



Department of Energy

Washington, DC 20585

July 23, 2018

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Subject: Final Pilot Study Report for In Situ Biosequestration for the Remediation of Uranium in Alluvial Groundwater at the Monument Valley, Arizona, Uranium Mill Tailings Radiation Control Act (UMTRCA) Site

Dear Ms. Roanhorse:

Enclosed is the final pilot study report prepared by the University of Arizona entitled *Pilot Study for In Situ Biosequestration for the Remediation of Uranium in Alluvial Groundwater at the Monument Valley, Arizona, UMTRCA Site*. This pilot study was conducted by the University of Arizona, in collaboration with Navarro Research and Engineering, Inc., contractor to the U.S. Department of Energy Office of Legacy Management, at the Monument Valley, Arizona, Processing Site. The timeframe of the study was between April 1, 2015, and September 30, 2017.

Please contact me at (970) 248-6621 or Angelita.Denny@lm.doe.gov if you have any questions. Please address any correspondence to:

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Office of Legacy Management
2597 Legacy Way
Grand Junction, CO 81503

Sincerely,

Angelita Denny, Site Manager
Office of Legacy Management

Enclosure

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File: MON 0100.02 (records)





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U.S. Nuclear Regulatory Commission
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Washington, DC 20555-0001

Subject: Pilot Study for In Situ Biosequestration for the Remediation of Uranium in Alluvial Groundwater at the Monument Valley, Arizona, Uranium Mill Tailings Radiation Control Act (UMTRCA) Site

To Whom It May Concern:

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Sites\MON6-26-18 MON Pilot Study for Uranium Biosequestration Study (NRC)



FINAL PROJECT REPORT

Pilot Study for In Situ Biosequestration for the Remediation of Uranium in Alluvial Groundwater at the Monument Valley, Arizona, UMTRCA Site

Period: April 1, 2015–September 30, 2017

Prepared for:

**Navarro Research and Engineering, Inc.
Contractor to the U.S. Department of Energy
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2597 Legacy Way
Grand Junction, CO 81503**

September 30, 2017

Prepared by:

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Contents

Abbreviations	ii
Executive Summary	1
1.0 Introduction	1
1.1 Background	1
1.2 Objective and Approach	2
2.0 Project Site	3
3.0 Bench-scale Tests	4
3.1 Methods	4
3.2 Results	8
4.0 Field Test	14
4.1 Test Methods	14
4.2 Results of Current Pilot Test	17
5.0 Comparison to Other Studies	22
6.0 Summary and Conclusions	23
7.0 Acknowledgements	24
8.0 References	24

Figures

Figure 1. Schematic of in situ biosequestration (modified from EURSSEM 2016).....	1
Figure 2. Result of prior in situ biosequestration pilot test conducted near the center of the nitrate/sulfate groundwater plume at the Monument Valley site. Time zero represents the injection of the electron donor (ethanol). Uranium (U) concentration is presented on the right vertical axis. Graph modified from Miao et al. (2014).	2
Figure 3. Site location map, Monument Valley, Arizona, processing site	5
Figure 4. Features associated with the former ore-processing area of the Monument Valley site. 6	
Figure 5. Location of the current and prior pilot tests at the Monument Valley site; concentrations reported represent mean values	7
Figure 6. Breakthrough curves of bromide, nitrate, sulfate, and uranium after injection of site groundwater. No electron donor added. For all relevant figures, C/C_0 represents the effluent concentration divided by the injection concentration; PV represents the number of pore volumes.	9
Figure 7. Breakthrough curves of bromide, sulfate, nitrate, and uranium after injection of site groundwater with ethanol as the electron donor. The numbers 1–4 represent the experiment stages described in the text.	10
Figure 8. Breakthrough curves of bromide, sulfate, nitrate, and uranium after injection of site groundwater with ethanol as the electron donor (replicate).....	10
Figure 9. Column before (left), during (center), and after (right) acclimation with intermittent injection of ethanol	11
Figure 10. Breakthrough curves of bromide, sulfate, nitrate, and uranium after injection of site groundwater with various electron donors.....	12
Figure 11. Column before (a), during (b), and after (c) acclimation by the intermittent injection of acetate	13
Figure 12. Breakthrough curves of bromide, sulfate, nitrate, and uranium after injection of site groundwater with ethanol and elevated nitrate (600 mg/L).....	14

Figure 13. Map of well and borehole locations for current pilot-test area. Arrows represent 1.5 m lengths unless otherwise noted.....	16
Figure 14. Storage tanks at the site (looking southwest)	16
Figure 15a. Photographs of sediment collected before and after ethanol injection	17
Figure 15b. Photographs of sediment collected 18 months after ethanol injection	17
Figure 16. Oxidation–reduction potential (ORP) per well as a function of time after ethanol injection.....	19
Figure 17. Dissolved oxygen (DO) per well as a function of time after ethanol injection.....	19
Figure 18a. Concentrations of sulfate, nitrate, sulfide, and uranium as a function of time after ethanol injection; 662 is the upgradient well; 699, 700, 701, and 702 are injection wells; 703 and 704 are downgradient monitoring wells.....	20
Figure 18b. Concentrations of uranium as a function of time after ethanol injection; 662 is the upgradient well; 699, 700, 701, and 702 are injection wells; 703 and 704 are downgradient monitoring wells	21
Figure 19a. Concentrations of iron in groundwater as a function of time after ethanol injection	21
Figure 19b. Concentrations of manganese in groundwater as a function of time after ethanol injection.....	21

Abbreviations

cm	centimeters
cm/hr	centimeters per hour
DOE	U.S. Department of Energy
EPA	U.S. Environmental Protection Agency
ft	feet
ft/yr	feet per year
g	grams
hr	hours
km	kilometers
L	liters
m	meters
m ²	square meters
m ³	cubic meters
m/yr	meters per year
µg/L	micrograms per liter
mg/L	milligrams per liter
mL/min	milliliters per minute
UMTRCA	Uranium Mill Tailings Radiation Control Act

Executive Summary

This report presents an overview of the results of a project designed to assess the efficacy of in situ biosequestration for the treatment of uranium-contaminated groundwater at the Monument Valley, Arizona, Uranium Mill Tailings Radiation Control Act (UMTRCA) site. The project was a collaborative, jointly funded effort, with funding provided by the U.S. Department of Energy through its contractor (Navarro Research and Engineering, Inc.), and the Superfund Research Program, funded by the National Institute of Environmental Health Sciences. A 1.5-year pilot test and associated laboratory experiments were performed. The test was conducted in the former ore-processing area of the site, where there is a small plume of elevated uranium concentrations in the groundwater. The laboratory experiments were conducted using groundwater and alluvial sediment collected from the site of the pilot test. The results of the current pilot test are compared to those obtained from a prior pilot test conducted several years ago near the center of the nitrate and sulfate plume. The concentration of uranium is much higher and the nitrate and sulfate concentrations are much lower at the site of the current test.

The efficacy of in situ biosequestration using four different electron donors, acetate, benzoate, ethanol, and glucose, was evaluated in laboratory experiments. The results of the laboratory experiments indicated that ethanol was the most effective electron donor. Uranium concentrations in solution decreased greatly during and after the acclimation phase. Specifically, concentrations decreased from approximately 400 to approximately 1 microgram per liter ($\mu\text{g/L}$), which is significantly below the regulatory standard of 44 $\mu\text{g/L}$ established by UMTRCA. Mass-balance calculations showed that approximately 76% of uranium input was sequestered. Uranium concentrations rebounded upon the introduction of oxygenated water with no electron donor. Approximately 80% of the sequestered uranium was released, with 20% of that originally sequestered remaining so.

Ethanol solution (0.5%) was injected over a 1-day period into several closely spaced wells at the site. The results of groundwater and sediment characterization conducted before, during, and after the injection demonstrated that reducing conditions were generated. Large decreases in nitrate, along with moderate decreases in sulfate, were observed. Concentrations of uranium at the downgradient monitoring wells decreased by approximately 25%, from approximately 600 to approximately 450 $\mu\text{g/L}$. Uranium concentrations rebounded approximately 1 year after ethanol injection. The concentrations were not reduced to below the UMTRCA regulatory standard.

The percent reduction in uranium concentration was lower for the current pilot test. However, the uranium concentration in groundwater at the site of the prior pilot test is approximately 30 times lower than that for the current test site. Accounting for the differences in concentrations, the mass of uranium sequestered per liter of groundwater was approximately 100 versus approximately 10 $\mu\text{g/L}$ for the current and prior tests, respectively. The sequestration was maintained for approximately 2.5 years for the prior pilot test, versus approximately 1 year for the current pilot test. It is noteworthy that reducing conditions and uranium sequestration were maintained for a notable period even though uranium-contaminated groundwater was continually flowing into the treatment zone. Differences in the sequestration periods are likely at least partly due to differences in constituent concentrations. The use of a 10-times-lower ethanol concentration for the current pilot test may also have impacted the results; the prior pilot test used a 5% ethanol solution compared to a 0.5% ethanol solution used for the current pilot test.

Overall, the results of the pilot tests indicate that ethanol injection successfully stimulated microbial activity and decreased groundwater concentrations of uranium at the site. Based on the results of this study, successful application of this biosequestration approach would likely require periodic electron-donor injections to maintain reducing conditions and associated sequestration effects. Additional testing would be required to determine optimal operational conditions for promoting cost-effective treatment at the site.

1.0 Introduction

1.1 Background

Natural restoration, the process of contaminant attenuation under the action of naturally occurring in situ processes, is not always effective in meeting regulatory levels for various groundwater contaminants. Very few alternatives to natural restoration (or monitored natural attenuation) are available for the remediation of large groundwater contaminant plumes containing uranium or similar constituents. Methods to enhance the rates of natural attenuation and improve the feasibility of monitored natural attenuation for inorganic contaminants are a current focus of research. One promising alternative, in situ biosequestration, has potential for the remediation of large, deep contaminant plumes containing uranium (Figure 1). This approach has been pilot tested, for example, at the U.S. Department of Energy (DOE) Rifle site in Colorado (Williams et al. 2011).

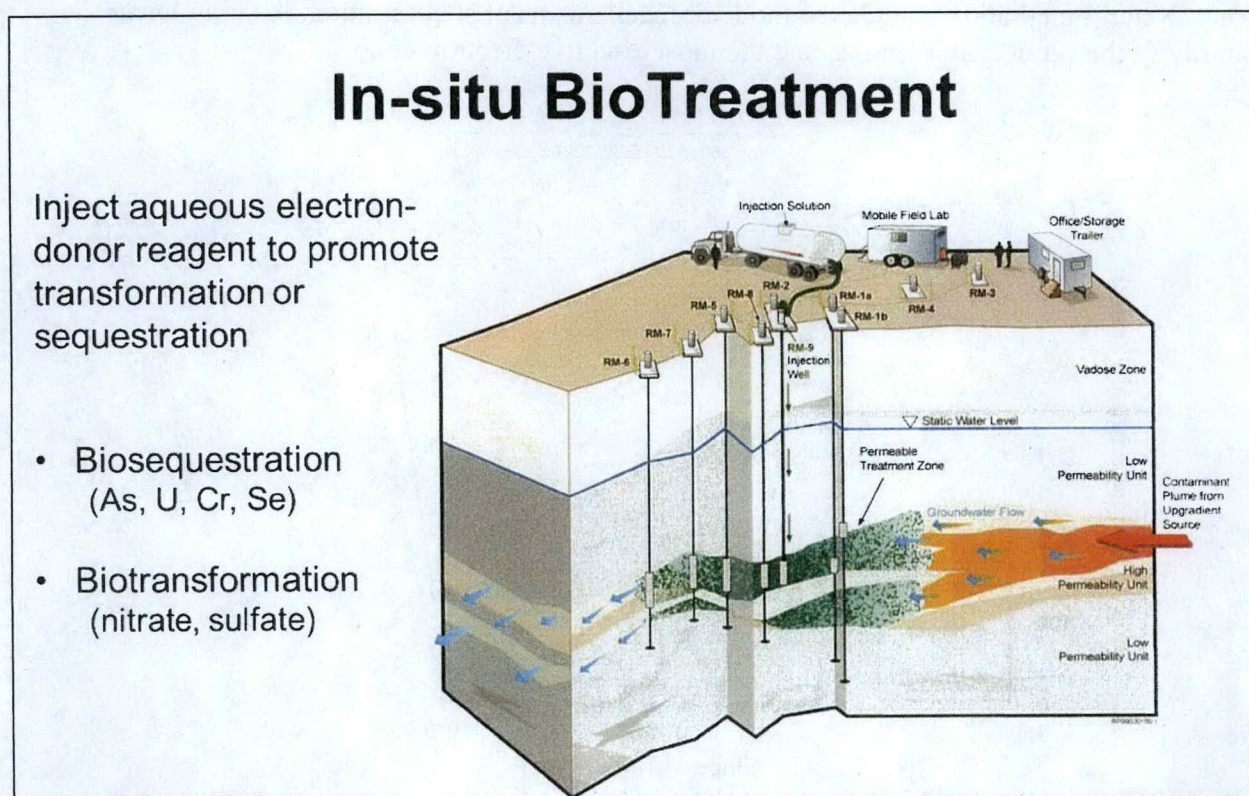


Figure 1. Schematic of in situ biosequestration (modified from EURSSEM 2016)

In situ biosequestration entails the injection of a reagent solution into a treatment zone to stimulate microbial activity and generate reducing conditions (Figure 1), which induces sequestration (via bioprecipitation and/or enhanced adsorption) of targeted contaminants. This sequestration in turn reduces the aqueous concentration and therefore the bioavailability of the contaminant.

