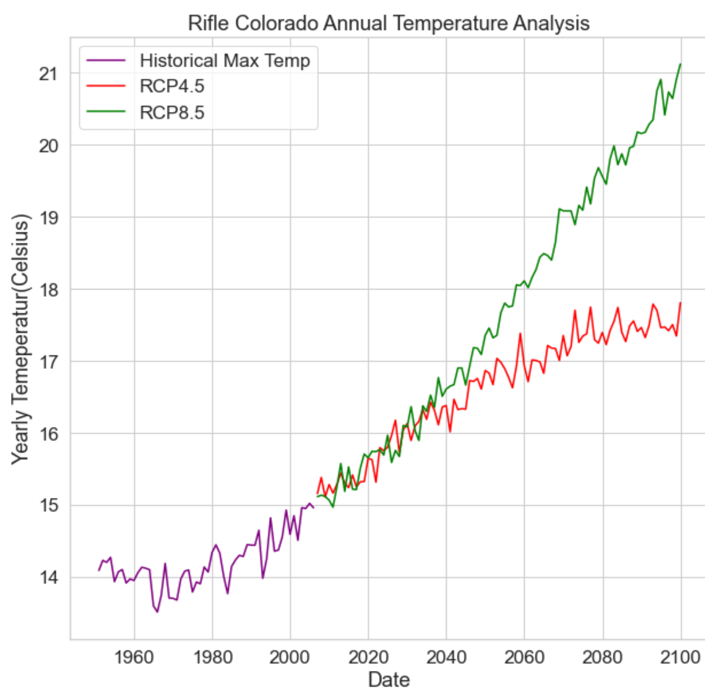

Figure 44. Average Rifle, Colorado annual temperature analysis.

Climate Analysis provided by Analysis of Record for Calibration (AORC):

The AORC is a gridded record of near-surface weather conditions, including total hourly precipitation, temperature, specific humidity, and wind components. The data collection period starts in 1979, which is sufficient for understanding the behavior of the historical climate of Rifle. Figure 45 graphs depict the results from the historical database from the AORC. The datasets range from the year 1979 to the near present on an hourly recorded basis and are plotted in a time-series format that shows the annual historical temperature and precipitation. Since the raw data is initially given on an hourly basis for the Colorado Basin River Forecast Center region. Python programming is implemented to convert the hourly climate variables to their yearly averages and the region is filtered solely on the disposal cell located in Rifle, Colorado.

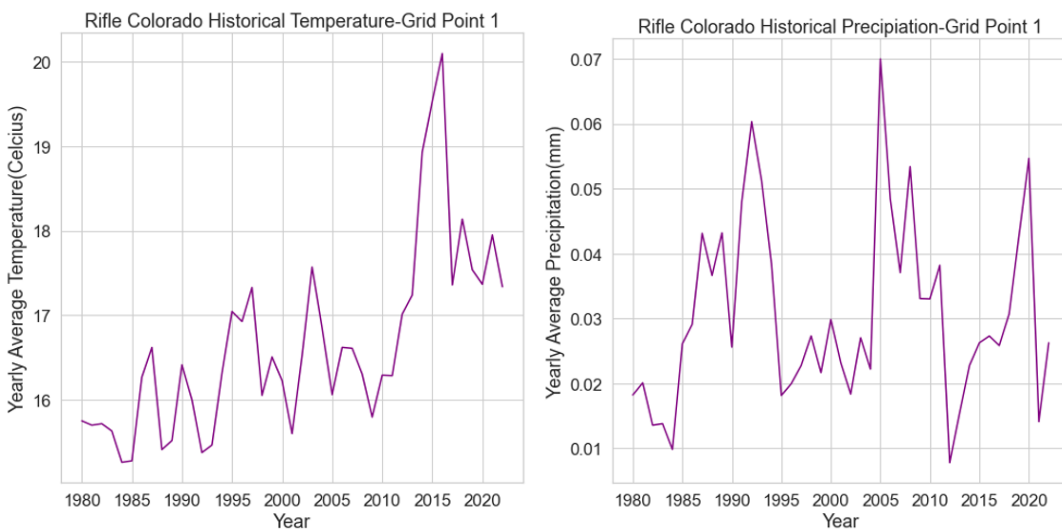

Figure 45. AORC historical temperature (left) and precipitation (right).

