


Apatite Injection for Sequestering Uranium (U) in Groundwater

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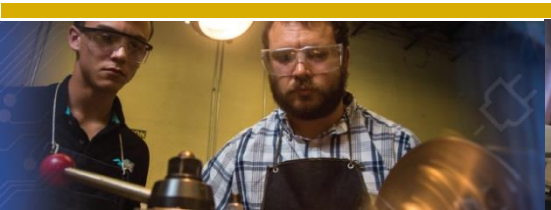


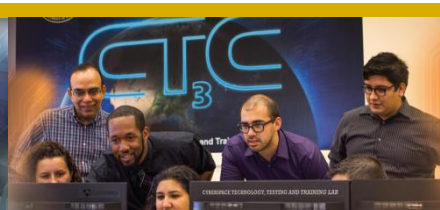

Project 5: Workforce Development and Training

Task 1 - Apatite Injection for Sequestering Uranium (U) in Groundwater

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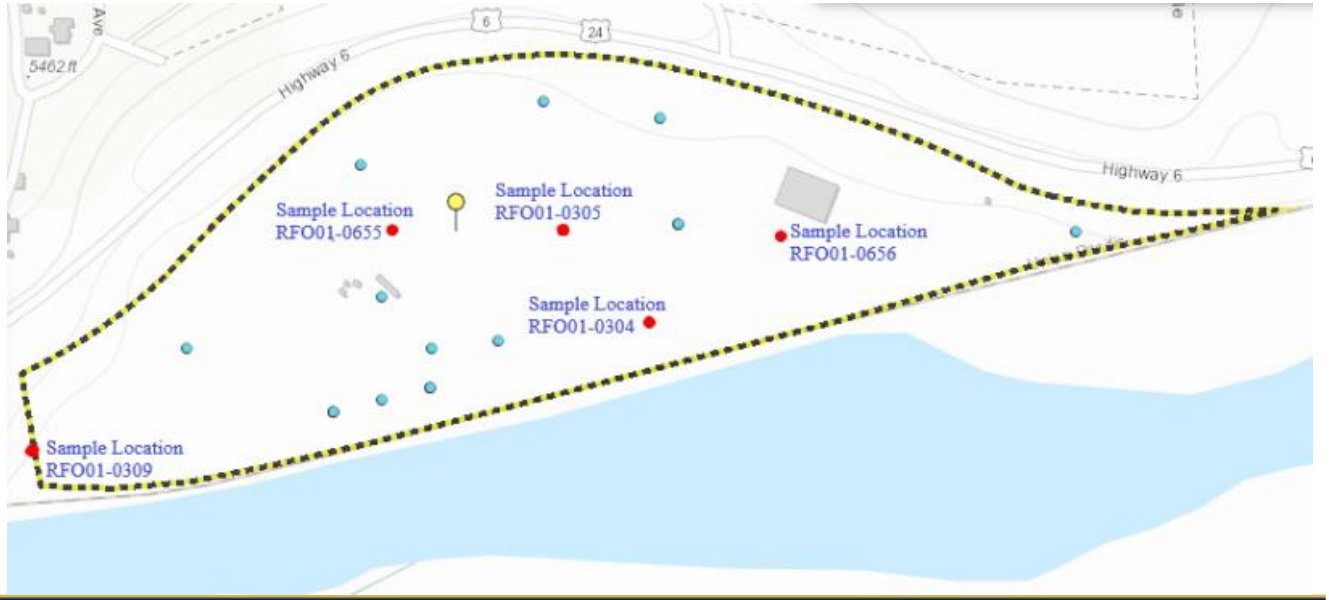
Site Needs:

The uranium remaining in the subsurface under the capped waste piles was predicted to be flushed by natural groundwater flow. However, uranium has persisted at elevated concentrations in groundwater much longer than predicted. Several studies proved that injection of apatite into groundwater have shown to sequester uranium. LM has implemented an in situ hydroxyapatite Permeable Reactive Barrier to remediate uranium at the DOE Old Rifle site in Colorado. While this process has proved to be effective, a better understanding of the uranium removal mechanisms behind the interaction is required.