The results from prior research efforts have demonstrated that in situ biosequestration can significantly influence natural and enhanced attenuation of constituents, including uranium, in groundwater. However, the results have also revealed a set of critical issues that must be addressed for broad-scale understanding of natural attenuation processes and for effective, successful application of in situ biosequestration for groundwater remediation. One such issue is the long-term efficacy of the process. For example, uranium concentrations in groundwater were observed to rebound within several weeks after the cessation of substrate injection at the Rifle, Colorado, test site (Williams et al. 2011). In contrast, Brusseau and colleagues conducted a prior pilot in situ biosequestration test at the DOE Monument Valley, Arizona, Processing Site (a Uranium Mill Tailings Radiation Control Act (UMTRCA) site) that attained longer-term sustainability of uranium sequestration, with concentration reductions maintained for approximately 2.5 years (Figure 2, Miao et al. 2014). This poses the question of why sites vary in efficacy of long-term biosequestration, and it highlights the need for improved understanding and prediction of remediation effects. Other critical unknowns, which are likely to be site-specific in many cases, for the effective application of biostimulated in situ biosequestration for groundwater remediation include the mode or mechanisms of sequestration, the long-term stability of the sequestered phases, and the most effective electron donor.

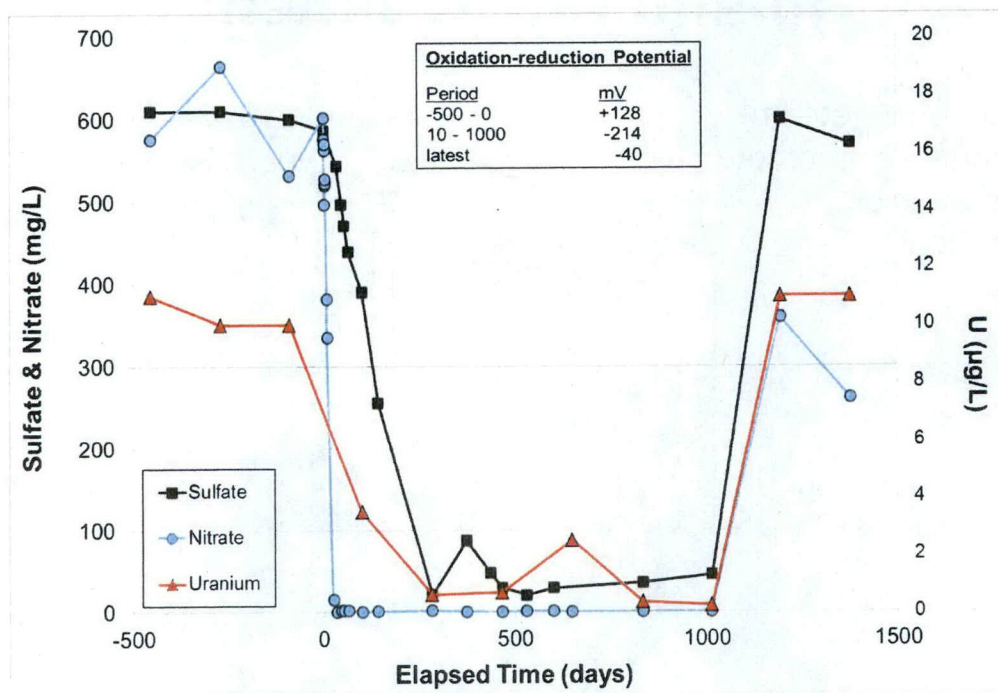


Figure 2. Result of prior in situ biosequestration pilot test conducted near the center of the nitrate/sulfate groundwater plume at the Monument Valley site. Time zero represents the injection of the electron donor (ethanol). Uranium (U) concentration is presented on the right vertical axis. Graph modified from Miao et al. (2014).

1.2 Objective and Approach

The current project consisted of A 1.5-year pilot test and associated laboratory experiments. The objective of the project was to investigate the feasibility and long-term efficacy of in situ biosequestration for the remediation of uranium-contaminated groundwater at the Monument

Valley site. We posit that the feasibility and effectiveness of in situ biosequestration are site dependent, influenced by specific conditions and properties of the site. The unique properties of subsurface environments in the southwest United States require focused investigation to evaluate the potential effectiveness of in situ biosequestration for this region. The project comprised a collaborative, jointly funded effort, with funding provided by DOE through its contractor (Navarro Research and Engineering, Inc. [Navarro]), and the Superfund Research Program, funded by the National Institute of Environmental Health Sciences.

This current pilot test was conducted within an area of elevated groundwater uranium concentrations. The results of this test are compared to the results obtained from a prior pilot test conducted near the center of the nitrate/sulfate plume. A set of bench-scale tests were conducted to supplement the current pilot test. Groundwater and sediment samples were collected before, during, and after injection of the electron donor. These samples were characterized for relevant chemical constituents and parameters. This report presents an overview of the study results.

2.0 Project Site

The Monument Valley processing site is located in the Navajo Nation in northeastern Arizona and is managed by DOE under Title I of the Uranium Mill Tailings Radiation Control Act (UMTRCA) of 1978. The site is located in Cane Valley, Arizona, 24 kilometers (km) (15 miles) south of Mexican Hat, Utah (Figure 3). The following details about ore processing activities conducted at the site are reproduced from the DOE report titled *Environmental Assessment of Ground Water Compliance at the Monument Valley, Arizona, Uranium Mill Tailings Site* (DOE 2005):

“From 1955 until 1964, ore at the site was processed by mechanical milling using an upgrader, which crushed the ore and separated it by grain size. During that period the only chemical used was minor amounts of flocculent (a substance used to consolidate particles within a liquid). The finer-grained material, which was higher in uranium content, was shipped to other mills for chemical processing. Coarser-grained materials were stored on site in the “old tailings pile.” Some ground water contamination may have resulted from water draining through the tailings piles during that period. From 1964 until 1968, batch leaching and heap leaching were used to process an estimated 1.1 million tons of tailings and low-grade ore at the site. In the batch-leaching process, sandy tailings were placed in lined steel tanks, and uranium and vanadium were leached by an upward flow of sulfuric acid solution. Heap leaching consisted of placing crushed, low-grade ore on polyethylene sheeting and percolating a sulfuric acid solution through the ore. Both heap-leaching and batch-leaching operations used ammonia and quicklime (calcium oxide) to produce a bulk precipitate of concentrated uranium and vanadium. Chemical solutions used in ore processing are believed to have been discharged to the “new tailings pile.” The new tailings pile contained both sandy tailings and processing solutions. An evaporation pond was on the east side of the new tailings pile. The purpose of the evaporation pond is unknown, but it may have been used to retain seepage from the new tailings pile. The former sources of ground water contamination at the site include (1) the old tailings pile and heap-leach area, (2) the new tailings pile, and (3) the evaporation pond. Surface

remediation at the site took place from 1992 through 1994 and resulted in the removal of these source materials and other site-related contamination. However, analysis of subpile soil samples (samples collected from beneath the “footprint” of the former tailings piles) indicates these soils may be a continuing source of ground water contamination.

The various features associated with the former ore-processing area are shown in Figure 4.

The site has a groundwater contaminant plume, approximately 2 km (1.2 miles) long, with elevated dissolved concentrations of nitrate and sulfate. Concentrations are as high as 600 milligrams per liter (mg/L) and 1800 mg/L for nitrate and sulfate, respectively (DOE 2017). Concentrations of heavy metals, uranium, and arsenic are relatively low (most values <10 micrograms per liter [$\mu\text{g/L}$]) within the study area. However, elevated uranium concentrations (>300 $\mu\text{g/L}$) are present in the alluvial aquifer near the old tailings pile (see red circle in Figure 5).

The unconsolidated alluvial aquifer system that is the focus of this study resides in a north-south-oriented paleovalley that is bounded by bedrock on the south and west sides as well as on the bottom. It consists of fine-grained alluvial sand. Bedrock is exposed at the southern and southwestern areas of the former ore-processing area, and it has been determined that infiltration at these areas serves as the primary source of groundwater recharge to the alluvium. It is estimated that only a minor fraction of the low annual precipitation recharges the aquifer in the center of the valley (where the nitrate/sulfate plume resides) due to loss from evaporation and plant uptake. Depth to groundwater is approximately 9–12 meters (m) (30–39 feet [ft]) for the alluvial aquifer.

The mean hydraulic gradient at the site is approximately 0.01 meters per meter (m/m) (ft/ft). Hydraulic conductivities range from 0.1 to 11 m/day for the alluvial aquifer (DOE 1999). The mean groundwater pore-water velocity is calculated to be 44 meters per year (m/yr) (144 feet per year [ft/yr]) with an assumed effective porosity of 0.25 and an assumed hydraulic conductivity of 3 m/day. Mean groundwater velocity directly measured from a tracer test near the center of the nitrate/sulfate plume was in the range of 10–30 m/yr (33–99 ft/yr) (Borden et al. 2012).

