YEAR-END TECHNICAL REPORT
September 29, 2020 to September 28, 2021

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, 2020 to September 28, 2021 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-2020-800012997-04b-009

Project 2: Environmental Remediation Science and Technology
Document number: FIU-ARC-2020-800013918-04b-004

Project 3: Waste and D&D Engineering and Technology Development
Document number: FIU-ARC-2020-800013919-04b-008

Project 4: DOE-FIU Science & Technology Workforce Development Initiative
Document number: FIU-ARC-2020-800013920-04b-017

Project 5: Long-Term Stewardship of Environmental Remedies: Contaminated Soils and Water and STEM Workforce Development
Document number: FIU-ARC-2020-800013922-04b-007

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.

The DOE LM Fellows Program inducted two (2) minority FIU STEM students during an induction ceremony held in November 2019. DOE LM officials, Mr. Carmelo Melendez, Dr. David Shaffer and Ms. Jalena Dayvault, attended the ceremony. Another FIU STEM student was introduced during a virtual ceremony held in November 2020.

The DOE LM Fellows have been engaged 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.

MAJOR ACCOMPLISHMENTS

Major accomplishments of this program to date include:

- Three 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 and virtually in November 2020.
- Completed the characterization of hydroxyapatite via XRD, SEM-EDS/XRF instrument for elemental composition.
- Characterized soil samples obtained from the Old-Rifle site via XRD, SEM-EDS and BET analyzer, accomplishing Milestone 2020-P5-M5. A report on the soil characterization of the Old-Rifle site sediment was submitted.
- Modeled a 3D-printed mount to attach the mid-range high-resolution imaging LiDAR (Ouster OS1-32) and its embedded computer onto FIU's high payload hexacopter (DJI S1000).
- Submitted a Draft Summary Document for the LM Needs for Remote Sensing Data Collection, accomplishing Deliverable 2020-P5-D3.
- DOE Fellows Olivia Bustillo and Eduardo travelled to Colorado in October to visit DOE-LM sites.
- FIU formally introduced DOE LM Fellow, Eduardo Rojas, during a virtual introduction ceremony held on November 19, 2020.
- DOE Fellow completed a study plan on Remote Sensing Technologies for LM Sites.
- The two DOE-LM Fellows attended the WM2021 Symposia virtually and presented posters based on their research along with 5-minute pre-recorded videos describing their posters during the WM2021 student poster competition.
- Two DOE Fellows conducted 8-week internships at LM sites in Colorado. Both LM Fellows completed a Summer Internship Plan in April 2021, made changes to the plan, and associated travel arrangements as requested by DOE LM. The DOE Fellows also deployed a drone and collected photogrammetry and LiDAR data, as well as soil/water samples during their site visits.
- DOE Fellows, Olivia Bustillo and Eduardo Rojas, graduated with Bachelor’s degrees in Environmental Engineering and Mechanical Engineering respectively.
- DOE Fellows prepared and presented their research accomplishments during the FIU Program Review held on September 14-15, 2021.

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

Task 1: Introduction

The Office of Legacy Management (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. 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 proved that injection of apatite into groundwater have shown 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 maximum contaminant limit (MCL). Apatite is a versatile tool regarding the immobilization of uranium, as it can potentially be used for 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 hydroxyapatite (HA) Permeable Reactive Barrier to remediate uranium at the Old Rifle site in Colorado (Szecsody et al. 2016). While this process has proved to be effective, a better understanding of the uranium removal mechanisms behind the interaction is required. The site is currently being reused by housing an operations and maintenance facility, as well as conducting biogeochemical research on constituents of concern.

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 on 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 pH, 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 and phosphate (PO_4^-) solutions. Phases two and three studies the interaction of uranium with apatite during and after formation of apatite and will study the mechanisms behind the interaction/sequestration. The mechanisms behind the interaction/sequestration of uranium and apatite could include adsorption of uranium onto apatite, precipitation of U-phosphate surface phases, phosphate precipitates coating uranium surface phases, or surface complexation. This year, the research has focused solely on the first phase of the experiment including the synthesis, kinetics, and characterization of hydroxyapatite and characterization of soil collected from Old Rifle Site.

Task 1: Methodology

Materials

This study utilized a solution containing sodium citrate, calcium chloride, and a phosphate solution. The phosphate solutions used in the experiment include trisodium phosphate, ammonium dihydrogen phosphate, disodium phosphate, and monosodium phosphate.

Approximately 1 lb., 5 oz. of surface level sediment samples were collected at the Old Rifle Site, CO from four different locations, as shown in Figure 1, and shipped to FIU to be used for the characterization studies.

Hydroxyapatite Synthesis

Synthesis of hydroxyapatite experiments consisted of creating stock solutions of calcium, phosphate, and citrate. Different Ca:Citrate:P ratios (Figure 2) were created to determine the optimum stoichiometric ratio for maximum yield of hydroxyapatite. Since HA takes between 3.5 to 5.3 weeks to form, the samples were monitored for 6 weeks before being prepared for analysis (Zsecsody et al. 2017). 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. Aqueous samples were diluted with 800 µL of 2% nitric acid to preserve the samples prior to analysis. At the end of 6 weeks, remaining supernatant was removed and samples were placed in an oven at 30°C until drying was complete. Dried solids were stored in small scintillation vials (Figure 3).

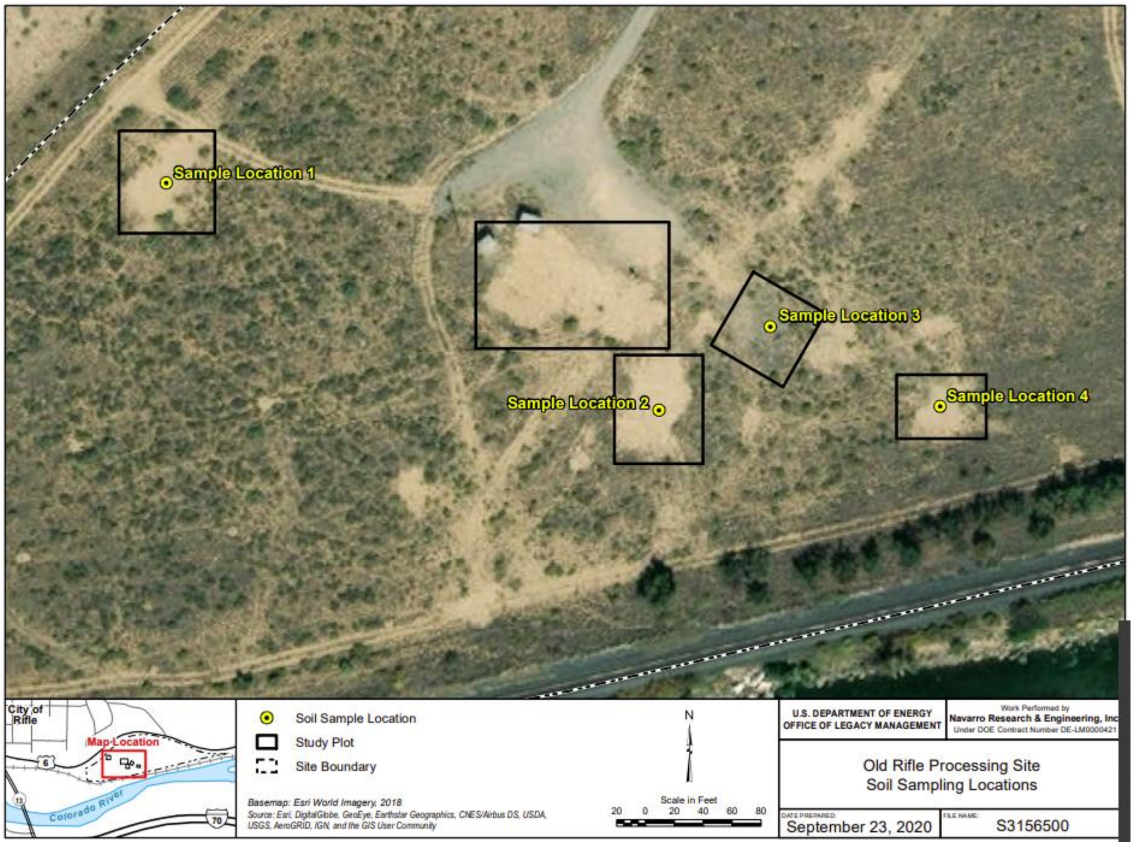

Figure 1. Map showing locations where sediment samples were collected at Old Rifle site.

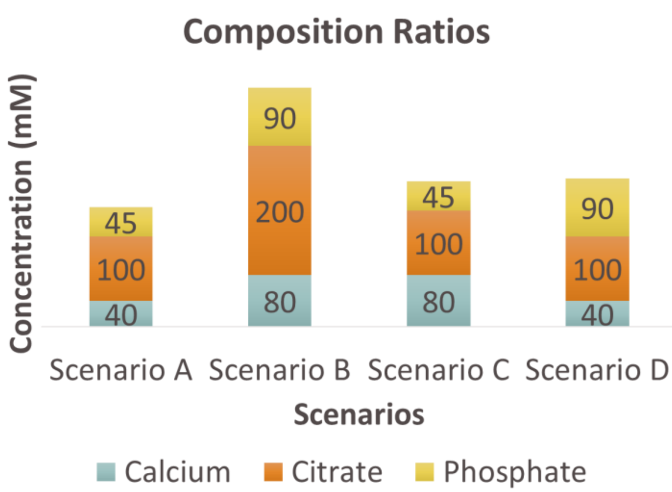

Figure 2. Composition of calcium, citrate and phosphate ratios tested during synthesis.

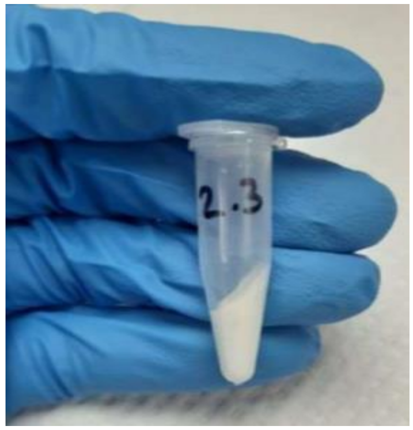

Figure 3. Dried HA precipitate formed during systhesis.

Characterization Studies

Prior to the characterization studies, the sediment samples were air dried and sieved through a 2-mm sieve (Figure 4) to remove gravel and larger sediment particles from the samples, since particles bigger than 2-mm are classified as rocks and will not be used in future experiments.

Figure 4. Sediment sieved through 2-mm sieve.

XRD analysis

A Bruker D2 PHASER XRD instrument (Figure 5) was used for characterization of the hydroxyapatite solids that formed throughout the experiments and sediment samples collected at Old Rifle Site. Sample were individually packed flat on to a sample holder (Figure 6 and 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.

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 - Figure 9). 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 soil 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). Hydroxyapatite samples will also be coated with gold in the future to obtain higher quality images.

Figure 5. Bruker D2 PHASER XRD instrument.

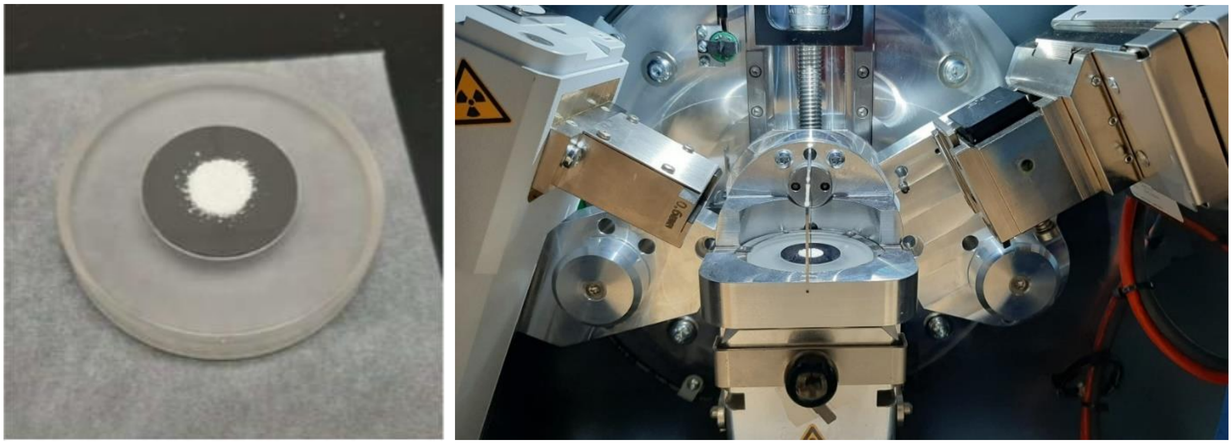

Figure 6. Hydroxyapatite powder on sample holder preprared for XRD analysis.

Figure 7. Plots 3 and 4 (left to right) sediment loaded onto sample holder prior to XRD analysis.

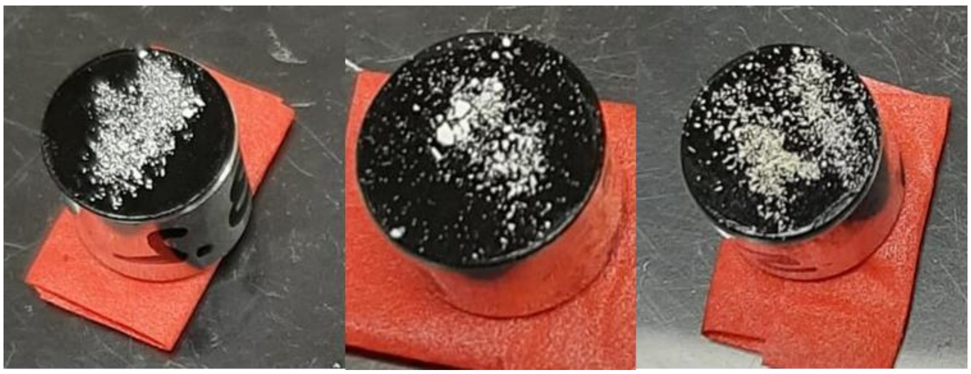

Figure 8. Dried HA Precipitate Prepared for SEM Analysis.

Figure 9. Instrument used to gold coat samples (left) and gold coated sediment samples (right).

Task 1: Results and Discussions

Hydroxyapatite Synthesis, Kinetics and Characterization Studies:

Hydroxyapatite formation studies were previously conducted in triplicates, to ensure reproducibility, with varying ratios of citrate, calcium and phosphate solution as shown in Figure 2. Samples were allowed to equilibrate for 6 weeks to complete precipitation of HA before preparing the samples for characterization. Throughout 6 weeks, pH was measured and aliquots were taken at regular intervals and stored in the fridge for future analysis via ICP-OES to measure the concentrations of total Ca and P. This data will be used to quantify the change in elemental concentration during the experiment. Scenarios 2 and 3 began to form an amorphous solid within the first week of the experiment before crystalline solids began forming (Figure 10 - Figure 11). Scenarios 4 and 5 (not pictured) also followed a similar trend of formation. After the 6 week time period, samples were centrifuged, the supernatant extracted, and the samples set to dry. Once the drying was complete, samples were analyzed through XRD and SEM-EDS instruments. The average total precipitate yielded was calculated for each scenario, as shown in Table 1. Scenario 3 yielded the highest amount, about 0.3 grams, while scenario 5 yielded the second highest of approximately 0.2 grams. Scenario 4 yielded the lowest amount of precipitate compared to the others (Table 1).

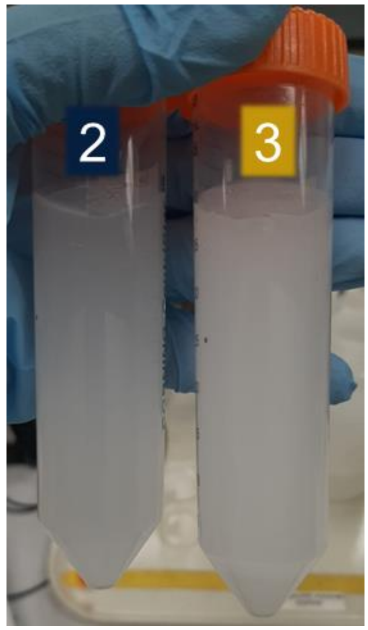

Figure 10. Apatite samples after week 1, showing onlt Scenario 2 and 3.

