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Washington, DC 20585

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U.S. Nuclear Regulatory Commission  
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Subject: U.S. Department of Energy Office of Legacy Management Report Entitled *Results of the Laboratory Batch Test of Phosphate Amendment Added to Shiprock Sediment and Groundwater* (NRC Docket No. WM-0058)

To Whom It May Concern:

Enclosed, for U.S. Nuclear Regulatory Commission (NRC) review, is a report prepared by the U.S. Department of Energy (DOE), Office of Legacy Management (LM) entitled *Results of the Laboratory Batch Test of Phosphate Amendment Added to Shiprock Sediment and Groundwater* (Document No. S24333).

This report provides results and interpretation of data collected during laboratory batch tests to evaluate the potential for in situ sequestration of uranium from groundwater using an injection of phosphate. Based on the results presented in this document LM is proceeding with laboratory column tests to further evaluate the suitability of this technique at the Shiprock site. This interim report will be followed by a final report that summarizes results for all the laboratory tests upon completion of the column tests.

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# Results of the Laboratory Batch Test of Phosphate Amendment Added to Shiprock Sediment and Groundwater

May 2019



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## Abbreviations

DOE	U.S. Department of Energy
ESL	Environmental Sciences Laboratory
µg/L	micrograms per liter
mL	milliliters
UMTRCA	Uranium Mill Tailings Radiation Control Act

## 1.0 Purpose and Scope

An in situ remedial technique being considered for use at the U.S. Department of Energy (DOE) Office of Legacy Management Shiprock, New Mexico, Disposal Site is to sequester uranium from groundwater and limit the mobilization of uranium from contaminated sediments. This technique involves the injection of phosphate amendment (Table 1) in groundwater to form hydroxyapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ ) and possibly whitlockite ( $\text{Ca}_3(\text{PO}_4)_2$ ). These minerals sequester uranium primarily by the adsorption of uranium to their surfaces independent of redox conditions. An initial evaluation of this technique using groundwater and sediment collected from the Shiprock site was recently completed at the Environmental Sciences Laboratory (ESL) in Grand Junction, Colorado. During the weeks of November 5 and 12, 2018, laboratory batch tests were conducted for the following objectives: (1) Determine whether hydroxyapatite and whitlockite will form in the subsurface with the injection of the phosphate amendment, (2) determine the amount of time required to form these minerals, and (3) determine if uranium concentrations in groundwater will decrease and the mobilization of uranium from sediments will be prevented. If these objectives are met, column tests, as described in DOE 2018, will be conducted to further evaluate the suitability of this technique at the Shiprock site.

Table 1. Composition and pH of the Phosphate Amendment

	$\text{Na}_2\text{HPO}_4$	$\text{NaH}_2\text{PO}_4$	$(\text{NH}_4)_2\text{HPO}_4$	$\text{CaCl}_2$	triNaCitrates	Total $\text{PO}_4^{3-}$	pH
(mM/L)	36.45	6.3	2.25	20	50	45.00	$7.52 \pm 0.30$
(g/L)	5.17	0.76	0.30	2.22	2.61	12.9	--

**Abbreviations:**

g/L = grams per liter

mM/L = millimoles per liter

## 2.0 Methods

San Juan River water, groundwater, and floodplain sediment used in the batch tests were collected at the Shiprock site during the week of September 3, 2018. San Juan River water was collected from sampling site 0899, groundwater was collected from well 1111, and sediment was collected from the area adjacent to well 1111. Groundwater was collected from and sediment was collected adjacent to well 1111 because this is one of four areas where high uranium concentrations persist despite several years of remedial pumping of contaminated groundwater (Figure 1). The chemical compositions of San Juan River water, groundwater, and the phosphate amendment are given in Table 2.