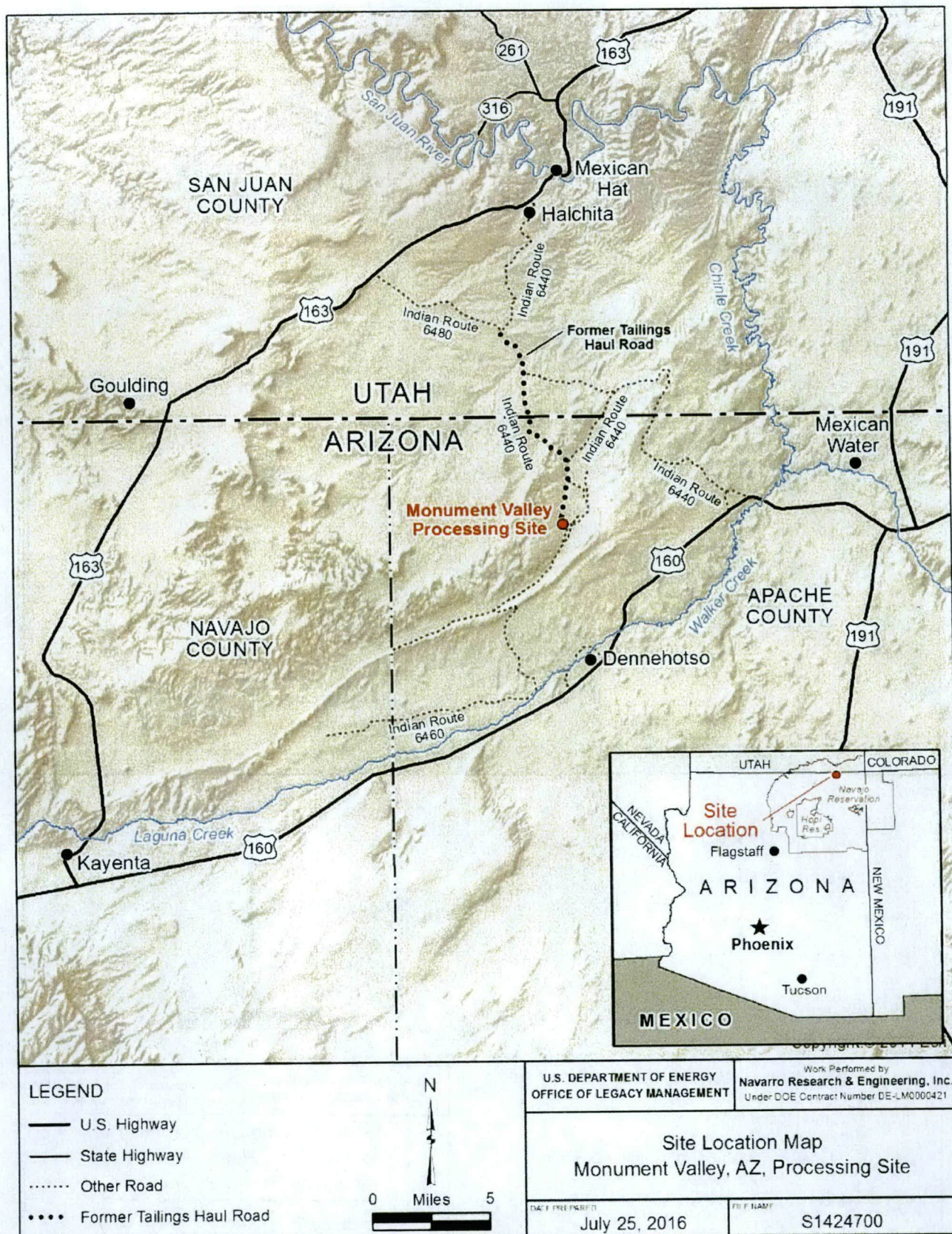
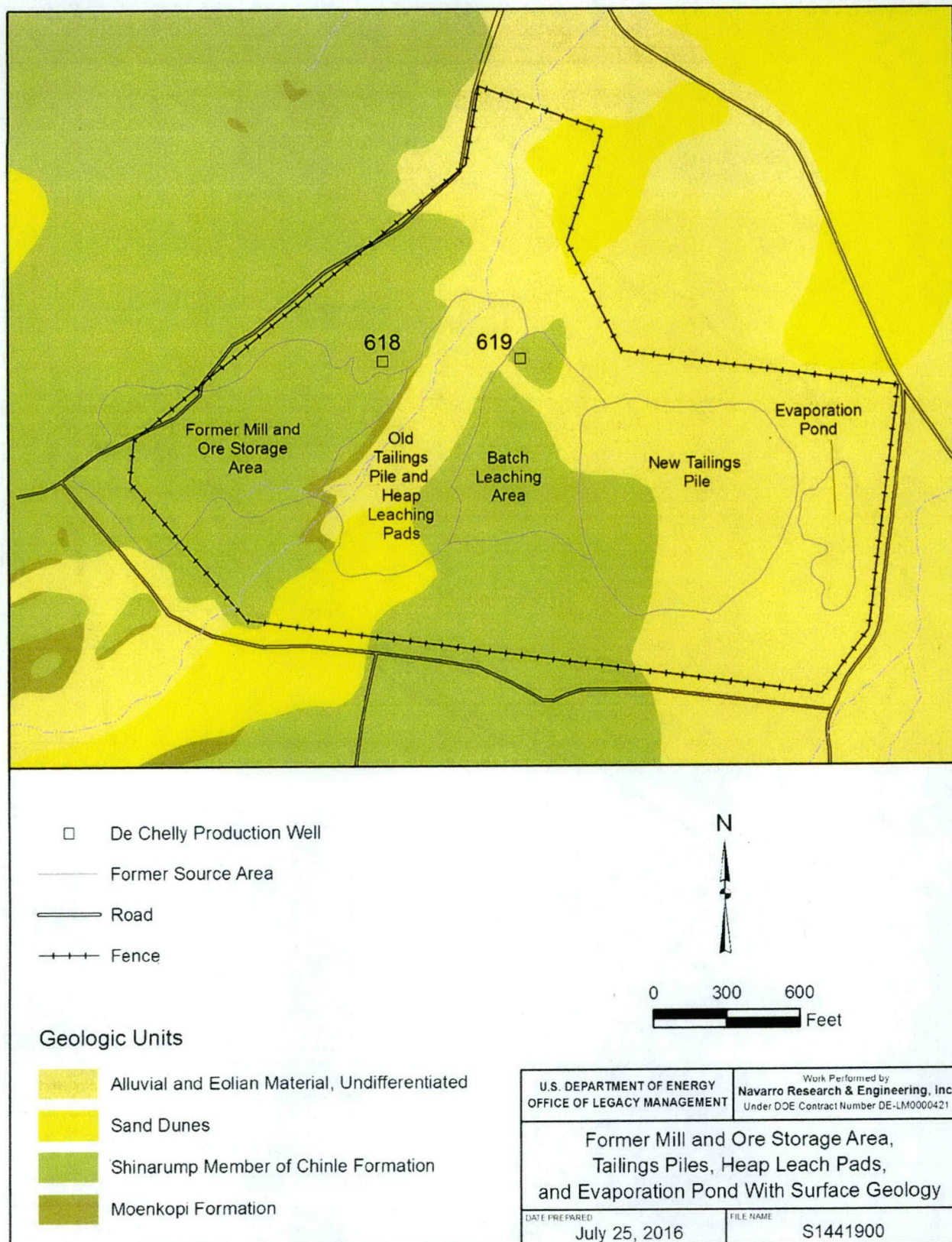


Figure 3. Site location map, Monument Valley, Arizona, processing site



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Figure 4. Features associated with the former ore-processing area of the Monument Valley site

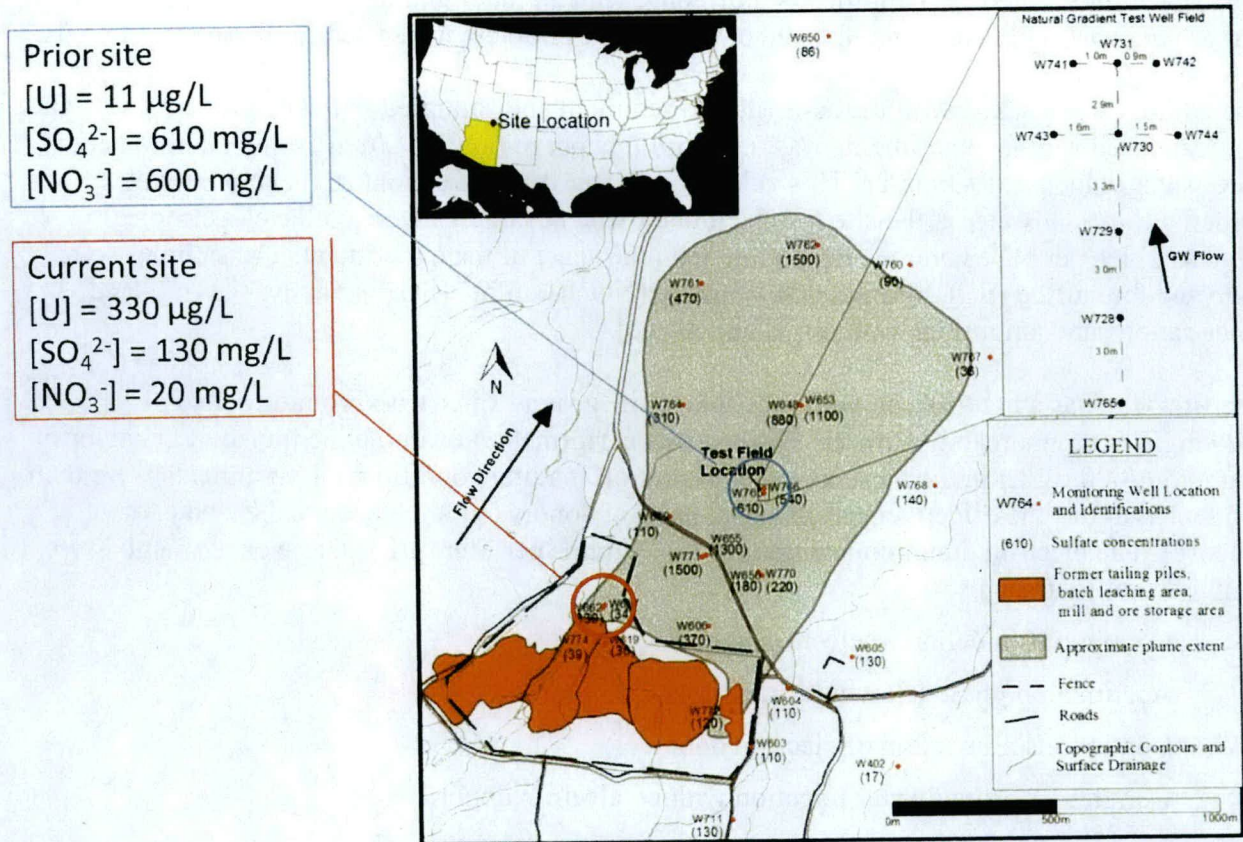


Figure 5. Location of the current and prior pilot tests at the Monument Valley site; concentrations reported represent mean values

The current pilot test was conducted within a small groundwater contaminant plume of elevated uranium concentrations that resides at the former ore-processing area of the site (Figure 5). Note that the prior pilot test was conducted near the center of the nitrate/sulfate groundwater contaminant plume (Figure 5). The uranium concentration is approximately 30 times higher and the nitrate and sulfate concentrations are approximately 30 and 5 times lower at the current pilot-test site compared to those from the site of the prior pilot test. These differences in concentrations are anticipated to cause some differences in results.

3.0 Bench-Scale Tests

3.1 Methods

The laboratory bench-scale experiments were conducted using miscible-displacement methods (i.e., column experiments). They were performed to test the effectiveness of different electron donors for uranium biosequestration and the effect of electron acceptors on uranium biosequestration and investigate uranium sequestration sustainability. The columns used in the experiment were glass columns with Teflon screens, Teflon end plugs, and plastic caps on each

end. The columns were 15 centimeters (cm) long, with an inner diameter of 2.6 cm. Sediment and groundwater collected from the site of the current pilot test were used for these experiments.

The column was packed with the as-is (damp) sediment and saturated with site groundwater. The flow rate used for the experiments was 0.1 milliliters per minute (mL/min), equivalent to a mean pore-water velocity of ~3 cm/hr. This velocity is larger than the estimated mean pore-water velocity of groundwater at the site (~0.5 cm/hr). Effluent samples were collected periodically, ~3–8 samples per pore volume, depending upon the stage of the experiment. The samples were analyzed for sulfide (S^{2-}), bromide (Br^-), nitrate (NO_3^-), sulfate (SO_4^{2-}), uranyl (UO_2^{2+}), and other cations and anions, as well as pH and ethanol.

The first test was a control run with injection of site groundwater with bromide added (100 mg/L) as a nonreactive tracer. This test was performed to examine the transport behavior of uranium (~400 μ g/L) in the absence of sequestration (natural conditions). Experiments were then conducted to test the effectiveness of select electron donors (ethanol, acetate, benzoate, or glucose). The electron donor concentration was 5 grams per liter (g/L). These experiments were conducted in four stages:

1. Continuous injection of electron donor.
2. Acclimation phase (flow interruption).
3. Continuous reinjection of electron donor.
4. Continuous groundwater injection with no electron donor.

