Monitoring of U(VI) Bioreduction After ARCADIS Demonstration at Savannah River Site F-Area

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Introduction

- The F/H Area Seepage Basins located in the center of Savannah River Site (SRS) (*Figure 1*) received approximately 1.8 billion gallons of acidic waste solutions. The acidic nature of the basin waste solutions triggered the mobilization of metals and radionuclides including soluble uranium (VI).

Figure 1. Aerial view of SRS

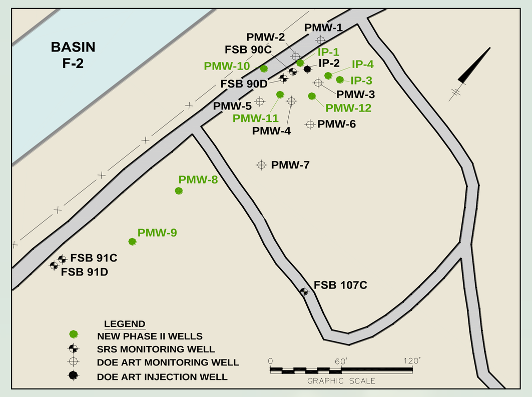

Figure 2. ARCAIDIS injection sites

- SRS F-Area sediments are acidic and composed predominantly of quartz sand with varying amounts of fine-grained minerals and iron-oxides.
- In 2010, ARCADIS implemented *in-situ* injections of a carbohydrate substrate to establish anaerobic reactive zones for metal and radionuclide remediation via the Enhanced Anaerobic Reductive Precipitation (EARP) process at the SRS F-Area (*Figure 2*).
- The addition of the molasses substrate solution to groundwater produces anaerobic conditions with redox values in the methanogenic or sulfate-reducing range conducive to the reductive precipitation of uranium.

$$UO2^{2+}(aq) + 2e^- = UO_2(s)$$

Objectives

- Determine the mineral composition of SRS fine clay fractions and identify all iron-oxide phases.
- Establish if ferrous carbonate and ferrous sulfide compounds will be present in the sediment after the bioreduction process has occurred. The presence of these compounds will indicate that anaerobic reductive conditions were established.
- Determine the types of reactions that might occur in the anaerobic aquifer.
- Determine if conditions will return to the initial state once samples are returned to aerobic conditions.

Methodology

- Microcosm studies were prepared with SRS sediments treated using a basal medium solution augmented with sulfate and molasses as well as a trace metal solution in the following amounts:

Batch 2			
Set #1	**Set #2**	**Set #3**	**Set #4**
20 mL of Soil	20 mL of Soil	20 mL of Soil	15 mL of Soil
12 mL of Basal Medium	12 mL of Basal Medium	12 mL of Basal Medium	12 mL of Basal Medium
500 ppm Sulfate	500 ppm Sulfate	-	-
5-10% by weight molasses	5-10% by weight molasses	5-10% by weight molasses	5-10% by weight molasses
0.5 mL of Anaerobic Bacteria	-	-	0.5 mL of Anaerobic Bacteria

Table 1. Batch 2 sample compositions

- To create anaerobic conditions necessary for the experiment, a vinyl anaerobic airlock chamber from COY Lab Products was used to ensure that no oxygen reached the samples.
- Half of the samples were augmented with sulfate in an attempt to create iron sulfide and stabilize reduced uranium.
- A pH evolution study was conducted to find the type of pH changes that occurred in the samples.
- Samples were sieved to 180 mm before X-ray Diffraction (XRD) analysis was conducted to identify any mineralogical changes in the samples. The experimental patterns were compared against known XRD patterns for siderite and pyrite.
- Liquid samples were filtered through 0.45 mm filters and were diluted by a factor of 200 in nitric acid (1%) for ICP-OES analysis to determine the ferrous iron concentration.

Results/Discussion

- XRD analysis indicated that the sediments contained quartz, kaolinite, montmorillonite, and goethite.
- All of the samples have followed a similar trend, with a decline in the pH values (*Table 2 and Figure 3*). It was noted that samples amended with sulfates had slightly higher pH than sulfate-free samples. The pH drop can be attributed to the fermentation process of molasses and the natural acidity of SRS soil used for the microcosm study. The low pH conditions are believed to have hindered the formation of bicarbonate/carbonate ions used to form the iron precipitates.
- XRD results confirmed the assumption that with low pH values no iron compounds would precipitate in the samples. The experimental patterns for each sample was compared with the patterns for siderite and pyrite; the results for these analyses were negative (*Figures 4-7*).

