

Article

Restoration Insights Gained from a Field Deployment of Dithionite and Acetate at a Uranium In Situ Recovery Mine

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Abstract: Mining uranium by in situ recovery (ISR) typically involves injecting an oxidant and a complexing agent to mobilize and extract uranium in a saturated ore zone. This strategy involves less infrastructure and invasive techniques than traditional mining, but ISR often results in persistently elevated concentrations of U and other contaminants of concern in groundwater after mining. These concentrations may remain elevated for an extended period without remediation. Here, we describe a field experiment at an ISR facility in which both a chemical reductant (sodium dithionite) and a biostimulant (sodium acetate) were sequentially introduced into a previously mined ore zone in an attempt to establish reducing geochemical conditions that, in principle, should decrease and stabilize aqueous U concentrations. While several lines of evidence indicated that reducing conditions were established, U concentrations did not decrease, and in fact increased after the amendment deployments. We discuss likely reasons for this behavior, and we also discuss how the results provide insights into improvements that could be made to the restoration process to benefit from the seemingly detrimental behavior.



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Keywords: restoration; uranium; in situ recovery; geochemistry; dithionite; acetate

1. Introduction

1.1. Historical Reductant Use for U ISR Restoration

Approximately 50% of uranium production worldwide is done using in situ recovery (ISR) [1], an aqueous mining technique used to extract uranium from lower-grade ores. ISR mining produces no hazardous dust or mine tailings such as those generated by conventional open pit mining [2,3]. During ISR, a lixiviant is injected into an ore body that is below the water table to dissolve uranium minerals. The lixiviant typically contains an oxidant, such as dissolved oxygen or hydrogen peroxide, and a complexing agent (usually CO_3^{2-} , added as either $\text{CO}_2(\text{g})$ or HCO_3^-). The oxidant reacts with mineralized U(IV), such as uraninite and coffinite, in the sandstone to form soluble U(VI) [2–6]. This aqueous U(VI) then combines with carbonate to form uranyl carbonate complexes, which often include Ca or Mg as well (e.g., $\text{UO}_2(\text{CO}_3)_2^{2-}$, $\text{UO}_2(\text{CO}_3)_3^{4-}$, $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$, $\text{CaUO}_2(\text{CO}_3)_3^{2-}$) [7–11]. These U(VI)-carbonate complexes are mobile and do not strongly adsorb to mining sediments. The water is pumped to surface facilities via production wells, and uranium is extracted using ion-exchange media [5]. This ISR process is generally considered more environmentally friendly than conventional mining, but it often leaves behind elevated groundwater concentrations of uranium and other constituents found in the ore zone [12].

To restore groundwater following ISR treatment, regulations typically call for lowering contaminant concentrations in the ore zone to pre-mining levels and providing monitoring data and model simulations that demonstrate that residual contaminant concentrations are stable and that the contaminants will not migrate beyond an aquifer exemption boundary.

Commonly, restoration first consists of groundwater sweep and reverse osmosis [3,13,14]. During groundwater sweep, water is pumped out of the ore zone and replaced with cleaner groundwater drawn in from outside the ore zone. Typically, groundwater sweep is accompanied by ion exchange recovery of residual uranium from the water pumped from the restoration zone, with some of the stream from which uranium has been recovered being returned to the restoration zone via injection wells. Following this step, groundwater is pumped to reverse osmosis units to remove U and other contaminants, which are disposed of while the “purified” water is returned to the ore zone via injection wells [3]. This process is continued until concentrations of the contaminants in the ore zone groundwater are at acceptable levels [5,6]. However, after reverse osmosis is stopped, the concentrations of some contaminants, particularly uranium, may rebound because of desorption or a change in redox conditions [4,5,12].

The prevailing geochemical conditions in ore zones prior to mining are highly reducing, with few electron acceptors available to oxidize sediments or aqueous species (these conditions are typically responsible for the formation of the uranium ore body in the first place). This makes in situ remediation with chemical reductants or biostimulants an attractive option for ISR restoration because once reducing conditions are re-established it is unlikely that they will become oxidizing again [5,6]. By re-establishing reducing conditions, any remaining U(VI) should be reduced back to the fairly insoluble and immobile U(IV) [3–5,14].

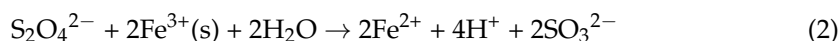
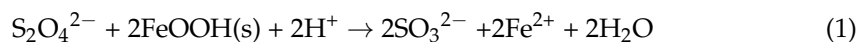
Several reductants have been explored for restoration after ISR mining. Biostimulants, such as acetate and molasses, have been tested at ISR sites [15]. While biostimulants were effective at stimulating microbial activity that lowered concentrations of certain redox-sensitive constituents, such as selenium, they had little impact on uranium concentrations. Hydrogen gas was used in a pilot study at a U ISR site in Texas, and it was found to be effective in reducing U(VI), but it induced reduction only very near the injection wells because it did not effectively distribute through the ore zone aquifer [16]. In south Texas, hydrogen sulfide (H_2S) has been injected with mixed indications of being effective in reducing U(VI) [12]. However, H_2S was reported to have little impact on groundwater quality at the Smith Ranch-Highland (SRH) U ISR site in Wyoming, where the work described in this paper was also carried out [17]. H_2S also has the disadvantage of being exceedingly hazardous, and it is currently difficult to obtain in the quantities needed for full-scale restoration. When sodium sulfide (Na_2S) was deployed on a large scale at SRH, no significant changes in uranium concentrations were reported [18]. Therefore, it has proven difficult to find an effective reductant that reliably reduces (“reduce” in this paper always refers to a redox reaction and not as a synonym for “decrease”) uranium as well as other contaminants to restore an aquifer following ISR mining.

One approach that, to our knowledge, has not been attempted at an ISR facility but has been used with some success at sites with shallow uranium contamination, is to inject a phosphate amendment to precipitate U(VI) as uranyl phosphate [19,20]. This strategy does not rely on reducing U(VI) to U(IV), but there are many unknowns regarding how well a phosphate amendment could be distributed throughout an ore zone at an ISR facility and how much the precipitation of $\text{Ca}_3(\text{PO}_4)_2$ (apatite) might interfere with the precipitation of uranyl phosphate (although uranyl would, in principle, still sorb strongly to apatite). The latter uncertainty is especially a concern at a location such as SRH, where native and post-mining waters contain high calcium concentrations. In a recent laboratory column study to evaluate remediation after U ISR [21], a phosphate amendment was found to be ineffective in removing uranium from solution.

1.2. Relating Previously Reported Small-Scale Tests to This Paper

As a prelude to the work reported in this paper, a small-scale study was performed at the SRH mine, where sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) was used to reduce uranium following ISR mining [22,23]. In this study, two single-well push-pull field experiments were conducted, in which dithionite was injected into an ore zone that had not undergone any restorative treatment, such as groundwater sweep or reverse osmosis. Sodium dithionite is a strong, rapidly reacting reductant that has been used to make heavy water for nuclear reactors, as a chemical intermediate and pulping agent in making paper, and in making dyes and other chemicals. It has also been shown to be effective in reducing Cr(VI) to Cr(III) in groundwater [24–28]. After the dithionite was deployed, the wells were “shut in” for ~3 days to allow it to react with ore-zone sediments, and then ore-zone water was drawn back into the wells until uranium concentrations returned to pre-test levels. This procedure enabled estimates of volumes of ore-zone water treated (i.e., volumes from which U had been removed) and moles of U reduced in each test [22,23]. Uranium reduction was confirmed by uranium isotope ratio measurements [22,23]. Interestingly, the two single-well dithionite deployments effectively treated similar volumes of ore-zone water per mole of dithionite introduced (460 and 530 L/mole dithionite), but the amounts of uranium reduced per mole of dithionite were significantly different (0.023 and 0.044 moles U/mole dithionite, with these values being approximately proportional to the U concentrations in the waters drawn into the two wells). These results suggest that uranium constituted only a small fraction of the electron acceptors in the ore-zone water after a dithionite treatment, and thus it is better to design dithionite deployments to treat target water volumes instead of target amounts of uranium.

The mechanisms inducing U(VI) reduction in the small-scale experiment were difficult to determine. One path for U(VI) reduction by dithionite addition is indirect through reduction of Fe(III) oxides to Fe(II) by reactions such as:



When the resulting Fe(II) adsorbs to aquifer minerals, the U(VI) reduction reaction is catalyzed since U(VI) reacts more quickly with adsorbed Fe(II) than aqueous Fe(II) [29,30]. Dithionite also produces many reduced sulfur species when it reacts with sediments and decomposes in aqueous solutions [24–27,31], and these reaction products likely also contribute to U reduction and removal. Important decomposition reactions producing other reductants, such as aqueous sulfide, include [31]:



Fe(II) can react with aqueous sulfide produced during the dithionite injection to form Fe(II) sulfides that, in principle, can reduce U(VI) [32–34].

Since dithionite appeared to be promising as a U(VI) reductant in the single-well field deployments, we tested its effectiveness to reduce U(VI) over a much larger aquifer volume by performing a multi-well field experiment in six contiguous five-spot well patterns in a previously mined ore zone at SRH. This experiment was intended to approximate a full-scale dithionite deployment at an ISR facility. Sodium acetate was also added as a biostimulant in two of the six well patterns to evaluate whether a follow-on biostimulation was beneficial after a dithionite treatment. Sodium acetate stimulates the growth of naturally occurring microbes, which effectively transfer electrons from acetate to many potential electron acceptors, including U(VI), resulting in reduction of U(VI) to U(IV).

2. Materials and Methods

2.1. Field Site

The SRH mine is located near Casper, WY, in Wyoming's Powder River basin (Figure 1). For many years, this mine was the largest ISR operation in the United States. Production occurred at numerous ISR mining units, where water with dissolved oxygen and carbon dioxide or sodium bicarbonate was injected to recover uranium contained in unconsolidated sandstone deposits.