Intermittent injections were used for the acclimation stage. After 1 pore volume of electron donor solution was injected to replace the aqueous solution in the column, the injection was stopped, and no flow occurred for several days. This was repeated a specific number of times.

Sulfide, sulfate, and pH in effluent samples were measured immediately after collection using a Hach DR2800 spectrophotometer (method Hach 8146 for sulfide and method Hach 8008 for sulfate) and an Orion pH meter. Other solutes in the effluent samples were all analyzed at the Arizona Laboratory for Emerging Contaminants (ALEC). Uranium and other cations were measured using inductively coupled plasma–mass spectrometry; anions were measured using ion chromatography. Total organic carbon was used to represent electron donor concentration and was measured using a carbon analyzer.

3.2 Results

The breakthrough curves for bromide, sulfate, nitrate, and uranium after injection of site groundwater into the column (first test) are presented in Figure 6. Bromide exhibited typical ideal transport, with a sharp, symmetrical breakthrough curve. Because of their anionic nature, the breakthrough curves for nitrate and sulfate are similar to that of bromide. In contrast to the anions, uranium shows significant retardation. This is because the major form of uranium in solution is UO_2^{2+} , which has measurable sorption potential. No significant reduction in nitrate, sulfate, or uranium was observed after the injection of site groundwater for ~37 pore volumes (210 hr). The results indicate that reduction of nitrate, sulfate, and uranium does not occur in the absence of an electron donor. This is consistent with the low natural dissolved organic carbon content in the site groundwater (~1 mg/L).

The breakthrough curves with ethanol as the electron donor are shown in Figures 7 and 8. Good reproducibility was demonstrated for the replicates. Nitrate reduction occurs rapidly at a hydraulic residence time of ~ 5 hr, and the production of nitrite confirms denitrification. A significant decrease in sulfate concentrations occurred during acclimation of the column, and the production of sulfide confirms sulfate reduction. Uranium concentrations decreased significantly during the acclimation phase, and uranium sequestration was maintained for several pore volumes of injection thereafter. Reducing conditions are illustrated by a color change of sediment during the acclimation phase (Figure 9).

The breakthrough curves with ethanol (duplicate run), acetate, benzoate, or glucose as the electron donor are presented in Figure 10. All four electron donors caused denitrification. Glucose caused decreases in both sulfate and uranium during the acclimation stage. However, the decreases were not as great as they were for ethanol, for which concentrations were reduced to almost zero. Sequestration of uranium was also observed after the continuous injection was resumed for ethanol and glucose. Acetate caused a moderate decrease in uranium during the acclimation stage, but no decrease in sulfate was observed. Acclimation of the column using acetate as the electron donor did not cause a color change of the sediment (Figure 11), indicating that formation of the black solid is associated with sulfate reduction. Benzoate did not cause a decrease in either sulfate or uranium during the acclimation stage. The results indicate that ethanol is the most effective electron donor of the four tested.

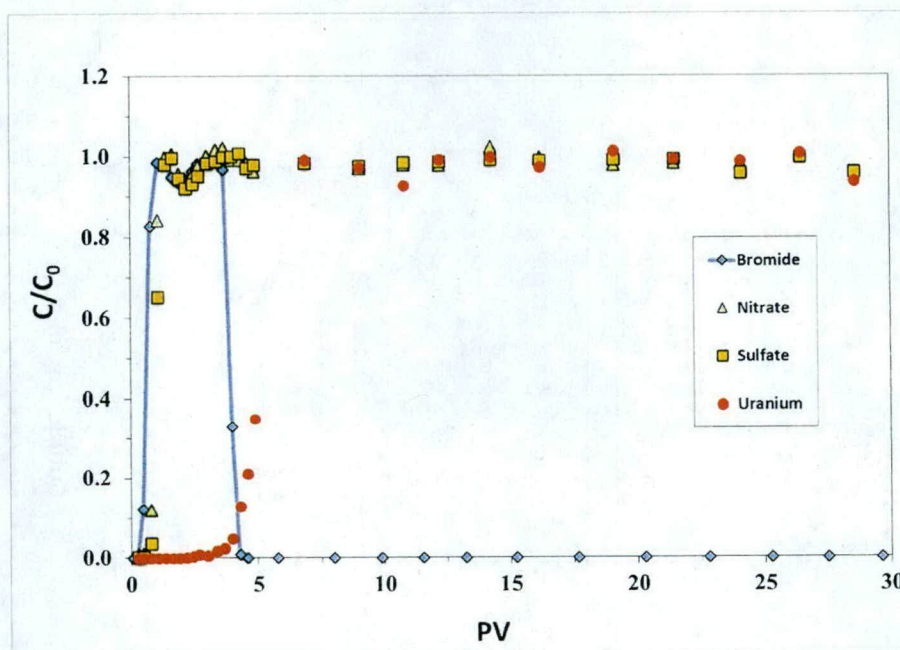


Figure 6. Breakthrough curves of bromide, nitrate, sulfate, and uranium after injection of site groundwater. No electron donor added. For all relevant figures, C/C_0 represents the effluent concentration divided by the injection concentration; PV represents the number of pore volumes.

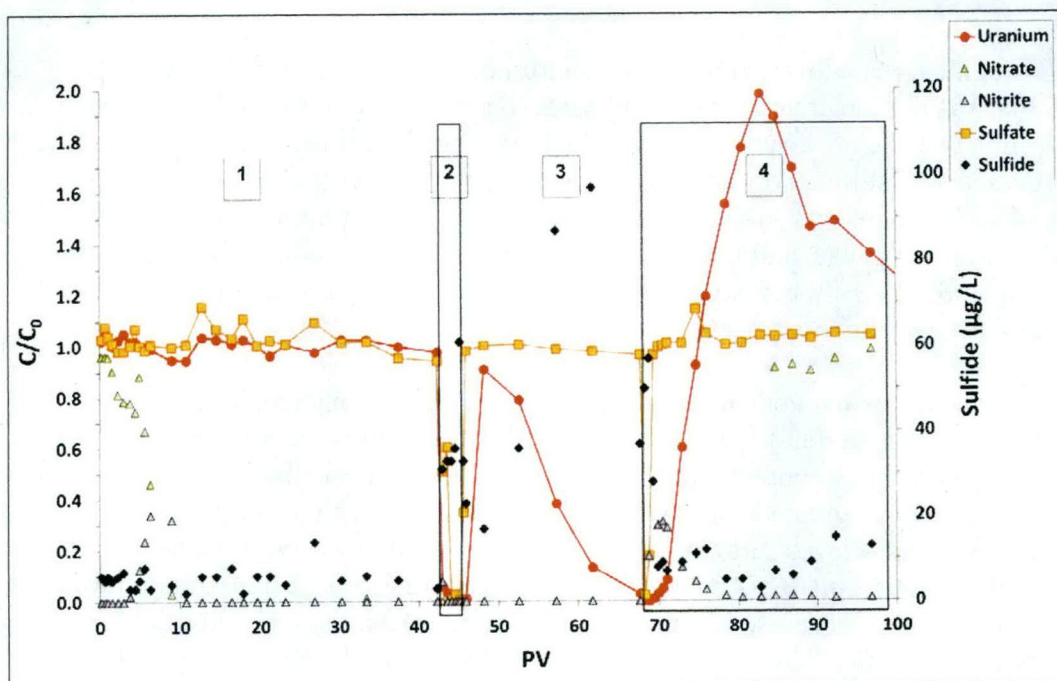


Figure 7. Breakthrough curves of sulfate, nitrate, and uranium after injection of site groundwater with ethanol as the electron donor. The numbers 1–4 represent the experiment stages described in the text.

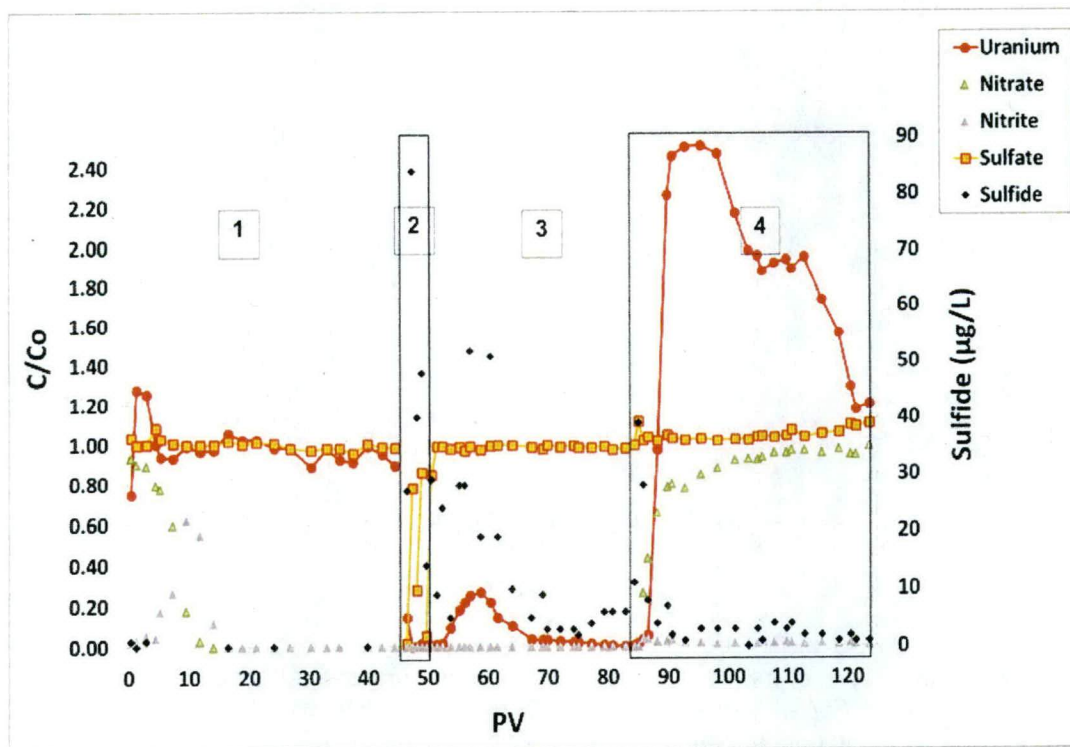


Figure 8. Breakthrough curves of sulfate, nitrate, and uranium after injection of site groundwater with ethanol as the electron donor (replicate)

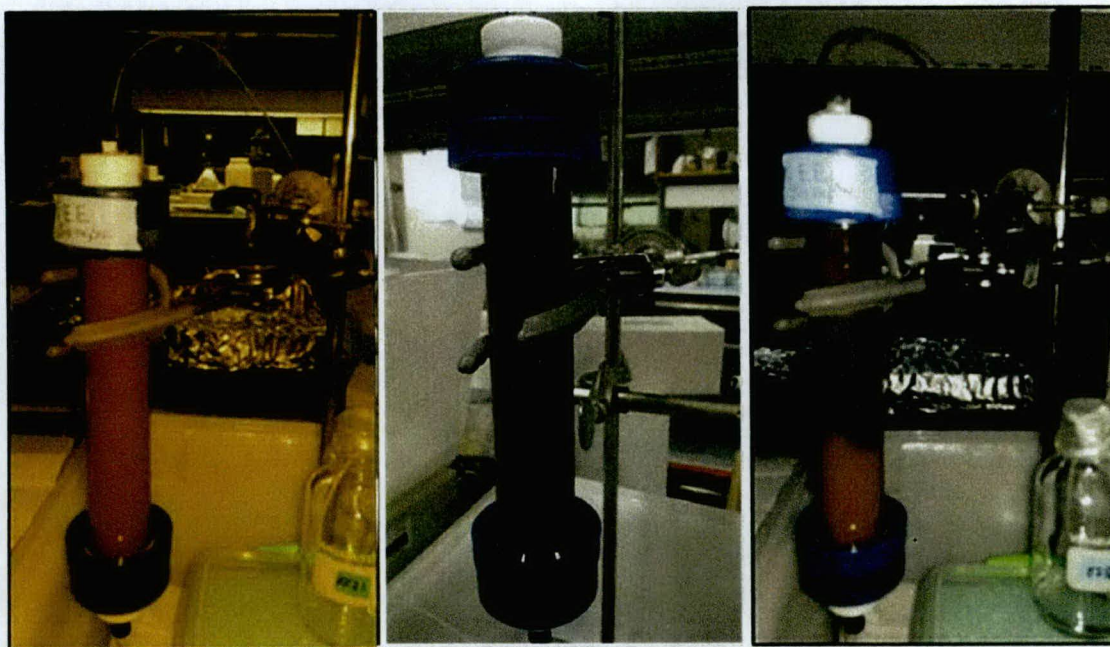


Figure 9. Column before (left), during (center), and after (right) acclimation with intermittent injection of ethanol