Task 2: Conclusions

Geophysical Survey Method for LM's Disposal Cells

For this task, FIU looked into several geophysical survey technologies that would possibly map the subsurface for LM's disposal cell. After reviewing commercially available geophysical survey systems, the ground penetrating radar has the most potential for surveying the disposal cells' subsurface and potentially mapping any subsurface depressions that occur and could occur.

Climate Trend Analysis

This study focused on compiling precipitation and temperature data to parse the historical impact of the forcing climate on the hydrology of DOE-LM sites. The information generated depicts not just the historical time series plots but also future predictions using known climate models. The information generated will help DOE-LM site managers correlate any hydrology issues of the Rifle, Colorado cell.

Task 2: References

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TASK 3: STEM WORKFORCE DEVELOPMENT

Task 3: Introduction

Florida International University (FIU), the largest Hispanic serving research-extensive institution in the continental United States, is one of the nation's leading producers of scientists and engineers from underrepresented groups. In 1995, the U.S. Department of Energy created a unique partnership with FIU to support environmental cleanup technology development, testing and deployment at DOE sites. This partnership spawned a research center at FIU dedicated to environmental R&D. The center, now known as the Applied Research Center, has tackled and helped solve multiple problems at many DOE sites. The DOE-FIU Science and Technology Workforce Development Program is designed to build upon this relationship by creating a pipeline of minority engineers specifically trained and mentored to enter the DOE workforce in technical areas of need. This innovative program was designed to help address DOE's future workforce needs by partnering with academic, government and DOE contractor organizations to mentor future minority scientists and engineers in the research, development, and deployment of new technologies addressing DOE's environmental cleanup challenges.

Task 3: Objectives

Under this project, FIU ARC proposed to expand the current DOE EM CA to include a new project (Project #5) within the already established DOE-FIU Cooperative Agreement to support LM's main goals and mission. It is projected that 2 FIU minority students will be competitively selected to become part of an initial cohort of STEM minority students selected for this program. It is also anticipated that half time of a Post-Doctoral Fellow will be needed to directly support and guide the selected students. To ensure that the students will be trained in pertinent technical areas that directly support LM's goals, FIU will work closely with LM management to define high target, high priority technical topics. Based on past performance, skill sets, and infrastructure at FIU, some of the technical areas of concentration may include long-term monitoring; technology identification, selection, testing/evaluation; big data/data analytics; IT tools for knowledge management and transfer; fate and transport modeling of contaminants of concern; and deactivation & decommissioning (D&D). The selected students will present their research in relevant conferences such as the Waste Management Symposia. The students will also participate in a summer traineeship program at selected LM sites. Students will use the research topics for their dissertation/thesis and publish their research results in appropriate peer-reviewed journals.

Task 3: Results and Discussion

DOE Fellows Recruitment

FIU conducted the fall 2021 recruitment campaign by setting up tables at the Engineering Center, as well as the Physics & Chemistry and Computer Science buildings to promote the DOE Fellows program and distribute flyers. Classrooms were also visited to promote the program and encourage interested and eligible students to apply. Emails were sent to students who signed up at the tables, informing them about the application deadline and providing links to the DOE Fellows website where application instructions and forms could be accessed. Shawn Cameron, a graduate student pursuing a master's degree in Mechanical Engineering, was selected to join the DOE Fellows Class of 2021.

DOE Fellows Induction Ceremony

DOE Fellows presented posters based on their research at the DOE Fellows Poster Exhibition and Competition held on November 9, 2021. Eduardo Rojas presented a poster titled *"Remote Sensing Technologies for Long Term Surveillance of DOE-LM Sites"* during the undergraduate poster session and won 2nd place. Olivia Bustillo presented a poster tilted *"Interaction of Hydroxyapatite and Uranium in Groundwater at the Old Rifle Site"* during the graduate poster session and won 3rd place.