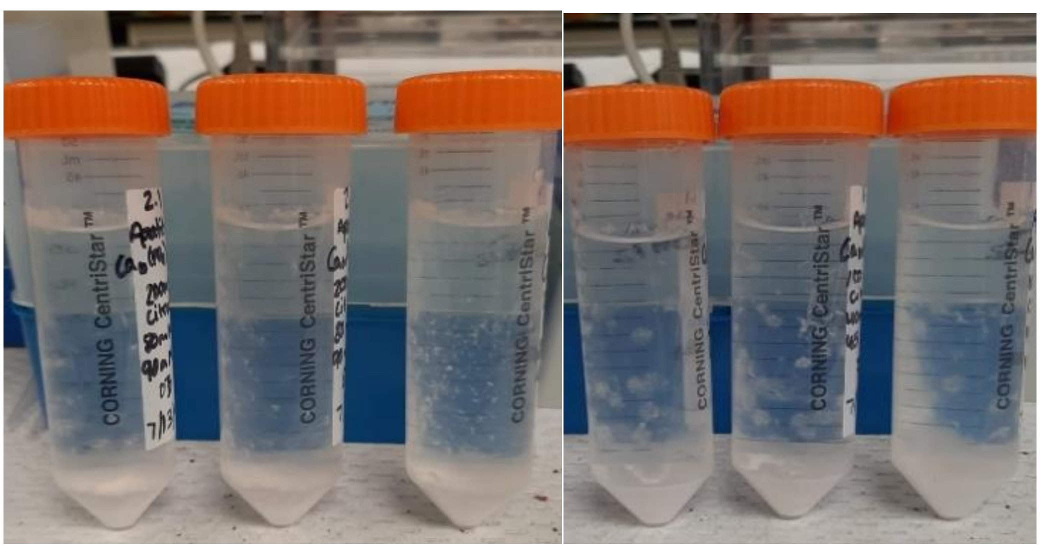

Figure 11. Scenario 2 and 3 apatite samples after Week 4 (left to right).

Table 1. Average total precipitate yield for each scenario

	Scenario 2	Scenario 3	Scenario 4	Scenario 5
Average Total Precipitate (g)	0.1083 ± 0.015	0.2993 ± 0.060	0.0393 ± 0.006	0.1845 ± 0.005

Dried apatite samples were characterized via XRD and observed patterns were matched with a known database of minerals to estimate the mineral composition to confirm the formation of HA. The synthesized samples matched to a hydroxyapatite Powder Diffraction File™ (PDF®) (01-074-0566) that was found during literature review. Figure 12 through Figure 15 show the XRD data obtained for Scenarios 2 - 5 matching with the hydroxyapatite PDF pattern. Even though all the XRD patterns matched with the PDF, Scenario 4 matched well with high intensity XRD while Scenarios 3 & 5 resulted in more precipitate. The high intensity XRD patterns obtained from the instrument for Scenario 4 were possibly due to impurities in the sample, so that sample was washed twice with deionized water, dried, and then analyzed again for comparison. The intensity remained about three times higher than the other scenarios indicating a different crystal size. XRD data from the HA analysis support that the samples had formed hydroxyapatite.

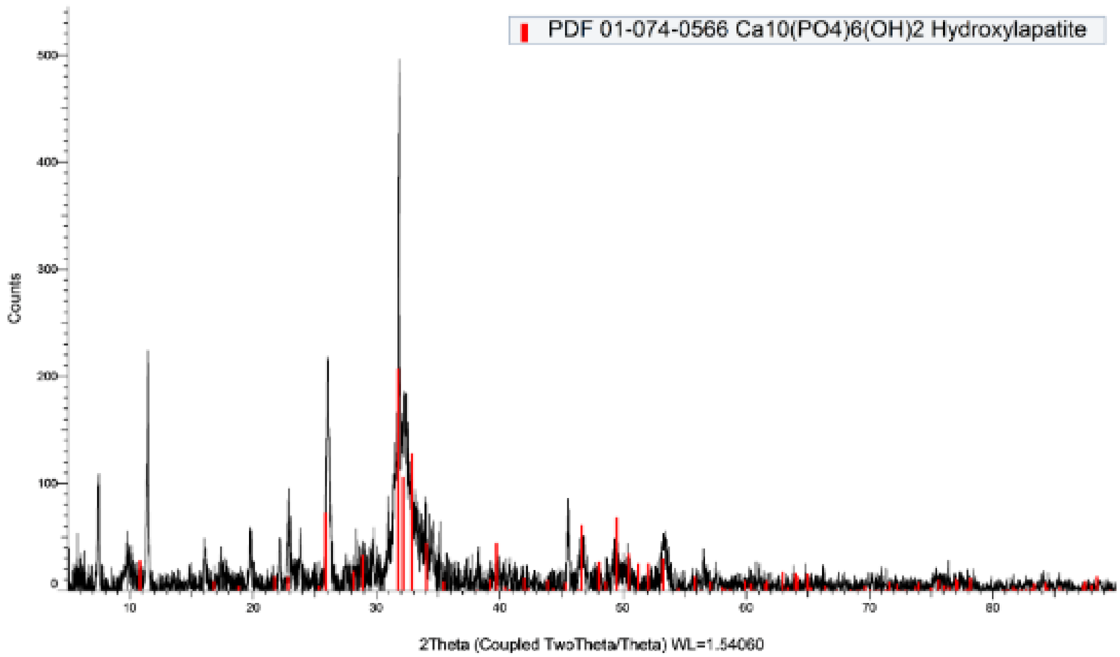

Figure 12. Scenario 2 XRD pattern matching with hydroxyapatite PDF.

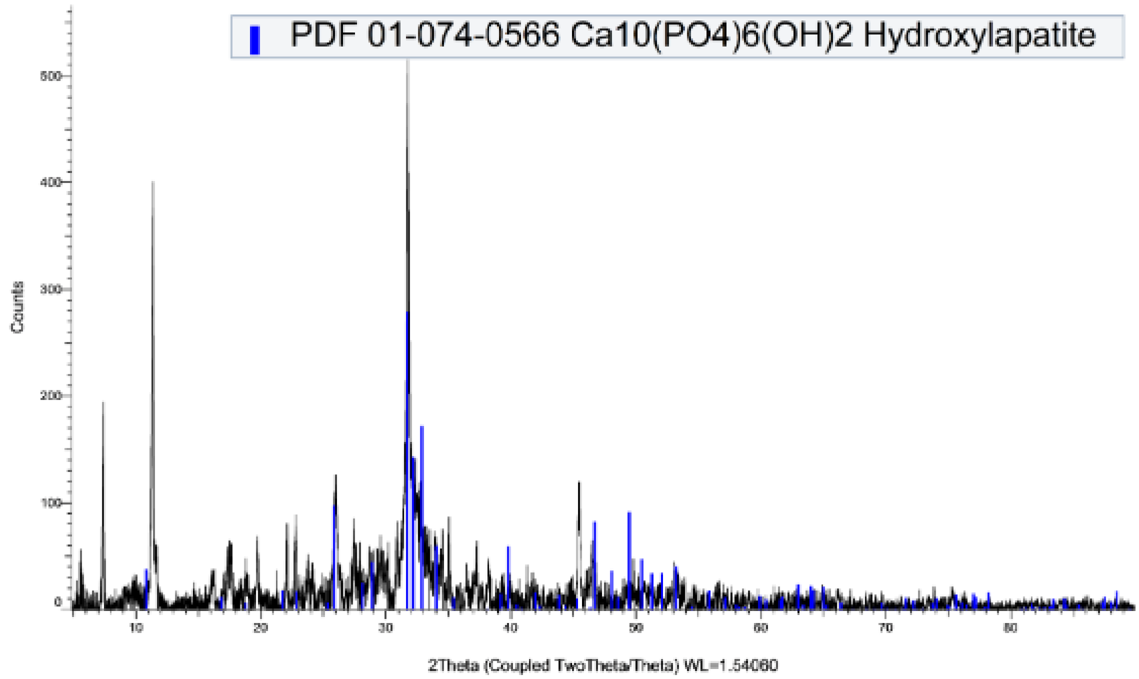

Figure 13. Scenario 3 XRD pattern matching with hydroxyapatite PDF.

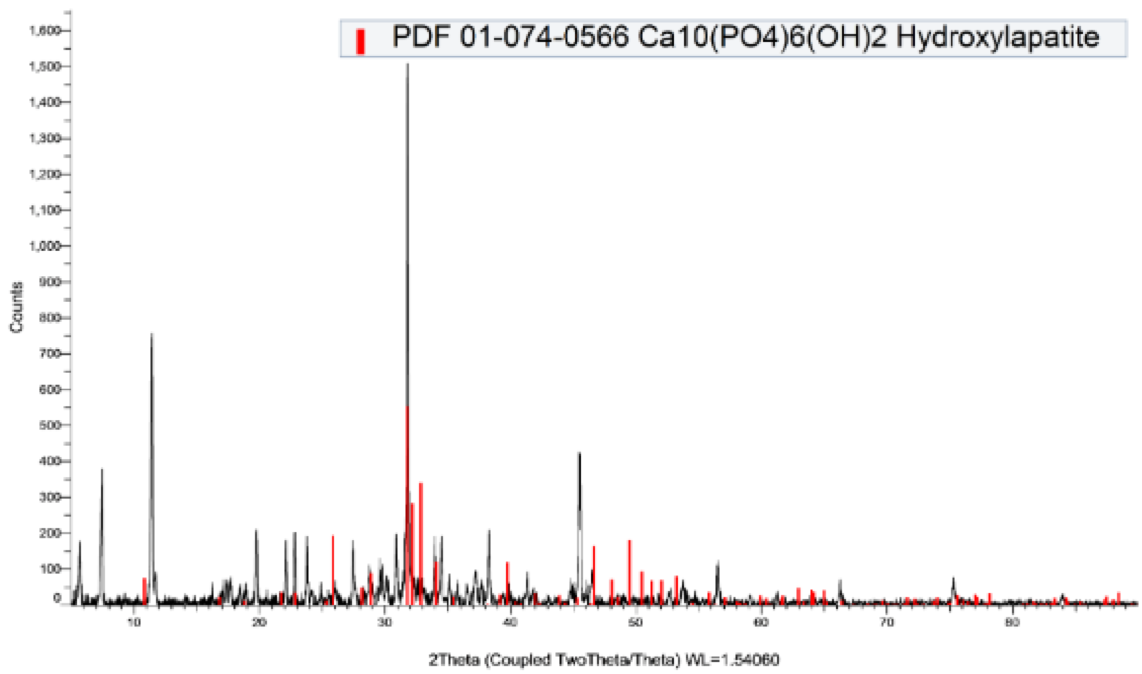

Figure 14. Scenario 4 XRD pattern matching with hydroxyapatite PDF.

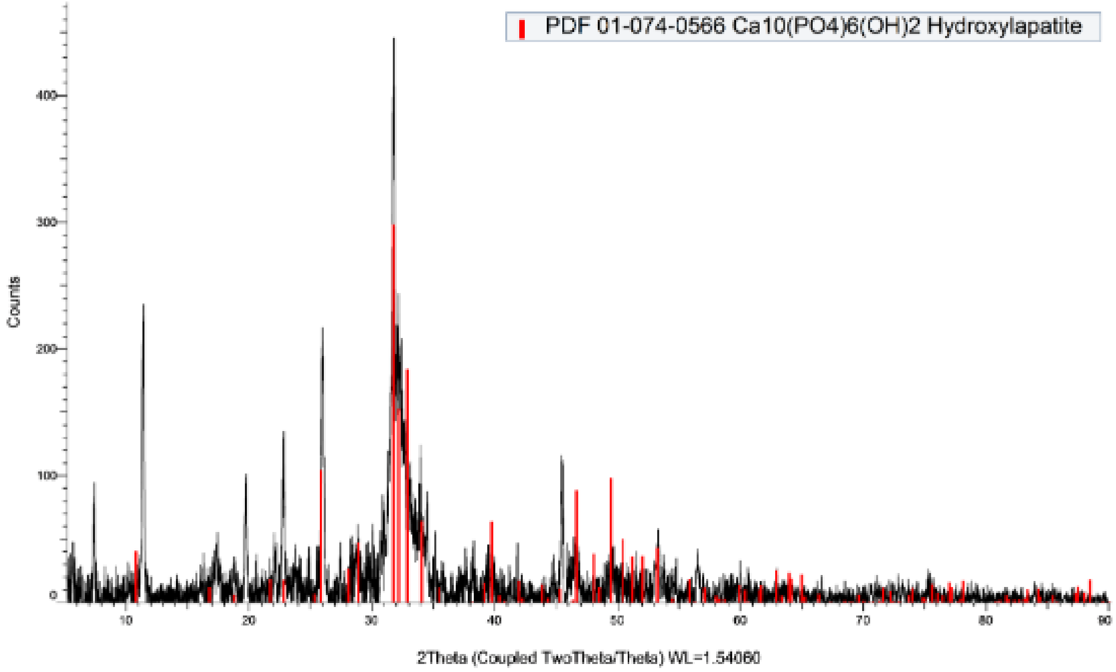

Figure 15. Scenario 5 XRD pattern matching with hydroxyapatite PDF.

The dried hydroxyapatite precipitate was analyzed via SEM-EDS to characterize the samples. Initially, data showed high amounts of carbon along with some other trace elements, which was unexpected for the given samples. Therefore, the samples were washed twice with deionized water and dried in the oven at 30°C to remove any impurities. When washing, a small amount of precipitate and DI water was placed in a microcentrifuge tube and mixed well. Following that, the samples were centrifuged, and the supernatant was removed thus removing impurities. This process was repeated twice to ensure precipitates are clean and free of impurities then the samples were set to dry. The samples were then re-analyzed to determine if the carbon is from the tape being used to hold the sample on the stud, and to also see if the analysis yields the same results. The analysis identified all elements present and the mass percentage of each. The prominent elements identified via EDS included oxygen, calcium, and phosphorus with trace amounts of sodium found, as shown in **Error! Reference source not found.**. Sodium 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 (Equations 1 and 2) and compared to the theoretical estimated value. The calculations that were performed are displayed within and under Table 2, which demonstrates an example computation. 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 3 below. The similarity indicates that impurities were removed after washing.

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

Eq. 1

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

Eq. 2

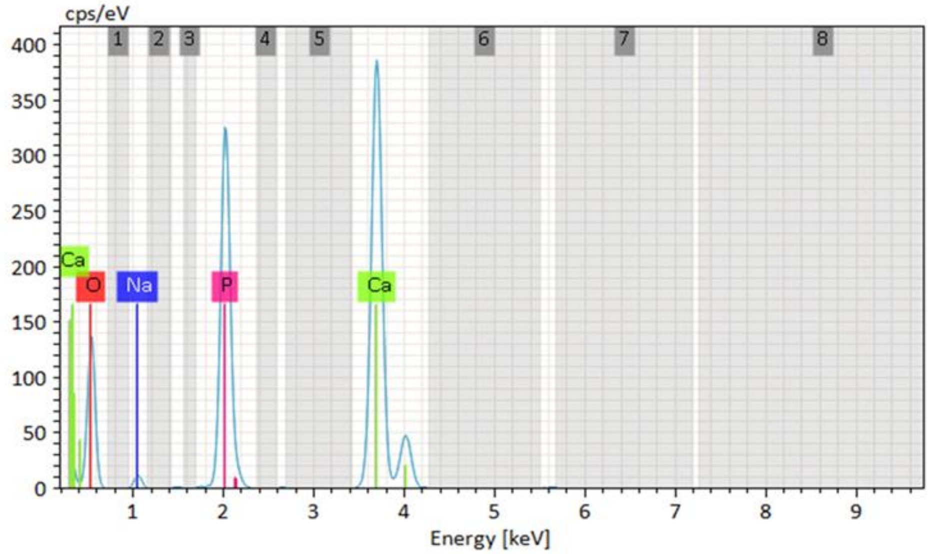

Figure 16. EDS element spectrum obtained for apatite formed during synthesis.