Objective:

- Study the mechanism of U removal/sequestration from groundwater by apatite
- Study the environmental factors influence the stability of the removal of uranium



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Experimental Plan

Subtask 1.1
Studies kinetics and characterization of the formation of apatite

Subtask 1.2
Studies how the uranium will interact when it is immediately injected, while the apatite is in the process of precipitation

Subtask 1.3
Studies how the uranium interacts with the apatite after it has precipitated and is flowing in the groundwater

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Accomplishments

- Completed literature review on using Apatite to sequester Uranium
- Compiled data gathered from Geospatial Environmental Mapping System (GEMS) in regard to the Old Rifle site, which helped identify the pH of the area, uranium, calcium and phosphate concentration
- Prepared a study plan, which details the objectives and importance of this task
- Drafted the experimental procedures to achieve three subtasks
- Reviewed additional literature to better understand this task and the mechanisms behind the interaction

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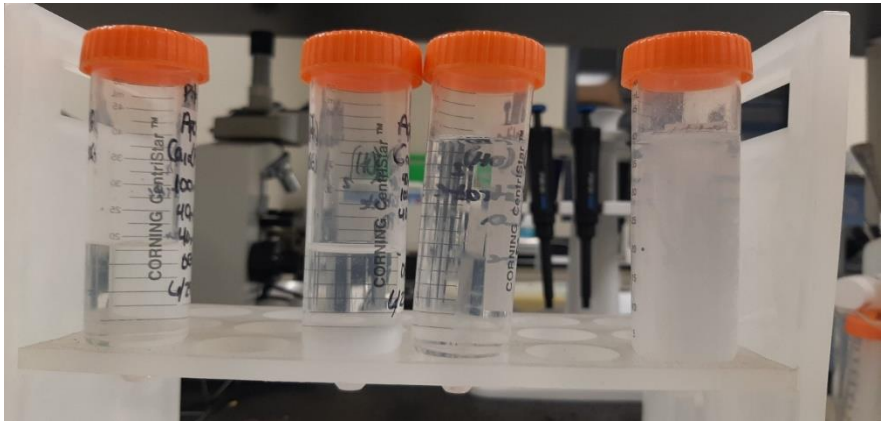
Trial Experiments

	Solution 1	Solution 2	Solution 3	Solution 4
Calcium Concentration	20mM	20mM	20mM	40mM
Citrate Concentration	50mM	50mM	50mM	100mM
Phosphate Concentration	20mM	20mM	22.5mM	45mM
Phosphate Salts	trisodium phosphate	trisodium phosphate	ammonium dihydrogen phosphate, disodium phosphate, monosodium phosphate	ammonium dihydrogen phosphate, disodium phosphate, monosodium phosphate
pH adjusted	yes	no	no	no
pH	7.50	11.59	7.50	7.40



- Target pH - 7.5
- Solution 1 met target pH but did not display formation of apatite
- Solution 2 did not meet target pH
- To meet target pH, phosphate solution was created with three salts instead of one
- Solutions 3 and 4 are made at different concentrations to test which is best for apatite formation
- Solutions 3 and 4 met target pH and began to show signs of apatite formation

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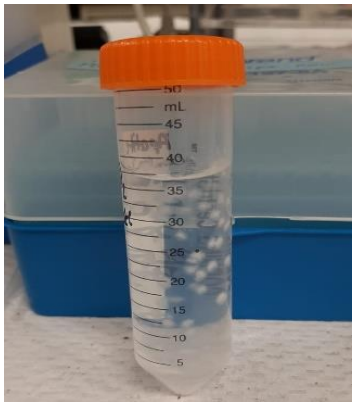
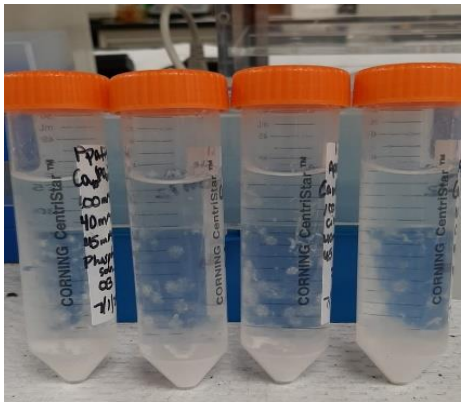
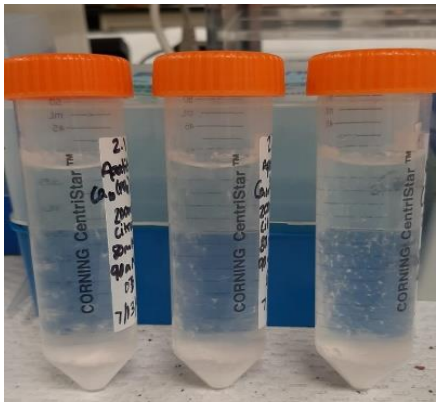
Current Samples