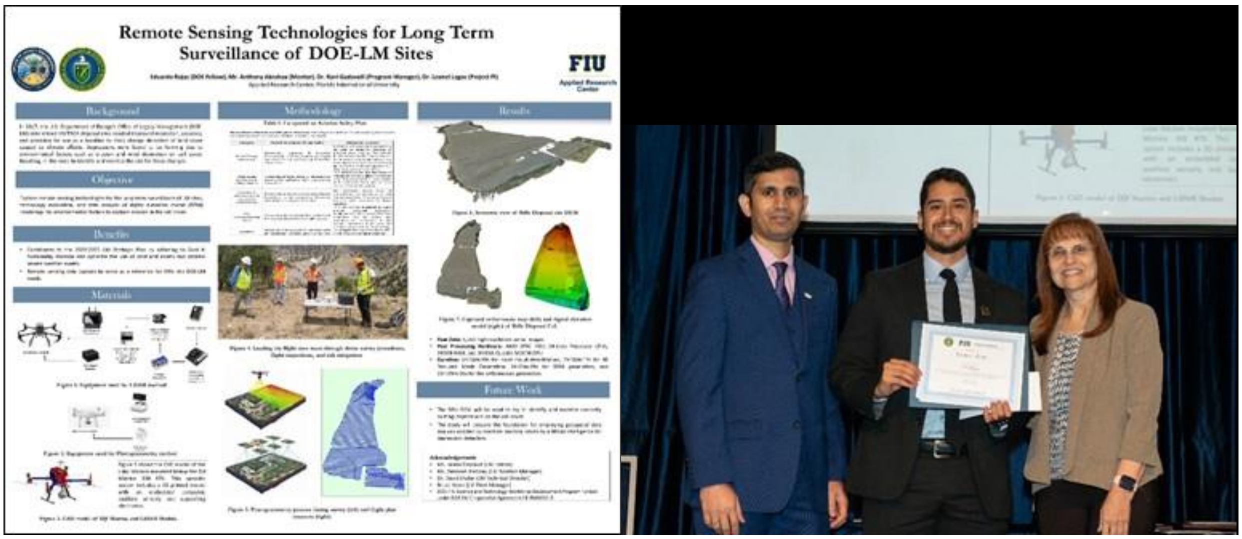

Figure 46. Poster prepared and presented by DOE Fellow Eduardo Rojas during the DOE Fellows Poster Exhibition (left) and Eduardo receiving the award during the induction ceremony (right).

Figure 47. Poster prepared and presented by DOE Fellow Olivia Bustillo during the DOE Fellows Poster Exhibition (left) and Olivia receiving the award during the induction ceremony (right).

Ms. Bustillo's oral presentation titled *"Investigating the Use of Hydroxyapatite as a Permeable Reactive Barrier to Remediate Uranium in Groundwater at the Old Rifle Site"* was presented on November 10, 2021 during the induction ceremony day.

Figure 48. DOE Fellow Olivia Bustillo presenting her work prior to the lab tours on the day of the induction ceremony.

DOE Fellows Eduardo Rojas (Class of 2020) and Shawn Cameron (Class of 2021) were officially inducted into the DOE Fellows program during the annual induction ceremony held on November 10, 2021. The DOE-LM office was represented by Ms. Jalena Dayvault, Site Manager.

Figure 49. DOE Fellows Eduardo Rojas (Class of 2020) and Shawn Cameron (Class of 2021) during the induction ceremony with Drs. Inés Triay and Ravi Gudavalli.

Awards were also presented for the DOE Fellow of the Year and the Mentor of the Year. The DOE Fellow of the Year Award was given to Ms. Olivia Bustillo (DOE Fellow Class of 2019).

Figure 50. DOE Fellow Olivia Bustillo receiving the DOE Fellow of the Year award, pictured with Dr. Inés Triay and Ravi Gudavalli.

DOE Fellows Conference Participation

DOE Fellow Olivia Bustillo attended the 2022 Waste Management Symposia held in Phoenix, Arizona from March 6-10th. At the conference, she presented her research in the form of an oral and poster presentation. Along with this, she had the opportunity to participate in a panel, "*Graduating Students and New Engineers – Wants and Needs- Are Companies Even Listening?*", where she discussed the shift in the workplace culture due to Gen Z becoming the majority within the workforce. All presentations were very well received and incited invigorating discussions about her research as well as the changes required due to the shift in the workforce. After returning from Waste Management, Ms. Bustillo penned her experience at the conference, which was posted on the DOE Fellows website (https://fellows.fiu.edu/my-wm2022-experience-by-olivia-bustillo/).

> Participation in the Waste Management Symposia (#WMSym2022), held in Phoenix, AZ (March 6-10, 2022), was an extraordinary experience. This conference provided a unique platform for discussing safe yet cost-effective solutions regarding the management and disposition of radioactive wastes and the decommissioning of nuclear facilities. This was my third time participating in the conference, yet every year I attend transcends the previous. This conference presents a distinctive opportunity to connect with professionals in the industry across the world and gain further insight into the multifaceted nature of the nuclear field.
>
> This year I was fortunate enough to present my current research, supported by the Department of Energy – Office of Legacy Management (DOE-LM), in a professional session in the form of an oral presentation and in the "Student Posters: The Next Generation – Industry Leaders of

Tomorrow" session in the form of a poster presentation. At Florida International University's Applied Research Center (FIU-ARC), under the mentorship of Dr. Ravi Gudavalli, I am investigating the interaction between hydroxyapatite and uranium to facilitate uranium remediation at the Old Rifle, CO site. These presentations stimulated discussions regarding the applicability of this technology at other DOE sites as well as other interesting bioremediation techniques.