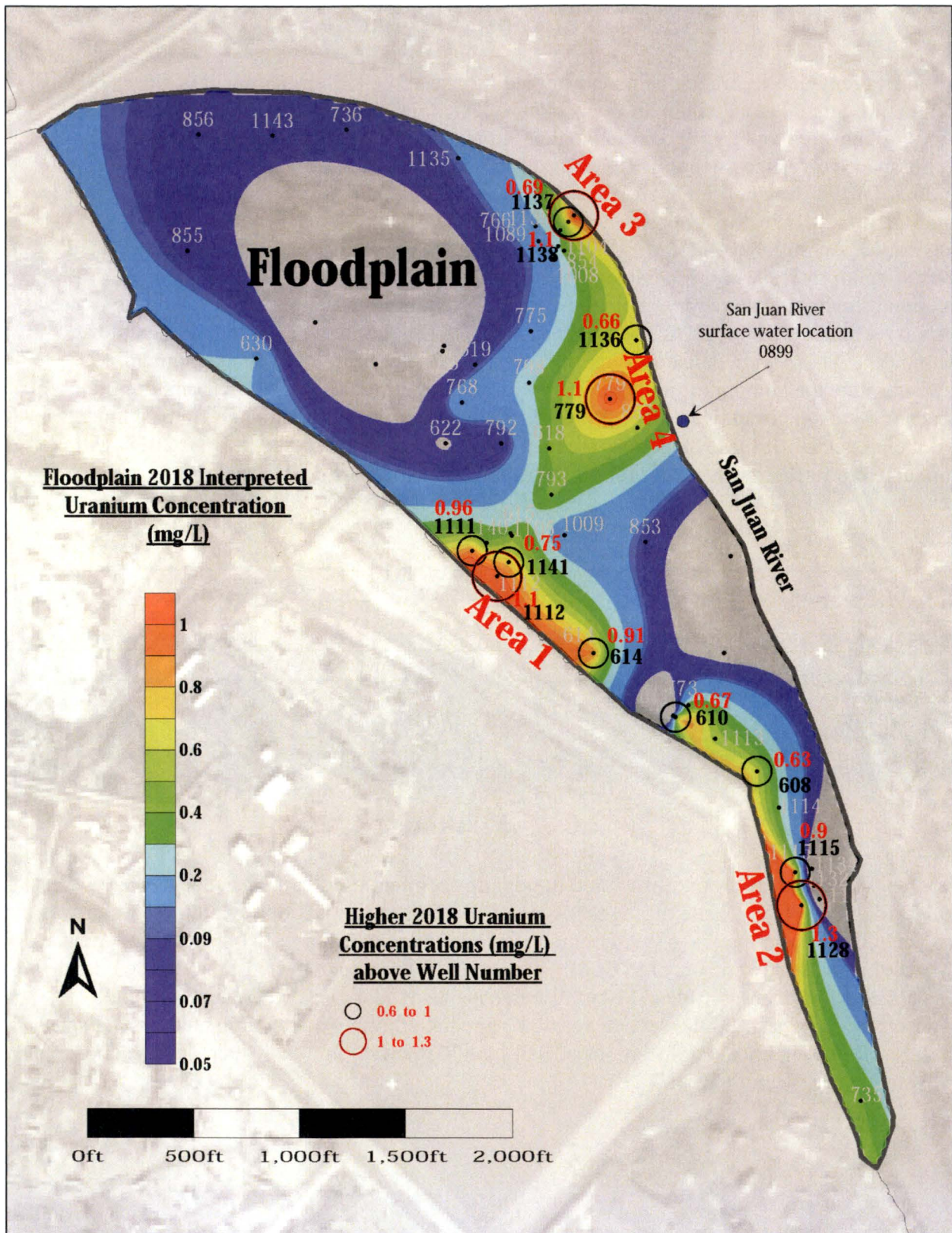


Figure 1. Location of the High Uranium Concentration Areas on the Floodplain at the Shiprock, New Mexico, Disposal Site



Table 2. Chemical Composition of San Juan River Water, Groundwater, and the Phosphate Amendment

	San Juan River	Well 1111	Phosphate Amendment, Filtered
pH (standard units)	8.19	6.76	7.57
Specific conductance ( $\mu\text{S}/\text{cm}$ )	445	14589	7770
Temperature ( $^{\circ}\text{C}$ )	20.28	23.47	23
Ca (mg/L)	45	430	320
Mg (mg/L)	5.8	1220	<8
Na (mg/L)	46	2620	2360
K (mg/L)	3.3	59	5.7
Alkalinity (mg/L as $\text{CaCO}_3$ )	107	1165	1808
Cl (mg/L)	8.8	413	583
$\text{SO}_4^{2-}$ (mg/L)	110	9202	110
$\text{NO}_3^-$ (mg/L)	3.2	185	<2.5
$\text{PO}_4^{3-}$ (mg/L as P)	<0.04	<0.4	550
$\text{PO}_4^{3-}$ (mg/L)	0.1	1.2	1686.6
U (ICP) ( $\mu\text{g}/\text{L}$ )	<100	790	<1000
U (KPA) ( $\mu\text{g}/\text{L}$ )	2	1040	<10

**Abbreviations:**

ICP = inductively coupled plasma

KPA = kinetic phosphorescence analysis

$\mu\text{S}/\text{cm}$  = microsiemens per centimeter

Batch tests were completed using method CB(WS-1) "Analysis of Water-Soluble Salt Deposits" described in Chapter 7 of the Legacy Management Support contractor *Environmental Sciences Laboratory Procedures Manual* (LMS/PRO/S04343). The batch tests were performed by placing 25 grams of air-dried sediment collected adjacent to well 1111 and 100 milliliters (mL) of groundwater in 250 mL Nalgene bottles and mixing with 100 mL of the phosphate amendment prepared in San Juan River water. The Nalgene bottles were placed on end-over-end stir bars for continuous agitation of the soil-water mix. The duration of the test was 7 days, and the bottles were removed from the end-over-end stir bars immediately after mixing, at intervals of 30 minutes, 1 hour, 4 hours, 8 hours, 1 day, and each day thereafter until the end of the week.