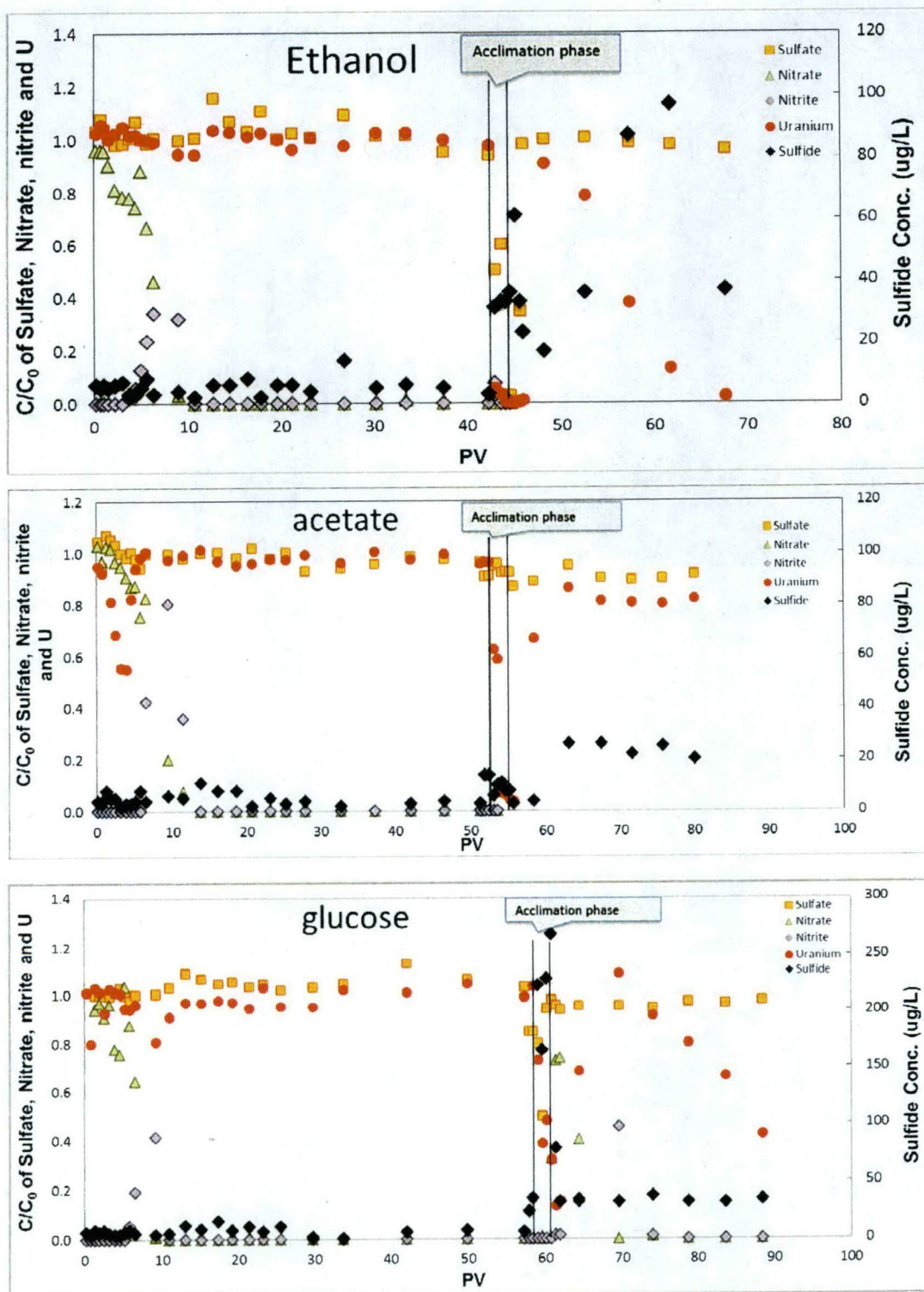


Figure 10. Breakthrough curves of sulfate, nitrate, and uranium after injection of site groundwater with various electron donors

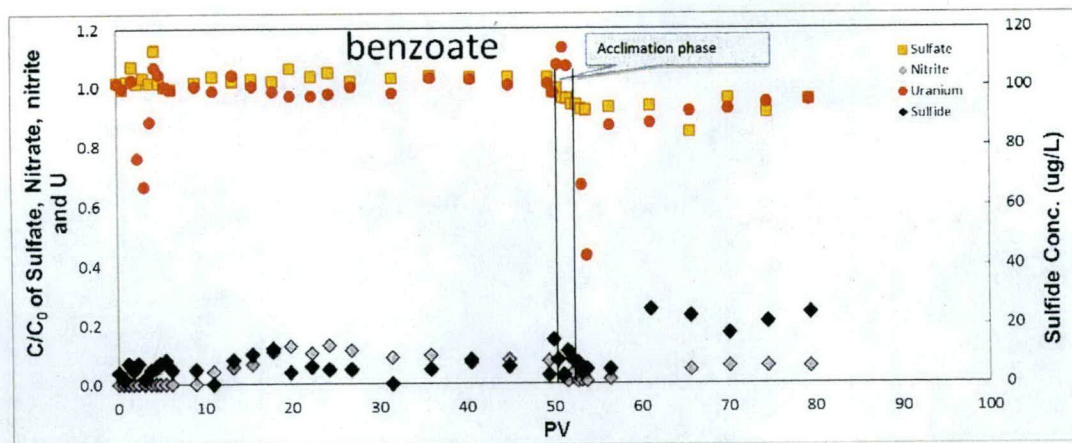


Figure 11. Breakthrough curves of sulfate, nitrate, and uranium after injection of site groundwater with various electron donors(continued)



Figure 12. Column before (left), during (middle), and after (right) acclimation by the intermittent injection of acetate

An experiment was conducted with elevated nitrate in the presence of ethanol (Figure 12). Compared to the standard ethanol tests (Figures 7 and 8), the additional nitrate delayed the rebound of uranium that occurred at the start of stage 3 but reduced the decrease in uranium concentration observed at the end of stage 3.

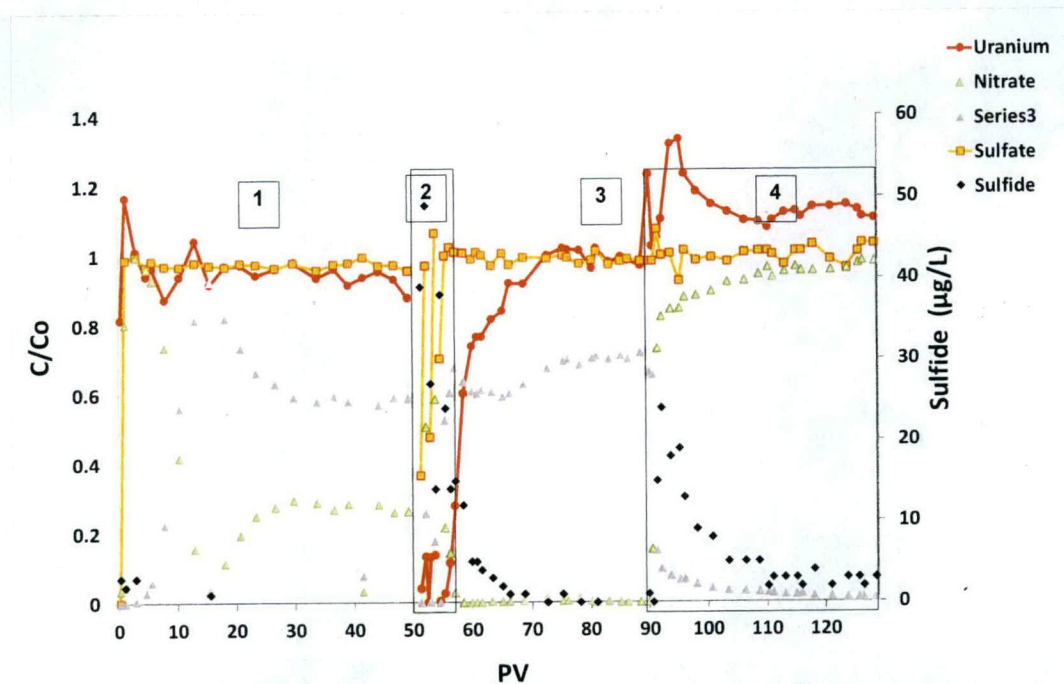


Figure 13. Breakthrough curves of bromide, sulfate, nitrate, and uranium after injection of site groundwater with ethanol and elevated nitrate (600 mg/L)

Uranium concentrations in the effluent solution decreased greatly during and after the acclimation phase (stage 2). Specifically, they decreased from ~400 to ~1 µg/L, which is significantly below the UMTRCA regulatory standard of 44 µg/L. Mass-balance calculations were conducted to determine the amount of uranium sequestered during the first three stages of the ethanol-injection tests. The results showed that 76% of the uranium injected into the column was sequestered.

Inspection of Figures 7 and 8 shows that uranium concentrations rebounded after the introduction of several pore volumes of oxygenated water containing no electron donor. The concentrations are observed to surpass the original injection concentrations, due to the release of sequestered uranium. Calculations showed that 20% of the sequestered uranium was retained after oxygenated water containing no ethanol was injected, with the other 80% released.

4.0 Field Test

4.1 Test Methods

The schedule of activities at the site was as follows:

- May 2015: Monitoring well installation, groundwater and core collection
- Aug. 2015: Field test, ethanol injection
- Sep. 2015: 1st postinjection groundwater sampling
- Oct. 2015: 2nd postinjection groundwater sampling

- Nov. 2015: 3rd postinjection groundwater sampling; core collection
- Jan. 2016: 4th postinjection groundwater sampling
- Mar. 2016: 5th postinjection groundwater sampling
- May 2016: 6th postinjection groundwater sampling
- Oct. 2016: 7th postinjection groundwater sampling
- Feb. 2017: 8th postinjection groundwater sampling; core collection

New injection/monitoring wells (0699 through 0704) configured with ~1.5 m (4.9 ft) horizontal grid spacing were constructed by Navarro at the site (Figure 13). Boreholes were developed with a Geoprobe rig, to a total depth in the alluvial aquifer of approximately 21 m (70 ft) below ground surface. Injection/monitoring wells were installed with 0.75-inch diameter Schedule 40 polyvinyl chloride (PVC) casings with 6 m (20 foot), 0.010-inch slotted screens from approximately 15 to 21 m (50 to 70 feet) below ground surface.

Ethanol at 0.5% concentration was used as the electron donor. To evaluate cost effectiveness for potential full-scale applications, compared to that used in the prior pilot test (5%), a lower concentration was used for the current pilot test. Approximately 19,000 L of solution was created by mixing the ethanol with site groundwater pumped initially from an upgradient well with elevated uranium concentrations (0662) and later additionally from the other injection wells. The solution was stored in tanks (see Figure 14). The solution was injected over ~21 hr into wells 0699, 0700, 0701, and 0702 at a total rate of 15 L/min using a peristaltic pump. Changes in concentrations of several water-quality constituents were observed for the upgradient well (0662), indicating that the radius of influence of the injection was at least ~1.5 m (4.9 ft).