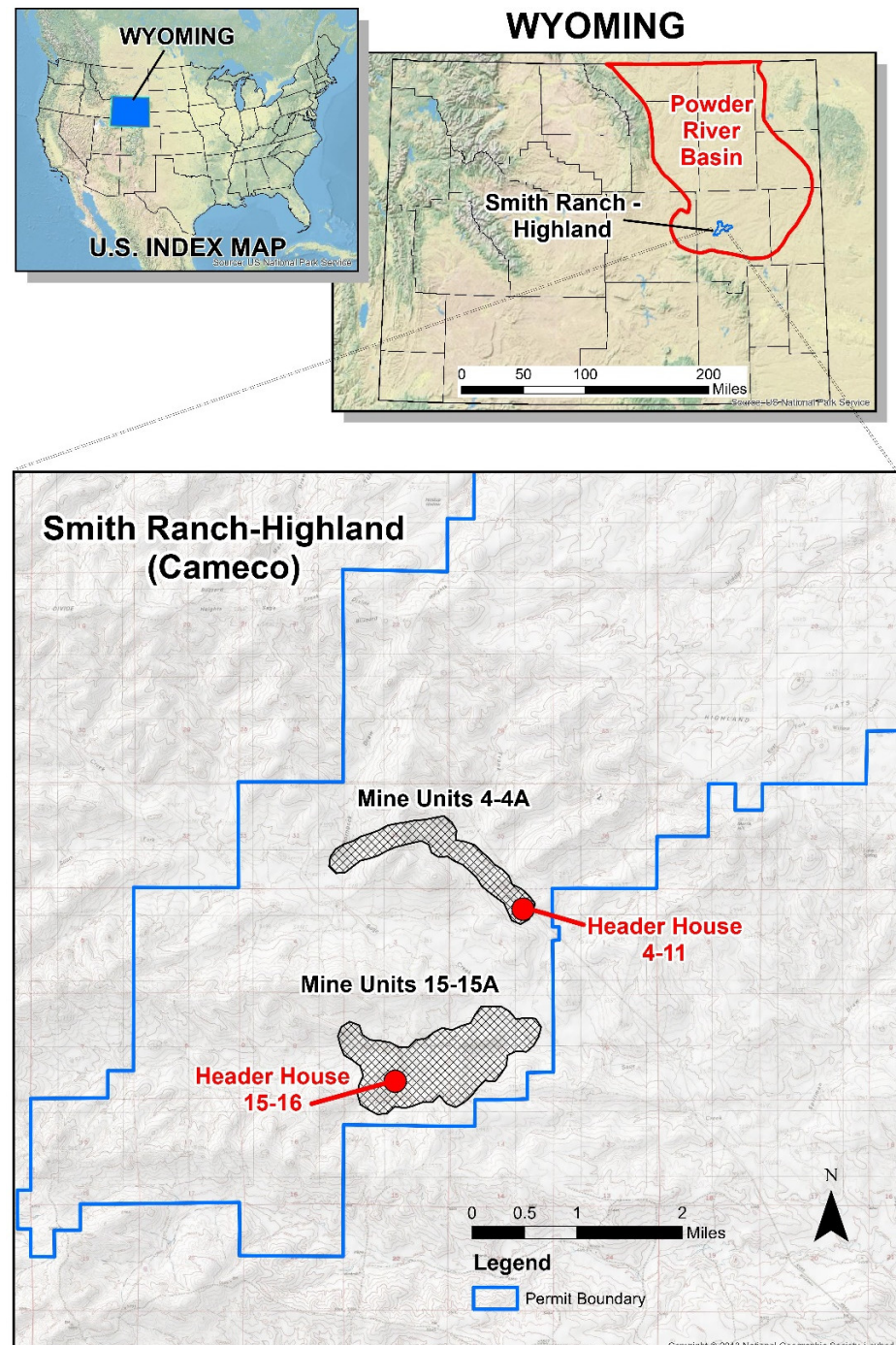


Figure 1. Location of Smith Ranch-Highland Facility in Wyoming, showing mining unit 4A and HH 4-11, where the multi-well reductive amendment test was conducted. Also shown is the location of HH 15-16 in mining unit 15, where the single-well push-pull dithionite tests discussed in Section 1.2 were conducted.

The multi-well reductive amendments experiment was conducted in mining unit 4A (MU 4A) in six five-spot well patterns served by Header House 4-11 (HH 4-11). HH 4-11 is located about two miles from the location of the single-well push-pull dithionite tests mentioned above (Figure 1), and the subsurface hydrology and geochemistry were quite similar at the two locations. Mining unit 4A had been actively solution-mined between 1995 and 2005 using water augmented with oxygen and carbon dioxide to oxidize and dissolve uranium. The 6 well patterns used for the amendment experiment consisted of a total of 18 wells, with 6 production wells and 12 injection wells (Figure 2). Appendix A contains information about these wells such as their completion interval depths and their water chemistries prior to the experiment. Each pattern forms roughly a 100×100 feet square, with a production well in the center and injection wells at each of the four corners, with many of the injection wells being shared by adjacent patterns. Production wells average about 70 feet from injection wells. All the injection wells were operating normally, except for well 4I-318, which was plugged and unavailable to use, so the test was conducted with only 11 injection wells. Every well was screened over a 13- to 20-foot interval at depths ranging from about 710 to 740 feet below land surface, with differences in depth varying slightly, mainly due to the surface topography (Table A1). The wells were screened at optimal depths to provide access to a confined transmissive sand layer containing uranium mineralization. The sediment mineralogy at the start of the amendment experiment was presumed to be very similar to that described in previous characterization studies of post-mining sediments from SRH mining unit 4 [5,6].

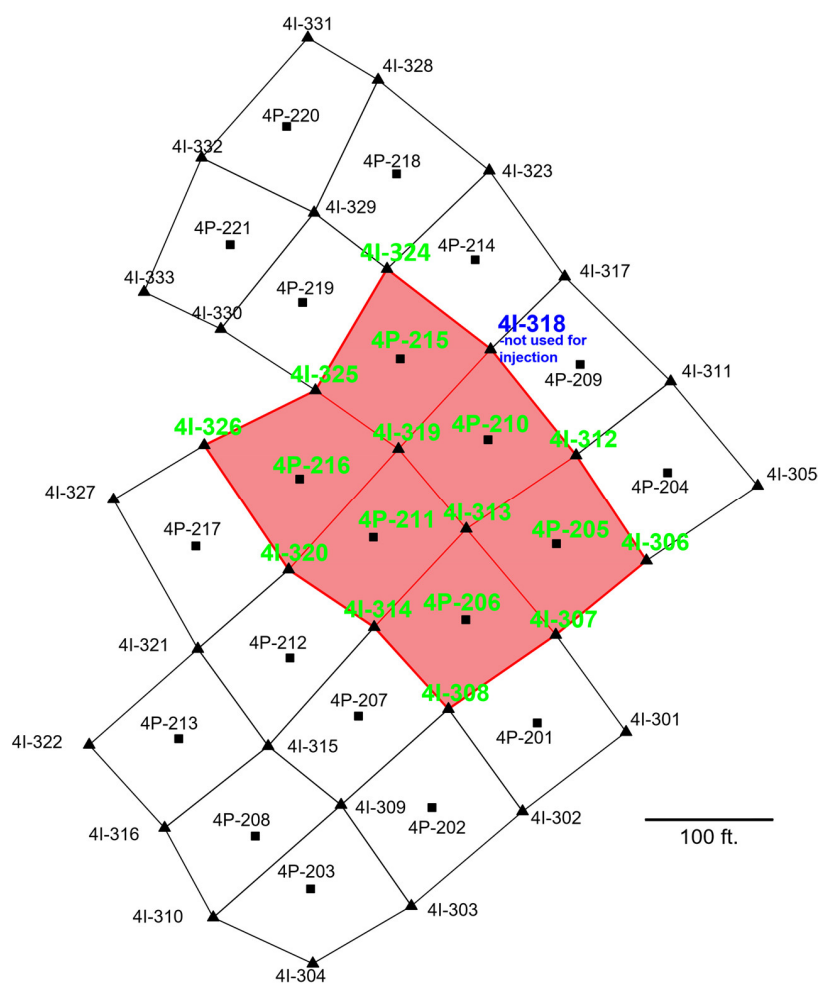


Figure 2. Wells served by HH 4-11, with the well patterns used in the multi-well amendments test shaded pink. The wells designated with a green font were used for the work described here. Note that 4I-318 was not used for these tests because it was plugged.

No restoration had been conducted in any of the well patterns served by HH 4-11 until approximately 13 months prior to the amendment test. At that time, water was pumped out of the ore zone, which drew cleaner water in from outside the ore zone in a classic groundwater sweep. The pumped water was sent through ion exchange columns to recover uranium, and then a portion of this water was reinjected into the ore zone, which significantly lowered the uranium concentrations (Figure A1). However, no reverse osmosis treatment was conducted in HH 4-11 before the start of the amendment test. The groundwater sweep was also effective in lowering the concentrations of many elements (Tables A2 and A3), but their concentrations at the time of the dithionite deployment remained elevated well above pre-mining concentrations (typified by Table A4). Restoration operations were stopped prior to the start of the dithionite injection and did not resume for the duration of the test.

2.2. Tracer Test

Six and a half months prior to the addition of the reductive amendments, a tracer test was conducted in the six well patterns that were designated for the amendment test. This test was carried out to provide an estimate of the aquifer volume accessed by the patterns (and thus an estimate of how much dithionite should be introduced). It was also used to identify any unusual groundwater flow patterns that might prompt changes to where or how the amendments should be introduced or whether flow rates in any of the wells should be altered to provide better distribution of amendments. Details of the implementation, results, and interpretation of the tracer test are provided in Appendix B.

The estimated aquifer volume swept by the tracers in the six well patterns was approximately 6900 m³, which compares well with the geometrically calculated volume of 7600 m³ (assuming a porosity of 25% and an ore-zone thickness in each well equal to the screened interval length). Additionally, the tracer test results indicated that while the flow distribution within the six patterns was not ideal, each injection well flow made a significant contribution to sweeping the patterns and there were no significant diversionary flows that would compromise the amendments test (Figures A9 and A10). Thus, no adjustments were made to improve the flow distribution, as any attempt to do so was deemed to be just as likely to be detrimental as beneficial.

2.3. Amendment Test

The reductant sodium dithionite was introduced into the injection wells in the six five-spot well patterns to investigate how effectively dithionite removed uranium and other contaminants from the groundwater in the patterns. Forty days after the addition of dithionite ended, sodium acetate was injected into two of the six well patterns to stimulate microbial growth and further promote reducing conditions. The following two sections describe these two injections in considerable detail, with frequent reference made to supporting material in Appendix C.

2.3.1. Dithionite Injection

In the amendment test, 8400 kg of nominally 90% purity sodium dithionite, or about 43,400 moles of dithionite, was used. Assuming about 500 L of water treated per mole of dithionite (estimated from the single-well dithionite tests [22,23]), this was enough dithionite to treat about 21,700 m³ of water, which was about 3.1 times the 6900 m³ estimated to be accessed by the six well patterns in the tracer test. The margin of a factor of around 3 was to allow for uncertainties in going from single-well tests to a multi-well configuration, and to compensate for some additional volume accessed in the aquifer because the dithionite injection was planned as a 10% over-injection into the injection wells (i.e., the combined injection flow rate into all injection wells would exceed the combined production flow rate from all production wells by 10%). Over-injection would result in a greater volume of aquifer accessed than during the tracer test, which had less than a 0.25% over-injection. The dithionite test was conducted with the six well patterns in a closed-loop

configuration, with the water produced from the production wells pumped directly into the injection wells without being sent out of the header house (in contrast to the tracer test, where the production flows were diverted to a surface facility and injection flows came in from this facility). The test was started using the same flow balance as in the tracer test (see Table A5), although balanced flow rates in each well were initially about 15% higher than in the tracer test, which was possible because of the closed-loop configuration.

The dithionite was mixed in fourteen ~1600-gallon batches in a plastic tank using potable water from a shallow well at the SRH mine. Once mixed in the ~1600-gallon batch tank, each batch of dithionite solution was transferred to a second larger tank that was plumbed directly into HH 4-11 (Figure A12). This configuration allowed batches to be prepared while continuously pumping the dithionite solution from the larger tank into the header house. The compositions of each of the 14 batches are listed in Table A7. The first two batches were prepared at approximately 0.5 M sodium dithionite, 0.65 M sodium sulfite, and 0.24 M sodium sulfide, which was expected to result in a dithionite injection concentration of about 0.05 M after the 1:10 dilution in the injection plumbing, thus roughly matching the injection concentration in the single-well dithionite tests. Sulfite and sulfide were added to the dithionite solution to slow the degradation of dithionite. They do this by keeping the pH of the solution elevated, scavenging oxygen (which reacts rapidly with dithionite), and helping to push the degradation reaction equilibria in the direction of the reactant dithionite (both sulfite and sulfide are degradation products of dithionite). Dithionite degradation decreases pH, which in turn results in a more rapid degradation of dithionite, so maintaining a higher pH is desirable [27,31]. A pH of 8.0 was the initial goal to stabilize the dithionite, while not being so high as to cause significant calcite precipitation in the aquifer (the pH was expected to drop to 7 or less after the 1:10 dilution with the injection flows).