Two other solutions were prepared and removed from the end-over-end stir bars at the same intervals as the bottles with sediment, groundwater, and phosphate amendment solution. These solutions were a duplicate of the sediment, groundwater, and phosphate amendment solution and a control mixture consisting of sediment, groundwater, and San Juan River water without phosphate amendment. The purpose of the duplicate sample is to assess the reproducibility of the analytical measurements, and the purpose of the control sample is to determine if uranium concentrations change over time in the absence of phosphate amendment.

The phosphate amendment chemicals were mixed following the methodology developed for the testing of the phosphate amendment at the Old Rifle, Colorado, Processing Site (Rigali 2018):

- [1] Mix the Ca citrate solution using the following procedure:
  - [a] Add citrate as sodium citrate into water and mix until dissolved.
  - [b] Add Ca as  $\text{CaCl}_2$ , and then mix until dissolved.
  - [c] Set solution aside.
- [2] In a separate container, mix the phosphate solution using the following procedure:
  - [a] Heat water to  $\sim 70$  °C using a stir bar and a magnetic hot plate.
  - [b] First, add the  $\text{NaH}_2\text{PO}_4$ .
  - [c] Add the  $\text{Na}_2\text{HPO}_4$ .
  - [d] Add the  $(\text{NH}_4)_2\text{HPO}_4$ .
  - [e] Allow solution to cool.
- [3] Mix the two solutions, and then add the mixed solution to the 250 mL Nalgene bottles. The mixed solution was not allowed to sit for more than 24 hours because the microbes in the river water will begin to degrade the citrate.

### 3.0 Results

Results of the batch test are provided in Table 3.

These results were input into the U.S. Geological Survey geochemical code PHREEQC to calculate saturation indexes for various minerals that could potentially precipitate from solution or dissolve during the batch test. These include phosphate-containing minerals other than hydroxyapatite and whitlockite, such as autunite ( $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2$ ), H-autunite ( $\text{H}_2(\text{UO}_2)_2(\text{PO}_4)_2$ ), Na-autunite ( $\text{Na}_2(\text{UO}_2)_2(\text{PO}_4)_2$ ), K-autunite ( $\text{K}_2(\text{UO}_2)_2(\text{PO}_4)_2$ ), and brushite ( $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ). Calcite ( $\text{CaCO}_3$ ), dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ), gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), and halite ( $\text{NaCl}$ ) were included to determine if the dissolution or precipitation of these minerals could contribute to the differences in the concentration of the major ions that were measured during the batch test.

Values of the saturation index for each of these minerals are presented in Table 4.

Table 3. Chemical Composition of the Batch Test Solutions

	Initial	30 minutes	1 hour	4 hours	8 hours	1 day	2 days	3 days	4 days	5 days	6 days	7 days
<b>Soil + Groundwater + Phosphate Amendment</b>												
pH (standard units)	7.12	7.19	7.19	7.16	7.14	7.2	7.1	7.17	6.98	6.91	6.92	6.94
Specific conductance (µS/cm)	10420	10140	10180	10350	10510	10520	10540	10500	11320	11800	11730	11670
Temperature (°C)	23	23	23	23	23	23	23	23	23	23	23	23
Ca (mg/L)	400	400	390	370	360	350	330	340	320	330	320	320
Mg (mg/L)	640	660	630	610	620	600	600	600	620	610	620	610
Na (mg/L)	2520	2590	2460	2530	2470	2460	2600	2500	2600	2420	2330	2360
K (mg/L)	38	39	38	38	39	36	36	36	35	37	37	37
Alkalinity (mg/L as CaCO <sub>3</sub> )	948	1316	1304	1352	1288	1352	1520	1524	1732	1876	1900	1884
Cl (mg/L)	464	462	467	469	481	472	441	447	454	451	451	460
SO <sub>4</sub> <sup>2-</sup> (mg/L)	4320	4437	4450	4277	4660	4481	4565	4443	4447	4583	4699	4579
NO <sub>3</sub> <sup>-</sup> (mg/L)	110	113	116	113	118	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5
PO <sub>4</sub> <sup>3-</sup> (mg/L as P)	280	270	250	240	210	200	170	180	170	150	150	150
PO <sub>4</sub> <sup>3-</sup> (mg/L)	858.6	828.0	766.6	736.0	644.0	613.3	521.3	552.0	521.3	460.0	460.0	460.0
U (ICP) (µg/L)	<500	<500	<500	<500	<500	<500	<500	<500	<500	<500	<500	<500
U (KPA) (µg/L)	510	360	300	140	71	56	59	67	67	34	38	22
<b>Soil + Groundwater + Phosphate Amendment Duplicate</b>												
pH (standard units)	7.18	7.16	7.22	7.16	7.14	7.19	7.13	7.16	7.12	7.11	6.93	6.95
Specific conductance (µS/cm)	10250	10160	10090	10340	10400	10420	10550	10520	11100	11250	11760	11690
Temperature (°C)	23	23	23	23	23	23	23	23	23	23	23	23
Ca (mg/L)	400	380	380	370	350	340	330	340	330	320	310	320
Mg (mg/L)	640	650	600	620	610	610	610	600	630	600	610	610
Na (mg/L)	2520	2640	2460	2460	2480	2530	2370	2410	2410	2450	2290	2380
K (mg/L)	37	39	38	39	40	37	36	37	37	36	37	37
Alkalinity (mg/L as CaCO <sub>3</sub> )	1340	1324	1312	1352	1344	1352	1552	1652	1640	1684	1876	1860
Cl (mg/L)	470	466	467	469	475	465	443	136	430	459	460	463
SO <sub>4</sub> <sup>2-</sup> (mg/L)	5529	4378	4958	5562	5474	4638	4453	4438	4665	4696	4669	4465