Groundwater levels for all wells were measured using a standard water-level meter. Groundwater samples were collected from all wells, using a compressed-air-driven bladder pump in most instances. A hand-operated ball-valve pump was used in some cases. Groundwater was analyzed for in situ temperature, dissolved oxygen, oxidation–reduction potential, pH, and electrical conductivity using YSI-plus and Orion (for pH) probes. Samples were collected after wells were purged to obtain stable water-chemistry parameters. Approximately 60 mL of groundwater was collected for immediate onsite sulfide measurements using a spectrophotometric method with a Hach DR2800 spectrophotometer. More than 1 L of groundwater was collected and split into different vials or bottles for analysis for cations (~20 mL, capped plastic vials, three duplicates), anions (~20 mL, capped plastic vials, three duplicates), and isotopes (~1 L, plastic bottle, one duplicate). The samples were preserved as necessary (e.g., with hydrochloric acid), stored in a cooler with ice, and transported back to the University of Arizona. Standard trip and field blanks were employed.

For sediment sample collection, the 5 ft plastic sleeve obtained from the Geoprobe rig was first cut to remove the segment with no sediment using a sterilized hacksaw. The remainder of the sleeve filled with sediments was subsequently cut into three pieces. Subsamples were then collected aseptically for microbial and geochemical analyses. Inductively coupled plasma–mass spectrometry was used for cation analysis. Ion chromatography was used for anion analysis. The sediment samples were microwave-assisted acid-digested before implementing the cation and anion analysis. Examples of the sediment collected are shown in Figures 15a and 15b.

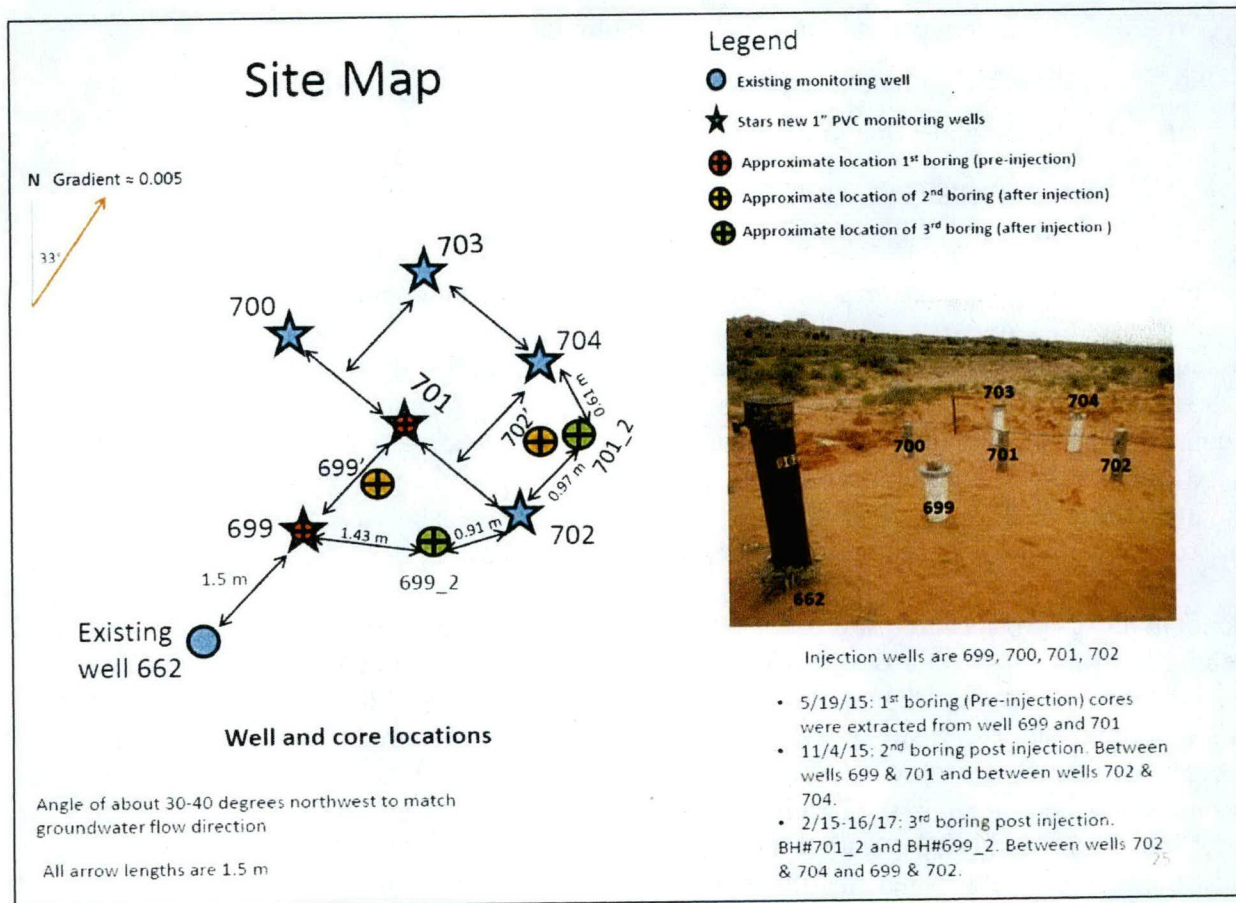


Figure 14. Map of well and borehole locations for current pilot-test area. Arrows represent 1.5 m lengths unless otherwise noted.

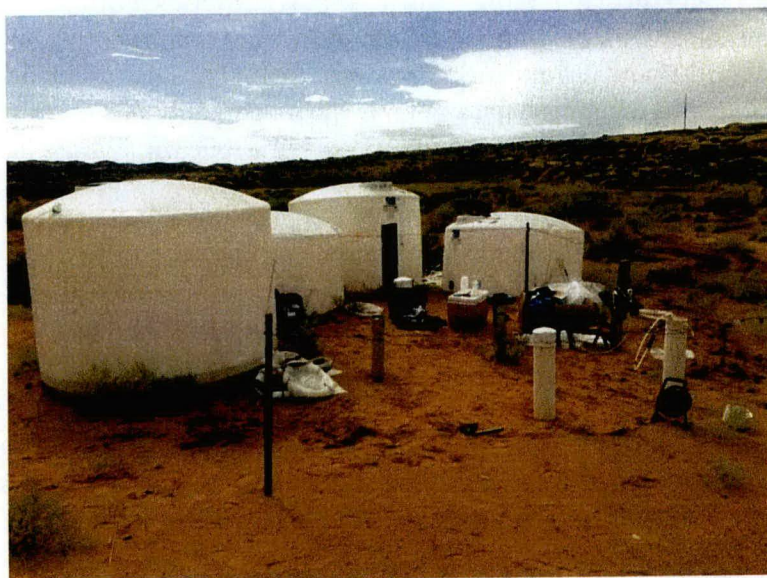


Figure 15. Storage tanks at the site (looking southwest)

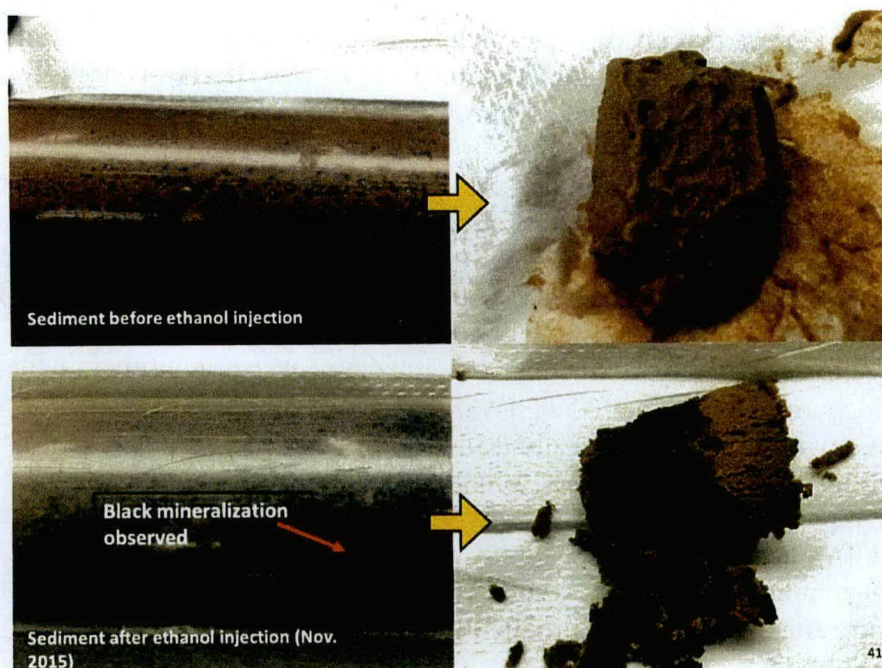


Figure 16a. Photographs of sediment collected before and after ethanol injection

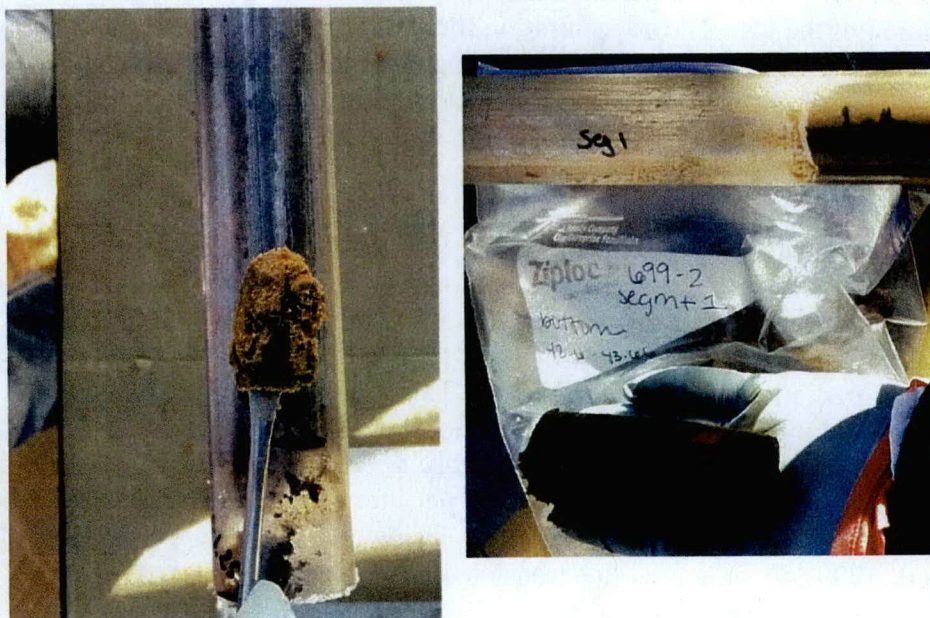


Figure 15b. Photographs of sediment collected 18 months after ethanol injection

4.2 Results of Current Pilot Test

The oxidation–reduction potential and dissolved oxygen concentration in all the wells after ethanol injection are presented in Figures 16 and 17, respectively. Oxidation–reduction potential

in all the wells decreased rapidly after ethanol injection and remained below 0 millivolts (i.e., had a negative value) for more than 400 days. Oxidation–reduction potential rebounded sometime prior to the last sampling round. Dissolved oxygen also decreased rapidly after ethanol injection, which corresponds to the decrease in oxidation–reduction potential.