After the first two batches were prepared, it became apparent that the initial batch recipe, which had been optimized in the laboratory, was not appropriate for the field study. This was due to a higher pH than expected and because of the formation of black precipitate that was believed to consist of elemental sulfur and perhaps other reduced sulfur species. The high pH prompted an immediate reduction in the dithionite injection rate so that the over-injection into the well patterns for these two batches was less than 5%. Sodium sulfide was removed from the mixture starting with batch 3, and several of the final batches also contained no sulfite because a sulfite precipitate began accumulating at the bottom of the mixing tank (Table A7). The black precipitate almost immediately caused pressure build-up in the injection wells, necessitating a decrease in pumping/injection flow rates and forcing deviations from ideal flow balance because injection wells accepting the most flow were experiencing the greatest flow rate decreases. Dithionite injection was interrupted for about 20 h after batch 3 and then again for nearly 3 days after batch 4, while closed-loop circulation (without dithionite injection) was continued during these time periods in an attempt to stabilize and hopefully decrease the injection pressures. While the pressures stabilized, they did not significantly decrease during these interruptions, and batches 5–14 were injected nearly continuously, with the overall injection and production flow rates being reduced to about half of their original targets to allow partial restoration of flow balance within the patterns.

The time sequencing and injection rates for all 14 dithionite batches, which occurred over a span of 9 days, are listed in Table A8. During the injection of batches 5–14, pumping rates of dithionite solution into the injection plumbing were adjusted to be slower in the evenings than during the day to avoid running the feed tank dry overnight, which resulted in significant fluctuations in the dithionite concentrations injected into the six well patterns, as well as fluctuations in the amount of over-injection into the patterns, ranging from about 10% at night to as much as 25% during the day. Figure A13 shows the combined injection and production flow rates during and immediately after the dithionite injection, and flow rates for individual wells during this period are shown in Figures A14 and A15, with Figure A14 showing the injection flows as fractions of the total injection flow.

Soon after the dithionite injection was completed, all flows were increased somewhat (Figure A13), and the six well patterns were circulated for a total of 40 days (or 49 days from the start of the dithionite injection) while maintaining approximately the same degree of flow balance as during the latter parts of the injection. This circulation continued up until the time of the acetate injection.

During the dithionite injection, the concentration of dithionite in the injection flow stream was qualitatively monitored in HH 4-11 by UV absorbance spectroscopy [31] using a fiber optics system. Dithionite concentrations remained stable throughout the batch injections with no obvious degradation from the start to the end of a batch. The oxidation-reduction potential (ORP) in the injection stream remained consistently very low due to the strong reducing conditions induced by the dithionite (ranging from -600 to -700 mV relative to Ag/AgCl electrode, which is -370 to -470 mV relative to standard hydrogen electrode, or Eh). Production wells were periodically sampled for alkalinity using a Hach titration kit and for ferrous iron and sulfide using Hach reagent kits with a Hach DR890 colorimeter (Hach Company, Loveland, CO, USA). The pH, ORP, temperature, and specific conductance in each of the production wells were also periodically measured using a YSI multiprobe system.

During and after the dithionite injection, water samples were collected from each production well three times per day. A sample for cations and trace metals and a second sample for anions were collected at each sampling time. All samples were filtered through a 0.45-micron filter into 125 mL low density polyethylene (LDPE) bottles. The cation sample was acidified with ultra-pure HNO_3 to a pH of 2, while the anion sample was not acidified. These samples were sent to Los Alamos National Laboratory for chemical analyses. Cations were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) using Environmental Protection Agency (EPA) Method 200.7 with a Perkin-Elmer Optima 2100 DV system. Selected elements, including U, were determined by ICP-mass spectrometry (ICP-MS) using EPA Method 200.8 with a Perkin-Elmer NexION system. Anions were measured by ion chromatography (IC) using EPA method 300.0 with a Dionex ICS-2100 system. A small number of samples were also collected for $^{238}\text{U}/^{235}\text{U}$ isotope ratio measurements to directly test for U(VI) reduction. Determinations of $^{238}\text{U}/^{235}\text{U}$ were performed on a Nu Plasma HR MC-ICP-MS at the University of Illinois, Urbana-Champaign. The 2σ precision of the ratio measurements was 0.11‰. Details of the isotope work, including descriptions of the sample purification procedure, spikes, and quality control, can be found in [23].

2.3.2. Acetate Injection

Forty days after the dithionite injection ended, the production flows from four of the six production wells in the test patterns (4P-210, 4P-211, 4P-215, and 4P-216) were stopped, and the flows from the other two production wells (4P-205 and 4P-206) were directed into their six adjacent injection wells (4I-306, -307, -308, -312, -323, and -314). Given the reduced overall flow rates relative to when all six production wells were operating, it was possible to achieve flow balance in the two remaining well patterns (Table A9). Sodium acetate was injected into these two well patterns through the six operational injection wells using the same mixing and injection system that was used for the dithionite. Four ~1500-gallon batches of 1000 kg of sodium acetate each (~1.07 M acetate, pH 7–8) were prepared, and these were injected into the combined injection flows over approximately 64 h (Table A10), resulting in an average injection concentration of about 0.075 M acetate and an average over-injection rate of about 7%. Five kg of the tracer sodium 2,6-difluorobenzoate was added to the first batch of acetate, and five kg of sodium pentafluorobenzoate was added to the third batch. These tracers were added to observe the consumption of acetate. The fluorinated benzoate tracers are resistant to biodegradation, so drops in total organic carbon concentrations relative to the tracer concentrations provided an indication of the microbial consumption of acetate. The tracers also allowed the injected water to be traced through the well patterns.

Following the 64 h acetate injection, the balanced circulation flows through the two well patterns were continued for 20 days, or 23 days from the start of the acetate injection. During this 23-day period, 3 samples per day were collected from wells 4P-205 and -206. The sampling protocol was the same as during the dithionite injection except that an additional 60 mL glass bottle was collected from each well at each sampling time for analyzing the tracers and total organic carbon. These samples were collected without filtration or acidification. Fluorinated benzoate tracers were analyzed by HPLC, while total organic carbon was chemically oxidized and then analyzed with a Xylem OI Analytical carbon analyzer.

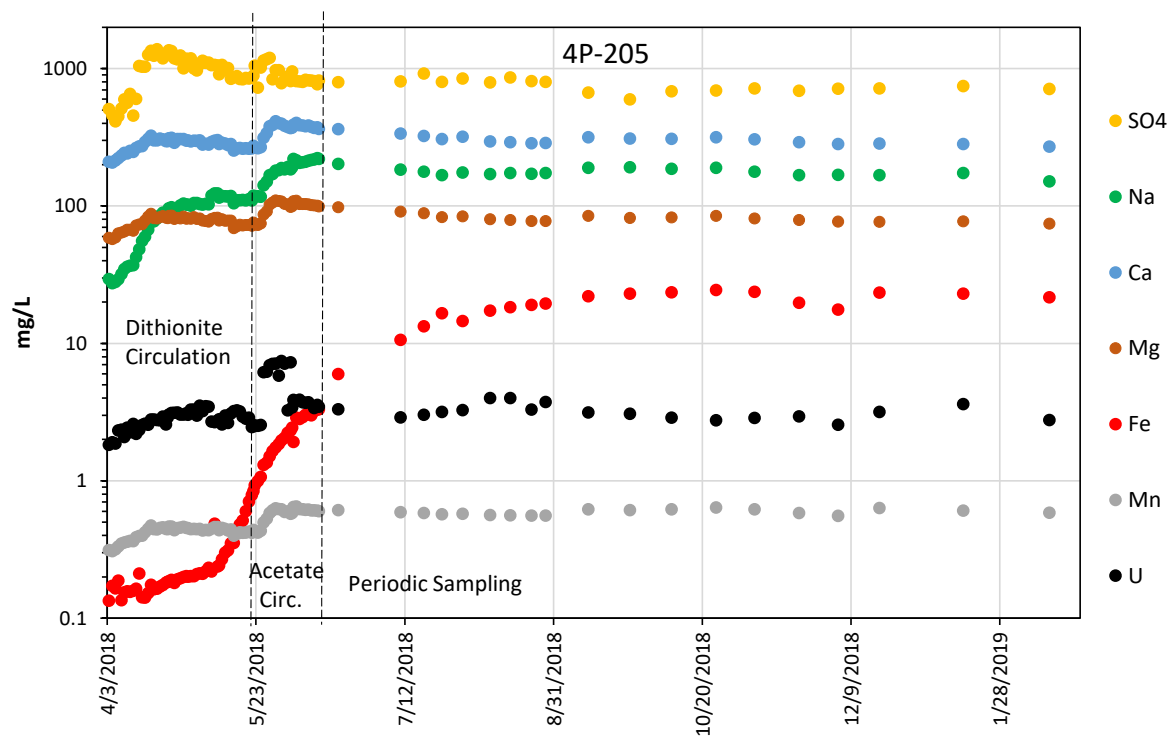
After the 23 days of acetate circulation, all flows in HH 4-11 were stopped. However, periodic sampling of each of the six production wells in the six test patterns was performed for another 8 months, with sampling intervals ranging from weekly to monthly (total of 19 samples in 8 months). Each sampling event was preceded by approximately one day of closed-loop circulation of all six patterns.

3. Results

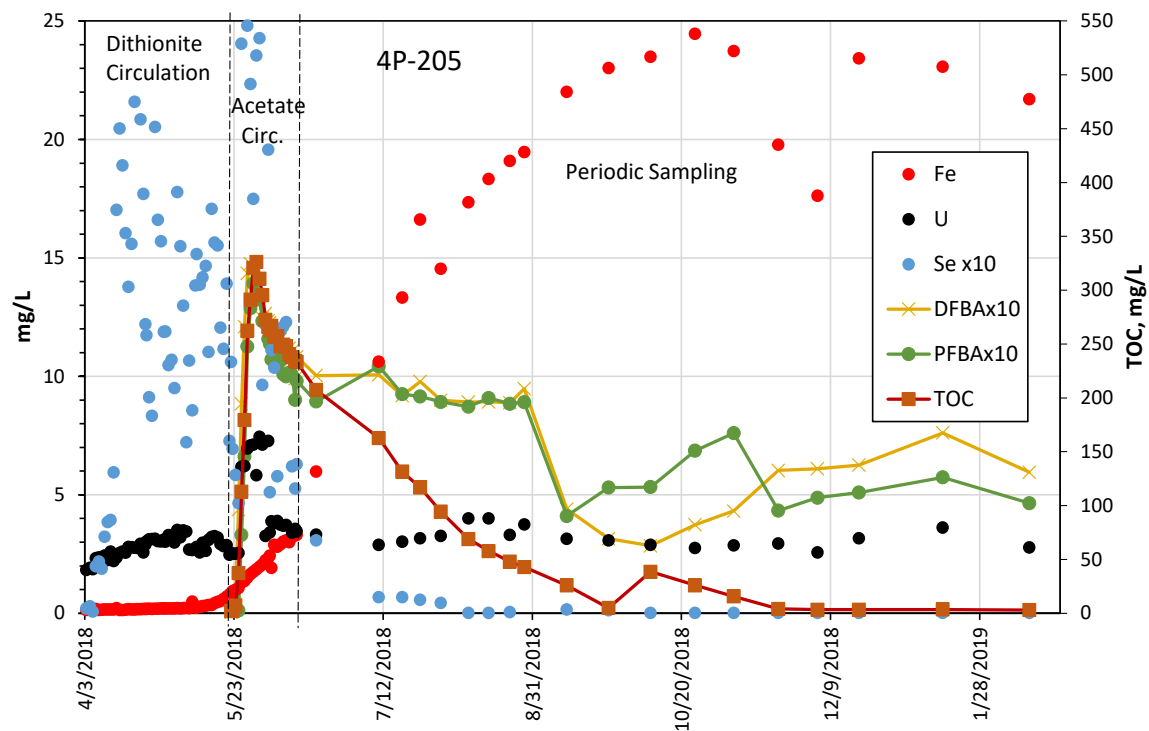
The results of the amendment experiment over the entire 10 months of the test, including both the dithionite and acetate injections and the 8 months of sampling after the injections, are described here. Appendix D contains supporting information referred to in this section.