I was also able to participate in a panel, "*Graduating Students and New Engineers – Wants and Needs – Are Companies Even Listening?"*, which explored the true wants and needs of recent graduates and new engineers in the nuclear field. My talk during the panel was focused on what the incoming generation, Gen Z, expects from companies as we are gradually becoming the majority within the workforce. This incited an invigorating conversation between students and professionals in the industry about how there has been a shift in the workplace culture which needs to be addressed. We discussed various approaches on how companies can attract, engage, and retain the younger generation as employees. It was a very empowering experience to be a voice for my peers and to provide insight to those that have been in the field for many years.

In addition, the opportunity for networking at this conference was ample. From attending sessions on different topics, such as women in science, or simply visiting the exhibition booths around the conference, there was always someone new to meet and learn from. The students and professionals that attended the conference were more than happy to share their personal experiences with others, which allowed attendees like myself to gain a fresh perspective of the numerous paths that are available after graduation. The exchange of ideas that occurred during these conversations was invaluable, often leading to personal opportunities such as internships or jobs.

Having been a DOE Fellow since 2019, I have become familiar with the governmental aspect within the nuclear field, staying on the technical and scientific side. However, at this conference I had the chance to speak with people from other branches of the government and industry professionals, which enlightened me to the political and societal aspects that are an integral part of making meaningful progress in this line of work. Waste Management provided the forum, which exposed me to the necessary stakeholder relations, as well as engagement of the community. I came away from this conference with many exciting opportunities and an eagerness to make impactful changes within society using what I have learned. I am very grateful for the DOE-FIU Fellowship that has allowed me to have this experience in the first place, and that has provided opportunities to participate in internships, engage with various sites, and partake in stakeholder meetings. My involvement in these activities has contributed substantially to my growth as a student and a budding professional.

Figure 51. (L to R) Mr. Carmelo Melendez (Director, DOE-LM), Dr. Ravi Gudavalli (DOE Fellows Program Manager & Mentor, FIU-ARC), Dr. David Shafer (Technical Director, DOE-LM), and Ms. Olivia Bustillo (DOE-LM Fellow).

Figure 52. (L to R) Ms. Olivia Bustillo speaking with Mr. Jay Mullis (Acting Associate Principal Deputy Assistant Secretary for Regulatory and Policy Affairs, DOE-EM) at the Speed Networking Event.

Figure 53. FIU's DOE Fellows and staff featuring Nicole Nelson-Jean (Associate Principal Deputy Assistant Secretary for Field Operations, DOE-EM) at Waste Management Symposia 2022.

Figure 54. (R to L) Ms. Olivia Bustillo (DOE-LM Fellow), Dr. Leonel Lagos (FIU-ARC Director of Research & DOE Fellows Program Director) and Dr. Ravi Gudavalli (Mentor, DOE Fellows Program Manager) after Ms. Bustillo's panel presentation (Wants and Needs of Recent Graduates and New Engineers - Are Companies Even Listening?).