The concentrations of sulfate, nitrate, sulfide, and uranium in groundwater samples collected from the wells at multiple times after ethanol injection are presented in Figure 18a. Rapid decreases of nitrate concentrations are observed (within the first sampling period) after ethanol injection for the more-upgradient wells. Conversely, nitrate concentrations decreased more gradually for the two most-downgradient wells (0703 and 0704). Rebound of nitrate concentrations occurred within approximately 100–200 days for the more-upgradient wells, whereas rebound occurred much later (>500 days) for the two most-downgradient wells (0703 and 0704). Relatively small decreases in sulfate concentration were observed, along with the production of sulfide. Significant increases were observed in dissolved iron and manganese after ethanol injection (Figures 19a and 19b, respectively). Sediment samples collected after ethanol injection showed dark discolorations (see Figure 15a). These discolorations persisted for at least 18 months after injection (Figure 15b). All of the changes in dissolved constituents and sediment presented above are consistent with the production of reducing conditions upon the injection of the 0.5% ethanol solution.

Uranium concentrations as a function of time for each well are compared in Figure 18b. The initial concentrations of uranium in the two most-upgradient wells (0662 and 0699) were approximately 332 $\mu\text{g/L}$. The concentration for well 0662 increased gradually to ~ 450 $\mu\text{g/L}$ during the duration of the test. The concentration for well 0699, the most-upgradient injection well, decreased to 250 $\mu\text{g/L}$ within the first sampling period and then rebounded by the next sampling period. The results indicate that sequestration processes did not persist extensively in the vicinity of well 0699, as would be anticipated given its relative location and associated lowest residence time for the reagent.

Initial uranium concentrations were approximately 607 $\mu\text{g/L}$ for the five downgradient wells (0700–0704). Concentrations decreased to values ranging from 411 to 480 $\mu\text{g/L}$, with a mean of 448 $\mu\text{g/L}$. The mean decrease was approximately 25%. The decreases in uranium concentrations occurred first for the most-upgradient row of wells (0700–0702), followed several weeks later for the most-downgradient wells (0703 and 0704). This downgradient propagation of the reactive zone was also observed for the prior pilot test (Miao et al. 2014). Unlike in the column experiments, uranium concentrations did not decrease to below the UMTRCA regulatory level of 44 $\mu\text{g/L}$. The overall mass of uranium sequestered per liter of groundwater was estimated to be approximately 100 $\mu\text{g/L}$ across the treatment zone. Using an assumed specific discharge of ~ 0.03 $\text{m}^3/\text{m}^2/\text{day}$ (DOE 1999), this removal rate translates to ~ 3 $\text{g}/\text{m}^2/\text{day}$.

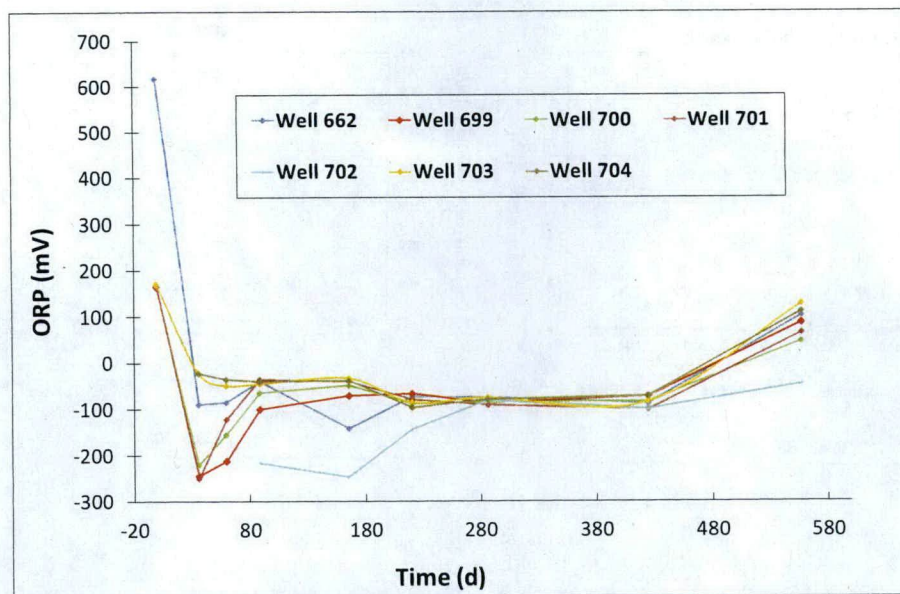


Figure 17. Oxidation–reduction potential (ORP) per well as a function of time after ethanol injection

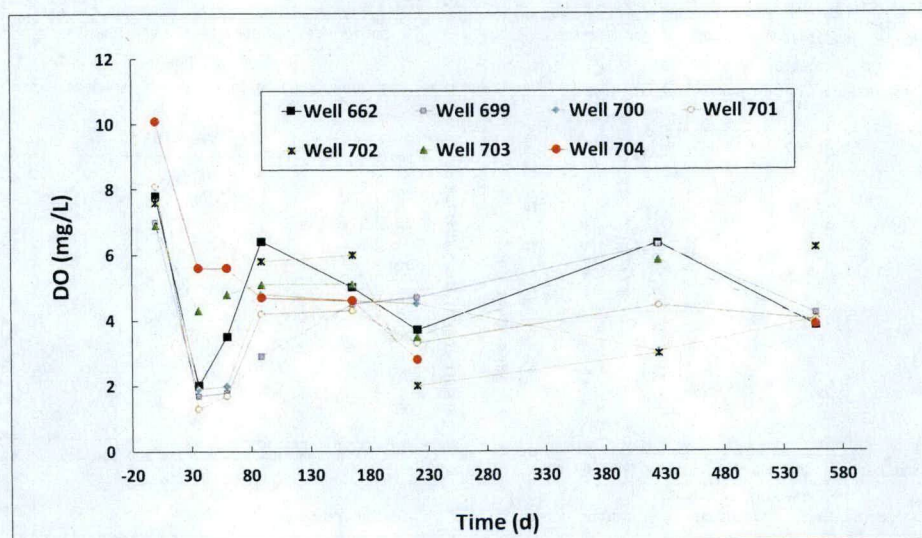


Figure 18. Dissolved oxygen (DO) per well as a function of time after ethanol injection

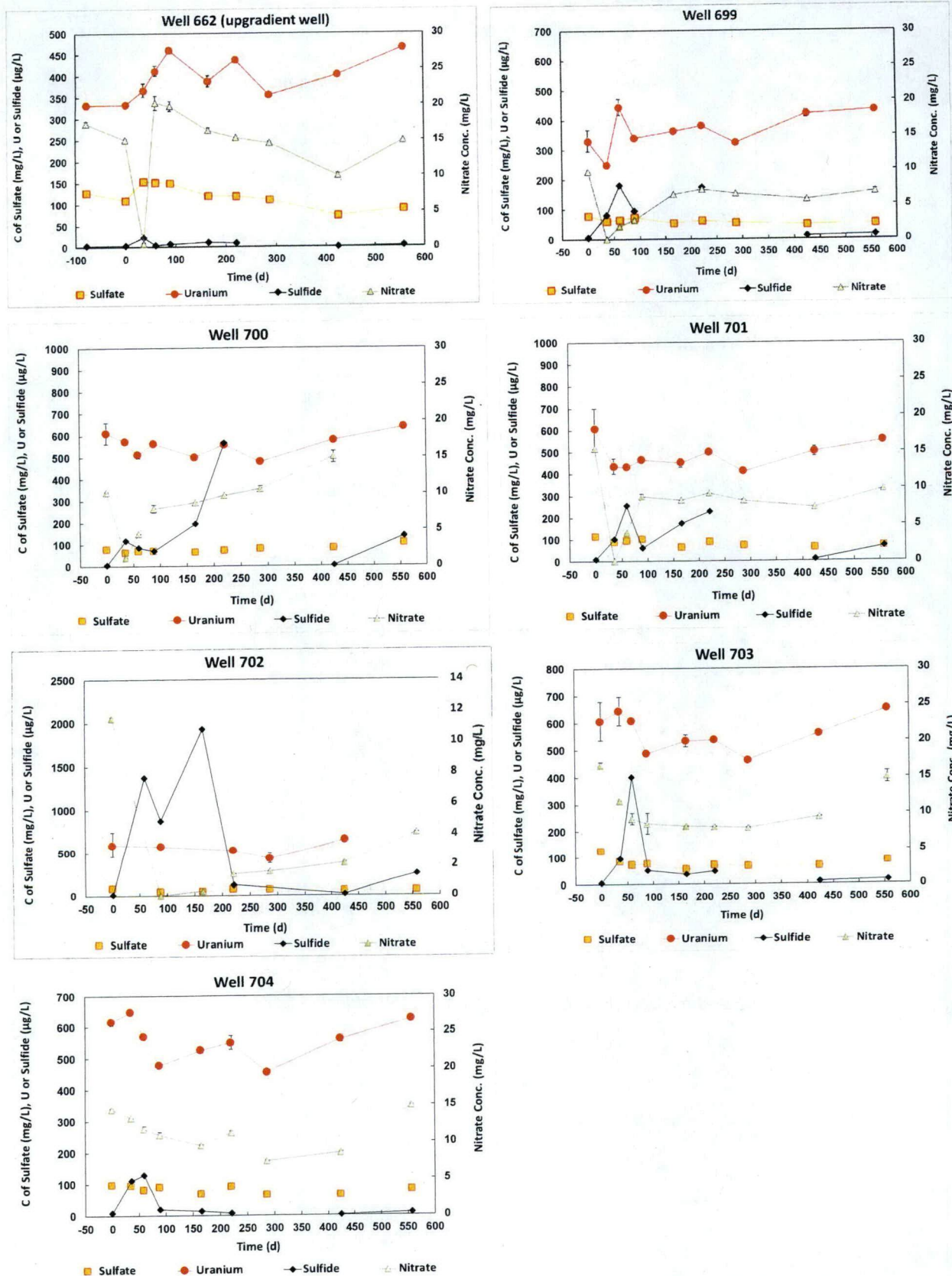


Figure 19a. Concentrations of sulfate, nitrate, sulfide, and uranium as a function of time after ethanol injection; 0662 is the upgradient well; 0699, 0700, 0701, and 0702 are injection wells; 0703 and 0704 are downgradient monitoring wells

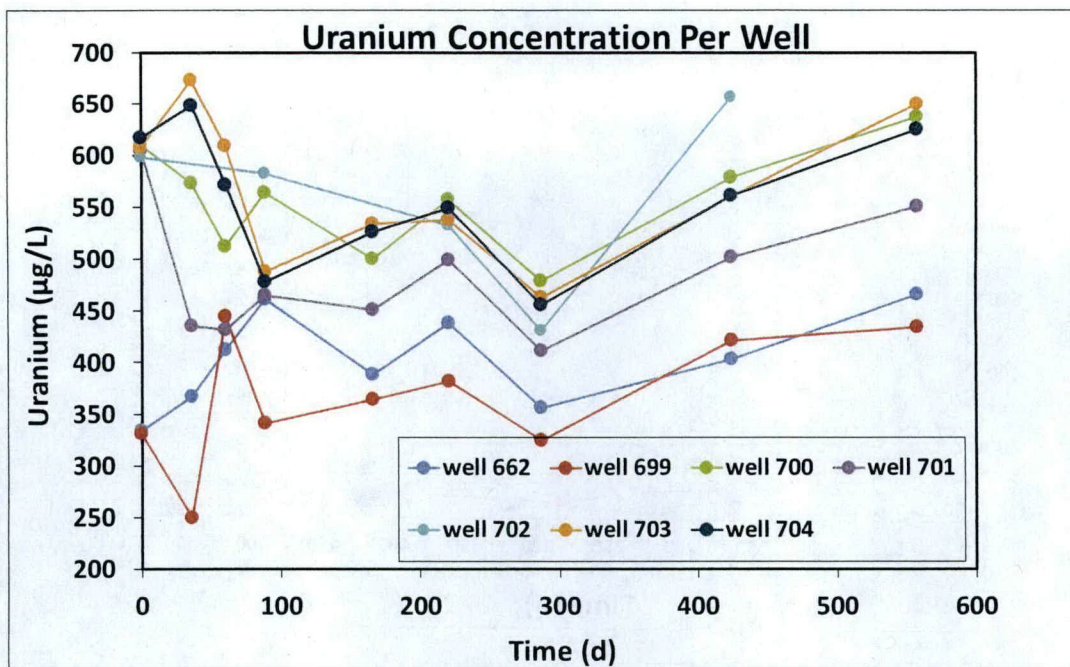


Figure 18b. Concentrations of uranium as a function of time after ethanol injection; 0662 is the upgradient well; 0699, 0700, 0701, and 0702 are injection wells; 0703 and 0704 are downgradient monitoring wells