Before discussing geochemical observations, we point out that the back-pressure problems encountered during the dithionite injection and the resulting flow imbalances mean that the aquifer volume accessed in this phase of the experiment should not be assumed to be the same as that determined during the tracer test. The flow distribution of dithionite was also obviously different than was the case for the tracers. Since a non-reactive tracer was not added with the dithionite, an alternative analysis involving the use of total cation charge as a surrogate tracer was carried out to estimate how much the affected aquifer volume and flow distribution changed during the dithionite injection (see Appendix D.1 of Appendix D). It was concluded that the swept volume was not significantly different after the dithionite injection than during the tracer test, but there was about 10% less recovery of injected fluids in the dithionite test (about 86% recovery vs. 95% recovery), indicating that the lack of flow balance resulted in about 10% more “flare-off” of dithionite solution. However, the dithionite mass that was introduced to the six patterns was a factor of 3.1 greater than what was estimated to treat the volume in the patterns, which should have more than made up for the unintentional flare-off. In contrast, the responses of the tracers injected with the acetate indicated that the flow balance and mass participation in the two patterns used for the acetate injection were nearly the same as in the tracer test (Figures A20 and A21). This is not surprising given that ideal flow balance was restored to these two patterns when the other four patterns were shut down.

Figures 3–5 show the concentration histories of several key constituents in three of the six production wells during the amendment test. Figure 3 represents a well pattern that received both dithionite and acetate, Figure 4 represents a pattern adjacent to a pattern that received both dithionite and acetate, and Figure 5 represents a pattern that was one pattern removed from a pattern that received both dithionite and acetate. There were two production wells corresponding to each of these three descriptions, and the trends observed in the two wells in each pairing were very similar. Figures for the companion production wells not shown in Figures 3–5 are provided as Figures A22–A24, respectively, in Appendix D.2 of Appendix D.



(A)



(B)

Figure 3. (A) Concentration histories of several key constituents in production well 4P-205 during the amendment test. (B) Concentration histories of redox-sensitive constituents (Fe(II), U, Se), TOC (as acetate surrogate), and tracers. Note that Se, difluorobenzoate (DFBA), and pentafluorobenzoate (PFBA) concentrations are multiplied by 10.

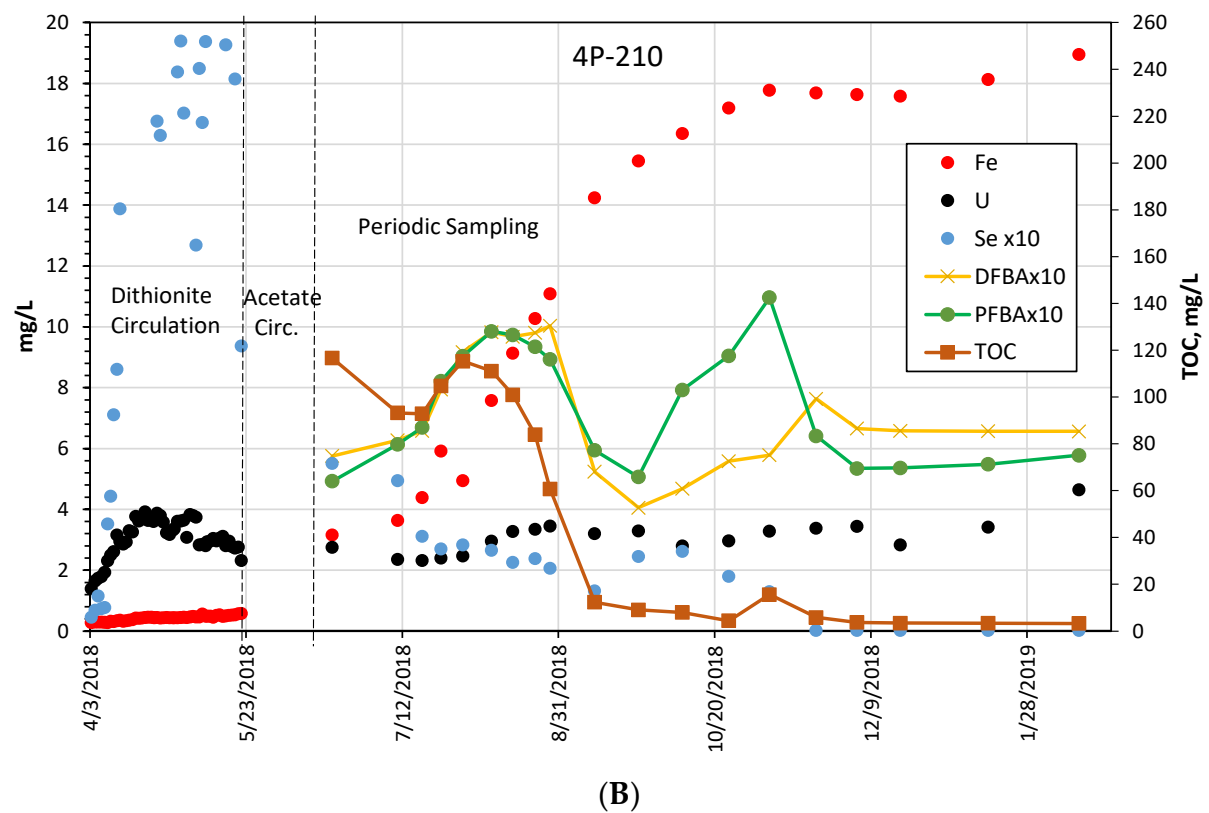
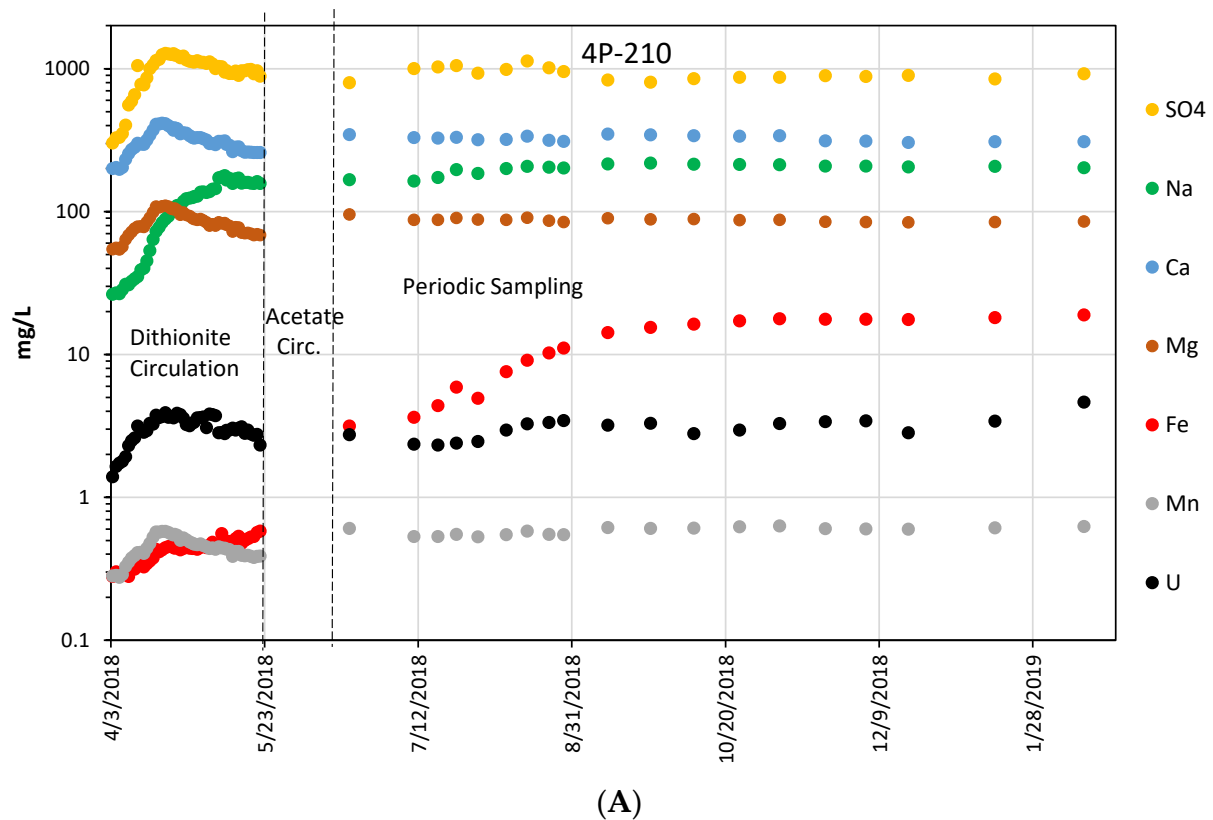
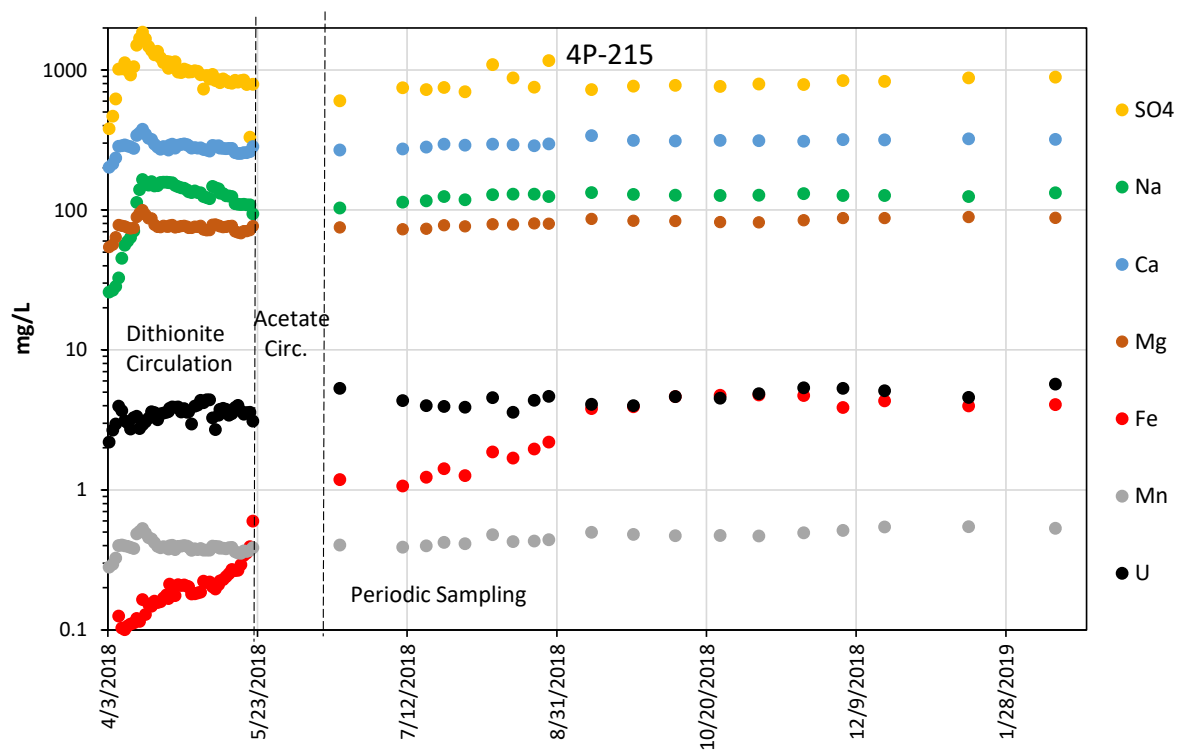
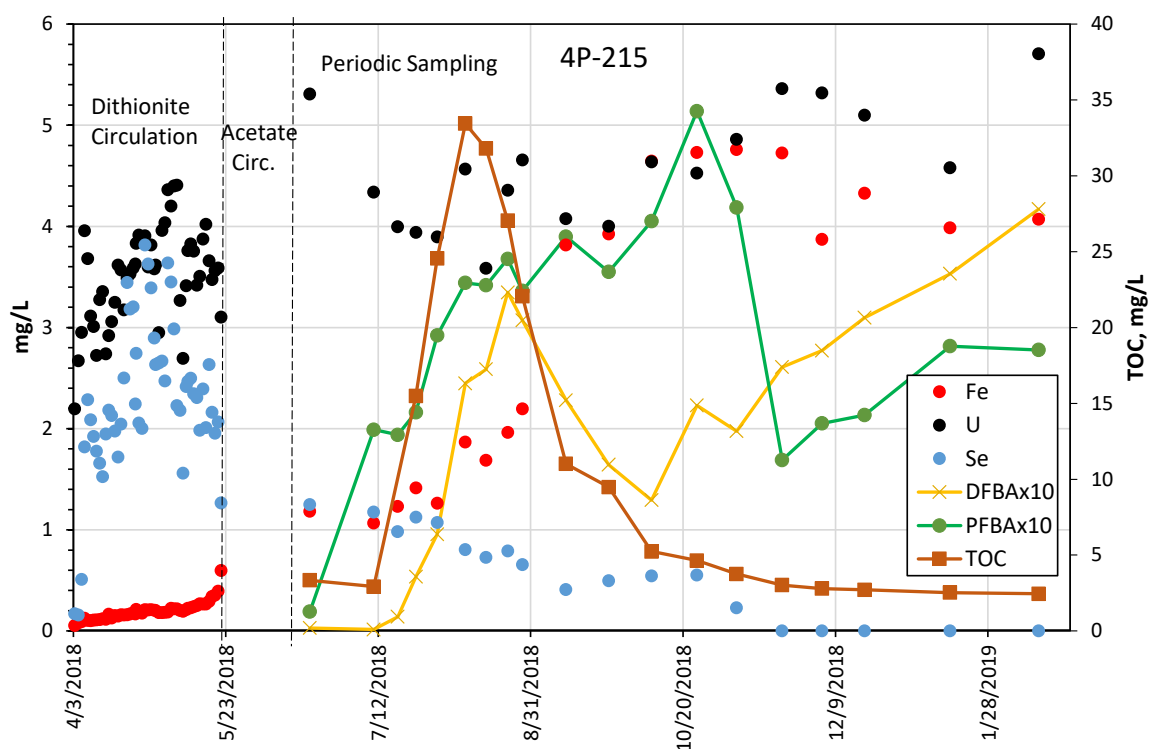