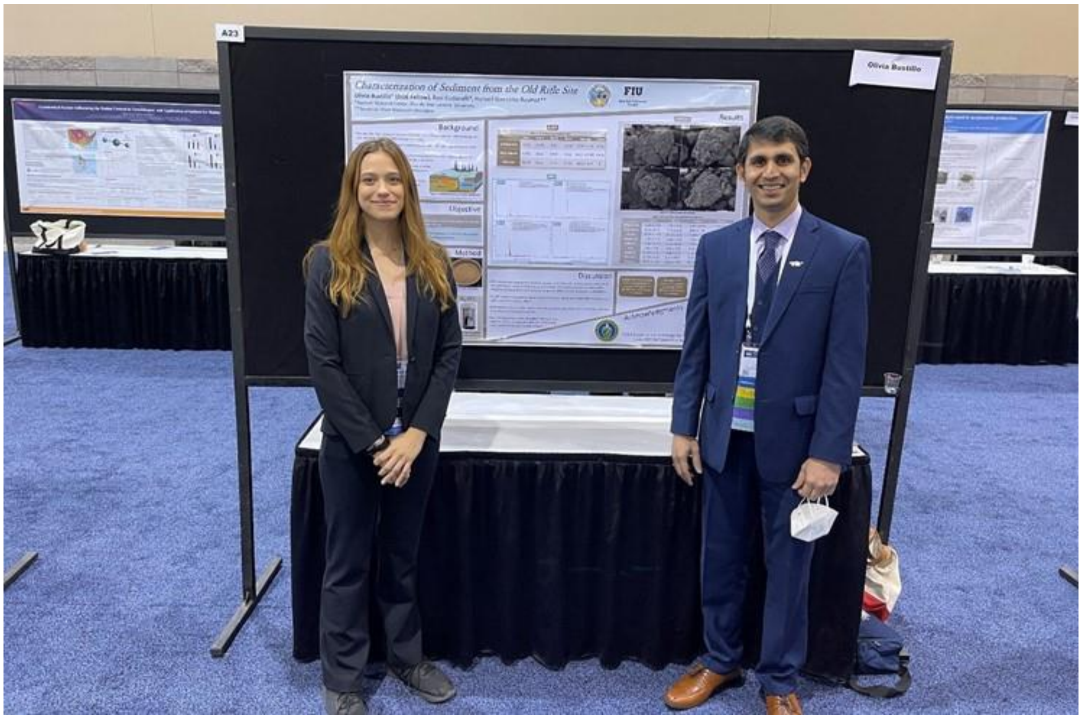

Figure 55. Ms. Olivia Bustillo (DOE-LM Fellow) and Dr. Ravi Gudavalli (Mentor) at the Student Poster Competition WM2022.

DOE Fellows Summer Internship

DOE Fellows Olivia Bustillo and Eduardo Rojas completed their summer 2021 internship reports and submitted them to DOE-LM as a deliverable after receiving approval from Ms. Jalena Dayvault, DOE-LM Program Manager.

DOE Fellow Olivia Bustillo completed her summer 2022 internship with Department of Energy’s Office of Legacy Management Grand Junction office. In the first week, she was able to complete all the required trainings, including those that would grant her access to the Environmental Sciences Laboratory (ESL). During the internship, she conducted experiments in the ESL to support the proof-of-principle hydroxyapatite study at the Moab, UT site for uranium remediation that will occur later in the year. The purpose of these experiments is to establish if the formulation used previously at the Old Rifle site would be suitable for application at Moab, given a different groundwater and sediment chemistry, to also determine if the formula can be simplified by utilizing the pre-existing elements within the groundwater and sediment and finally, to evaluate whether pre-stimulating the sediments with organic carbon prior to the introduction of hydroxyapatite has a positive effect on uranium uptake time. The overall objective of this project is 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.