Table 3. Chemical Composition of the Batch Test Solutions (continued)

	Initial	30 minutes	1 hour	4 hours	8 hours	1 day	2 days	3 days	4 days	5 days	6 days	7 days
<b>Soil + Groundwater + Phosphate Amendment Duplicate (continued)</b>												
NO <sub>3</sub> <sup>-</sup> (mg/L)	115	114	112	114	114	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5
PO <sub>4</sub> <sup>3-</sup> (mg/L as P)	280	270	270	240	220	190	170	180	170	150	150	150
PO <sub>4</sub> <sup>3-</sup> (mg/L)	858.6	828.0	828.0	736.0	674.6	582.6	521.3	552.0	521.3	460.0	460.0	460.0
U (ICP) (µg/L)	<500	<500	<500	<500	<500	<500	<500	<500	<500	<500	<500	<500
U (KPA) (µg/L)	500	430	320	160	86	53	58	76	74	70	40	37
<b>Soil + Groundwater + San Juan River Water</b>												
pH (standard units)	7.42	7.23	7.19	7.25	7.34	7.54	7.39	7.36	7.34	7.39	7.31	7.33
Specific conductance (µS/cm)	8070	7920	7910	8270	8230	8200	8320	8180	8740	8580	8570	8610
Temperature (°C)	23	23	23	23	23	23	23	23	23	23	23	23
Ca (mg/L)	280	300	310	340	330	330	300	330	320	320	310	310
Mg (mg/L)	660	660	630	630	640	620	610	590	610	620	610	610
Na (mg/L)	1440	1470	1340	1480	1360	1310	1310	1280	1300	1260	1260	1270
K (mg/L)	38	38	36	38	38	36	36	33	37	37	36	38
Alkalinity (mg/L as CaCO <sub>3</sub> )	680	672	660	712	692	720	704	696	744	708	712	688
Cl (mg/L)	204	211	201	220	208	212	193	191	195	197	196	196
SO <sub>4</sub> <sup>2-</sup> (mg/L)	4640	4717	4470	5896	4838	4647	4550	4465	4568	4693	4531	4931
NO <sub>3</sub> <sup>-</sup> (mg/L)	113	116	112	121	116	115	109	109	110	111	110	111
PO <sub>4</sub> <sup>3-</sup> (mg/L as P)	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
PO <sub>4</sub> <sup>3-</sup> (mg/L)	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
U (ICP) (µg/L)	<500	<500	<500	<500	<500	<500	<500	<500	<500	<500	<500	<500
U (KPA) (µg/L)	480	560	500	530	540	560	540	530	560	560	550	540

**Abbreviations:**

ICP = inductively coupled plasma  
 KPA = kinetic phosphorescence analysis  
 µS/cm = microsiemens per centimeter

Table 4. Saturation Indexes for Various Minerals in Each of the Batch Test Solutions