Figure 4. (A) Concentration histories of several key constituents in production well 4P-210 during the amendment test. (B) Concentration histories of redox-sensitive constituents (Fe(II), U, Se), TOC (as acetate surrogate), and tracers. Note that Se, difluorobenzoate (DFBA), and pentafluorobenzoate (PFBA) concentrations are $\times 10$.



(A)



(B)

Figure 5. (A) Concentration histories of several key constituents in production well 4P-215 during the amendment test. (B) Concentration histories of redox-sensitive constituents (Fe(II), U, Se), TOC (as acetate surrogate), and tracers. Note that difluorobenzoate (DFBA) and pentafluorobenzoate (PFBA) concentrations are $\times 10$.

In the A panels of each of Figures 3–5 (and Figures A22–A24), a log concentration scale is used to accommodate the nearly 4 orders of magnitude range in concentrations (note that K^+ , Cl^- , and HCO_3^- were other main contributors to total charge that are not shown— K^+ and Cl^- changed very little during the test, while HCO_3^- could not be accurately measured, as discussed below). The B panels of these figures serve to illustrate the consumption of acetate (inferred from TOC concentrations) and the effects of the resulting biostimulation on the concentrations of the redox-sensitive species Fe(II), U(VI), and Se (a mixture of Se(IV) and Se(VI) as determined by geochemical model calculations—see Appendix E) in each of the well patterns. The Fe(II) and U(VI) concentration histories are common to both the A and B panels of Figures 3–5 (and Figures A22–A24), with a log concentration scale used in the A panels and a linear concentration scale used in the B panels.

In Figures 3A, 4A and 5A, it is apparent that sodium, calcium, and magnesium concentrations all rose almost immediately in all wells after the dithionite was injected. Sodium levels increased because sodium dithionite, sodium sulfite, and sodium sulfide were the major constituents of the injectate. Calcium and magnesium likely increased due to cation exchange with sodium on aquifer sediments. The concentrations of these constituents rose further after the sodium acetate injection for the same reasons. Calcite dissolution could have also contributed some calcium during both injections, although the injectate solutions had a pH that was high enough that they should not have promoted this. However, the pH in the production wells dropped somewhat during the test (Table 1), so some calcite may have dissolved.

Table 1. pH and Eh (mV, adjusted from measured ORP in mV relative to Ag/AgCl) in the six production wells measured at various times during the test. Shaded columns indicate well patterns receiving acetate.

Date	4P-205		4P-206		4P-210		4P-211		4P-215		4P-216	
	pH	Eh	pH	Eh	pH	Eh	pH	Eh	pH	Eh	pH	Eh
3 April 2018	6.4	355	6.4	347	6.4	341	6.4	334	6.4	343	6.4	337
7 April 2018	6.4	248	6.4	249	6.4	247	6.4	245	6.4	257	6.4	288
12 April 2018	6.4	176	6.5	238	6.5	210	6.5	205	6.3	198	6.5	191
21 May 2018	6.2	207	6.2	194	6.2	181	6.2	167	6.2	166	6.1	171
19 June 2018	6.0	120	6.0	114	6.0	105	6.1	176	6.1	130	6.1	136
28 August 2018	6.0	36	6.1	26	6.0	48	6.0	58	6.1	67	6.1	45

Note that 3 April 2018 was prior to injection of any amendments, 12 April 2018 was the end of the dithionite injection, 21 May 2018 was just prior to the acetate injection, and 19 June 2018 was the time of the first sampling of all six wells after the acetate circulation stopped.

Sulfate concentrations increased significantly and remained elevated during and after the dithionite injection (Figures 3A, 4A and 5A). This is not surprising, as sulfate is one of many degradation products of dithionite. It is also generated by oxidation of sulfite and sulfide, which were injected directly and are also degradation products of dithionite. Although considerable sulfide was injected and more was expected to be produced from dithionite decomposition [31], sulfide concentrations in all production wells (measured using a Hach colorimeter kit) never exceeded about 0.02–0.03 mg/L. This is similar to what they were before the test and also consistent with what was observed during the single-well dithionite tests [22,23]. Apparently, most of the injected or produced sulfide reacted with the excess Fe^{2+} that was generated (see the next paragraph) to form insoluble Fe(II) sulfides, such as mackinawite or pyrite. However, some of the sulfide might have also reacted with Mn^{2+} , which also became elevated during the test, to form insoluble manganese sulfides.

Iron concentrations (determined with ICP-OES and assumed to be all Fe^{2+} because of the extremely low solubility of Fe^{3+}) increased throughout the dithionite injection and then increased further after the acetate injection (Figures 3–5). This was expected, as large amounts of Fe^{2+} appeared during the single-well dithionite tests [22,23], and Fe^{2+} generation has also been observed in laboratory dithionite studies investigating Cr(VI) reduction [24,28]. It is also consistent with the decreases in oxidation-reduction potentials

in all production wells during the test (Table 1). Most of the Fe^{2+} was likely produced when abundant Fe(III) oxides, left behind by the oxidation of pyrite and other reduced iron phases during mining, were reduced first by dithionite and its degradation products and then by microbial processes after the acetate injection. Fe^{2+} concentrations may have also been enhanced as a result of Fe^{2+} being displaced from aquifer cation exchange sites when sodium and other cation concentrations increased.

While dithionite can promote reduction and removal of uranium, U concentrations increased slightly after the addition of dithionite, and concentrations never appreciably dropped (Figures 3–5). There was also a significant spike in uranium concentrations after the acetate addition in the two patterns that received acetate (Figures 3 and A22). Only a few samples for $^{238}\text{U}/^{235}\text{U}$ isotope ratio measurements were collected during the amendments test, including 6 from well 4P-205, 5 from 4P-210, and 4 from 4P-215 (Figure 6). This isotope

ratio, expressed as $\delta^{238}\text{U} = \left(\frac{\left(\frac{^{238}\text{U}}{^{235}\text{U}} \right)_{\text{sample}}}{\left(\frac{^{238}\text{U}}{^{235}\text{U}} \right)_{\text{standard}}} - 1 \right) \times 1000\text{‰}$, would be expected to decrease

over time if significant U(VI) reduction was occurring [22,23,34–40], and while there is a hint of a slight drop for the last two samples collected (Figure 6), the uncertainty in the measurements indicate that the drop is not significant relative to the earlier measurements. This suggests that U(VI) reduction was not significant, which is in contrast to the dithionite push-pull tests conducted at the SRH mine, in which there was a strong $^{238}\text{U}/^{235}\text{U}$ isotopic signal of reduction [22,23] and corresponding removal of U(VI).

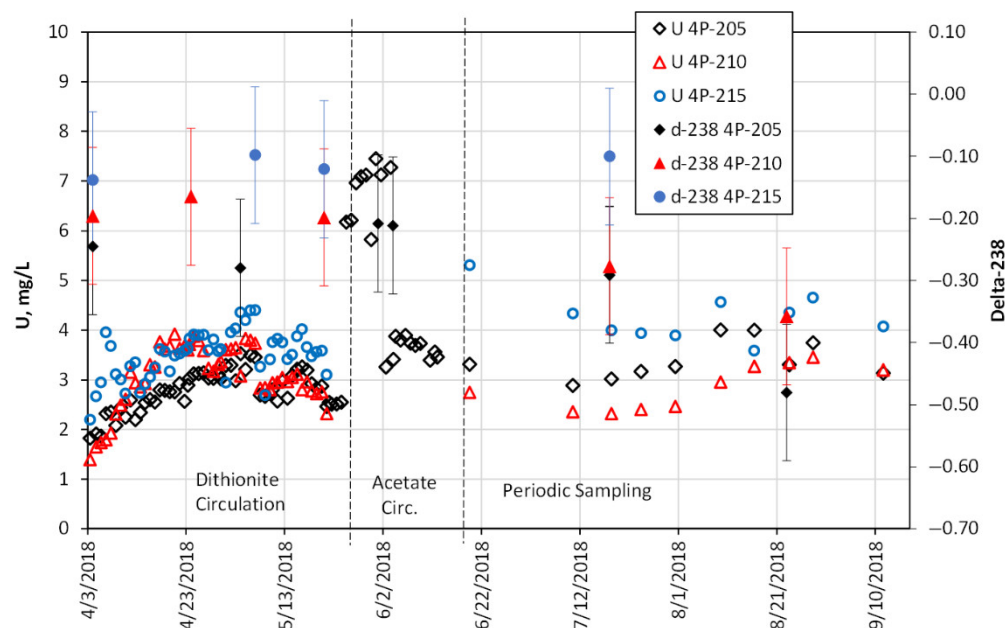


Figure 6. U concentrations and $\delta^{238}\text{U}$ in wells 4P-205, -210, and -215 during the amendments test. Error bars for $\delta^{238}\text{U}$ represent the analytical uncertainty (± 2 standard deviations) of the isotope measurements.

For both multi-well and push-pull tests, dithionite was likely consumed rapidly in sediments near the injection well bores, creating a reaction zone or “halo” around them. In the single-well push-pull tests, aquifer water was drawn through these reaction zones after the dithionite injections, which made it easy to see the effects of uranium reduction because the reaction zones were the last thing seen by the pumped water. However, in the multi-well test, any uranium reduction that occurred in the reaction zones would have taken place as the uranium was injected into the aquifer rather than being pulled out, and once the injected water moved out of the reaction zones and made its way to the production wells, it had plenty of opportunity to interact with aquifer sediments that were unaffected by dithionite. Apparently, any uranium reduction that occurred close to the injection wells

was more than offset by the desorption of U(VI) from aquifer sediments, including possibly the liberation of U(VI) after reductive dissolution of U(VI) adsorbents such as Fe(III) phases (discussed below), once the injected water moved outside the reaction zones.