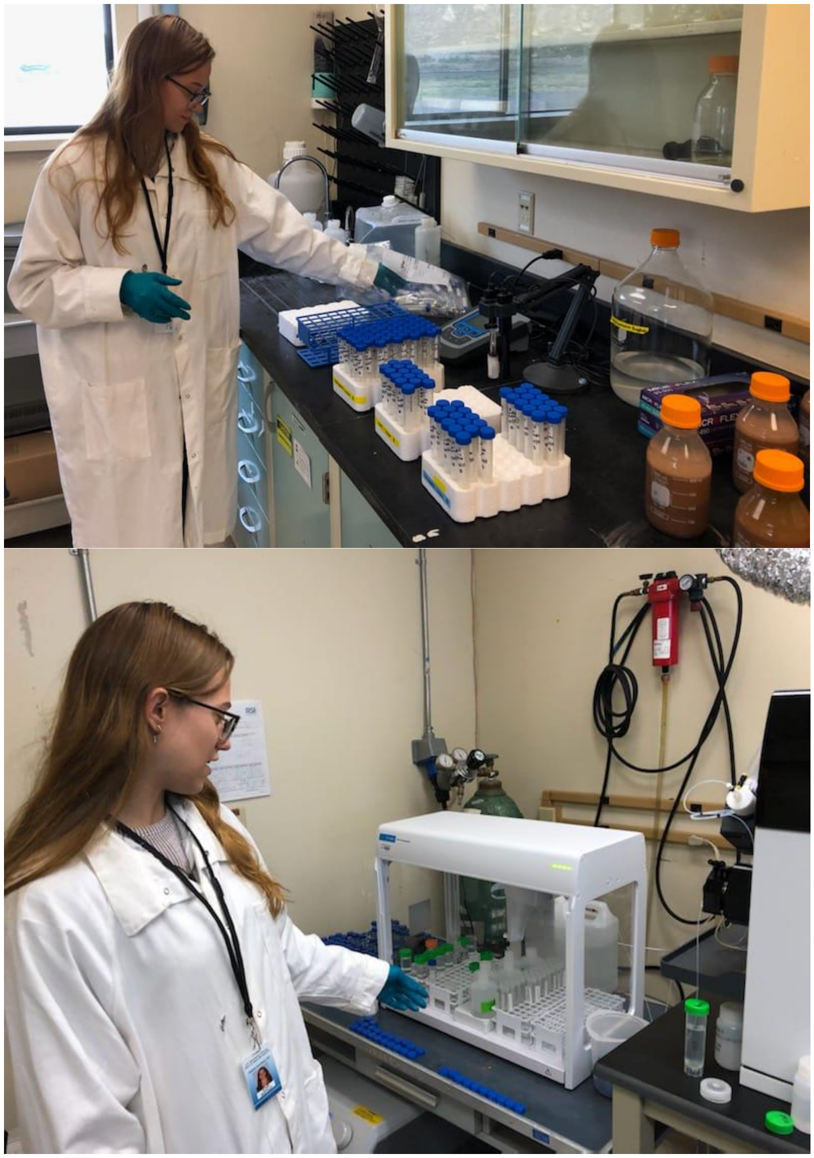

Figure 56. Ms. Olivia Bustillo at ESL preparing and analyzing samples.

DOE-LM Fellow Shawn Cameron participated in the inspection for Rifle, Colorado, and Mexican Hat, Utah Disposal Cell that Legacy Management does annually. Shawn was able to accompany LM inspectors on both trips to check the integrity of the cell and their surrounding conditions.

At the start of the inspection of the Rifle disposal cell, the Fellow was able to view a 2022 inspection field drawing for Rifle location as illustrated in Figure 57. This illustration depicts important land markers such as new observations identified during the previous annual inspection, previous observations currently monitored, basic site features, and site features not required to be inspected. The inspection field drawing along with the 2022 inspection checklist is discussed in a group meeting which is depicted in Figure 57. During the meeting, the scheduled inspectors discussed the issues for the condition of the cell that was previously noticed and what action needs to be taken to account for each issue. Once the protocol meeting is accomplished, the scheduled inspectors split into groups to traverse the Rifle cell to assess its integrity depicted in the 2022 inspection checklist (Figure 58). LM Fellows, Shawn Cameron and Olivia Bustillo, along with LM's Jalena Dayvault and mentor Anthony Abrahao, began the inspection at the toe of the cell's rip rap rock layer. The main objective of the inspection is to check for evidence of erosion, settling, slumping rock degradation, vegetation, and bio-intrusion. Keeping a lookout for these abnormalities, nothing was observed that would cause the disposal cell to function outside of its normal operation.

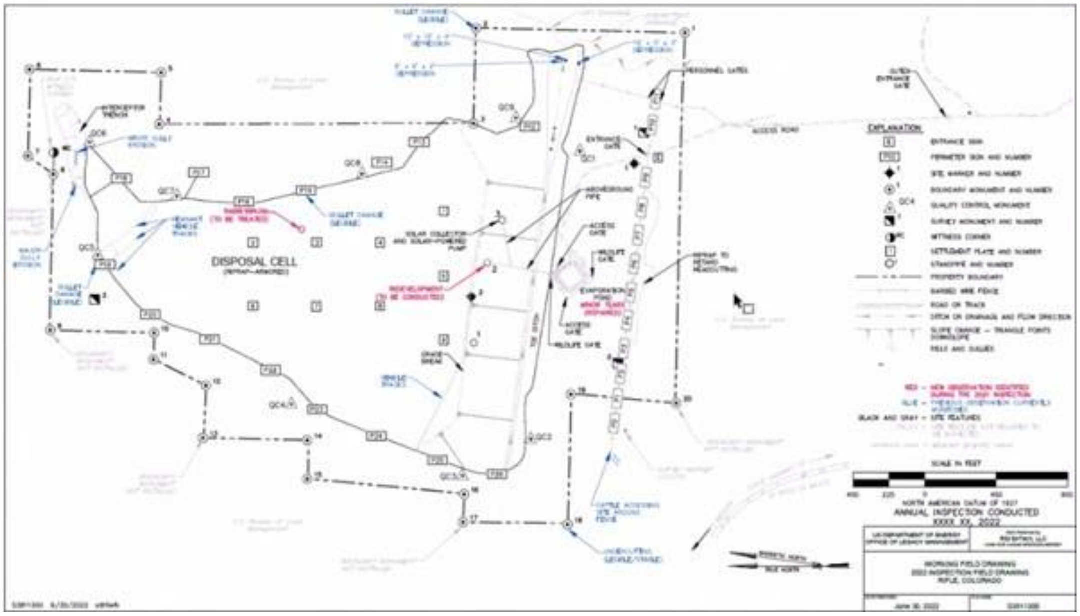

Figure 57. 2022 Inspection Field Drawing - Rifle, Colorado.