Date	Sample 1 pH Basal medium, 500 ppm sulfate, molasses, bacteria	Sample 2 pH Basal medium, 500 ppm sulfate, molasses	Sample 3 pH Basal medium, molasses	Sample 4 pH Basal medium, molasses, bacteria
11/24/2014	7	7.02	7	6.99
11/30/2014	4.98	4.92	4.98	5.14
12/11/2014	5.28	5.13	5.23	5.41
12/18/2014	4.71	4.62	4.63	4.74

Table 2. pH evolution study of Batch 2

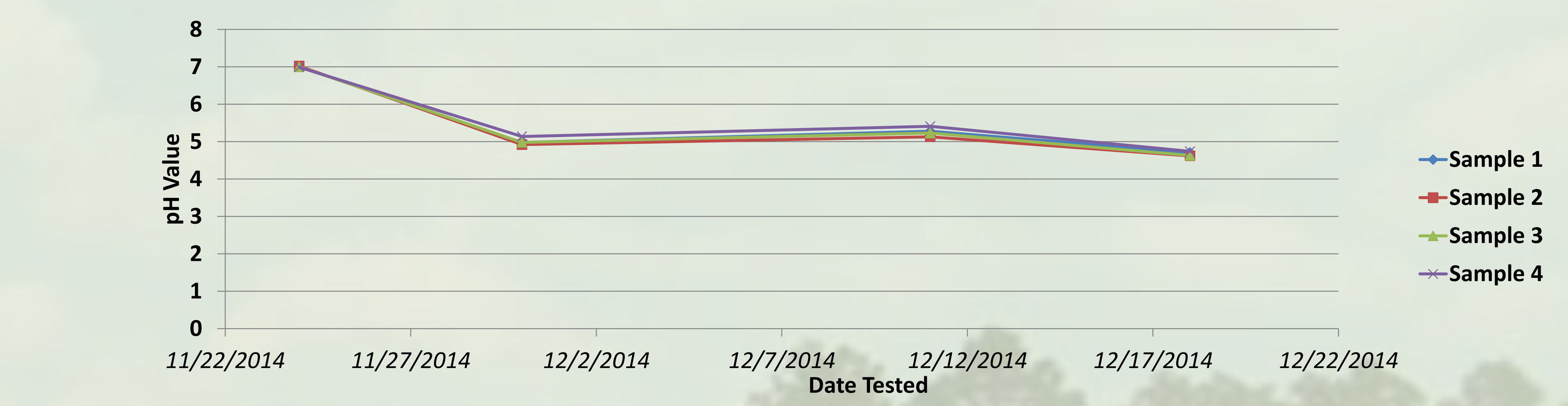

Figure 3. Graph of pH evolution study of Batch 2

Batch 2 – XRD Results

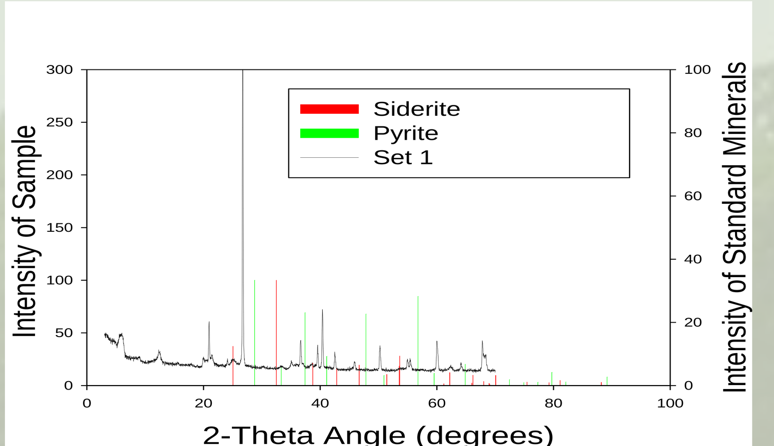

Figure 4. Set 1 XRD results vs Siderite and Pyrite

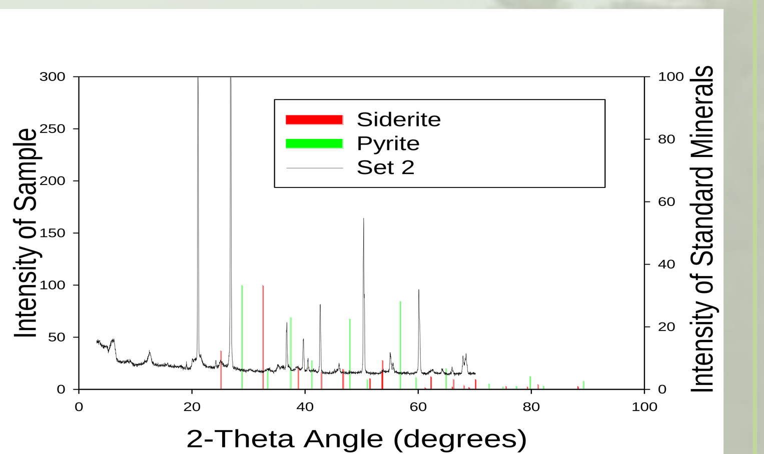

Figure 5. Set 2 XRD results vs Siderite and Pyrite

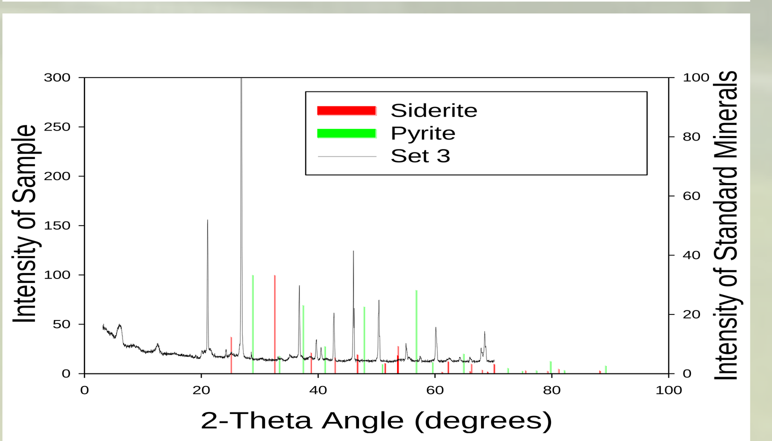

Figure 6. Set 3 XRD results vs Siderite and Pyrite

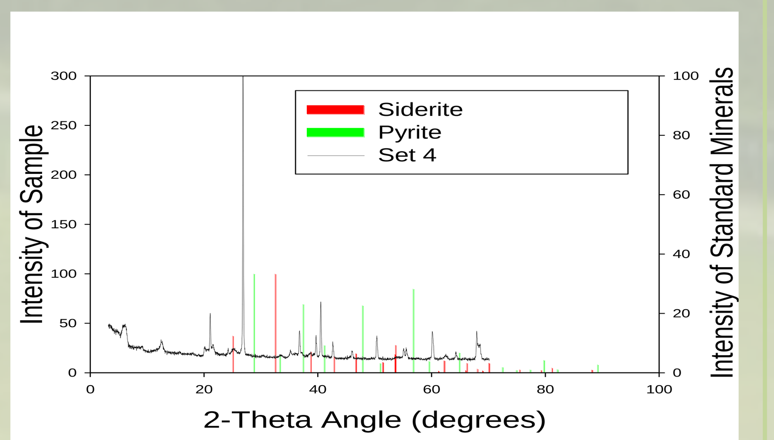

Figure 7. Set 4 XRD results vs Siderite and Pyrite

- ICP-OES analysis confirmed that there is ferrous iron present in the samples. The highest iron concentration being 13312.8 ppb for Batch 1, Sample 1-2, the lowest were in Batch 2 Samples 2,3, and 4 which may be below the calibration curve. This may also be an indication that the iron has precipitated in these samples.

Description	Fe Concentration, ppb	Description	Fe Concentration, ppb
Batch 1, Sample 1-1	1650.875	Batch 1, Sample 3-3	5349.698
Batch 1, Sample 1-2	13312.8	Batch 1, Sample 4-1	5494.83
Batch 1, Sample 1-3	8462.025	Batch 1, Sample 4-2	6118.962
Batch 1, Sample 2-1	4705.947	Batch 1, Sample 4-3	7596.792
Batch 1, Sample 2-2	4757.759	Batch 2, Sample 1	8651.304
Batch 1, Sample 2-3	5815.257	Batch 2, Sample 2	-
Batch 1, Sample 3-1	5730.317	Batch 2, Sample 3	-
Batch 1, Sample 3-2	4343.13	Batch 2, Sample 4	-

Figure 8. ICP-OES data

Future Work

- Conduct ICP analysis on the Batch 2 samples using a lower dilution factor.
- Determine the types of reactions that might occur in the anaerobic aquifer.
- Verify the continued sequestration of U(VI) in relation to the possible re-oxidation of minerals from the bioreduction zone.
- Sulfate concentrations will be examined using an ion analysis technique.
- Determine pH levels, sulfate concentrations, and iron concentrations after re-oxygenation.

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