	Autunite	H-Autunite	Na-Autunite	K-Autunite	Brushite	Calcite	Dolomite	Gypsum	Halite	Hydroxyapatite	Whitlockite
<b>Soil + Groundwater + Phosphate Amendment</b>											
Initial	-13.15	-20.61	-9.08	-12.36	-12.30	0.42	1.34	-0.20	-4.70	9.03	4.20
30 min	-13.32	-20.91	-9.22	-12.50	-12.32	0.69	1.90	-0.20	-4.69	9.23	4.29
1 hour	-13.44	-21.02	-9.37	-12.63	-12.35	0.69	1.89	-0.20	-4.71	9.11	4.21
4 hours	-14.14	-21.64	-10.03	-13.31	-12.39	0.67	1.86	-0.23	-4.69	8.85	4.06
8 hours	-14.67	-22.12	-10.57	-13.81	-12.47	0.62	1.78	-0.22	-4.69	8.49	3.84
1 day	-14.75	-22.31	-10.64	-13.94	-12.48	0.70	1.95	-0.24	-4.70	8.67	3.93
2 days	-15.36	-22.67	-11.15	-14.51	-12.33	0.57	1.69	-0.28	-4.71	8.62	3.98
3 days	-14.57	-22.05	-10.43	-13.75	-12.55	0.74	2.03	-0.25	-4.72	8.34	3.73
4 days	-14.84	-21.92	-10.64	-14.02	-12.64	0.60	1.79	-0.28	-4.70	7.24	3.14
5 days	-15.42	-22.37	-11.30	-14.56	-12.70	0.58	1.74	-0.26	-4.73	6.80	2.88
6 days	-15.33	-22.28	-11.23	-14.46	-12.72	0.58	1.76	-0.26	-4.75	6.76	2.85
7 days	-15.78	-22.77	-11.66	-14.90	-12.71	0.60	1.79	-0.27	-4.73	6.88	2.92
<b>Soil + Groundwater + San Juan River Water</b>											
Initial	-13.52	-21.46	-9.80	-12.59	-15.53	0.67	2.02	-0.26	-5.29	0.29	-1.79
30 min	-12.70	-20.28	-8.99	-11.80	-15.53	0.50	1.66	-0.22	-5.26	-0.40	-2.13
1 hour	-12.64	-20.17	-9.04	-11.81	-15.50	0.48	1.59	-0.21	-5.32	-0.44	-2.14
4 hours	-12.93	-20.56	-9.24	-12.07	-15.50	0.55	1.68	-0.12	-5.26	-0.21	-2.02
8 hours	-13.26	-21.10	-9.66	-12.40	-15.47	0.66	1.92	-0.17	-5.30	0.27	-1.77
1 day	-14.11	-22.37	-10.55	-13.31	-15.45	0.89	2.36	-0.19	-5.31	1.18	-1.30
2 days	-13.43	-21.34	-9.82	-12.58	-15.49	0.69	2.00	-0.22	-5.35	0.36	-1.73
3 days	-13.38	-21.27	-9.84	-12.65	-15.45	0.70	1.96	-0.18	-5.36	0.46	-1.66
4 days	-13.40	-21.24	-9.83	-12.56	-15.47	0.69	1.97	-0.19	-5.35	0.27	-1.77
5 days	-13.45	-21.39	-9.91	-12.61	-15.47	0.71	2.02	-0.19	-5.36	0.46	-1.67
6 days	-13.17	-20.94	-9.62	-12.34	-15.48	0.63	1.87	-0.21	-5.36	0.09	-1.86
7 days	-13.13	-20.92	-9.56	-12.24	-15.49	0.62	1.84	-0.19	-5.36	0.11	-1.86

**Note:**

A negative sign indicates that the solution is undersaturated with respect to a mineral. A positive sign indicates that the solution is saturated with respect to a mineral.

### 3.1 Objectives 1 and 2. Determine if Hydroxyapatite and Whitlockite Will Form and the Amount of Time Required to Form These Minerals

A calculation of saturation indexes using PHREEQC indicates that throughout the experiment the soil plus groundwater plus phosphate amendment solution was saturated with respect to hydroxyapatite and whitlockite, was undersaturated with respect to gypsum, halite, autunite, H-autunite, Na-autunite, K-autunite, and brushite ( $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ), and was saturated with respect to calcite and dolomite. Additional evidence for the formation of hydroxyapatite and whitlockite in the soil plus groundwater plus phosphate amendment solution is the change in the concentration of calcium and phosphate relative to the change in the soil plus groundwater plus San Juan River water solution over time (Figure 2). In the soil plus groundwater plus phosphate amendment solution, calcium and phosphate decrease over time, but in the soil plus groundwater plus San Juan River water solution, calcium varies slightly throughout the experiment and is slightly higher at the end of the experiment than at the beginning, and phosphate is consistently below the reporting limit.