	Scenario 1	Scenario 2	Scenario 2.1	Scenario 2.2	Scenario 2.3	Scenario 3.1	Scenario 3.2	Scenario 3.3
Calcium Concentration	20 mM	40 mM	40 mM	40 mM	40 mM	80 mM	80 mM	80 mM
Citrate Concentration	50 mM	100 mM	100 mM	100 mM	100 mM	200 mM	200 mM	200 mM
Phosphate Concentration	22.5 mM	45 mM	45 mM	45 mM	45 mM	90 mM	90 mM	90 mM
pH	7.50	7.40	7.27	7.30	7.32	7.15	7.10	7.18

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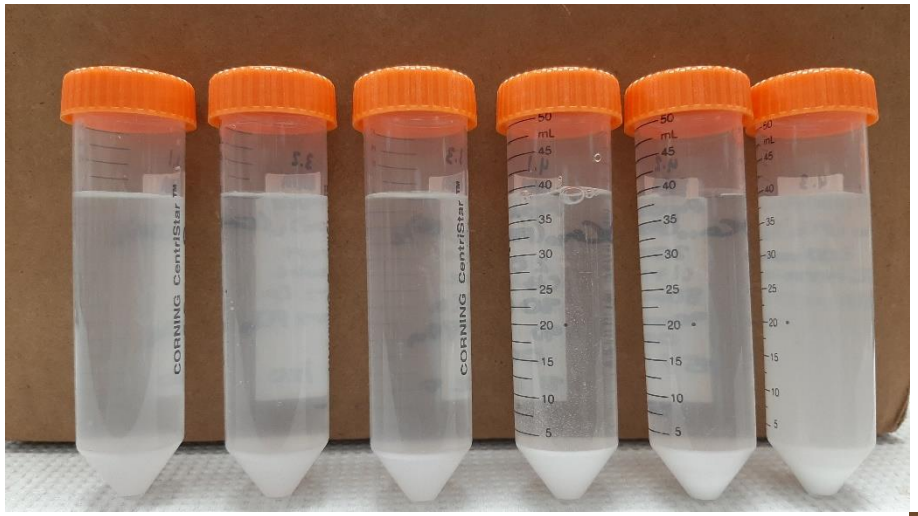
Additional Samples

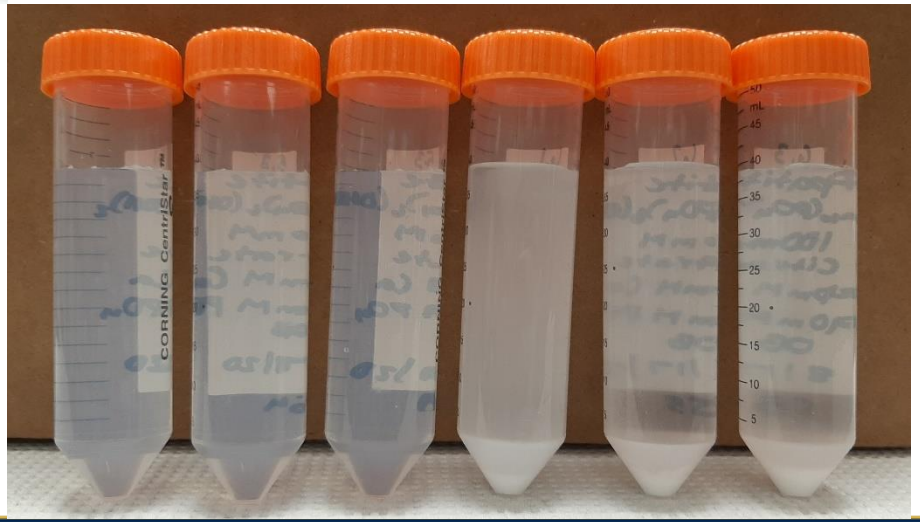
	Sample 3.1-3.3	Sample 4.1-4.3	Sample 5.1-5.3	Sample 6.1-6.3
Calcium Concentration	40 mM	80 mM	80 mM	40 mM
Citrate Concentration	100 mM	200 mM	100 mM	100 mM
Phosphate Concentration	45 mM	90 mM	45 mM	90 mM
pH	7.33 - 7.40	7.24 - 7.27	6.94 - 6.97	7.28 - 7.30