Table 2. Atomic ratio example computation

	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 3. Calculated vs theoretical atomic ratio for all scenarios

Atomic Ratio					
Element	**Theoretical**	**Scen. 2**	**Scen. 3**	**Scen. 4**	**Scen. 5**
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

The SEM analysis was conducted at FIU's Florida Center for Analytical Electron Microscopy (FCAEM) facility to obtain clear images that could show the structure of the HA precipitate. The structures found in Figure 17 show a crystalline structure for scenarios 2, 4, and 5 while scenario 3 displays more flakes than crystals. These images will be used for comparison in future experiments after the introduction of uranium to note any changes.

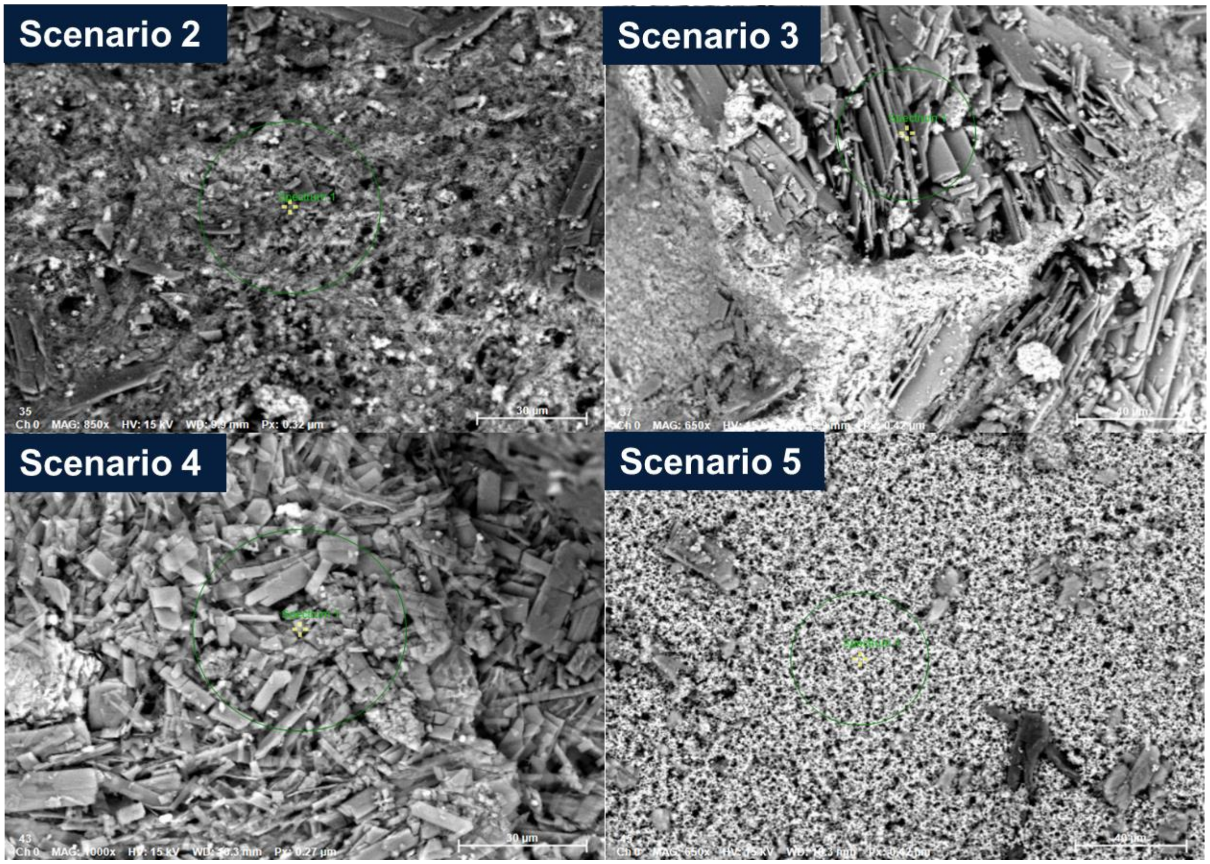

Figure 17. SEM Images of hydroxyapatite formed during synthesis via different scenarios.

Additionally, to conduct ICP-OES analysis, FIU prepared aliquots collected during the synthesis of hydroxyapatite in phase one of this study. Aliquots (200 µL) from each sample were collected three times a week for the duration of the experiment and stored in the refrigerator. Aqueous samples were analyzed via ICP-OES to determine the concentration of total calcium and phosphorus over time for each scenario tested. There were four scenarios studied during the kinetics experiment to establish the optimum stoichiometric ratio of calcium to citrate to phosphate. Since the samples have very high concentrations, establishing a proper calibration curve so that the instrument can measure the samples accurately is necessary. A calibration curve for calcium ranging from 0.5 - 10 ppm and for phosphorus from 0.5 - 20 ppm was established prior to analysis. Calibration standards were prepared by diluting two stock solutions containing 1,000 ppm of Ca and P with 2% HNO_3 to obtain 50 mL solutions. The stock and HNO_3 volumes used to create each calibration standard are listed in Table 4. Based on the initial concentrations used to synthesize apatite, aliquots were diluted according to the information provided in Table 5 to reduce the amount of Ca and P in the samples to values that were within the calibration range. 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 off the previous weeks' analysis.

It was observed that the aliquots had begun to form a precipitate while in storage. This could negatively affect the data obtained since the samples would no longer be representative of the concentration at the time they were collected due to the reaction continuing. Due to the precipitation, the samples were centrifuged, and the supernatant was removed to prepare dilutions for analysis. The analysis produced unreliable data, which confirms that the precipitation that occurred during storage interfered with the intended analysis. Therefore, hydroxyapatite was resynthesized for all four scenarios to obtain valid data for HA formation kinetics. 200 µL aliquots were taken three times a week and immediately diluted with 800 µL of 2% HNO_3 and analyzed via ICP-OES on a weekly basis. Data was processed to visualize the formation over time as seen in Figure 18 - Figure 19.

Table 4. Ca and P calibration standards used for ICP-OES calibration

Ca Conc. (ppm)	Volume of 1000 ppm stock	P Conc. (ppm)	Volume of 1000 ppm stock	Volume of 2% HNO_3
0.5	0.025	0.5	0.025	49.950
1.0	0.05	1.0	0.05	49.900
2.5	0.125			49.875
5.0	0.25	5.0	0.25	49.500
7.5	0.375			49.625
10	0.5	10	0.5	49.000
		15	0.75	49.250
		20	1.0	49.000

Table 5. Dilution factors for week 1 through 4.

	Week 1	Week 2	Week 3	Week 4
Scen 2	400	300	300	200
Scen 3	400	400	300	300
Scen 4	400	400	400	400
Scen 5	400	300	300	200

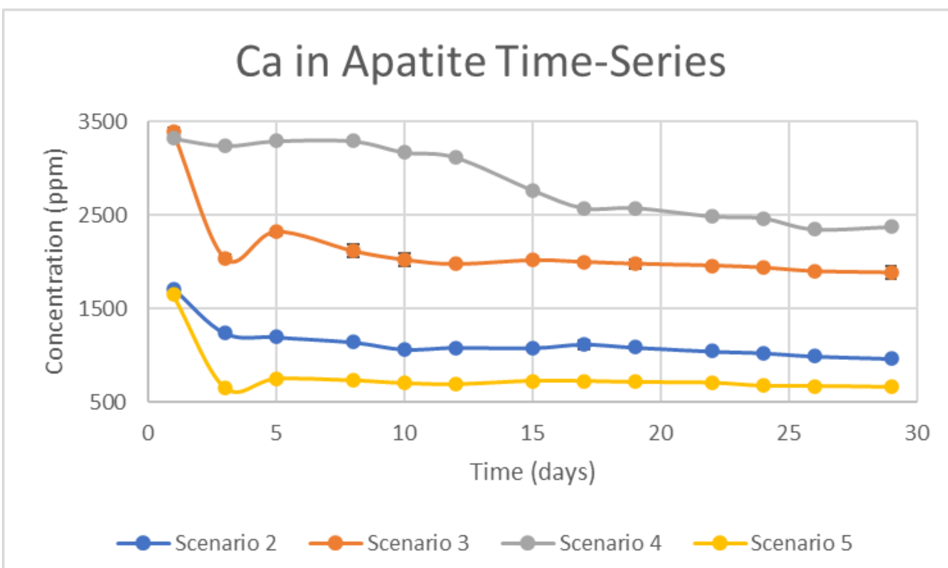

Figure 18. Calcium concentrations during apatite formation.

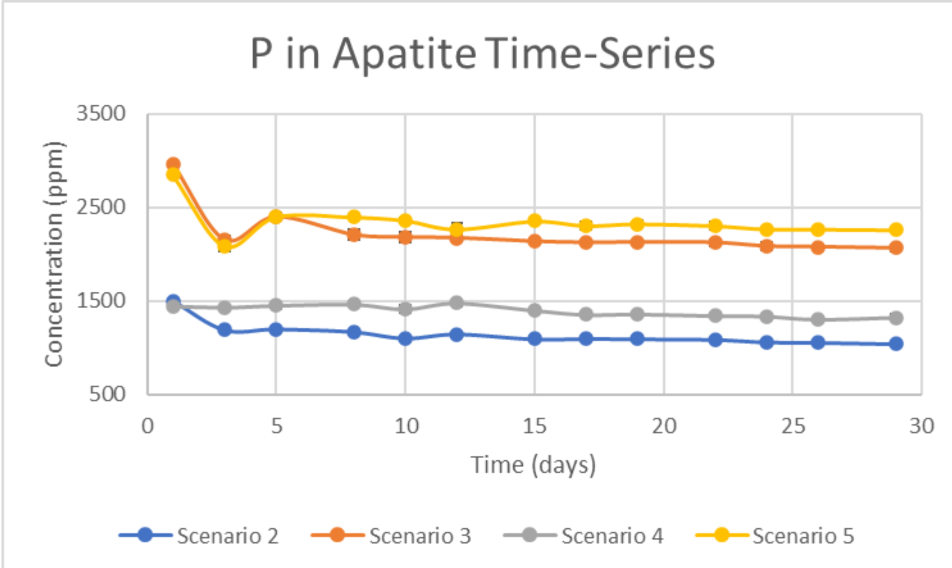

Figure 19. Phosphorus concentrations during apatite formation.

Sediment Characterization

During the initial analysis via SEM, samples were not gold coated, and instead the images were collected in parallel with EDS data. However, the images collected were not clear and the structure of the sediment could not be easily viewed. Therefore, the procedure was altered in order to conduct these analyses separately. Once the sediment was gold coated, the images obtained were much clearer and the structure could be identified. Images were taken at varying magnifications and at different locations on the sample (Figure 20). Overall, SEM analysis provided higher magnification images of the particles and sets a baseline of what the sediment structure is prior to any manipulation. In the next phases of apatite inclusion studies for uranium (U) sequestration in groundwater, these images will help identify any changes that occur during experimentation.

BET surface area analysis showed that surface areas, pore volumes, and pore sizes between soils from Plots 1, 2, and 4 were similar, while Plot 3 soil had slightly different values than the others, as shown in Table 6. The data obtained from this analysis is in agreement with the images obtained from SEM analysis.

Table 6. Bet surface area analysis data

	Plot 1	Plot 2	Plot 3	Plot 4	Average	Units
Surface area	12.98	14.02	9.81	13.66	12.62 ± 1.66	m^2/g
Pore volume	0.020	0.023	0.018	0.020	0.02 ± 0.002	cm^3/g
Pore size	64.53	69.58	77.51	62.82	68.61 ± 5.71	Å

When samples were initially analyzed via EDS, data showed that high amounts of carbon were present, which was unexpected for the given samples. Therefore, the samples were re-analyzed to determine if the carbon present was a result of the carbon tape used to load the samples. It was established that the large amount of carbon that first appeared was due to the tape used, so carbon was therefore deconvoluted during interpretation of the data in order to ensure accurate results. Ultimately, EDS data revealed that oxygen, silicon, and aluminum were the prominent elements while iron, potassium, calcium, magnesium, sodium, titanium, and phosphorus were found in trace quantities (Table 7).

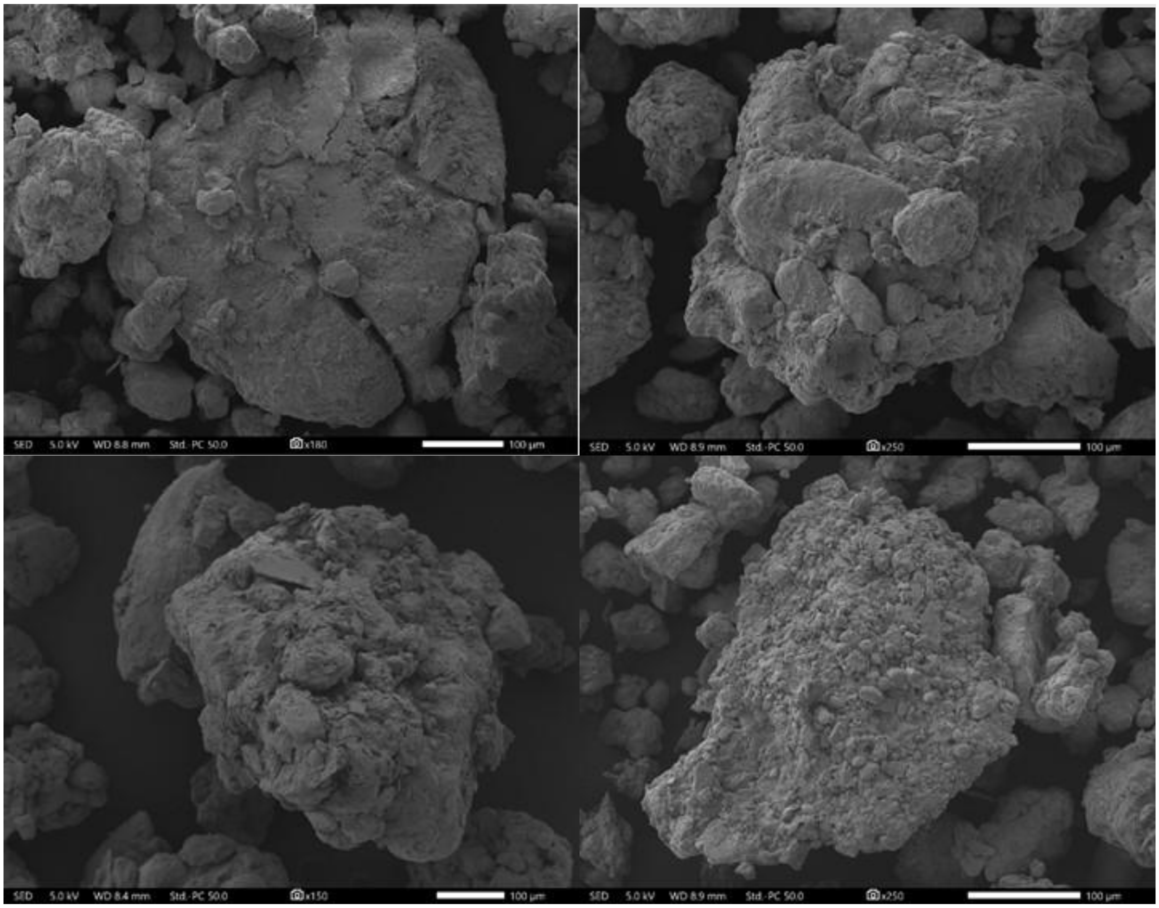

Figure 20. SEM images of soil samples from Plots 1-4.