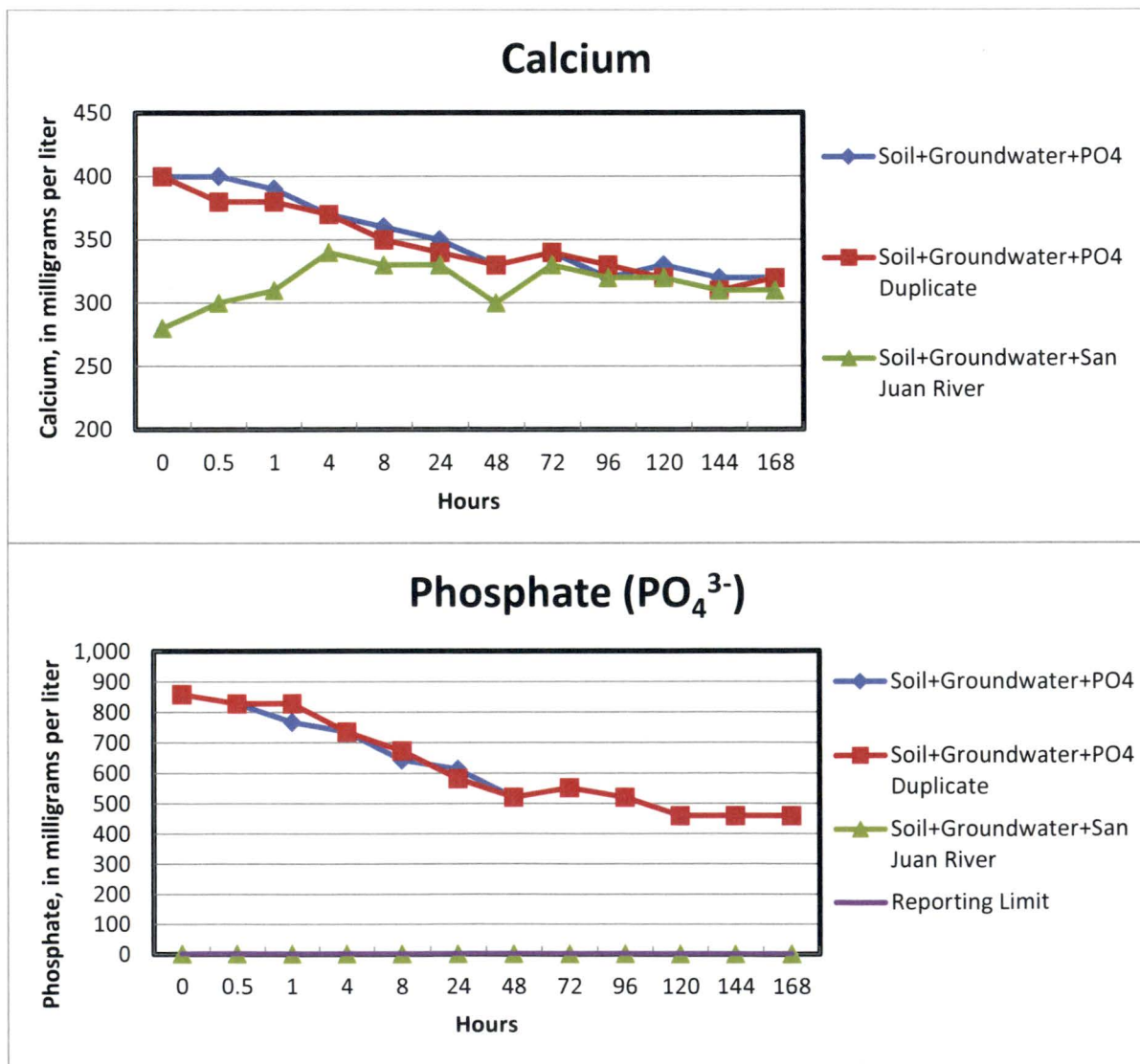


Figure 2. Concentrations of Calcium and Phosphate During the Batch Test

The soil plus groundwater plus San Juan River water solution throughout the experiment was undersaturated with respect to gypsum, halite, autunite, H-autunite, Na-autunite, K-autunite, brushite and whitlockite, saturated with respect to calcite and dolomite, but interestingly was saturated with respect to hydroxyapatite throughout most of the experiment.

The soil plus groundwater plus San Juan River solution appears to have been slightly saturated or in equilibrium with respect to hydroxyapatite beginning with the sample collected at 8 hours. The concentration of uranium, however, did not decrease over time in this sample. This indicates that either hydroxyapatite did not form, or it formed in amounts small enough that it had no effect on uranium concentrations. The kinetics of a reaction (the speed at which a reaction occurs) also influences when a reaction will occur. A positive saturation index does not mean that a reaction will occur immediately, kinetic effects may prevent a reaction from occurring in a reasonable time frame.

The amount of time required to form hydroxyapatite is needed to determine the minimum stop-flow time that allows hydroxyapatite to form during the column tests (DOE 2018). ESL staff noticed a small amount of precipitate upon mixing the amendment solution, but the water in the flasks did not start to get cloudy until around the 8–24 hour sample and became cloudier over time. The phosphate amendment used in this experiment results in the rapid formation of calcium phosphate compounds such as whitlockite or amorphous calcium phosphate compounds, but hydroxyapatite can take days to weeks to form (Szecsody et al. 2016). Geochemical modeling of the addition of phosphate amendment to groundwater at the Old Rifle site indicated that whitlockite would form first followed by apatite (Rigali 2018). Based on the values of the saturation indexes and the changes in the concentration of calcium and phosphate shown in Figure 2, it appears that whitlockite and hydroxyapatite could have formed immediately upon mixing and kept forming until day 5.

To determine the sequence of the formation of whitlockite and hydroxyapatite and the processes controlling the concentration of the major ions, the inverse modeling function of PHREEQC was used to model the changes in solution chemistry between each time increment. The inverse modeling function usually produces many solutions to account for the changes in the chemistry between the modeled solutions. It is up to the user to select the model that is the most valid based on geochemical principles and knowledge of the system. Since the solution was consistently saturated with respect to calcite, whitlockite, and hydroxyapatite, these phases were allowed to precipitate in the inverse model. Although the solution was consistently saturated with respect to dolomite, it was not included because the kinetics of dolomite formation would preclude the formation of dolomite during the duration of this experiment (Drever 1997).