The fact that uranium concentrations spiked significantly in wells 4P-205 and -206 almost immediately after the sodium acetate injection (Figures 3 and A22) suggests that some of the U(VI) desorption occurred as a result of cation exchange processes, with all the injected sodium displacing calcium, magnesium, and possibly some U(VI) from cation exchange sites in the aquifer. The same thing happened to a lesser extent after the sodium dithionite injection. U(VI) desorption would be enhanced by elevated calcium and magnesium concentrations due to the formation of highly stable Ca-U(VI)-CO₃ and Mg-U(VI)-CO₃ complexes, with the calcium ternary complexes expected to dominate (Table 2, which lists predominant U aqueous species predicted in water chemistries representative of various stages of the amendments test and generally relevant to the SRH site). These U(VI) complexes are also known to inhibit U(VI) reduction [11,41].

Table 2. Calculated fractions of dissolved uranium species present in a typical background water, a typical post-mining ore-zone water, and at various stages during the amendment test at SRH. Also shown is the U speciation in a water that approximates ore-zone water after typical reverse osmosis treatment.

Species	Background Water *	Post-Mining Water *	Pre-Amendment Water *	Post-Dithionite Water *	Post-Acetate Water *	Post-RO Water *
Ca ₂ UO ₂ (CO ₃) ₃	0.517	0.742	0.690	0.728	0.710	0.477
CaUO ₂ (CO ₃) ₃ ^{−2}	0.467	0.244	0.291	0.258	0.264	0.416
MgUO ₂ (CO ₃) ₃ ^{−2}	0.011	0.007	0.008	0.006	0.007	0.009
UO ₂ (CO ₃) ₃ ^{−4}	0.004	0.003	0.003	0.004	0.005	0.003
UO ₂ (CO ₃) ₃ ^{−2}	0.002	0.005	0.008	0.004	0.013	0.079
UO ₂ CO ₃	5.6 × 10 ^{−6}	1.7 × 10 ^{−4}	3.7 × 10 ^{−4}	1.3 × 10 ^{−4}	0.001	0.015
All Others	2.4 × 10 ^{−5}	9.2 × 10 ^{−5}	3.3 × 10 ^{−5}	1.0 × 10 ^{−5}	1.2 × 10 ^{−4}	2.90 × 10 ^{−4}

* See Appendix E, Table A12, for representative water chemistries. Calculations were performed using PHREEQC [42], with the minteq.v4 database (11091, 4-21-2016, <https://github.com/ufz/iphreeqc/blob/master/database/minteq.dat>, accessed on 10 May 2022). The minteq.v4 database was supplemented with additional reactions for aqueous U chemistry [43] and uranyl ternary complexes [8,44].

Another factor contributing to U(VI) desorption may have been increases in alkalinity after both the dithionite and acetate additions, which along with Ca²⁺ contributes to the formation of the stable Ca-U(VI)-CO₃ complexes. Some sodium bicarbonate was included as a stabilizing agent in the bulk sodium dithionite powder that was used in the test, although the percentage was listed as a rather wide range on the drum labels (2–25%, despite the nominal 90% purity of the sodium dithionite). Unfortunately, it was not possible to accurately monitor groundwater alkalinity during the test because the abundant sulfite that was added with the dithionite, and generated by dithionite degradation, interfered with alkalinity titrations, resulting in unrealistically high alkalinity measurements. Some alkalinity may have also been generated as a result of calcite dissolution in the aquifer when the pH slightly dropped (Table 1). Finally, after the acetate addition, there was likely some microbial conversion of acetate to CO₂, which then becomes bicarbonate or carbonate, increasing alkalinity [45].

A final likely contribution to the U(VI) concentration increases after both the dithionite and acetate injections was the reductive dissolution of Fe(III) oxides, which are strong sorbents of U(VI) [46]. Reduction of Fe(III) would be expected to occur before reduction of U(VI), and this would have resulted in the liberation of U(VI) from the Fe(III) oxides without significant reduction of U(VI).

The consumption of acetate to promote microbial growth in the two well patterns receiving acetate is evident from the divergence of the concentration trends of total organic carbon (TOC) and the fluorinated benzoate tracers, which were injected with the acetate, in these patterns (Figures 3B and A22B). The fluorinated benzoates make a trivial contribution

to the TOC, so the TOC concentrations almost exclusively reflect acetate concentrations, and the TOC concentration trends start to diverge from the tracer concentration trends at about the time the acetate circulation in the two injection patterns stopped (Figures 3B and A22B). The reducing effects of the biostimulation are most apparent from the sudden drop in selenium concentrations almost as soon as the TOC and tracer concentrations start to diverge (Figures 3B and A22B), indicating reduction of Se(VI) to Se(IV), which adsorbs to sediments more strongly than Se(VI) [47]. Selenium could have also been further reduced to elemental selenium (Se(0)), which is insoluble. Similar effects are seen in the well patterns that did not receive acetate due to its spillover into these patterns when all six patterns were circulated together for about 24 h prior to each subsequent sampling event (Figures 4B, 5B, A23B and A24B). The selenium concentrations in all wells dropped to below detection limits before the end of the test. However, the disappearance of selenium from the four patterns not receiving acetate occurred much later than in the two patterns that received acetate, which is likely a reflection of both the later arrivals and the lower concentrations of acetate in the four patterns. Interestingly, Se concentrations in all well patterns initially increased after the dithionite injection, which may reflect a liberation of selenium that was adsorbed to Fe(III) solids [48] after the Fe(III) was reduced and dissolved by the dithionite.

The biostimulation also probably contributed to the reduction of Fe(III) solids, resulting in continued increases in Fe^{2+} concentrations in all production wells after the acetate addition, although they were already increasing dramatically after the dithionite addition (Figures 3–5). The increases were most prominent in the two well patterns into which acetate was injected (Figures 3 and A22). Of the other four well patterns, the highest Fe^{2+} increases were observed in the pattern that experienced the highest acetate/TOC concentrations during subsequent circulation and sampling of the patterns (well 4P-210, Figure 4), which may have seen higher TOC concentrations in part because of flaring of TOC from the adjacent 4P-205 pattern during the acetate injection. However, it is apparent that the biostimulation had virtually no effect on U(VI) concentrations, and little, if any, effect on sulfate concentrations in any of the well patterns throughout the test (Figures 3–5 and A22–A24). Biostimulation can often lead to significant U(VI) and sulfate reduction [45,49,50], and we believe that the reason it did not do so in the multi-well test was the abundance of Fe(III) solids in the aquifer sediments, which showed no sign of being fully consumed by the end of the test.

Based on thermodynamic considerations, as long as significant amounts of ferric solids remained in the aquifer, U(VI) and sulfate would not be expected to be appreciably reduced. It may be that to achieve significant U(VI) reduction, more acetate biostimulation (and/or more dithionite injection) would have been necessary to consume all or most of the ferric solids. However, even if more than enough acetate had been added to dissolve all of the Fe(III), the subsequent reduction of Ca-U-CO₃ would likely have been inefficient since even microbial reduction is inhibited by the extraordinary thermodynamic stability of these complexes [10,40]. Acetate appeared to be almost completely consumed in all well patterns before the end of the test (Figures 3B, 4B, 5B and A22B, A23B, A24B), and it appeared that iron concentrations in the well patterns leveled off at about the same time that TOC concentrations dropped to very low levels. Even if some U(VI) reduction occurred, it was obviously offset by liberation of U(VI) when Fe(III) adsorbents were reduced and by U(VI) desorption enhanced by increases in calcium concentrations and alkalinity. These additional sources of U(VI) would have also swamped any U reduction signal from $^{238}\text{U}/^{235}\text{U}$ isotope ratios.

Appendix E describes PHREEQC [42] geochemical model calculations performed to determine the potentials for important redox couple transitions in the restoration process. The upshot of these calculations is that Se(IV)/Se(VI), Fe(II)/Fe(III), U(IV)/U(VI), and S(–II)/S(+VI) each have a midpoint of transition (where there are equal amounts of reduced and oxidized forms) in the order listed. Appendix E also contains Eh-pH diagrams for these four elements generated using the Geochemist's Workbench software package [51].

The Eh-pH diagrams are consistent with the PHREEQC calculations over the pH range of the specific water chemistries simulated with PHREEQC. As reducing conditions are re-imposed by the restoration process, Se is the first to be reduced and precipitated, while the others follow in approximately a stepwise fashion as Eh decreases. We use the qualifier “approximately” because the redox transitions occur over ranges of Eh potentials that have some overlap. The relatively large separation in the reduction values of Fe and U (Table A11) is important because of the significant quantities of ferric solids generated by the mining process as a result of pyrite oxidation. The Fe(III)/Fe(II) couple is thus likely to consume large amounts of reductant before a low enough Eh is reached to cause large-scale U(VI) reduction. We do not consider here the possibility of kinetic limitations in any of the redox transitions, but the field observations align well with the thermodynamic calculations, suggesting no significant kinetic bottlenecks for any of the transitions.

It is informative to estimate the total amount of uranium and iron mobilized by the dithionite and acetate over the entire time of the amendment test (Table 3). This calculation uses the iron and uranium concentrations of all six production wells during the test, with the concentrations multiplied by production flow rates to obtain masses of iron and uranium removed from each well over time. It also assumes no repeat appearance of uranium or iron in production wells after pumped water was recirculated into injection wells. For uranium, both a total recovery (72.0 kg) and a background-corrected recovery (29.5 kg) are estimated. The background-corrected recovery represents the excess uranium mobilized after subtracting the pre-test concentrations from the measured concentrations in all production wells.

Table 3. Mass recoveries of uranium and iron in each of the production wells. Total recoveries are listed in the last row of the table. “U-bkgd” is the U recovery in excess of what would have been recovered if the concentrations in all wells had remained at their pre-test levels throughout the test. Shaded rows indicate well patterns receiving acetate.

Well	U Recovery, kg	U-Bkgd Recovery, kg	Fe Recovery, kg
4P-205	15.2	6.7	16.6
4P-206	22.1	12.3	19.6
4P-210	3.2	1.6	4.5
4P-211	7.3	2.9	4.2
4P-215	12.8	4.6	3.1
4P-216	11.5	1.4	3.7
Total	72.0	29.5	51.7

The total amount of iron mobilized (51.7 kg) during the amendments test was about 0.022 moles iron/mole dithionite injected, which is much smaller than the ~0.34 moles iron/mole dithionite observed in the earlier single-well push-pull dithionite tests [22,23]. This is not surprising since the iron generated in the multi-well test had to move over much greater distances through the aquifer than in the single-well tests before being extracted, and it would have been significantly attenuated by cation exchange and perhaps other sorption or precipitation processes along the way. Seventy percent of the iron was recovered from the two well patterns that received acetate, so acetate biostimulation likely contributed to iron production, although some of the additional iron production in these patterns may have also been a result of displacement of Fe²⁺ from cation exchange sites by all the sodium that was injected with the acetate. These same two patterns received only 43% of the total dithionite injected. The recoveries of both U(VI) and Fe²⁺ would have been higher if pumping/circulation had continued longer, as concentrations of both constituents were at or near their highest in all production wells at the end of the test.