Table 7. Average elemental mass percentage composition from EDS analysis

	Plot 1	Plot 2	Plot 3	Plot 4
Magnesium	1.421	1.301	1.866	1.148
Aluminum	8.483	7.319	8.637	9.780
Silicon	27.51	26.36	24.68	25.83
Potassium	2.350	1.918	1.982	2.571
Calcium	1.442	2.518	2.739	3.936
Iron	3.844	3.483	3.632	3.510
Sodium	0.155	0.301	1.186	0.907
Titanium	0.359	0.269	0.323	0.385
Oxygen	52.29	56.53	54.89	51.83

The XRD pattern collected from the Plot 3 sediment had a significantly lower intensity compared to the XRD patterns from other sediment plots (Figure 21 - Figure 24), therefore the sample was re-analyzed. Plot 3 intensities remained approximately 6,500 counts while Plots 1, 2, and 4 were in the range of 13,000 to 17,500 counts. This is an indication that Plot 3 may have different characteristics. Preliminary analysis of the XRD patterns showed a significant amount of silicon dioxide present, as well as the possibility of albite, calcite, muscovite, and anorthoclase. Once EDS data was collected, XRD graphs were interpreted again, with the goal of confirming that all prominent elements found via EDS also appeared in the XRD results. XRD analysis confirmed that elements found via EDS are present in all samples in the form of silicon dioxide, calcite, albite, kaolinite, and muscovite.

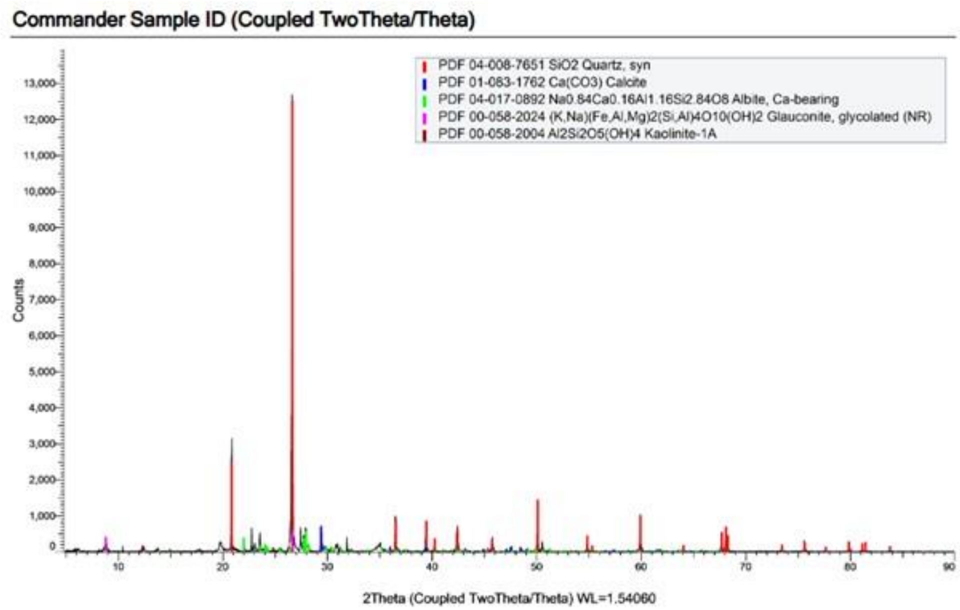

Figure 21. Matched XRD pattern for sediment sample from plot 1.

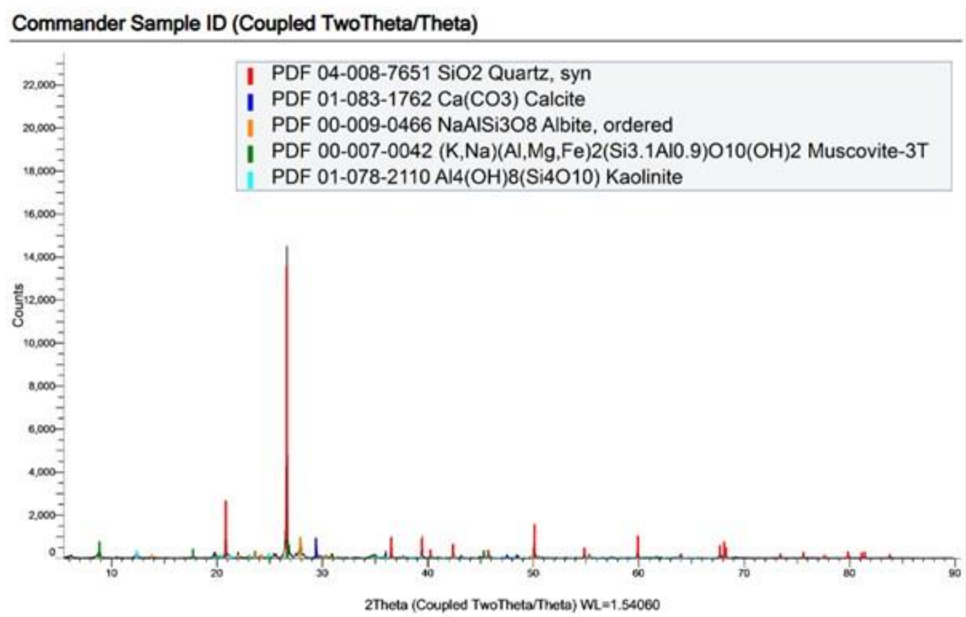

Figure 22. Matched XRD pattern for sediment sample from plot 2.

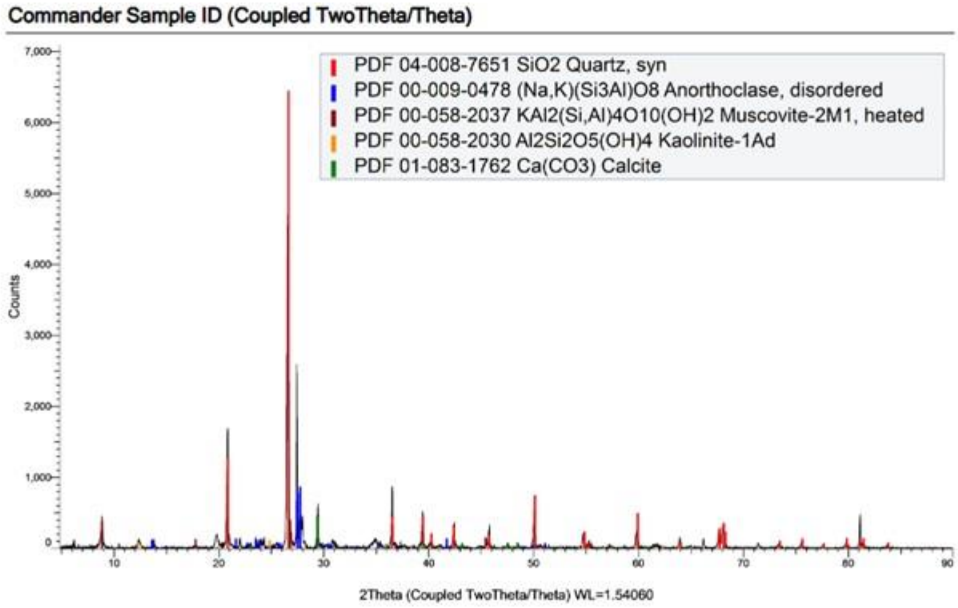

Figure 23. Matched XRD pattern for sediment sample from plot 3.

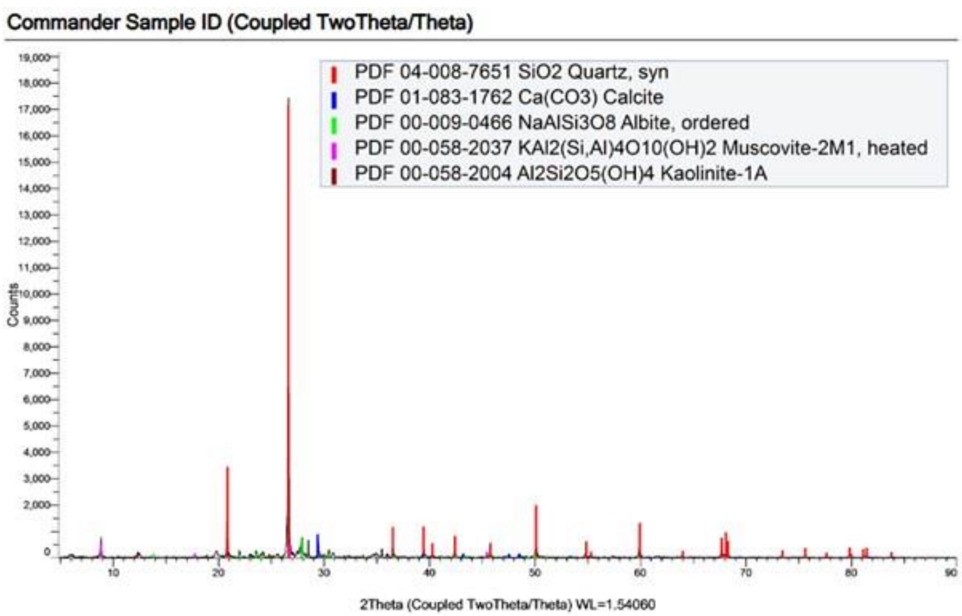

Figure 24. Matched XRD pattern for sediment sample from plot 4.

Task 1: Conclusions

Hydroxyapatite Synthesis, Kinetics, and Characterization Studies

Based on results, synthesis 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. The synthesis portion of this experiment is being concluded. From the current experiment, scenario 3 appears to precipitate the most solid and has the potential to be the optimal stoichiometric ratio.

Sediment Characterization

This study investigated the chemical composition, structure, and surface area of the sediment samples obtained from four different locations at the Old Rifle Site, CO. Experimental data showed that soil from all four plots were comparable, however Plot 3 samples consistently displayed anomalies during analysis. The analysis conducted via EDS and XRD revealed that the same elements were being identified in each method, confirming the presence of silicon, oxygen, aluminum, iron, potassium, calcium, magnesium, and sodium. Phosphorus was only found via EDS in trace quantities for Plots 3 and 4, while titanium was found in trace quantities for all locations, but neither was identified via XRD analysis. This could be due to the small amount detected. SEM and N2-BET analysis confirmed the surface area and structure were similar for all samples, with Plot 3 contrasting the most. The deviation of Plot 3 from all other locations could be due to varying soil conditions. Overall, the soil samples have comparable characteristics. The data obtained will help fill the knowledge gaps on 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 mechanism of U removal from groundwater using apatite as well as the environmental factors that influence the stability of that removal.

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.

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: REMOTE SENSING TECHNOLOGIES FOR LONG-TERM SURVEILLANCE OF DOE-LM SITES

Task 2: Introduction

Fulfilling the Department of Energy's (DOE) post-closure responsibilities and ensuring the future protection of human health and the environment poses a considerable long-term challenge. In this scenario, remote sensing technologies can be effective tools for informed decision-making as geospatial data and trends are taken into account so that managers can base their decisions on more accurate information.

A fast-growing trend in remote sensing surveys uses on-demand photogrammetric analysis and light detection and ranging (LiDAR) scans deployed by autonomous robotics platforms. These technologies provide a cost-effective, centimeter-level precision with a shorter time frame compared to traditional methods. Three-dimensional mapping strategies provide valuable data, such as orthomosaic maps, 3D point clouds, volumetric measurements, slope monitoring, erosion trends, digital surfaces, and terrain models. However, the choice (or combination) of methods is situational and depends on factors such as time, budget, and capturing conditions, among others.

Department of Energy Office of Legacy Management (DOE-LM) has used LiDAR to measure changes in landfill profiles and disposal cells at Old Rifle and Mexican Hat sites. These changes in LiDAR profiles could be early indicators of erosion of the cell cover or compaction of waste. Sites that endured maintenance issues can benefit from LiDAR surveys, such as Rocky Flats Landfill slumping, Grand Junction Disposal volumetric estimation, and Mexican Hat Disposal erosion issues.

Florida International University (FIU), in collaboration with DOE-LM, is investigating robotic platforms and remote sensing methods suitable for long-term monitoring of DOE-LM sites considering their environmental characteristics. The study will prepare the foundation for potential continued collaborations in employing geospatial data analysis frameworks assisted by Artificial Intelligence driven by Machine Learning. The frameworks will provide DOE-LM sites with tools for tracking long-term effects on land cover and land use dynamics and issues related to climate change, resilience, and extreme weather events, helping to detect maintenance issues early on. Thereby, the FIU study contributes to the 2020-2025 Strategic Plan by adhering to Goal 4: Sustainably manage and optimize the use of land and assets and address severe weather events.

Task 2: Objectives

This study's primary goal is to compile a matrix containing the appropriate remote sensing technology adequate for surveying specific features present in DOE-LM sites across the country. The investigations will pursue the following objectives:

- Compile current land feature characteristics of DOE-LM sites across the U.S., such as arid, semi-arid, wet, semi-wet environments, vegetated or barren lands, elevation, topography, and weather.
- Investigate specific needs in DOE-LM sites for remote sensing data collection, combining data from questionnaires addressed to site manager, visits, existing publicly available aerial photography from DOE-LM, and on-demand in-house surveys.

- Evaluate commercially available robotic systems, state-of-the-art in remote sensing technologies suitable for UAVs, UGVs, and wearables.
- Explore remote sensing technologies for the long-term surveillance of LM sites, technology evaluation, and data analysis of digital elevation model (DEM) renderings for environmental factors to capture erosion in the cell cover.

In the first year, this study mainly focused on photogrammetry and LiDAR remote sensing applications using autonomous unmanned aerial vehicles (UAVs) and unmanned ground vehicles (UGVs). Even though UAVs are popular remote sensing tools, battery life is a concern and especially in vast areas, a ground platform or wearable system might be better suited. A ground system has fewer constraints with payload capacity and can even be gas-powered.

The scope of this study was to explore remoting sensing applied to site monitoring, such as mobile platforms for sensor delivery, optimal mission planning for imaging acquisition, sensor integration, in-house surveys and field validation, photogrammetry and LiDAR mapping frameworks, intelligent point cloud management algorithms, object detection techniques, and artificial intelligence focusing on topics related to statistical learning and remote sensing.

Task 2: Methodology

Materials

The study utilized four different UAVs for conducting drone training and surveys. The DJI Phantom 3 equipped with a RGB camera and gimbal and DJI S1000 Spread Wings was used for in-house UAV flight. The DJI Phantom 4 RTK equipped with a RGB camera and gimbal was used for a Photogrammetry survey at the Rifle Disposal Site Deployment and the DJI Matrice 300 RTK was utilized equipped with an in-house 3D printed mount embedded with a Jetson Xavier NX (computer), Ouster OS1 LiDAR (auxiliary sensory), and supporting electronics.

Literature Review on Remote Sensing, Platforms, and Current Industry Applications

The literature review summarized relevant state-of-the-art imaging technologies, such as mid-range LiDAR imaging systems and several camera types such as thermal, multispectral, 3D, depth, and tracking cameras, including fundamental concepts in image interpretation and geospatial data management. The review also focused to identify techniques to improve precision versus coverage and adequacy of using ground, airborne, space-borne based platforms, and guidelines in acquiring remote sensing data using multi-rotor versus fixed-wing UAVs.

The review focused on applications using photogrammetry and LiDAR mapping, depending on a particular use case and time, budget, and capturing conditions, among others. LiDARs are active sensors suitable for surveying narrow structures such as power lines or telecom towers and mapping areas below tree canopies. In contrast, photogrammetry uses passive cameras better for projects that require visual data such as construction inspections, asset management, and agriculture. Lastly, the study explored the popular supporting software for autonomous systems, mission planners, and custom builds using the Robot Operating Systems (ROS) software frameworks.

LM Site Characterization

A total of 84 LM sites were examined for characteristics such as location (state-territory), regulatory driver, land cover, land features, elevation, weather conditions, hydrology, winds, current land use, and a climate summary incorporating data from Weather Spark [1]. Climate summary provides detailed weather reports of typical climate characteristics from sources such as the National Oceanic and Atmospheric Administration (NOAA). As shown in Figure 25, the site characterization can assist in selecting suitable remote sensing methods and platforms for Legacy Management sites. This simple searchable database performed within an Excel framework can be used as a reference by site personnel to find site characteristics of a location.