To account for changes in the concentration of sulfate (mostly increases over time), gypsum was allowed to either precipitate or dissolve, because the solution was slightly undersaturated with respect to gypsum. Changes in the concentration of magnesium, sodium, and potassium were accounted for by cation exchange because (1) overall, the changes in concentration were small and variable, increasing slightly between some time increments and decreasing in others, (2) the sediments in the batch experiment were clay to silt size, which would favor cation exchange reactions, and (3) magnesium and sodium could not precipitate from solution because dolomite was not included in the model and the solution was consistently undersaturated with respect to halite. None of the autunite minerals or brushite was included in the inverse models because all

solutions were well undersaturated with respect to these minerals so they would not precipitate from solution. Selected results of the inverse modeling are presented in Table 5.

Table 5. Results of the Inverse Modeling of Selected Time Increments of the Batch Test (in mol/L)

Phases Transferred	Dissolved	Precipitated	Adsorbed	Desorbed
<b>Hour 4–8</b>				
Gypsum	0.0024	-	-	-
Whitlockite	-	0.0004879	-	-
CaX2	-	-	0.001186	-
MgX2	-	-	-	0.001173
NaX	-	-	-	-
KX	-	-	-	0.00002617
CO <sub>2</sub> (g)	0.000345	-	-	-
<b>Day 3 to 4</b>				
Gypsum	0.001858	-	-	-
Whitlockite	-	0.0001620	-	-
CaX2	-	-	0.001873	-
MgX2	-	-	-	-
NaX	-	-	-	0.003771
KX	-	-	0.00002549	-
CO <sub>2</sub> (g)	0.00719	-	-	-
<b>Day 4 to 5</b>				
Gypsum	0.0006626	-	-	-
Hydroxyapatite	-	0.0002175	-	-
CaX2	-	-	-	0.0006771
MgX2	-	-	-	-
NaX	-	-	0.001406	-
KX	-	-	-	0.0000517
CO <sub>2</sub> (g)	0.005126	-	-	-
<b>Day 5 to 6</b>				
Gypsum	0.001095	-	-	-
CaX2	-	-	0.001347	-
MgX2	-	-	-	0.001347
NaX	-	-	-	-
KX	-	-	-	-
CO <sub>2</sub> (g)	0.0004119	-	-	-

**Abbreviation:**

X2 or X = Quantity of the exchange species in moles per liter

Up to day 4, the majority of models produced indicated that whitlockite formation was occurring. Between day 4 and 5, more of the models indicated that hydroxyapatite was forming. Between days 5 and 6 and 6 and 7, neither whitlockite nor hydroxyapatite was formed in the inverse models, and this is consistent with the analytical data, as the concentrations of calcium and phosphate do not change from day 5 to day 7 (Table 2 and Figure 2). Therefore, it is possible that whitlockite and hydroxyapatite were forming immediately upon mixing, but perhaps whitlockite formed first, followed by the formation of hydroxyapatite between days 4 and 5. This would be in agreement with the findings at the Old Rifle site.



The inverse modeling presents a general understanding of reactions that could be occurring and not an exact quantitative description of the reactions. Cation exchange most likely is responsible for the changes in the concentration of the cations, but most of the changes appear to be within analytical error ( $\pm 0.1\%$ ) based on differences between the soil plus groundwater plus phosphate amendment solution and the duplicate (Table 2). The large increase in alkalinity that occurred during the batch test (Table 3) cannot be explained on the basis of the dissolution of calcite because each solution was saturated with respect to calcite (Table 4). The source of the alkalinity must be the degradation of sodium citrate, but was not included in the inverse models because this chemical is not in any of the PHREEQC databases.

### 3.2 Objective 3. Determine Changes in the Concentration of Uranium

A comparison of uranium concentration in the soil plus groundwater plus phosphate amendment solution with the uranium concentration in the soil plus groundwater plus San Juan River solution shows that the addition of the phosphate amendment rapidly resulted in an immediate reduction in uranium groundwater concentration from 1040 to 510  $\mu\text{g/L}$  (Figure 3). Uranium concentrations continued to decline with time and were lower than the Uranium Mill Tailings Radiation Control Act (UMTRCA) groundwater standard of 44  $\mu\text{g/L}$  by day 5 and remained below this concentration until the end of the batch test.