Figure 58. Group Meeting for the 2022 Inspection Checklist.

Figure 59. DOE Fellows Shawn Cameron and Olivia Bustillo performing Rifle Disposal Cell inspection.

Noticeable cobbles of cracked rocks were seen among the top layer of the cell which is a common occurrence and not an issue since the rock degradation is not in a bundle but instead is occurring individually. The different stages in rock degradation are seen in Figure 60. Patterns of the weather conditions can cause the rocks to crumble to the point that the rocks will turn into dust. This dust formation can be seen in Figure 60 where the condition of the rock is extremely eroded.

Figure 60. Stages of rock degradation.

In addition to the Rifle, Colorado inspection, Shawn also took part in the annual inspection of the Mexican Hat disposal cell location. The inspection of the Mexican Hat location did have similar protocols related to the Rifle location such as an initial group meeting depicted in Figure 61 to discuss the 2022 annual checklist of the cell. In addition, an inspection field drawing of the cell was given and can be seen in Figure 62.

Compared to the field drawing of the Rifle site, the Mexican Hat site does have different features that needs to be accessed such as the surrounding gates and seep flow. Figure 63 shows the DOE Fellow inspecting the surrounding fence to check for any damage to the fence or damaged site surveillance features that could potentially affect the disposal cell's integrity or security. Figure 64 and Figure 65 show 2 of the seeps that surround the cell. The seep conditions are monitored to ensure that significant increase in flows does not occur. Annual seep flow monitoring is done by observation, photographic documentation, and description of the total seven seeps.

Figure 61. Group Meeting for the 2022 Mexican Hat inspection checklist.

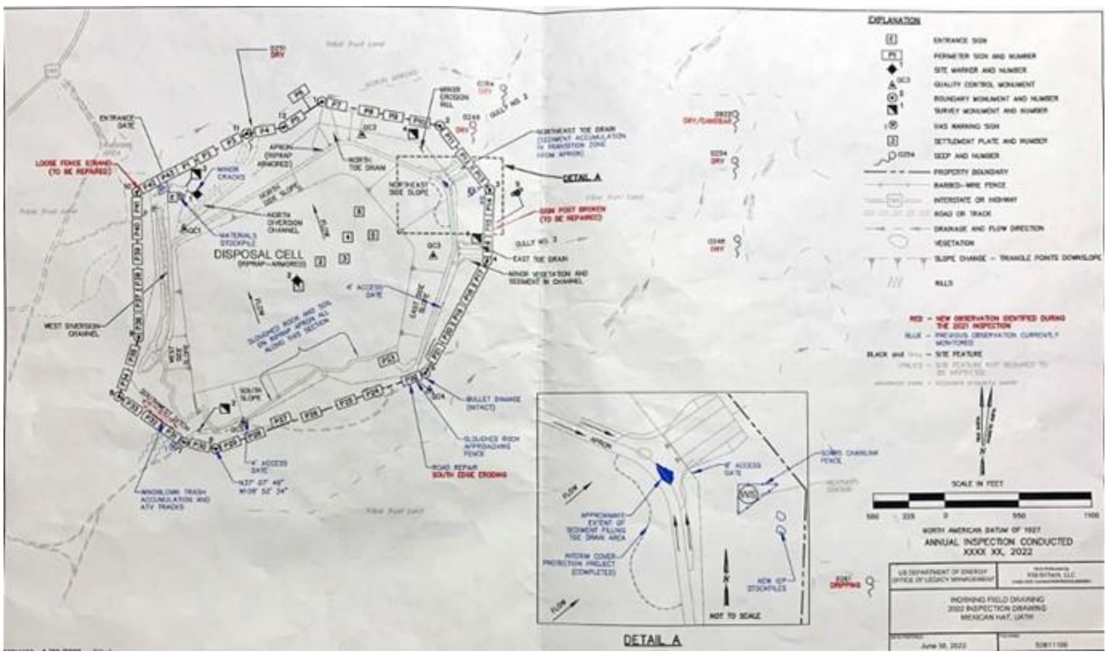

Figure 62. 2022 Inspection field drawing Mexican Hat, Utah.