- Samples created with varying Ca:P ratio
- Aliquots taken throughout the length of the formation time period to see the concentration over time
- All pH values are within the optimum range for apatite formation and are monitored

Additional Samples Continued



From left to right: Sample 3.1, 3.2, 3.3, 4.1, 4.2, 4.3



From left to right: Sample 5.1, 5.2, 5.3, 6.1, 6.2, 6.3

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- Ongoing
  - Monitor pH of all samples and take 200 µL aliquots 3x a week
  - Dry solids from aliquots and analyze to monitor concentration
  - Prep trial samples for analysis
  - Begin prepping and analyzing the first set of samples

- Future work
  - Determine the characteristics of the apatite samples
  - Establish the kinetics of the formation of apatite, which is needed for the upcoming subtasks

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Acknowledgments

FIU ARC Mentor

Dr. Ravi Gudavalli

DOE-LM Collaborators

Ms. Jalena Dayvault

Dr. David Shafer

DOE-FIU Science and Technology Workforce Development Program

Dr. Leonel Lagos

Sponsored by the U.S. Department of Energy, Office of Legacy Management, under Cooperative Agreement #DE-EM0000598.

Backup Slides

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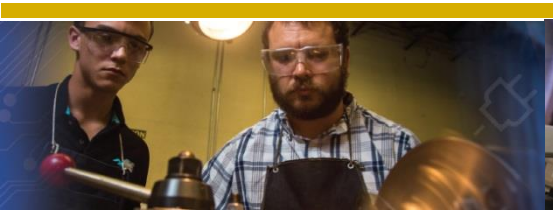

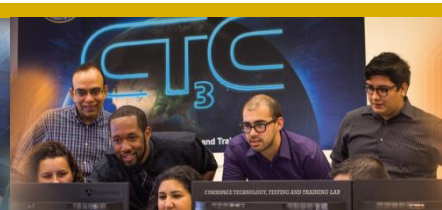

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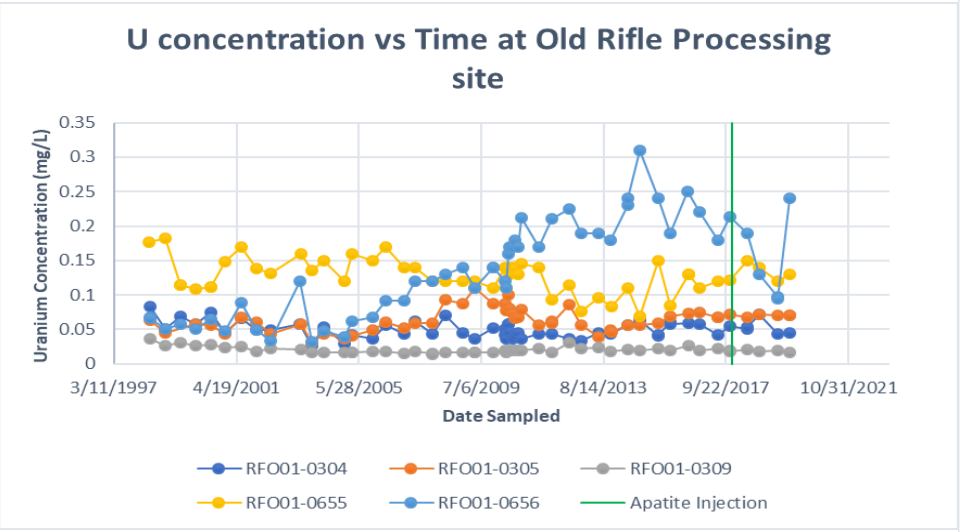