Fernald Preserve, OH, Site	Ohio	CERCLA/RCRA	Level I: 6. Wetland (Man-made) Level II: 61. Forested wetland	Open water, upland forests, a lengthy riparian corridor, and 385 acres of grassland, including tallgrass prairie and savanna	The geographical coordinates of Hamilton are 39.400 deg latitude, -84.561 deg longitude, and 591 ft elevation.	Fernald Preserve located in Hamilton, OH. In Hamilton, the summers are warm and humid, the winters are very cold and windy, and it is partly cloudy year-round. Over the course of the year, the temperature typically varies from 23°F to 86°F and is rarely below 6°F or above 93°F.	The clearer part of the year in Hamilton begins around June 12 and lasts for 4.7 months, ending around November 3. On August 22, the clearest day of the year, the sky is clear,	The windier part of the year lasts for 7.0 months, from October 16 to May 17, with average wind speeds of more than 8.0 miles per hour. The windies day of the year is January 15, with an average hourly wind speed of 10.2 miles per hour. The calmer time of year lasts for 5.0 months, from May 17 to October 16. The calmest day of the year is July 31, with an average hourly wind speed of 5.8 miles per hour.
Laboratory for Energy-Related H	California	CERCLA/RCRA	Level I: 1. Urban or built-up Level II: 12. Commercial and Services 76. Transitional Areas	LEHR Facility. Property owned by UC Davis for tran	About 46 ft. The topography within 2 miles of Davis is essentially flat, with a maximum elevation change of 30 feet and an average elevation above sea level of 46 feet.	In Davis, the summers are hot, arid, and mostly clear and the winters are short, cold, wet, and partly cloudy. Over the course of the year, the temperature typically varies from 39°F to 93°F and is rarely below 31°F or above 102°F.	The clearer part of the year in Davis begins around May 14 and lasts for 5.3 months, ending around October 23. On July 19, the clearest day of the year, the sky is clear	The clearer part of the year in Davis begins around May 14 and lasts for 5.3 months, ending around October 23. On July 19, the clearest day of the year, the sky is clear, mostly clear, or partly cloudy 91% o the time, and overcast or mostly cloudy 9% of the time. The cloudier part of the year begins around October 23 and lasts for 6.7 months, ending around May 14. On January 11, the cloudiest day of the year, the sky is overcast or mostly cloudy 56% of the time, and clear, mostly clear, or partly cloudy 44% of the time.
Maxey Flats, KY, Disposal Site	Kentucky	CERCLA/RCRA	Level I: 1. Urban or Built-up Land Level II: 12. Commercial and Services 76. Transitional Areas	The Maxey Flats site is located in the Knobs physiographic region, which is characterized by hills and relatively flat-topped ridges.	463 - 600 ft.	In Morehead, the summers are hot and muggy, the winters are very cold and wet, and it is partly cloudy year-round. Over the course of the year, the temperature typically varies from 28°F to 88°F	The clearer part of the year in Morehead begins around June 15 and lasts for 4.6 months, ending around November 4	The windier part of the year lasts for 6.9 months, from October 20 to May 15, with average wind speeds of more than 7.0 miles per hour. The windies day of the year is February 25, with an average hourly wind speed of 9.0 miles per hour. The calmer time of year lasts for 5.1 months, from May 15 to October 20. The calmest day of the year is July 30, with an average hourly wind speed of 5.0 miles per hour.

Figure 25. Site characterization compilation of LM's sites. [2]

Regarding the DOE-LM site characterization, the study characterized the selected Legacy Management site conditions and its corresponding geographical setting via the Land Use Classification Systems from the United States Geological Survey (USGS), which provides standardization for categorizing land use. The classification levels range from general to specific uses. The characterization selected levels suitable for remote sensing applications. The classification includes identifying weather conditions and wind speeds to consider remote platforms best suited for their location. The compilation encompasses all CERCLA/RCRA, NWPA, D&D, and FUSRAP sites, including different environmental characteristics also classifying them according to land features, vegetation, elevation and weather conditions, and type of contamination at the sites, including radiological, chemical, and hazardous materials.

UAV Surveys

In the study, two UAVs, shown in Figure 26 were used for in-house flight trainings and surveys. The DJI Phantom 3 is a small quadcopter coupled with a gimbal camera suitable for photogrammetry surveys. The DJI S1000 is a larger octocopter with improved flight performance and better loading capacity (about 30 lbs.), essential in carrying a LiDAR mapping system and supporting embedded computers.

Figure 26. FIU's photogrammetry (left) and LiDAR (right) mobile mapping systems.

The in-house mapping surveys worked as a testbed to evaluate remote sensing techniques, sensors, mission planning patterns, and collect data for testing geospatial analysis software. The aerial surveys were also used to contextualize the research and training efforts. The efforts included the integration of a mid-range high-resolution imaging LiDAR into the large UAV. Table 8 shows the specifications of the procured LiDAR that will be used throughout the study.

Table 8. LiDAR Specifications

Parameter	**Ouster OS1**
Weight (g)	455
Beams	32
Temperature (c)	-20 to +50
Vertical FOV (^{o})	45
Range (m)	120
Precision (cm)	+- 1.5 to 5
Points per second	2,621,440
Rotation Rate (Hz)	10 or 20
Power (W)	14-20
Vertical Resolution (^{o})	0.01
Horizontal Resolution (^{o})	0.01

To facilitate the goal of deploying remote sensing technologies for LM’s needs. The study required photogrammetry survey training using a quadcopter coupled with a high resolution gimbled camera. Figure 27 shows the aircraft and the surveyed testing area at the FIU campus.

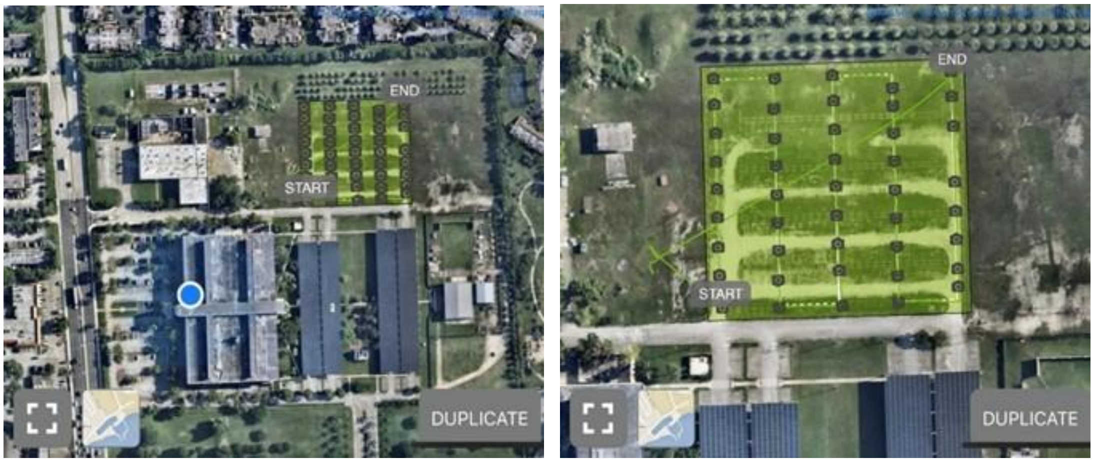

Figure 27. Photogrammetry aircraft and the surveyed testing.

The study then focused on learning about UAV systems and their main components. As sketched in Figure 28, the main components are the flight controller, GPS, IOSD, Camera, Receiver, ESC, Motor, Video Transmitter, and Video Receiver.

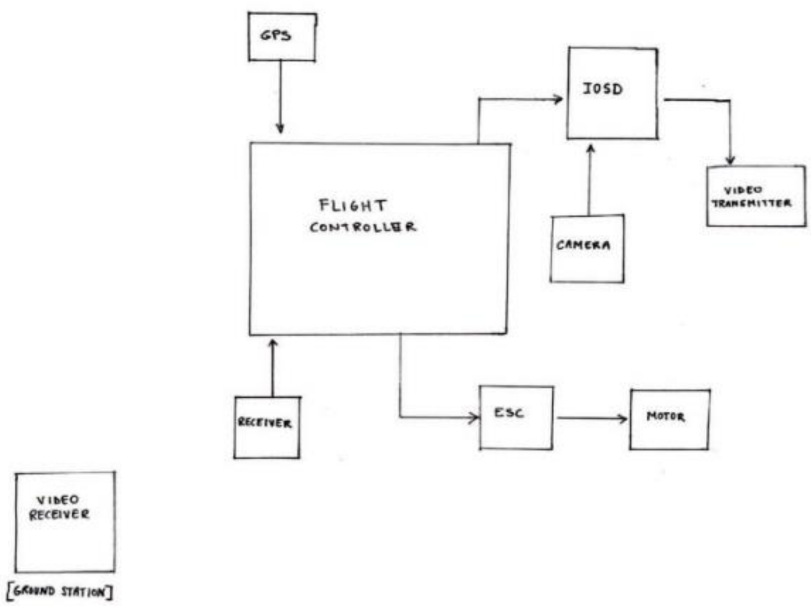

Figure 28. Typical main components in UAV systems.

UAV survey training included the fundamentals of radio controls, takeoff, in-flight, and landing procedures using flight simulators and physical models demonstrated in Figure 29.

Figure 29. UAV flight training in preparation of deployment.

The study also examined potential flight planner software suitable for surveying outdoor missions guided by a GPS autonomously. Ongoing flight trainings with DJI S1000 hexacopter were crucial to be familiarized with using a larger drone to perform LiDAR surveys. Since a bigger aircraft is needed to carry the payload of a LiDAR module.

The photogrammetry training process entailed conducting surveys of the student parking lot at the university's engineering center. The initial step was to verify flight regulations around the facility by checking the controlled airspace at the coordinates of interest. Assessing the weather and wind conditions to assert the cloud coverage would not impede data capture as well as allow proper flight conditions respectively. This could be determined using B4UFLY, a mobile application that shows the flight conditions based on GPS location. The next step was conducting a UAV gear checklist such as making sure batteries are full, performing IMU (Inertial Measuring Unit) and Compass calibration, and examining propellers are in suitable condition for flight.

Furthermore, a preflight checklist was conducted prior to initiating the flight plan. The setting would be observed for hazards such as light posts and power lines that may be in way of the flight route. Landing zones were established in case of an emergency where the UAV would have to land. Next, the DJI Phantom 3 would be programmed to fly a desired flight path of the land cover that wanted to be surveyed. The photogrammetry software utilized called Pix4D, is a mobile application that links with the UAV. The application ran its own automated preflight check prior to giving permission for takeoff. Upon selecting the dimensions of the proposed surveyed area on the web mapping platform of Pix4D, the flight plan conditions would be selected. The conditions include adjusting the flight altitude and speed, as well as the angle of the camera. Once the flight plan was initiated the UAV would fly to the starting point and fly through the predetermined flight path. Every so often a picture would be taken of the land cover to capture the aerial photography for post processing shown in Figure 30. Once all images were captured and the UAV had traversed the entire flight path; the drone would return to the initial landing zone also known as the home point.

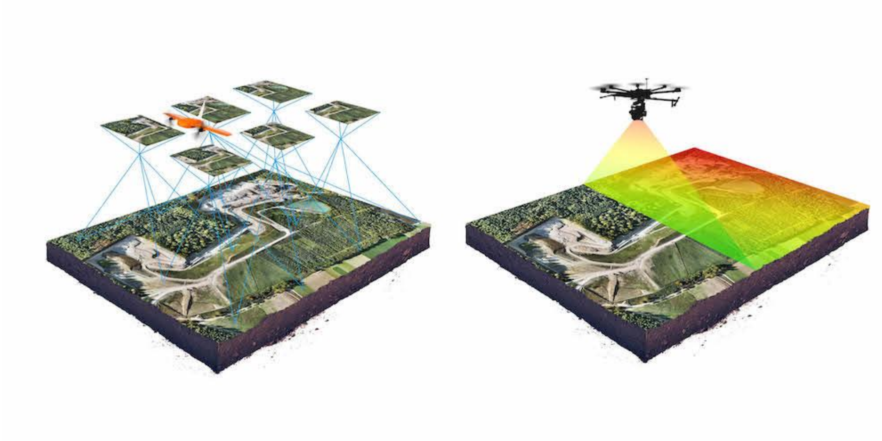

Figure 30. UAV collecting aerial photographs from different locations along flight plan which provides digital elevation model when post processed. [3]

LM Aviation Safety Plan

The Aviation Safety Plan (Table 9) was finalized in accordance with the Legacy Management (LM) Aviation Program's standards to perform a drone baseline survey of the Rifle Disposal Site. A project overview was prepared including lists of equipment specifications, the purpose and goal of the deployment, and an itinerary to establish the flight strategy with the visual observers and attending LM flight observers. A drone mission statement, including terrain and aeronautical sectional maps which the fellow had to learn to read as part of his Part 107 - Small Unmanned Aircraft Systems certification, was also incorporated into the safety plan. An important part of the program was to identify the controlled airspace of the site as well as assure the location of the drone deployment was not within a 5-mile radius of the airport. A preflight inspection of the site to determine 3 different flight termination points for the drone to land was performed to account for emergency landings. The Aviation Safety Plan also included necessary logistics, drone mission hazards, and pre/post-mitigation measures for prioritizing safety and being prepared for any outcome. This is one of the biggest priorities for Legacy Management when conducting their work procedures.

Table 9. Composed an Aviation Safety Plan to LM Aviation and FAA Standards

Drone Mission Hazards and Mitigation Measures Following is a matrix which addresses typical hazards for sUAS operations at remote LM sites in western Colorado.

Category	Hazard Description (if applicable	Mitigation Measure
Stored Energy (Batteries)	Lithium-Ion batteries if misused, mishandled, and improperly packaged can short circuit, overheat, and possibly cause a fire.	Batteries are inspected periodically as well as properly charged to prevent short circuits. The lithium-ion batteries used for the survey will be housed in a portable battery case to mitigate the risk of overheating or igniting a fire. A fire extinguisher will also be present in case of fire.
Drop Zones (strikes from falling objects)	Awareness of drop zones is important to avoid sUAS collisions with parachuting operations	This hazard will be avoided because the survey will take place in a remote area. The sectional chart was viewed and confirmed there are no drop zones in the working area.
Proximity to overhead power lines and/or obstructions	Powerlines and obstructions are deemed hazardous to air navigation. Proximity with drones can cause collisions.	No overhead power lines or obstructions are located on or near the surveyed site. Therefore, there is no risk with proximity to drone surveys.
Fall Hazards/Elevated Work	The surveyed site is located on an inclined hill slope and therefore has fall hazards.	This risk will be mitigated by using proper personal protective equipment for this hazard. The crew members will be aware and attentive to inclinations in the terrain. Members must pace the distance they cover to avoid falling.
Wildfires	Smoke caused by wildfires interfere with air navigation visibility specially for the	To mitigate the risk of wildfires, the flight crew will monitor wildfires

<u>LM Rifle Technology Deployment:</u>

Following the finalization of the Aviation Safety Plan, the first drone baseline survey of the Rifle Disposal Site located in Rifle, Colorado was successfully conducted as the remote pilot in command (Figure 31). During this experience, the importance of effective communication with flight crew to mitigate any risk and enforce safety was learned. Drone survey procedures, pre-flight and post-flight inspections (Figure 32), and risk mitigation were coordinated and led by the fellow and the assisting flight crew team through for the duration of 5 days (Figure 33). Lessons on leadership and risk mitigation throughout the survey process were learned from Mr. David Morton, an experienced pilot from LM. LM's Aviation Program Manager, Ms. Deborah Steckley provided the study with the resources needed for preparing the Aviation Safety Plan, as well as supported the drone deployment. Mr. Anthony Abrahao (mentor and Research Scientist from Florida International University) and Mr. Bruce Akers, LM Fleet Manager, served as visual observes in capturing the photogrammetry data of the 71-acre site. Their efforts were necessary to have a constant visual line of sight with the aircraft and remain within the project site boundary.