4. Discussion

4.1. Adjusting Restoration Methods to Achieve Large-Scale U(VI) Reduction

Although the multi-well amendments test did not result in lowering the U(VI) concentrations in the testbed well patterns, some of the results and observations suggest that the amendments could be more effective if deployment strategies were altered and/or integrated better with some of the restoration methods in current use. The most obvious improvement would be to add more of the reductive amendments, as it was apparent the amounts added in the multi-well test were insufficient to achieve significant U(VI) reduction in the well patterns. In principle, enough dithionite was added to remove U(VI) from all the groundwater in the patterns (based on the volumes of water treated per mole of dithionite in the single-well push-pull dithionite tests [22,23] and the volume of water in the six well patterns estimated from the tracer test), but most of the U(VI) in the patterns was apparently adsorbed to sediments rather than being dissolved in the groundwater. While U(VI) reduction undoubtedly occurred in dithionite reaction zones close to the injection wells, it was more than offset by U(VI) desorption outside the reaction zones, which was enhanced by increases in Ca^{2+} concentrations (promoting the formation of very stable Ca-U- CO_3 complexes) and by reductive dissolution of Fe(III) phases (releasing large amounts of U(VI) that were adsorbed to these phases). The sodium acetate amendment was likewise not added in sufficient quantities to result in significant reduction of U(VI), and its addition caused further increases in Ca^{2+} concentrations and additional reductive dissolution of Fe(III) that caused more desorption of U(VI). Both amendments may have also promoted U(VI) desorption by increasing alkalinity through a combination of carbonate addition with the dithionite, calcite dissolution, and microbial conversion of acetate to CO_2 .

Instead of simply increasing the amounts of reductive amendments, which could become cost prohibitive and would require extensive cleanup efforts to decrease concentrations of many constituents, the multi-well test results suggest that the effectiveness of the amendments might be improved by integrating them better with conventional restoration approaches. In the multi-well test, the amendments were deployed after some groundwater sweep had lowered U(VI) concentrations but before any reverse osmosis that would have significantly lowered the concentrations of other constituents. Most importantly, the concentrations of Ca^{2+} and alkalinity remained very high, thus favoring the formation of very stable Ca-U- CO_3 complexes, which likely promoted U(VI) desorption and also stabilized U(VI) against reduction [7–11,40]. If sodium dithionite and/or sodium acetate were deployed after Ca^{2+} concentrations and alkalinity were lowered, they should be more effective at reducing U(VI), possibly even reducing significant amounts of U(VI) before all Fe(III) is reduced. Besides reverse osmosis, vacuum or forced-draft degassing to remove CO_2 gas from ore-zone water, which has been performed previously at the SRH mine, could be employed to help lower alkalinity levels. Sodium dithionite or sodium acetate would still be expected to cause increases in Ca^{2+} concentrations (because of cation exchange with the sodium), which would likely induce some desorption of U(VI) from sediments, but this desorption should be less when Ca^{2+} and alkalinity concentrations are initially much lower. However, U(VI) liberated by reduction and dissolution of ferric solids might still be a problem. Additionally, some additional follow-up groundwater sweep and reverse osmosis would likely be needed to meet restoration target concentrations, or modified targets would have to be negotiated with regulators.

An alternative approach may be to apply sodium dithionite or sodium acetate early in a restoration sequence, possibly even at the end of a mining campaign. This would be performed not to lower U(VI) concentrations, but rather to cause as much U(VI) desorption and as much dissolution of Fe(III) solids as possible. That would set the stage for a more effective subsequent restoration by standard methods of groundwater sweep and reverse osmosis. The multi-well amendments test results suggest that U(VI) recoveries from ore zones can be enhanced after dithionite or acetate injections relative to what is achievable by the standard method of groundwater sweep, and any additional recovery of U(VI) means that there will be less U(VI) left behind to serve as a long-term source of persistent elevated

U(VI) concentrations. Additional U(VI) recovery also has an economic benefit to offset restoration costs. A potential downside to this approach, at least in the case of acetate or another biostimulant, is that if initial U(VI) concentrations are much higher than in the multi-well amendment test, they might inhibit microbial growth and thus the establishment of reducing conditions that cause the beneficial reduction of Fe(III) [52].

Another potential low-cost improvement to any restoration process, suggested by the dramatic increases in U(VI) concentrations immediately after the sodium acetate injections into the 4P-205 and -206 well patterns, would be to introduce an inexpensive salt, such as NaCl or KCl, before adding any other amendment. The cations in these salts will have the effect of displacing Ca^{2+} from cation exchange sites, which should in turn induce U(VI) desorption from sediments via the formation of Ca-U(VI)- CO_3 complexes. The resulting decreased inventory of adsorbed U(VI), in principle, should improve the effectiveness of any subsequent restorative treatment process, and by removing Ca^{2+} from aquifer sediments, there should be less of an increase in Ca^{2+} concentrations when reductive amendments are deployed. This addition of Na^+ or K^+ might also cause the release of Ra^{2+} from cation exchange sites, which would decrease residual Ra^{2+} concentrations in the ore zone. Although a bit more expensive than NaCl, KCl would be even more effective at displacing Ca^{2+} (and Ra^{2+}) from cation exchange sites because K^+ is a stronger cation exchanger than Na^+ . K^+ also has the advantage of being less likely to cause swelling of clays than Na^+ (clay swelling could be detrimental to aquifer permeability).

4.2. Site-Specific Considerations

While the above suggestions should be generally applicable to any uranium ISR site where an alkaline lixiviant is used, their effectiveness may depend somewhat on local geochemical conditions. At uranium ISR sites with lower natural and post-mining Ca^{2+} , Mg^{2+} , and SO_4^{2-} concentrations than SRH, it might be easier to reduce U(VI) using reductive amendments. On the other hand, lower Ca^{2+} (and Mg^{2+}) concentrations may also increase the amount of U(VI) that is initially adsorbed to sediments, resulting in a greater inventory of U(VI) to be desorbed and/or reduced. Total amounts of Fe(III) generated by mining may also vary significantly from one location to another.

Operations using an acidic lixiviant rather than an alkaline lixiviant may pose a different set of restoration challenges, with U(VI) being inherently easier to address than many other mobilized constituents (because of its more efficient removal during mining and the ultra-low alkalinity left behind in the ore zone after mining). Ultimately, the best approach to take at a given location should be informed by pilot field tests, such as the one described here. Laboratory column testing, such as the dithionite column studies described in chapter 2 of [22], can also be informative and serve as a useful complement to field work. However, the much larger scale of field tests allows for a better understanding of the interplay between hydrology and geochemistry to address such issues as the distance from an injection borehole that a reductant can reach in significant quantities.

4.3. Comparing Dithionite to Acetate

Regarding the relative merits of sodium dithionite and sodium acetate (and by extension, many other biostimulants) as reductive amendments, it appears from the results of the single-well push-pull tests [22,23] that dithionite is more effective and efficient at directly reducing both Fe(III) and U(VI). However, the results of the multi-well test suggest that dithionite accomplishes this reduction only at a very short distance from injection wells because of how rapidly it reacts with aquifer sediments. Acetate, on the other hand, can impart reducing conditions over a much greater aquifer volume because it has an induction period before it stimulates microbial growth, meaning that it can be distributed over a large area before it promotes reducing conditions. This induction period appeared to be about a month in the case of the two well patterns that directly received acetate, and 2–3 months in the other well patterns that eventually received smaller amounts of acetate (via flaring and recirculation/mixing of all six well patterns during periodic sampling).

From an operational perspective, handling and injection of acetate is inherently easier and safer than handling and injection of dithionite. The rapid degradation of dithionite complicates its deployment, but the field test performed for this study demonstrates that this problem can be overcome.

4.4. Optimizing Restoration Strategy with Field Testing

Devising an optimal restoration strategy involving reductive amendments after uranium ISR would benefit from additional field research, in which some of the strategies suggested above are tested, and as mentioned above, the best approach will be site-specific. Devising such an approach would also benefit from more rigorous geochemical and transport modeling than was possible for this study. Multi-well tests are recommended over single-well push-pull tests because they reveal many more potential issues, and they also more closely replicate practical full-scale amendment deployments. Single-well tests are less expensive and have fewer potential impacts than multi-well tests, but they are not considered as desirable. To the extent possible, ISR mining companies should consider the incorporation of multi-well tests involving 4–6 well patterns into conventional restoration operations that are being conducted on a much larger scale (e.g., the scale of an entire mining unit). This would allow evaluation of various restoration approaches with minimal potential impact on the overall restoration of a much larger area, and it would also allow the opportunity to recover from unintended or unforeseen consequences.

5. Conclusions

The following points are key takeaways from the field study that should be considered when devising more effective uranium ISR restoration strategies involving reductive amendments.

- Higher Ca^{2+} concentrations, coupled with high alkalinity, cause the formation of Ca-U(VI)-CO_3 complexes that are thermodynamically stable and thus inhibit U(VI) reduction. These complexes also decrease U(VI) sorption to aquifer sediments. Lowering Ca^{2+} and alkalinity concentrations will likely decrease the quantities of reductants needed to complete restoration.
- Ca^{2+} concentrations in restoration waters increased during the addition of the sodium salts of acetate, dithionite, and sulfite, thus promoting the formation of Ca-U(VI)-CO_3 complexes. The Ca^{2+} concentration increases can be explained as the result of cation exchange of Na^+ with Ca^{2+} in clays.
- A flush of the restoration zone before reductant addition using a KCl or NaCl solution may mobilize much of the Ca^{2+} sequestered in clays and have the added benefit of extracting Ra^{2+} from them. These cations can then be pumped to the surface and removed using reverse osmosis, which should make subsequent restoration easier.
- The data presented in this study clearly show that reducing conditions were established, yet dissolved U concentrations increased. This is likely caused by a combination of the extreme stability of the Ca-U(VI)-CO_3 complexes and the reductive dissolution of ferric solids, which liberates U(VI) adsorbed to these solids. The reduction of abundant ferric solids occurs before significant reduction of U(VI).
- Se(VI) and U(VI) are the most important dissolved elements of concern resulting from the oxidation process used for U ISR mining at SRH. Ferric solids are also produced during mining. The field amendment test results and the PHREEQC calculations presented in Appendix E both imply that Se(VI), Fe(III), and U(VI) are reduced in a sequential fashion in the order listed. Ferric solids likely represent the greatest portion of the oxidized equivalents, and most of the reductants were probably consumed converting these solids into ferrous iron, while reducing very little U(VI).
- Dithionite reduces ferric solids and U(VI) more rapidly than biostimulation with acetate. However, dithionite is more complicated to handle. Acetate has a greater half-life within the formation and can thus be used to treat larger volumes of aquifer

around the injection points. Both reductants can work for restoration, and the choice of which to use (or choosing to use both) requires further investigation.

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Appendix A. Multi-Well Amendment Field Testbed Information

Table A1. Completion intervals and depths of screened intervals in wells used in the HH 4-11 amendments test (see Figure 2 for well layout). BGS = Below ground surface.

Well	Screen Top (ft BGS)	Screen Bottom (ft BGS)	Screen Length, ft
4P-205	718	736	18
4P-206	718	738	20
4P-210	723	742	19
4P-211	716	734	18
4P-215	724	741	17
4P-216	717	737	20
4I-306	725	740	15
4I-307	715	732	17
4I-308	722	739	17
4I-312	725	742	17
4I-313	717	734	17
4I-314	723	736	13
4I-318 *	727	742	15
4I-319	723	741	18
4I-320	726	743	17
4I-324	727	745	18
4I-325	717	734	17
4I-326	727	746	19

* Well 4I-318 was plugged and could not be used in the test.

Table A2. Major ion chemistry in production wells used in the amendments test in September 2017, prior to the start of the tracer test (U not measured, but see Figure A1 for U trends over time in 4P-216).