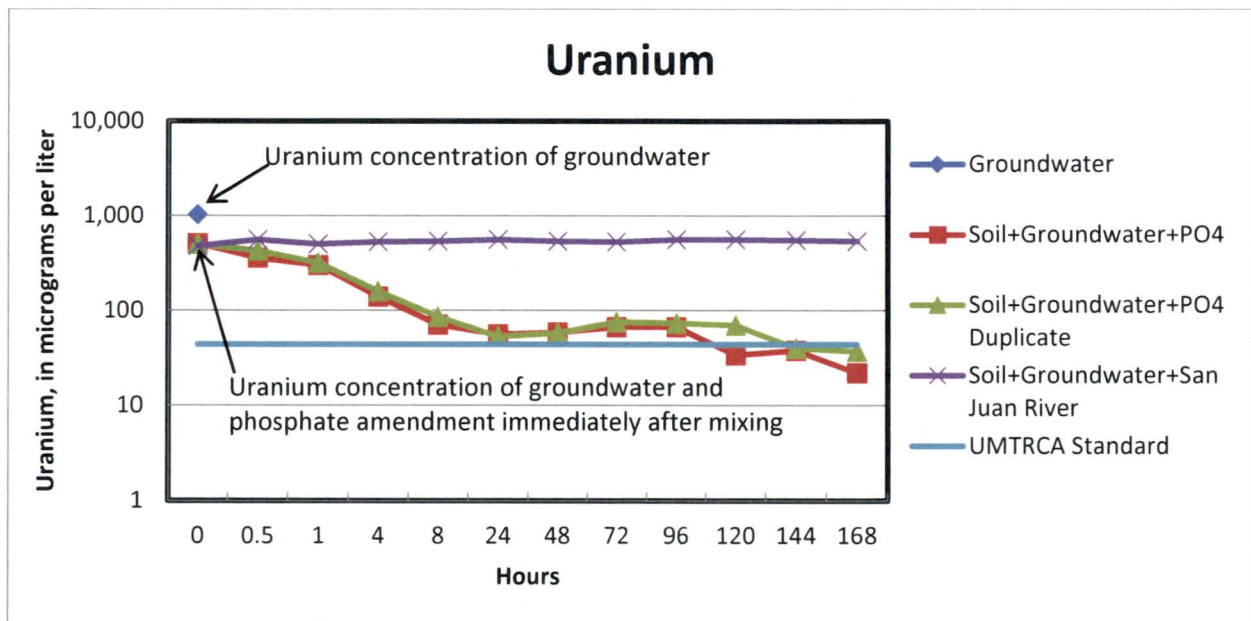


Figure 3. Uranium Concentrations During the Batch Test

The initial decrease in the concentration of uranium was a result of mixing 100 mL of groundwater with 100 mL of the phosphate amendment with a uranium concentration of less than the reporting limit of 10  $\mu\text{g/L}$ . A 1:1 mixing ratio would decrease uranium concentration in well 1111 groundwater at a concentration of 1040 to 520  $\mu\text{g/L}$ . The difference between the predicted concentration and measured concentration of 510  $\mu\text{g/L}$  is within the typical analytical error of 5%.

Throughout the experiment, the concentration of uranium in the duplicate sample was nearly identical to that in the solution containing the phosphate amendment. The concentration of uranium in the soil plus groundwater plus San Juan River solution varied slightly over the duration of the experiment, with an initial concentration of 480 µg/L and final concentration of 540 µg/L. Perhaps this is an indication that a small amount of uranium was leached from the soil during the experiment or that there was some analytical error.

### 3.3 Reaction Mechanism

The saturation indexes indicate that adsorption of uranium to whitlockite and hydroxyapatite is the mechanism causing the decrease in the concentration of uranium following the initial dilution caused by mixing groundwater with the phosphate amendment. Inverse modeling indicates that whitlockite formed first followed by the formation of hydroxyapatite starting at day 4. It is possible that both compounds formed throughout the batch test. Stable concentrations of calcium and phosphate from days 5 to 7 indicate that the formation of phosphate minerals was complete by day 5.

Another possible mechanism that can reduce the concentration of uranium is coprecipitation with calcite (uranium could substitute for calcium or adsorb to calcite as calcite precipitates out of solution) since the soil plus groundwater plus phosphate amendment solution is saturated with respect to calcite throughout the experiment. The soil plus groundwater plus San Juan River water solution, however, is also saturated with respect to calcite throughout the experiment, but neither calcium nor uranium decreased in this solution, so perhaps calcite precipitation is not occurring. Also, inverse modeling can explain changes in solution chemistry between each time increment without the precipitation of calcite.

## 4.0 Conclusion

Results of the batch test show that the addition of phosphate amendment to groundwater collected from the floodplain of the Shiprock, New Mexico, Disposal Site with an initial uranium concentration of 1040 µg/L decreased uranium to below the UMTRCA groundwater standard of 44 µg/L within 5 days. The concentration of uranium remained below the UMTRCA standard until the end of the batch test at 7 days. All available evidence indicates that the mechanism by which this reduction in concentration occurred was the adsorption of the constituent to whitlockite and hydroxyapatite. It is likely that whitlockite formed immediately and that hydroxyapatite formed starting at day 4, but based on the saturation indexes, it is also possible that both compounds were forming simultaneously. Regardless of the timing of the formation of these compounds, it appears that the formation of these phosphate minerals ceased by day 5. The large increase in alkalinity that occurred throughout the batch test was attributed to the breakdown of sodium citrate.

These results indicate that further evaluation of the use of this technique at the Shiprock site by column tests as described in DOE 2018 is warranted. Stable concentrations of calcium and phosphate from days 5 to 7 indicate that the formation of phosphate minerals was complete by day 5. Thus, a minimum stop-flow time of 5–7 days for the column tests seems reasonable.

## 5.0 References

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