Figure 31. Successfully conducted first drone baseline survey of Rifle Disposal Site as the remote pilot in command.

Figure 32. Performing onsite preflight inspection of Phantom 4 RTK.

Figure 33. Coordinating and leading flight crew team through drone survey procedures and risk mitigation. Pictured from left to right: Eduardo Rojas, Bruce Akers, Deborah Steckley, and David Morton.

Task 2: Results and Discussions

Photogrammetry Training Data Post Processing:

Figure 34 presents the captured digital elevation model (DEM) of the testing area post-processed using specialized photogrammetry software, Pix4D and the collected aerial images.

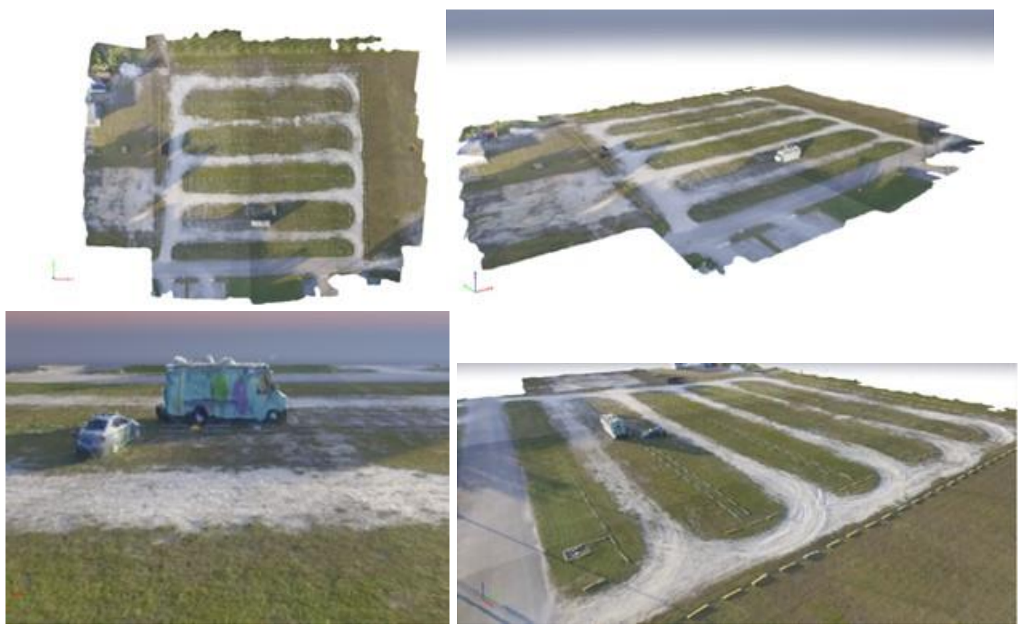

Figure 34. Processed 3D maps of parameters.

Finally, preliminary automated object detection tests using machine learning, seen in Figure 35, were also successfully performed for initial examination of the use of machine learning to detect objects using acquired data. The tests used an in-house aerial footage, and showed promising results. The reason for employing statistical methods tailored to remote sensing data's temporal and spatial data analysis come after LM communicated the possibility of looking into a prospective database to store acquired data assisted by machine learning.

Figure 35. Preliminary aerial object detection tests.

LiDAR Module Software Integration

The in-house integration of the LiDAR to the high payload octocopter was designed with a setup similar to the one illustrated by Figure 36.

Figure 36. FIU's UAV LiDAR mapping systems conceptual design.

To evaluate the setup, the conceptual design was simulated using the Robotic Operating Systems (ROS) toolset. The virtual model was used to assist in the performance evaluation of the mapping system beforehand. Figure 37 illustrates the system's mapping potential, in which a virtual UAV carries the selected multichannel LiDAR while scanning a synthetic environment capturing its environment producing virtual point clouds.

Figure 37. Simulated UAV (left), point cloud results (middle), and synthetic environment (right).

Figure 38 shows preliminary laboratory test results of the procured Ouster OS1-32 LiDAR, as well as the DJI S1000 UAV setup. The LiDAR's integration efforts involved designing and testing mechatronic systems, sensors, embedded hardware, and supporting software.

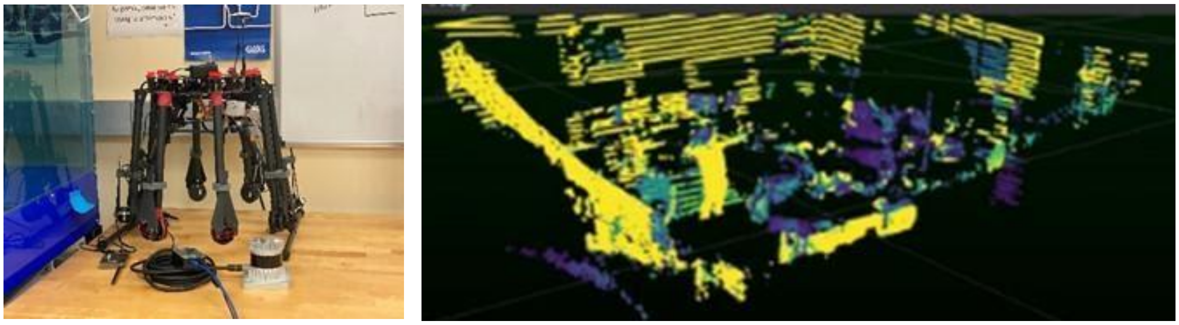

Figure 38. LiDAR and DJI S1000 UAV (left) and preliminary LiDAR testing (right).

LiDAR Module Bracket Development

Figure 39. LiDAR system main components.

FIU conducted modeling of a 3D printed mount to attach the mid-range high-resolution imaging LiDAR (Ouster OS1-32, Figure 39) and its embedded computer into the high payload hexacopter (DJI S1000). Figure 40 shows the 3D printed l-shaped mount's original conceptual design, illustrating the module's major components.

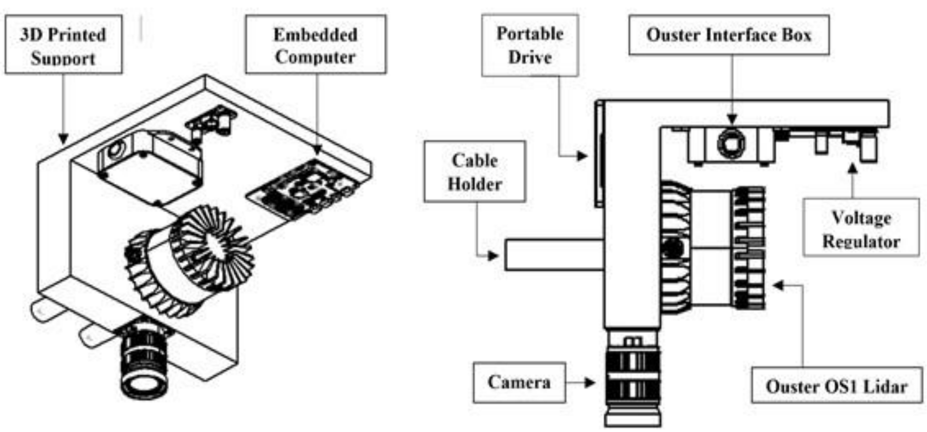

Figure 40. LiDAR mount conceptual design.

As illustrated in Figure 41, the LiDAR module is an agnostic self-contained remote sensing package, translatable to any other delivery platform, such as backpacks, ground, and aerial vehicles. Figure 42 shows the imaging system integrated into our aircraft. The module also houses a high-resolution camera.

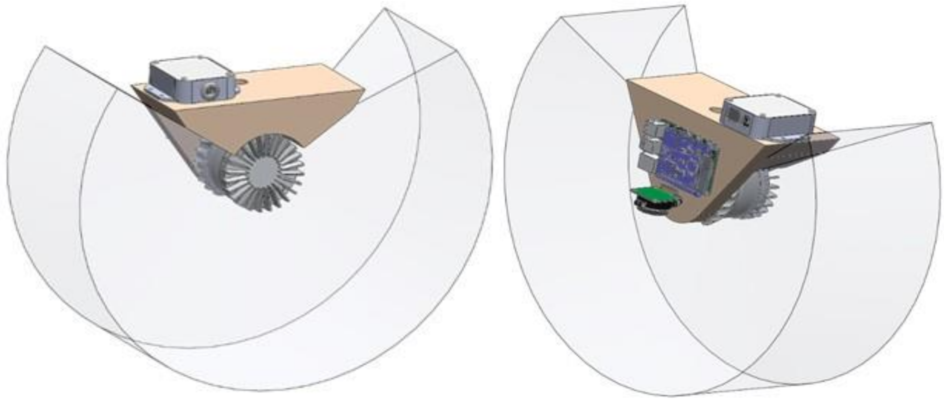

Figure 41. FIU's remote sensing agnostic LiDAR package.

Figure 42. LiDAR and aircraft integration preliminary design.

A topological optimization of the bracket mount was performed to identify critical areas in the frame that must remain intact for adequate structural support after removing material to produce a lighter assembly (Figure 43).

Figure 43. Lidar bracket original design (left) and optimized (right).

An optimal UAV was later obtained for the study thereby replacing the prior model selected. This new model provides superior battery efficiency to conduct the survey and a stable flight planning software to perform both photogrammetry and LiDAR depending on a customized mount application. Figure 44 shows the new model, DJI Matrice 300 RTK, for the brief LiDAR survey planned for the deployment.

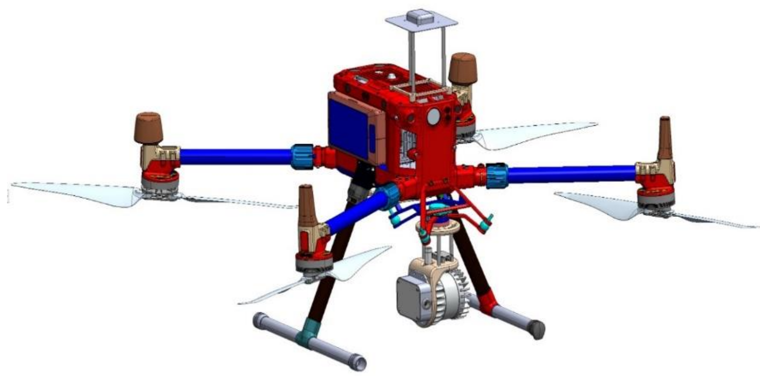

Figure 44. CAD model of the Lidar module mounted below the DJI Matrice 300 RTK. This agnostic system includes a 3D printed mount with an embedded computer, auxiliary sensory, and supporting electronics.

Figure 45 and Figure 46 show the materials and UAV equipment for technology deployment and data retrieval using the LiDAR and Photogrammetry methods. This initiative will try to aid LM's need to combat the creation of depressions on the top cell cover of the Rifle Deposal Site caused by erosion and other environmental factors.

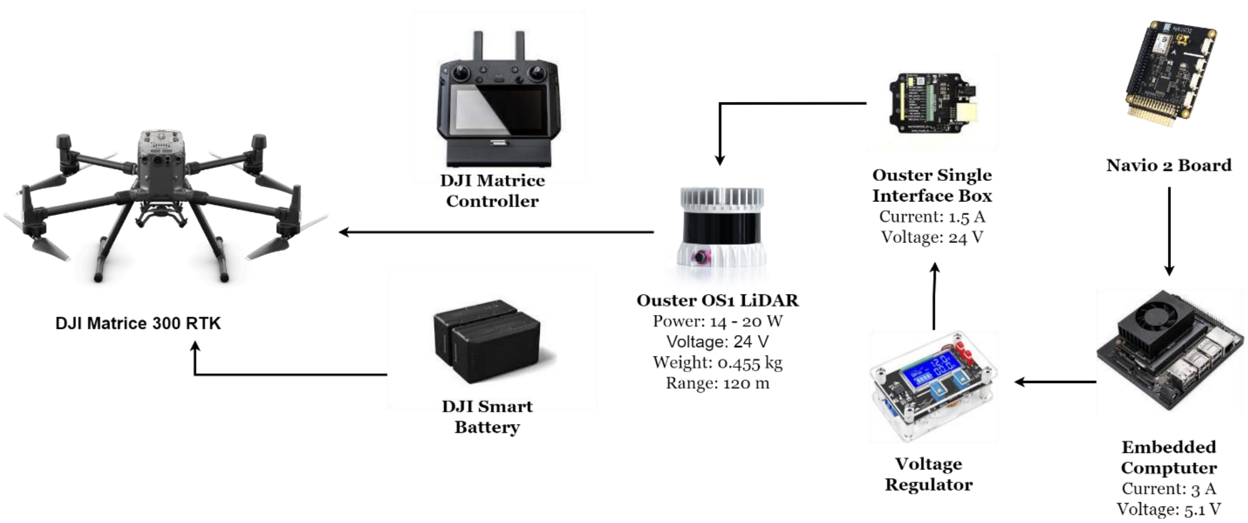

Figure 45. Equipment used for LiDAR method

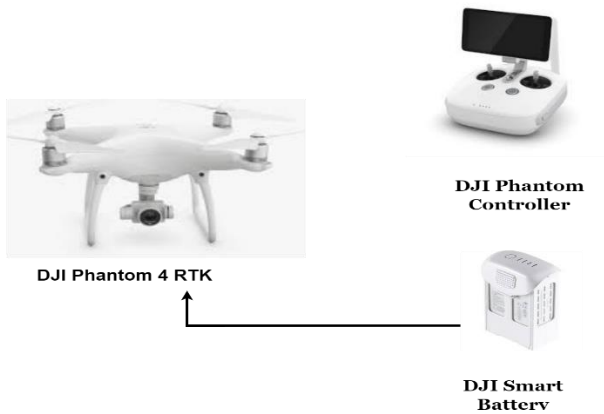

Figure 46. Equipment used for Photogrammetry method.

The culmination of the study's efforts led to the execution of surveys for LM's Rifle Disposal Cell (Figure 47) piloting two UAVs.

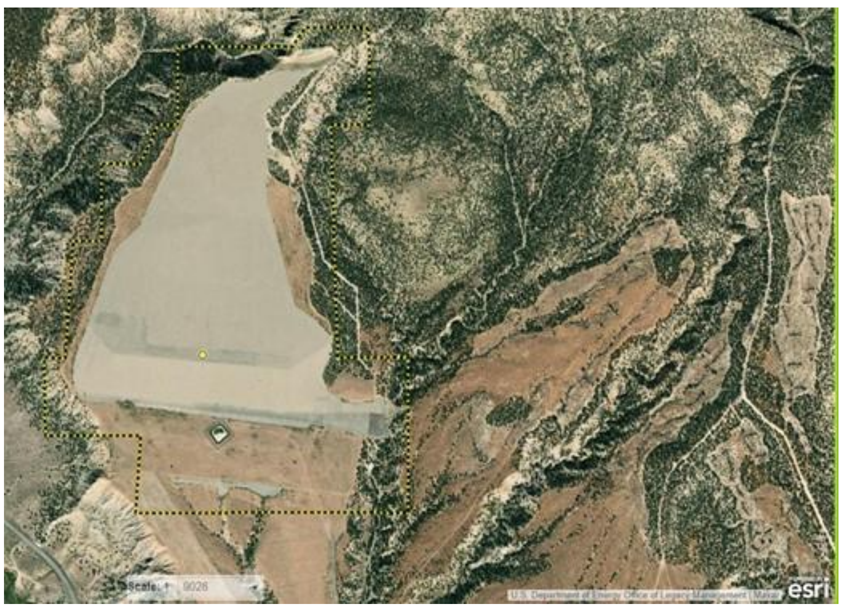

Figure 47. LM's Rifle Disposal Cell.

A complete photogrammetry workflow generating an accurate DEM (Digital Elevation Model) and an orthomosaic map of the cell, presented in Figure 48 was obtained by post-processing the aerial photography and data acquired.