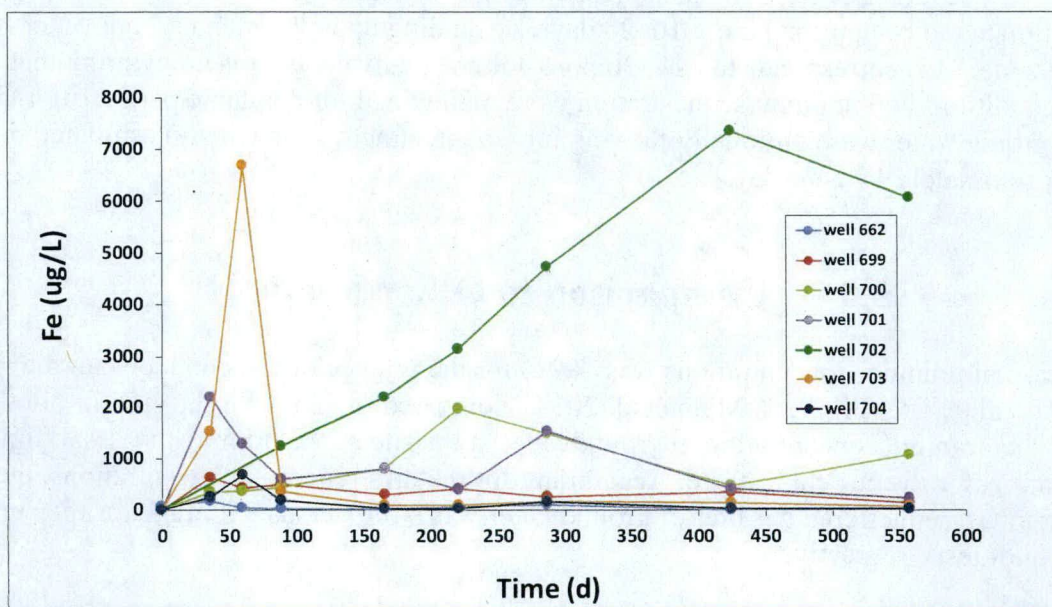


Figure 20a. Concentrations of iron in groundwater as a function of time after ethanol injection

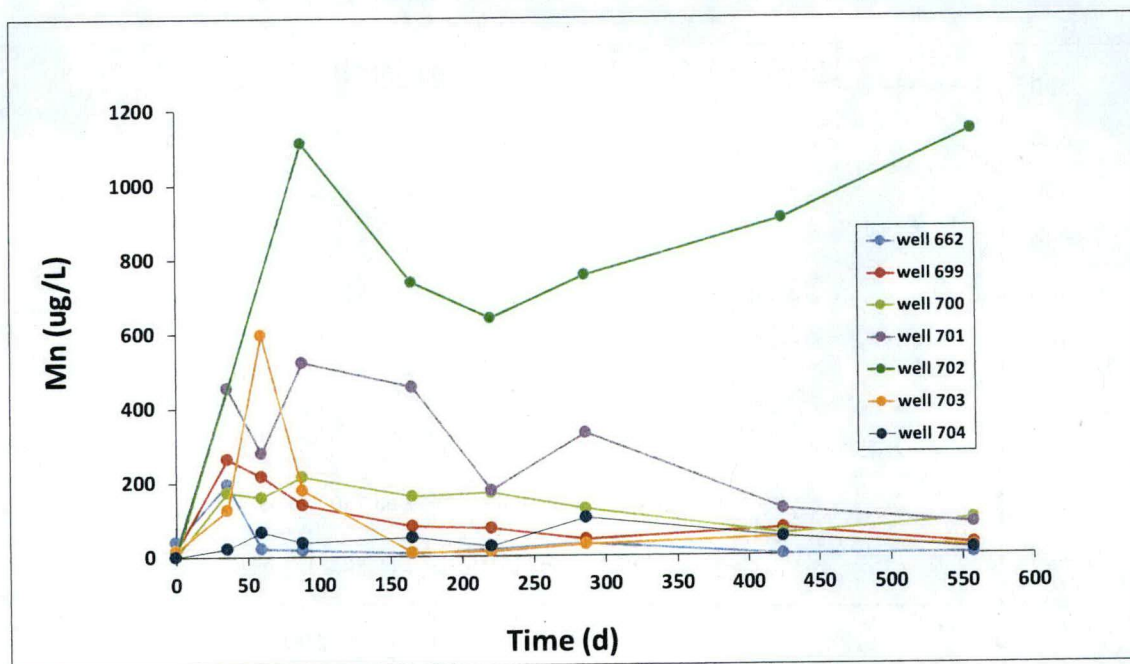


Figure 19b. Concentrations of manganese in groundwater as a function of time after ethanol injection

Rebound of uranium concentrations was observed to begin after approximately 300 to 400 days for the five downgradient wells. The mean residence time of the reagent solution in the treatment zone is estimated to be approximately 10–20 days, depending upon the mean groundwater flow rate in the zone. This corresponds to ~18–36 pore volume equivalents. It is noteworthy that reducing conditions and uranium sequestration were maintained for a notable period even though untreated groundwater was continually flowing into the treatment zone with an estimated mass flux of approximately 18 g/m²/day.

5.0 Comparison to Other Studies

The decrease in uranium concentrations was >99% for the prior pilot test conducted at the Monument Valley site (Figure 2, Miao et al. 2014), compared to ~25% for the current pilot test. However, the uranium concentration in groundwater at the site of the prior test was ~30 times lower than it is for the current test site. Accounting for the differences in concentrations, the mass of uranium sequestered per liter of groundwater was ~100 versus ~10 µg/L for the current and prior pilot tests, respectively.

Uranium sequestration was maintained for ~2.5 years for the prior pilot test, versus ~1 year for the current pilot test. Differences in the sequestration periods are likely due, at least in part, to differences in constituent concentrations. The use of a 10-times-lower ethanol concentration for the current pilot test may also have impacted the results.

Results obtained from two pilot tests conducted at the DOE Rifle site are used for comparison (Williams et al. 2011). Uranium concentrations at the Rifle site are similar to those of the current pilot test site at the Monument Valley site. Notable differences are observed between the Rifle tests and those conducted at the Monument Valley site. First, acetate was used as the electron

donor for the Rifle tests. Second, the electron donor was injected for 30 or 110 days for the Rifle tests, compared to approximately 1 day for the Monument Valley pilot test. Second, rebounds in uranium concentrations were observed after 30–160 days for the Rifle site. The sequestration periods for the Rifle site are shorter than those observed for the Monument Valley pilot test, although the reagent-injection periods were much longer.

6.0 Summary and Conclusions

This report presents an overview of the results of a project designed to evaluate the efficacy of in situ biosequestration for the treatment of uranium-contaminated groundwater at the Monument Valley site in northeastern Arizona. The project comprised a 1.5-year pilot test and associated laboratory experiments. This test was conducted within a small plume of elevated uranium concentrations. Bench-scale experiments were conducted using groundwater and alluvial sediment collected from the test site.

The results of the bench-scale experiments indicated that ethanol was the most effective electron donor of the four tested. Uranium concentrations in solution decreased greatly during and after the acclimation phase. Specifically, these concentrations decreased from approximately 400 to approximately 1 $\mu\text{g/L}$, which is significantly below the UMTRCA regulatory standard of 44 $\mu\text{g/L}$. Mass-balance calculations showed that approximately 76% of uranium input was sequestered. Uranium concentrations rebounded upon the introduction of oxygenated water with no electron donor. Approximately 80% of the sequestered uranium was released.

Ethanol solution (0.5%) was injected over a 1-day period. The results of groundwater and sediment characterization conducted before, during, and after the injection demonstrated that reducing conditions were generated. Large decreases in nitrate, along with moderate decreases in sulfate, were observed. Concentrations of uranium decreased at the downgradient monitoring wells by approximately 25%, from approximately 600 to approximately 450 $\mu\text{g/L}$. The decrease was sustained for approximately 1 year, after which uranium concentrations rebounded. The concentrations were not reduced to below the EPA regulatory standard.

The results obtained from the current pilot test were compared to those obtained from a prior pilot test conducted near the center of the nitrate and sulfate groundwater contaminant plume at the site. Relative concentration reductions for uranium were lower. However, the uranium concentrations in groundwater at the prior pilot test site are approximately 30 times lower than those at the current pilot test site. Accounting for the differences in concentrations, the mass of uranium sequestered per liter of groundwater was approximately 100 $\mu\text{g/L}$ versus approximately 10 $\mu\text{g/L}$ for the current and prior pilot tests, respectively.

Uranium sequestration was maintained for approximately 2.5 years for the prior pilot test, versus approximately 1 year for the current pilot test. It is noteworthy that reducing conditions and uranium sequestration were maintained for a notable period even though untreated groundwater was continually flowing into the treatment zone. Differences in the sequestration periods are likely due, at least in part, to differences in constituent concentrations. The use of a 10-times-lower ethanol concentration for the current pilot test may also have impacted the results.

Overall, the results of the pilot tests indicate that ethanol injection successfully stimulated microbial activity, generated reducing conditions, and decreased groundwater concentrations of uranium at the site. The decreases in uranium concentrations observed for the current pilot test were not to levels below the UMTRCA regulatory standard of 44 µg/L. However, the results obtained from the bench-scale tests show that decreases to as low as approximately 1 µg/L were achieved. Hence, it is possible that greater concentration reductions could be obtained in the field with optimal application conditions. Additional testing would be required to determine optimal operational conditions for promoting cost-effective treatment at the site. Factors to consider include the concentration of electron donor and the means and length of its application. Application of this biosequestration approach will likely require periodic electron-donor injections to maintain reducing conditions and associated sequestration effects.

7.0 Acknowledgments

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8.0 References

- DOE (U.S. Department of Energy), 1999. *Final Site Observational Work Plan for the UMTRA Project Site at the Monument Valley, Arizona*, U0018101.
- DOE (U.S. Department of Energy), 2005. *Environmental Assessment of Ground Water Compliance at the Monument Valley, Arizona, Uranium Mill Tailings Site*, DOE/EA-1313, Office of Legacy Management.
- Borden, A.K., M.L. Brusseau, K.C. Carroll, A. McMillan, N.H. Akyol, J. Berkompas, Z.H. Miao, F. Jordan, G. Tick, W.J. Waugh, and E.P. Glenn, 2012. "Ethanol addition for enhancing denitrification at the uranium mill tailing site in Monument Valley, AZ," *Water, Air, and Soil Pollut.* 223(2):755–763.
- EURSSEM, 2016. *The Environmental Radiation Survey and Site Execution Manual* (URSSEM), Chapter 4.5.2, "Immobilisation & solidification (CT)," <http://eurssem.eu/pages/4-5-2-immobilisation-solidification-ct>, accessed 2017.
- Miao, Z., C. Carreón-Diazconti, K.C. Carroll, and M.L. Brusseau, 2014. "The impact of biostimulation on the fate of sulfate and associated sulfur dynamics in groundwater," *J. Contamin. Hydrol.* 164:240–250.
- Williams, K.H., P.E Long, J.A. Davis, M.J. Wilkins, A.L. N'Guessan, C.I. Steefel, L. Yang, D. Newcomer, F.A. Spane, L.J. Kerkof, L. McGuinness, R. Dayvault, and D.R. Lovely, 2011.

"Acetate availability and its influence of sustainable bioremediation of uranium-contaminated groundwater," *Geomicrobiol. J.* 28:519–539.