Figure 63. Shawn Cameron and Pieter Hazenberg inspecting the security fence.

Figure 64. First seep sighting.

Figure 65. Second seep sighting.

DOE Fellow Shawn also took measurements of the various rock sizes of the two-disposal cells. The purpose of this is the future development of the Fellows' robotic platform drive train. Figure 66 and Figure 67 show the different features of the rocks that are used for each disposal cell. Different shapes of rock are used with each cell. This differentiation needs to be accounted for, for the platform development.

Figure 66. Mexican Hat, Utah rock measurements.

Figure 67. Rifle, Colorado rock measurements.

DOE Fellows Other Activities

DOE Fellow Olivia Bustillo 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. She also had the opportunity to meet with Dr. Ken Williams to set up her experiments and review the progress on her internship experiments. Olivia also traveled to Moab, UT to participate in a tour of the site and collect groundwater from the UPD22 injection well that will be used in her experiments. 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, Ken Williams.

Figure 68. Moab site tour, sample collection and tracer test.

DOE Fellow Olivia Bustillo was able to attend the DOE-LM All Hands meeting in St. Louis, Missouri. The week-long meeting consisted of various leadership trainings, a tour of the Weldon Spring, MO site, and a variety of team-building exercises. Through this meeting, Ms. Bustillo was able to gain a wealth of information that she can apply to her own career and future leadership positions. Additionally, Ms. Bustillo took part in the IAEA (International Atomic Energy Agency) 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 collaboration across different entities. She was also able to submit her professional abstract for Waste Management 2023.

Figure 69. DOE Fellow Olivia Bustillo at DOE-LM All Hands Meeting in St. Louis, Missouri

Figure 70. DOE Fellow Olivia Bustillo with IAEA Delegtion.

DOE Fellows participated in the Annual FIU Research Review held on 9/27 - 9/28 with DOE-HQ and site POCs. Additionally, DOE Fellows Olivia and Shawn presented their research accomplishments. The titles of their presentations are as below:

- Hydroxyapatite Injection for Sequestering Uranium (U) in Groundwater - Olivia Bustillo
- Climate Resiliency and Long-Term Surveillance of DOE-LM Disposal Cells - Shawn Cameron

Task 3: Conclusion

This project is successfully meeting its objectives by providing research training and mentoring for students from underrepresented groups on environmental problems at DOE LM.

ACKNOWLEDGEMENTS

Funding for this research was provided by U.S. DOE Cooperative Agreement #DE-EM0005213. Office of Legacy Management provided the funding for FIU Project 5 this year. During this period of performance, three (3) new DOE LM Fellows were hired and participated in the new pilot program between DOE LM and FIU. The FIU researchers and STEM students are grateful to DOE LM for initiating this new program at FIU.

APPENDIX

The following documents are available at the DOE Research website for the Cooperative Agreement between the U.S. Department of Energy Office of Environmental Management and the Applied Research Center at Florida International University:
https://doeresearch.fiu.edu/SitePages/Welcome.aspx

FIU Year 2 Annual Research Review Presentations:

1. FIU Research Review - Project 1
2. FIU Research Review - Project 2
3. FIU Research Review - Project 3 – D&D
4. FIU Research Review - Project 3 – IT ML
5. FIU Research Review - Project 4 & 5
6. FIU Research Review - Project 4 - DOE Fellow Aubrey Litzinger
7. FIU Research Review - Project 4 - DOE Fellow Aurelien Meray
8. FIU Research Review - Project 4 - DOE Fellow Joel Adams
9. FIU Research Review - Project 4 - DOE Fellow Mariah Doughman
10. FIU Research Review - Project 4 - DOE Fellow Nicholas Espinal
11. FIU Research Review - Project 4 - DOE Fellow Philip Moore
12. FIU Research Review - Project 5 - DOE Fellow Olivia Bustillo
13. FIU Research Review - Project 5 - DOE Fellow Shawn Cameron
14. FIU Research Review - Wrap Up - Project 1
15. FIU Research Review - Wrap Up - Project 2
16. FIU Research Review - Wrap Up - Project 3 – D&D
17. FIU Research Review - Wrap Up - Project 3 – IT ML
18. FIU Research Review - Wrap Up - Project 4
19. FIU Research Review - Wrap Up - Project 5