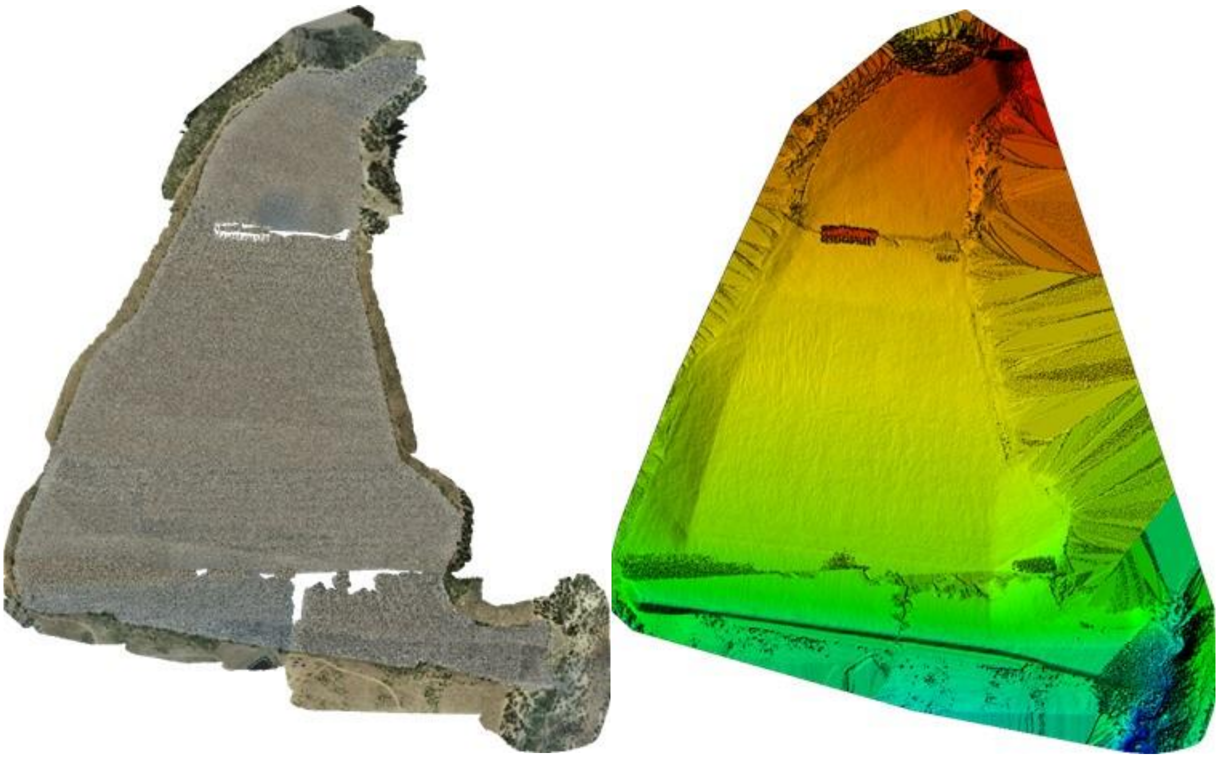

Figure 48. Captured orthomosaic map (left) and digital elevation model (right) of Rifle Disposal Cell.

Figure 49 shows the transects and image positions captured during the photogrammetry study. The photogrammetry post-processing used 5,266 high-resolution aerial images, computed using a computer with AMD EPYC 7451 24-Core Processor CPUs, 192GB RAM, and NVIDIA Quadro M2000 GPU, taking 6h:56m:49s for point cloud densification, 2h:58m:17s for 3D Textured Mesh Generation, 1h:55m:48s for DEM Generation, and 23h:39m:36s for Orthomosaic Generation.

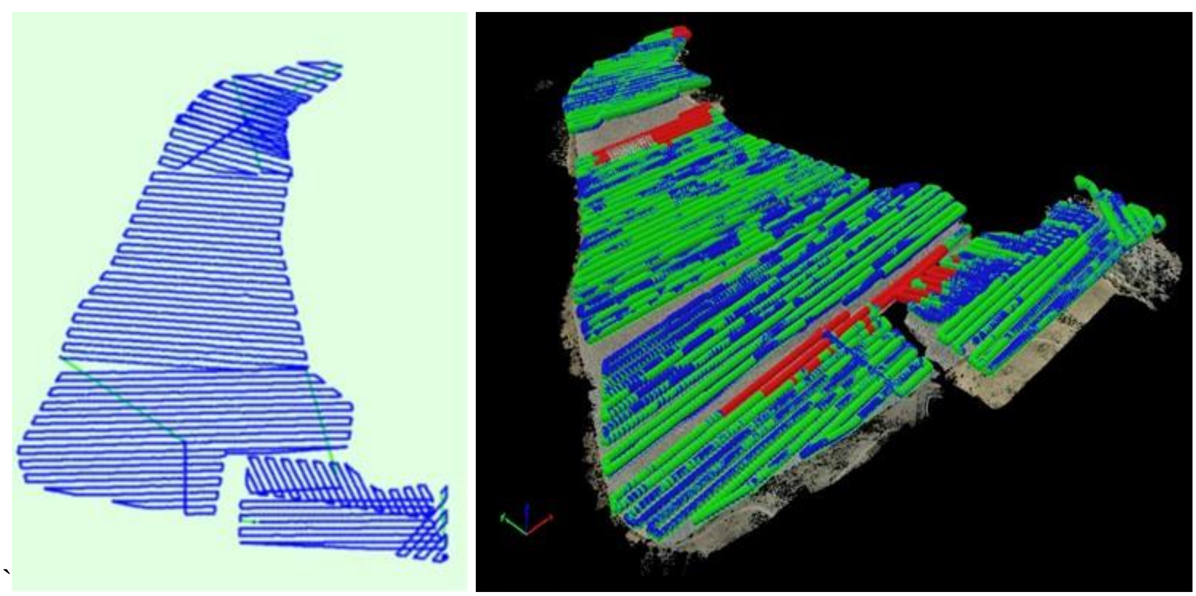

Figure 49. Aerial image positions and transects.

The study then conducted a literature review to identify existing algorithms suitable to detect early depressions in cell top layers using the DEM generated during his summer flyover at the Rifle Disposal Site in Colorado.

Figure 50 shows a basic workflow to estimate depressions using existing DEMs based on Gomez, Liedl, and Stefan, 2019 published as "A New GIS-Based Model for Karst Dolines Mapping Using LIDAR; Application of a multi-depth Threshold Approach in the Yucatan Karst, Mexico" [4].

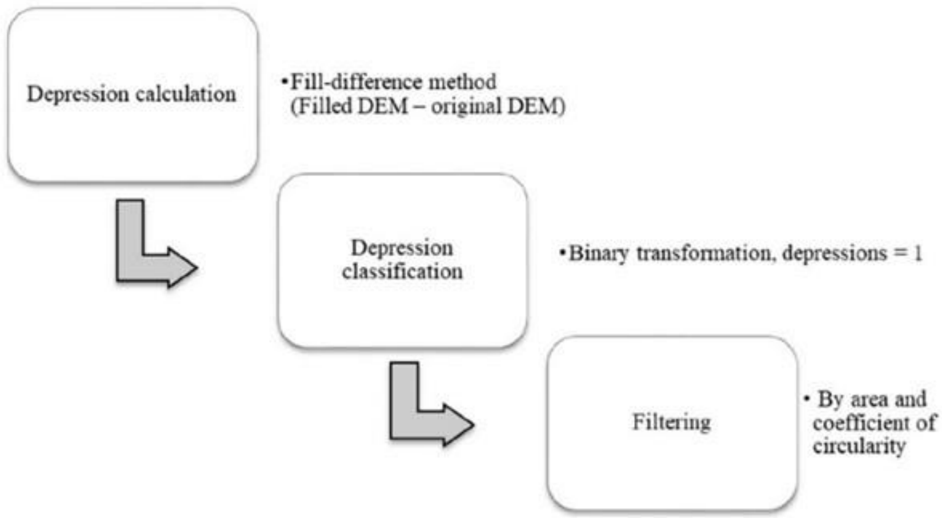

Figure 50. Basic workflow to estimate depressions using DEMs.

The method provided 63% accuracy after testing various parameters. The goal of the method is to classify depression intervals to identify dolines at variable depths statistically. Dolines, also known as *sinkholes*, are topographical features linked to groundwater vulnerability, and their identification is optimal for determining novel environmental and hydrological management strategies. Doline mapping provides critical insight to assessing the proper risk management practice. The method also considers essential factors for estimating doline mapping: the map scale, doline size, and contour interval. The technique can help analyze and post-process the Disposal Cell’s DEM without a prior baseline.

The study’s rendered elevation models (Figure 51) were requested by the Rifle Site Manager, Nicole Keller, assisting her in preparing a presentation for the national laboratories.

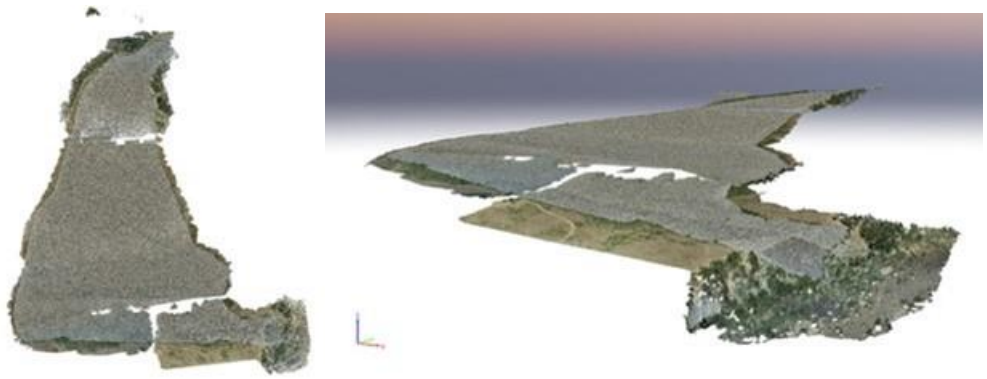

Figure 51. Isometric (left) and top (right) views rendering of the elevation model of Rifle Disposal Site.

The study then explored ArcGIS functionalities to attempt implementing early depression detection and sinkhole identification at disposal cell coverages.

Literature review was conducted on doline mapping detection, by reviewing Zhang et al., 2019 "Karst Sinkhole Detecting and Mapping Using Airborne LiDAR" [5]. Authors explored sinkhole mapping using airborne LiDAR data supplemented with auxiliary context information for better accuracy. This auxiliary context information includes specifying the terrain having sinkholes or not and characterizing the type of setting like rural vs urban.

The application of a toolset developed through ArcGIS, an online geographic information system (GIS) used for manipulating data, was examined. An important principle to take into consideration when using GIS-based processes for depression identification is the quality and parameters of the data being collected. This is an important factor to consider when gathering data for project needs. The capturing of high-resolution data does not correlate with better identification results. A high-resolution DEM tends to have an increase in number of depressions, thereby requiring further analysis to remove artificial depressions in the rendering. Contrastingly, coarse DEMs impact depression estimation because depressions smaller than the grid size cannot be defined.

Task 2: Conclusions

For this task, FIU laid the foundation necessary to carry out a study which involved the compilation of remote sensing platforms and technologies to determine the most suitable for characterization of environmental and topological features at LM sites to assist DOE LM meet its post-closure responsibilities for the management, long-term monitoring and protection of human health and the environment. FIU developed and proposed a cohesive study plan relevant to DOE-LM needs and successfully completed UAV flight and remote sensing training for image data retrieval, deploying UAV technology in-house at FIU and then at LM's Rifle Disposal Site using photogrammetry and LiDAR remote sensing methods. The data collected was post-processed to develop a 3D DEM with the possibility of employing depression detection techniques in future. These major accomplishments demonstrate the advancements of this research effort.

During the next year, primary focus will be to evaluate commercially available geophysical systems and state-of the-art sensors, such as ground penetrating radar, electrical resistivity imaging (ERI) and electromagnetic surveys, and explore the use of geophysical techniques for environmental mapping to facilitate the formation of depressions on the Rifle Disposal Site. FIU will also compile precipitation and temperature data and parse the historical impact of this climate forcing on the hydrology of DOE-LM sites across the country. Other ground platforms and wearables will be considered as well. The compilation efforts regarding the different environmental characteristics of DOE-LM sites will be finalized and tailored, sorting information requested from the sites and managers.

Task 2: References

1. *The weather year round anywhere on Earth*. The Weather Year Round Anywhere on Earth - Weather Spark. (n.d.). Retrieved December 6, 2021, from https://weatherspark.com/.
2. *LM sites*. Energy.gov. (n.d.). Retrieved December 6, 2021, from https://www.energy.gov/lm/lm-sites.
3. Torres, G. (2021, March 16). *Drone photogrammetry vs. LIDAR: what sensor to choose for a given application.* [Digital Image]. Wingtra. https://wingtra.com/drone-photogrammetry-vs-lidar/
4. Moreno-Gómez, M., Liedl, R., & Stefan, C. (2019). A New GIS-Based Model for Karst Dolines Mapping Using LiDAR; Application of a Multidepth Threshold Approach in the Yucatan Karst, Mexico. *Remote Sensing*, *11*(10), 1147. doi:10.3390/rs11101147
5. Zhang, S., Bogus, S., Baros, S., Neville, P., & Dow, R. (2019). Karst sinkhole detecting and mapping using Airborne Lidar - A conceptual framework. *MATEC Web of Conferences, 271*, 02005. https://doi.org/10.1051/matecconf/201927102005

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 initiated the Fall 2021 recruitment campaign, starting August 30, 2021, which is anticipated to run through October 1, 2021. During the recruitment period, FIU will set up tables at the Engineering Center, the Physics and Chemistry building, as well as the Computer Science building to promote the program and distribute flyers. FIU is also visiting classrooms 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. Interviews and selection of new DOE Fellows to join class of 2021 will be completed prior to an induction ceremony planned for November 11, 2021.

Figure 52. DOE Fellows promoting the program and recruiting new students.

DOE Fellows Introduction Ceremony

In November 2020, FIU conducted a virtual introduction ceremony in lieu of the traditional induction ceremony, welcoming DOE LM Fellow Eduardo Rojas. Mr. Carlos Melendez, Director of the Office of Legacy Management, gave an inspiring keynote to the new DOE Fellow inductees. Other DOE EM and LM colleagues included Mr. Kurt Gerdes, Mrs. Genia McKinley, Mr. Jean Pablo Pabon, Mrs. Jalena Dayvault, and Mr. David Shafer.

In addition, DOE LM Fellows presented their research being conducted at FIU. Ceremony participants and guests heard research presentations by LM Fellows Olivia Bustillo and Eduardo Rojas. LM Fellow Bustillo presented her investigation of the use of hydroxyapatite for U Sequestration while Fellow Rojas demonstrated some of the training he has received related to the use of remote sensing technologies for long-term surveillance of DOE-LM sites.

DOE Fellows Conference Participation

DOE LM Fellows Olivia Bustillo and Eduardo Rojas attended and presented at the Waste Management Symposia held virtually from March 8-12, 2021. The Waste Management Symposium is the world’s largest conference on radioactive waste management & disposal, decommissioning, packaging & transportation, facility siting and site remediation. After the conference, they met with Legacy Management leadership (director Carmelo Melendez and Jalena Dayvault) to discuss updates on their research and possible future work.

This year, DOE Fellow Olivia Bustillo also prepared and submitted an abstract titled “Characterization of Sediment from the Old Rifle Site” for the Waste Management Symposia 2022 student poster session.

DOE Fellows Summer Internship

DOE Fellows Olivia Bustillo and Eduardo Rojas completed their 8-week summer internship with DOE-LM at Grand Junction, CO, which served as the main office from which they traveled to several LM sites to perform sampling and surveys.