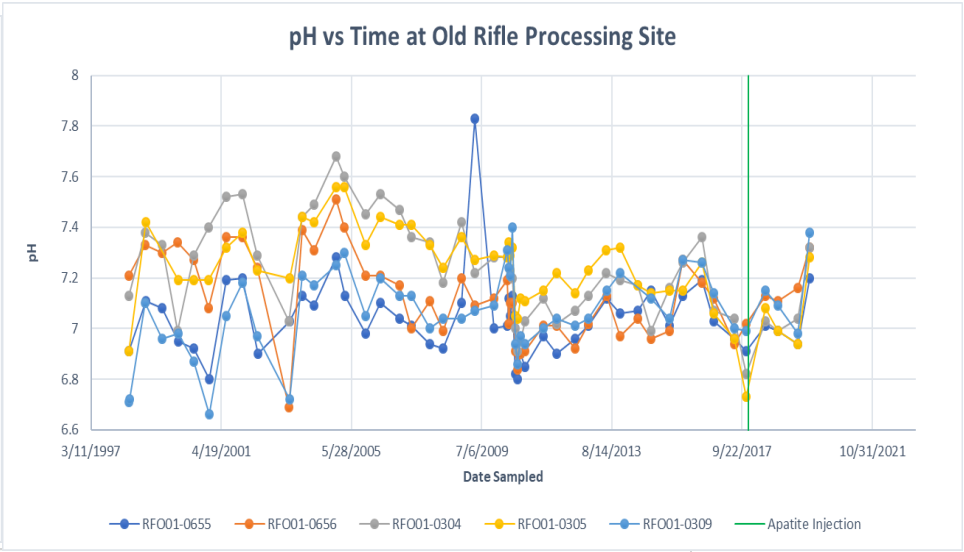

		Location									
		RFO01-0655		RFO01-0304		RF01-0305		RFO01-0309		RFO01-0656	
Condition	Dates	5/18/1998	11/7/2019	5/19/1998	11/7/2019	5/19/1998	11/7/2019	5/19/2020	11/7/2019	5/20/1998	11/7/2019
	pH	6.91	7.2	7.13	7.32	6.91	7.28	6.71	7.38	7.21	7.32
	Ca Concentration (mg/L)	164	190	196	210	207	180	154	180	200	180
	P Concentration (mg/L)	.1 ('07)	N/A	0.055 ('07)	N/A	0.065 ('07)	N/A	0.064 ('07)	N/A	n/a	0.091 ('07)
	ORP (mV)	-75	173.4	-52	115.7	-305	160.1	-364	74.5	204	71.2
	Temperature (°C)	10.9	14.2	8.8	13.8	10.3	14.7	11.6	15.58	8.4	17.91
	Uranium (mg/L)	0.177	0.13	0.0833	0.045	0.064	0.07	0.0367	0.017	0.0671	0.24
	Zone	Alluvium		Alluvium		Alluvium		Alluvium		Alluvium	

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Literature Review

Performance of an In Situ Hydroxyapatite Permeable Reactive Barrier at the Old Rifle Uranium Processing Mill Site

- Provided their injection formulation which contained the concentrations used, which was 40mM Ca, 100mM citrate, and 40mM phosphate
- Had graphs of the uranium concentrations in different wells at the old rifle site

Use of a Ca-Citrate-Phosphate Solution to Form Hydroxyapatite for Uranium Stabilization of Old Rifle Sediments: Laboratory Proof of Principle Studies

- Described the role of citrate in the solution, which is to keep Ca in the solution long enough for injection and transport of the reagents to the target area. Without citrate, a solution containing just Ca^{2+} and phosphate will rapidly form mono- and di-calcium phosphate
- Provided the specific location, depth, and type of soil used from the Old Rifle site
- Used a mix of phosphate salts (ammonium dihydrogen phosphate, disodium phosphate, and monosodium phosphate) and their concentrations used to get a solution at pH 7.5
- Optimum pH range for apatite formation is within 6.9 - 7.8

Influence of Ca-Citrate-Phosphate Mixtures on Rifle Sediment Treatment for Uranium Remediation

- Found that Ca-phosphate precipitation was most rapid at 7.5, with slower precipitation at lower pH