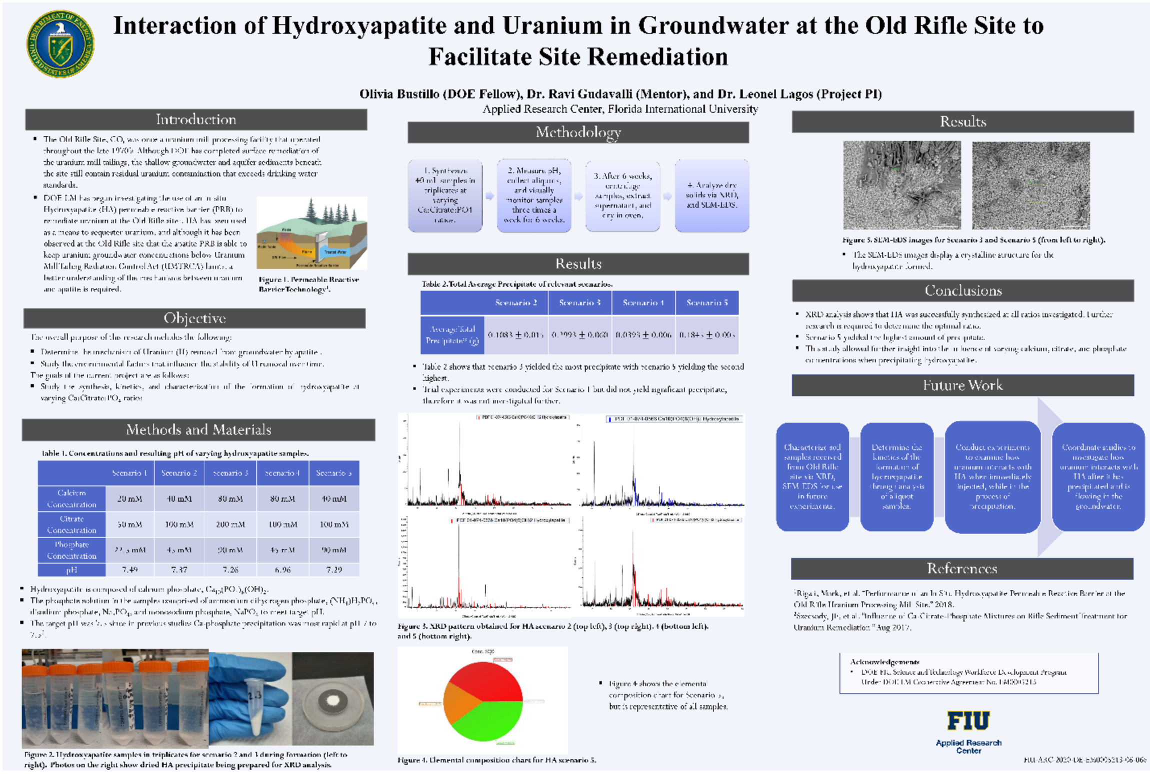

Figure 53. Poster prepared by DOE Fellow Olivia Bustillo for Waste Management Symposia 2021.

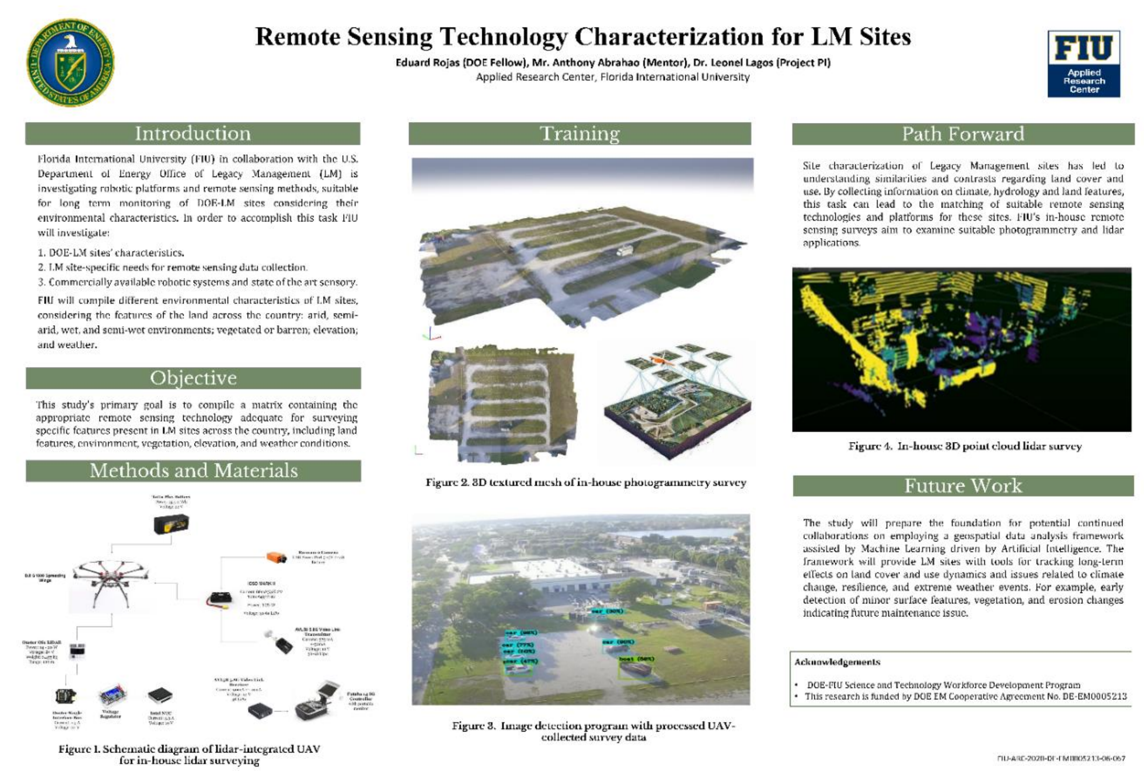

Figure 54. Poster prepared by DOE Fellow Eduardo Rojas for Waste Management Symposia 2021.

DOE Fellow Olivia Bustillo worked in the Environmental Sciences Laboratory at the Grand Junction, CO office alongside Peter Steves. While working in the lab, she was able to witness firsthand the process of collecting groundwater and surface water samples from the field and analyzing them in the lab. She also learned how to operate new instrumentation in the lab such as an ion chromatograph (IC) and a kinetic phosphorescence analyzer (KPA). In addition, being able to 'follow' the samples from the field to the lab provided Olivia the opportunity to learn about the importance of data integrity and proper sampling techniques.

Figure 55. DOE Fellow Olivia Bustillo learning to run the ion chromatograph in the Environmental Science Laboratory at the Grand Junction office with Peter Steves.

Olivia performed groundwater and surface water sampling activities with John Boylan and George Squibb at the Rocky Flats, CO site. She also learned about the procedures involved in different types of sampling activities that are ongoing at the site and how the different sampling activities assist the site in continuing to meet the requirements. This provided a perspective on sampling and how the site needs and history impact the sampling and preservation techniques.

Figure 56. DOE Fellow Olivia Bustillo conducting an alkalinity test at the Rocky Flats site during groundwater sampling.

DOE LM Fellow Eduardo Rojas worked and finalized his Aviation Safety Plan in accordance with the Legacy Management (LM) Aviation Program's standards to perform a drone baseline survey of the Rifle Disposal Site. Following the finalization of the Aviation safety plan, the DOE Fellow successfully conducted his first drone baseline survey of the Rifle Disposal Site located in Rifle, Colorado as the remote pilot in command.

Figure 57. Fellow with Principal Environment Engineer, George Squibb, performing fieldwork at Rocky Flats site to collect water samples.

Figure 58. Fellow accompanying Riverton Site Manager, Bill Frazier, and Principal Environmental Engineer, Sam Campbell, along with RSI contractors to view current Riverton water sampling.

Eduardo traveled to Rocky Flats, CO where he aided DOE Fellow Olivia with field sampling at the Rocky Flats site to collect groundwater samples to meet compliance and noncompliance standards along with Principal Environmental Engineer, George Squibb. He also met with Senior Ecologist, Jody Nelson, to learn about the vegetation and environmental transition of Rocky Flats from a site to a natural environment.

The final portion of the summer learning experience took place in Riverton, WY. The DOE Fellows accompanied Bill Frasier on a site visit, which consisted of meeting with various stakeholders to discuss the site. Throughout the various meetings, the Fellows met with different offices within the local tribal community (Shoshoni and Arapahoe representatives) as well as the local church officials and discussed the potential of future projects at the site, which aim to provide assistance for the local tribal community if certain funding is awarded to DOE. The church was involved to inform them of the history of the site, the ongoing activities, as well as this potential new project. During this trip, the Fellows were exposed to the importance of constant clear communication with the stakeholders as well as meeting the needs of the community. Lastly, the Fellows successfully presented their internship accomplishments and experience to LM Senior Management and FIU ARC staff. The DOE Fellows drafted summer internship reports based on their 8-week summer learning experiences with DOE-LM. Draft reports will be sent to LM collaborators for review and approval prior to submitting to DOE-HQ.

DOE Fellows Other Activities

FIU's Department of Energy (DOE) Office of Legacy Management (LM) Fellows, Olivia Bustillo and Eduardo Rojas, went to Colorado the week of October 19, 2020 to visit several LM sites. The three main sites visited include the Old Rifle Site, the Grand Junction Disposal Site, and the Rocky Flats site. The week began at the DOE LM Westminster office with Jalena Dayvault and Brian Stewart, where the students were given a tour of the office and attended a Job Safety Analysis (JSA) briefing.

<u>Old Rifle Site Visit</u>

On Tuesday October 20, 2020, the Fellows drove to the Old Rifle Site where they met with Tashina Jasso and Ken Williams. Jasso is a site manager for the Old Rifle site and Williams is a scientist, currently working for Lawrence Berkley National Laboratory, who has conducted experiments at the Old Rifle site relating to hydroxyapatite (HA) and uranium (U). Jasso and Williams discussed the site history and the hydroxyapatite technology they are exploring to remediate uranium. At the site, a small area was used to test this technology by strategically installing several wells so that the water can be tested at points up- and down-gradient from the point that the hydroxyapatite was injected to sequester uranium. The hydroxyapatite was injected using two different tanks, each containing a phosphate solution and calcium citrate. Once injected, the apatite forms in the area around the well and acts as a sponge, sequestering uranium as the groundwater passing through this area. Due to the low levels of uranium found at the site, this apatite barrier will take many decades to reach its maximum capacity. Williams expressed his belief that this technology has a lot of potential for remediating uranium in the groundwater. He also expressed his interest in developing a general procedure for this technology, so that it can be slightly modified for each site instead of needing to do a site-specific study every time it will be implemented. Williams also suggested it would be intriguing to explore how this process would be influenced with brackish water, characteristic of some sites. After the tour at the Old Rifle Site, the Old Rifle Disposal Site was visited. This vast site contains tailings from the former site, under five protective layers, each with their own purpose. The site also has several monitoring wells in place to ensure everything is functioning properly. DOE LM had previously conducted a UAV survey of the disposal cell cover to monitor any effects of erosion. Site Manager, Tashina Jasso, expressed when surveying the site that battery life of the UAV proposed a slight hindrance in time duration for the conventional topographic survey. Exploring a suitable and practical method to monitor the riprap layer for future potential erosion was of interest to DOE LM, as well as the opportunity to use LiDAR scanning to collect and detect the progressive changes.

Figure 59. DOE Fellows with Ken Williams (left to right): Olivia Bustillo, Eduardo Rojas, Ken Williams (top left), DOE Fellows with Tashina Jasso at the Old Rifle Disposal Site (top right), DOE Fellows with Tashina Jasso and Jalena Dayvault at the Old Rifle Disposal Site (bottom).

<u>Grand Junction Disposal Site</u>

On Wednesday October 21, 2020, pictures were taken of the Fellows with Jalena Dayvault for their social media page in front of the Atomic Legacy Cabin. The cabin was then briefly toured, which held information on the history of uranium mining and processing in Colorado, as well as relevant details about the Manhattan Project and the Cold War. Later, the Grand Junction disposal site tour was conducted with Bill Frazier. The disposal site, which is a Uranium Mill Tailings Radiation Control Act (UMTRCA) Title I site, is a vast area covering 360 acres of land. The large disposal cell, accounting for 94 acres, still has a remaining capacity of 223,000 CY as of 2020. This would take over 90 years to meet maximum capacity at the rate that they currently accept waste. Despite this, the site might be shut down in the next few years. This represents only one of the many challenges that LM has to face besides the ones found in their research. Although the site is functioning properly and is a vital resource for many in need of their disposal cell, they are waiting on approval from Congress to stay open. There is uncertainty regarding the reason for the delay, especially since keeping the site open is the most economically and environmentally smart decision for all involved. If the site is closed, the cost of the same waste disposal for their customers will be exponentially higher, as well as the environmental impact. The site is also currently conducting an Enhanced Cover Assessment Project. This project involves investigating options for allowing vegetation to grow on a few select patches of rock-armored, low-permeability UMTRCA covers. These covers are treated as evapotranspiration covers which control the percolation of precipitation into the tailings below. These patches are currently being monitored to determine if these methods are efficient enough.

Figure 60. Fellows with Jalena Dayvault and Bill Frasier at the Grand Junction Disposal site (top left); Grand Junction Disposal site cover (top right); Grand Junction Disposal site overview (bottom).

<u>Rocky Flats Site Tour:</u>

The final day in Colorado, October 22, 2020, consisted of traveling to the Rocky Flats site for a tour with Andy Keim, George Squibb, and John Boylan. Andy Keim is the site manager for Rocky Flats. George Squibb is a Principal Environmental Engineer and John Boylan is a Senior Hydrogeologist currently monitoring the Rocky Flats site. They provided extensive information on the history of the site, and then took the Fellows to key points at the site. The Fellows were able to visit their operating groundwater treatment systems, groundwater and surface water monitoring areas, along with the erosion control and monitoring systems. They were also able to see the Preble's meadow jumping mouse habitat that is being monitored and learned about site management activities. This site has also had many challenges other than the remediation at hand. The public has not always favored the site, and at times has feared it. There have been several misconceptions about the site and what has actually occurred there. There was even an episode on the television show Nightline where they claimed the site held America's most dangerous building. There are people who also want to construct a road through part of the site, so there are a lot of people interested in the site and its future. Overall, the trip was very beneficial for the Fellows to learn more about the history of LM and the challenges that they face other than the science at hand. Every LM site and office that was visited had a wonderful work environment, which was a great experience for the Fellows.

Figure 61. Overview of the water treatment system and the Rocky Flats site.

On August 4, 2021, DOE Fellows Olivia Bustillo and Eduardo Rojas graduated from FIU with Bachelor's degrees in Environmental Engineering and Mechanical Engineering respectively. Olivia has begun a Master's program in Environmental Engineering at FIU. She will be continuing her research with the Fellows program, which will include work for her thesis. Eduardo is pursuing employment opportunities while supporting his research topic at FIU.

Figure 62. DOE Fellows Oliva Bustillo and Eduardo Rojas during graduation Ceremony.

In addition, DOE Fellows participated in the FIU Program Review presentations held on 9/14 - 9/15 with DOE-HQ and site POCs and presented their research accomplishments. Below are the titles of their presentations.

- Hydroxyapatite Injection for Sequestering Uranium (U) in Groundwater - Olivia Bustillo
- Remote Sensing Technologies for Long-Term Surveillance of DOE-LM Sites - Eduardo Rojas

Figure 63. DOE LM Fellow Eduardo Rojas (Top-center) and FIU-ARC staff during the annual research review with DOE Officials.

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

FIU Year 1 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 Aurelien Meray
7. FIU Research Review - Project 4 - DOE Fellow Gisselle Gutierrez
8. FIU Research Review - Project 4 - DOE Fellow Jeff Natividad
9. FIU Research Review - Project 4 - DOE Fellow Mariah Doughman
10. FIU Research Review - Project 4 - DOE Fellow Philip Moore
11. FIU Research Review - Project 4 - DOE Fellow Sebastian Story
12. FIU Research Review - Project 5 - DOE Fellow Eduardo Rojas
13. FIU Research Review - Project 5 - DOE Fellow Olivia Bustillo
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