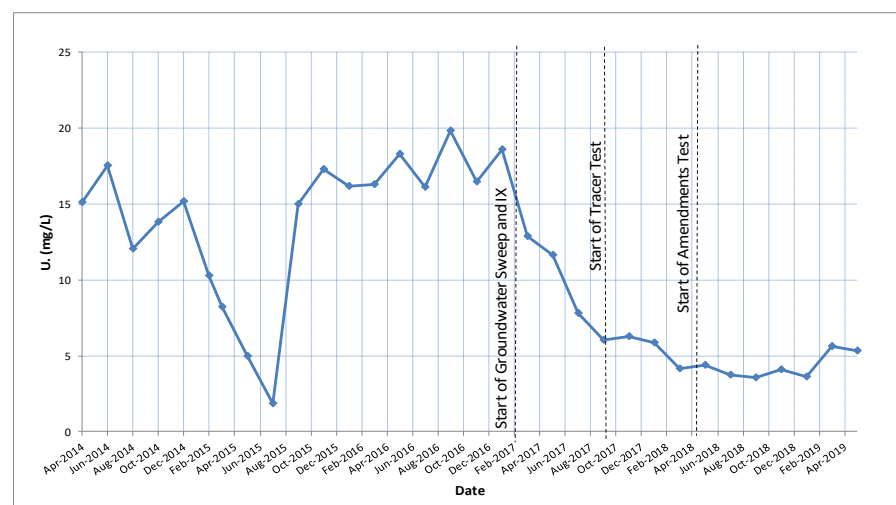
Species (mg/L)	4P-205	4P-206	4P-210	4P-211	4P-215	4P-216
Cl [−]	121	134	132	134	133	135
SO ₄ ^{2−}	570	619	598	600	599	608
HCO ₃ [−]	745	690	725	722	689	752
Ca	347	354	355	354	352	366
Mg	95	97	97	99	93	99
Na	43	44	44	44	43	44
K	17	17	18	17	17	18
pH (standard units)	6.2	6.2	6.2	6.2	6.2	6.2

Table A3. Major ion chemistry in production wells used in the amendments test in early April 2018, prior to the start of the amendments test.

Species (mg/L)	4P-205	4P-206	4P-210	4P-211	4P-215	4P-216
U	1.9	2.0	1.5	1.8	2.4	4.0
Cl [−]	64	63	60	64	63	78
SO ₄ ^{2−}	457	378	341	372	376	455
HCO ₃ [−]	365	390	415	470	460	550
Ca	208	206	202	212	207	251
Mg	58	57	55	59	55	68
Na	28	27	27	28	27	31
K	12	12	12	12	12	13.5
pH (standard units)	6.4	6.4	6.4	6.4	6.4	6.4

Table A4. Major and minor ion chemistry in two background monitoring wells in mining unit 4, which are typical of pre-mining groundwater chemistry in ore zones.

Species (mg/L)	4S-413	4P-402
U	0.06	0.03
Cl [−]	7.0	4.2
SO ₄ ^{2−}	235	75.6
HCO ₃ [−]	269	198
Ca	111	51.1
Mg	31.1	13.0
Na	20.6	18.8
K	7.8	5.9
Fe ²⁺	0.11	0.00
NO ₃ [−]	<0.01	<0.01
NO ₂ [−]	<0.01	<0.01
pH (standard units)	7.94	8.20

**Figure A1.** Uranium concentrations in well 4P-216 as a function of time. Dashed lines show the start of groundwater sweep and ion exchange, start of the tracer test, and start of the amendments test.

Appendix B. Implementation, Results, and Interpretation of Pre-Amendment Tracer Test

Prior to the addition of amendments, a tracer test was performed in the six well patterns of HH 4-11 that were to be used. The tracer test was conducted in September and October of 2017, and it involved injecting unique tracers into each of the 11 operational injection wells while running the 6 well patterns in a “balanced” fashion at close to the maximum flow rates that the production wells could sustain. During this time, all restoration operations were suspended, and all other well patterns in HH 4-11 were idled. Balancing was performed assuming that injection well flow was apportioned equally among its nearest-neighbor production wells. For example, for injection wells 4I-307 and 4I-313, the balanced injection flow rates are given by, respectively:

$$\text{Flow 4I-307} = (\text{Flow 4P-205})/4 + (\text{Flow 4P-206})/4 \quad (\text{A1})$$

$$\text{Flow 4I-313} = (\text{Flow 4P-205})/4 + (\text{Flow 4P-206})/4 + (\text{Flow 4P-210})/3 + (\text{Flow 4P-211})/4 \quad (\text{A2})$$

In Equation (A1), the flows of 4P-205 and 4P-206 are each divided by 4 because each has 4 nearest-neighbor injectors (see the map of Figure 2). In Equation (A2), 4P-210 is divided by 3 because, as noted earlier, 4I-318 was not operating. This approach ensures that the theoretical injection flow rate into each well pattern equals the flow rate being pumped from the pattern (by the single production well), and it also ensures overall equality of injection and production flow rates in the combined patterns. The target flow rates in each well, which were more or less maintained throughout the tracer test, are listed in Table A5, along with the tracers that were injected into each well and the time it took to inject each tracer. The sodium fluorinated benzoate tracers were obtained from Synquest Laboratories, with reported purities greater than 98 wt.%, and the sodium iodide and sodium bromide were obtained from Eastar Chemical Corp., with reported purities of greater than 99 wt.%.

Importantly, the flows from the production wells were not routed directly back into the injection wells during the test (i.e., the test was not operated in a closed-loop fashion). Rather, the production well flows were diverted to a surface facility, and the flows into the injection wells likewise came from a surface facility. For the tracer test, this operational configuration has the advantage of not having to worry about accounting for recirculation of the tracers through the well patterns in the interpretation of the test. The tracers basically make only one pass through the well patterns and then effectively “disappear” from the test once they are pumped out.

The purpose of the tracer test was to identify any diversionary flows within the patterns that might be desirable to avoid in the amendments test. For instance, if a tracer from a given injector never made it to any of the producers, then there would be little point in using that injector in an amendments test because the effects of the amendment injected into that well would not be observable in the test. Conversely, if there were an extreme short circuit between a given injector and producer, it may be desirable to make flow rate adjustments (i.e., operate the patterns partially “out of balance”) during the amendments test to avoid the “parasitic” behavior between the two wells. A secondary purpose of the tracer test was to obtain an estimate of the swept volume of the ore zone accessed by the six patterns so that an appropriate amount of amendment could be applied. The tracer test was also desirable from the standpoint of allowing qualitative evaluations of whether the introduction of the amendments had any effects on the distribution of flow within the patterns (by comparing tracer responses in the tracer test with responses of various constituents during the amendments test).

Each tracer (approximately 5000 g as a sodium salt) was dissolved in approximately 50 gallons of water that was diverted from one of the production wells, and these concentrated solutions were metered into a given injector at a rate that never exceeded about 400 mL/min (see the photo in Figure A2). Two high-pressure peristaltic pumps (Larox, Inc., Lappeenranta, Finland) were used for the metering, and because of the low metering rates, the tracer concentrations were never high enough to induce density-driven flow of the injection solutions (threshold of about 0.1 wt.% density contrast with groundwater). The low metering rates also ensured that the patterns stayed in flow balance (i.e., there was trivial over-injection in any given injector during tracer introduction). Table A6 lists the times at which tracers were injected into each injection well, as only two injections could be performed at any given time. Note that one tracer, sodium bromide, was used in two different injection wells that were in opposite corners of the six patterns to avoid interference between the tracer signals.

Table A5. Target flow rates and tracers injected into each injection well for the HH 4-11 tracer test. All tracer injection masses were ~5 kg (as sodium salts).

Well	Flow Rate, gpm	Tracer
4P-205	11.9	N/A
4P-206	11.9	N/A
4P-210	6.7	N/A
4P-211	7	N/A
4P-215	9.6	N/A
4P-216	7.3	N/A
4I-306	3.0	Na-2,3,4,5 tetrafluorobenzoate
4I-307	6.0	Na-2,4 difluorobenzoate
4I-308	3.0	NaBr
4I-312	5.2	NaI
4I-313	9.9	Na-2,6 difluorobenzoate
4I-314	4.7	Na-2,3,4 trifluorobenzoate
4I-318	plugged	N/A
4I-319	9.0	Na-pentafluorobenzoate
4I-320	3.6	Na-2,5 difluorobenzoate
4I-324	3.2	NaBr
4I-325	5.0	Na-2,4,5 trifluorobenzoate
4I-326	1.8	Na-3,4 difluorobenzoate

After the introduction of the first tracer, samples were collected in 60 mL glass bottles from each production well at a frequency averaging about 3 times per day. The samples were shipped to Los Alamos National Laboratory for analysis. All tracers except bromide were analyzed by high-performance liquid chromatography (HPLC) using a Dionex Ultimate 3000 RS Variable Wavelength Detector. The primary analytical column was an Acclaim C-18 (4.6 mm × 150 mm). Typical analytical parameters were as follows: 60/40 *v/v* 30 mM KH₂PO₄ buffer/methanol, 25 °C 0.8 mL/min flow rate, 200 µL injection volume, and analyte detection at 222 nm. Bromide was analyzed by ion chromatography using EPA method 300.0 on a Dionex ICS-2100 system.



Figure A2. Two tracers being injected from 55-gallon drums into injection wells using high-pressure peristaltic pumps (red units on the floor) in HH 4-11.

Table A6. Times of tracer injections into each injection well.

Well	Tracer	Start Time	End Time	Duration, h
4I-306	Na-2,3,4,5 tetrafluorobenzoate	19 September 2017 10:40	19 September 2017 16:45	6.1
4I-307	Na-2,4 difluorobenzoate	20 September 2017 11:50	20 September 2017 19:25	7.6
4I-308	NaBr	20 September 2017 19:40	21 September 2017 8:10	12.5
4I-312	NaI	21 September 2017 7:50	21 September 2017 15:20	7.5
4I-313	Na-2,6 difluorobenzoate	21 September 2017 13:00	21 September 2017 17:00	4
4I-314	Na-2,3,4 trifluorobenzoate	19 September 2017 17:45	20 September 2017 9:35	15.8
4I-318	N/A			
4I-319	Na-pentafluorobenzoate	21 September 2017 8:30	21 September 2017 12:30	4
4I-320	Na-2,5 difluorobenzoate	20 September 2017 10:00	20 September 2017 18:00	8
4I-324	NaBr	20 September 2017 18:40	21 September 2017 6:30	11.8
4I-325	Na-2,4,5 trifluorobenzoate	19 September 2017 23:00	20 September 2017 11:30	12.5
4I-326	Na-3,4 difluorobenzoate	19 September 2017 10:15	19 September 2017 22:35	12.3

Figures A3 and A4 summarize the results of the tracer test. Figure A3 shows approximate first arrival times, in days, for each tracer associated with each injector-producer combination (the arrival times are shown next to arrows indicating flow directions). Figure A4 shows estimated fractional tracer recoveries for each injector-producer combination presented in the same graphical manner as the first arrival times in Figure A3. Note that the recoveries were not the actual observed tracer recoveries during the test, but rather they are the estimated recoveries if the test had continued indefinitely (obtained by the standard method of log-linear extrapolation of the tails of the breakthrough curves). The actual breakthrough curves of each tracer in each production well are shown in Figures A5–A10 (one figure for each production well), with the concentrations plotted as a function of volume produced from the wells since the time of injection of each tracer. This is generally more useful than plotting as a function of time, as flow rates can vary over time and flow interruptions often occur as a result of power outages or other operational disruptions.

The tracer responses shown in Figures A3–A10 indicate that some injection–production well pairs had relatively rapid flow connections, while others had much slower connections. It is also apparent that tracers from a given injection well often preferentially moved toward one adjacent production well at the expense of another adjacent one. No tracer was detected in a production well that was not immediately adjacent to the injection well into which it was injected. Total recoveries in all adjacent production wells for a tracer injected into a given injection well were generally quite high, with the lowest recoveries typically being associated with corner injection wells that supplied only one producer. The lowest total recovery of any tracer was 70%. The tracer injected into well 4I-313 had a recovery of approximately 110% (in 4 adjacent production wells), which is obviously impossible and clearly reflects a combination of analytical measurement uncertainties, flow rate measurement uncertainties in each of the producers, and uncertainties associated with the log-linear extrapolation of the tracer breakthrough curves.

Based on the tracer test results, it was decided that no changes needed to be made to the injection and production flow rates in the six patterns for the amendments tests. There were no non-participating injection wells, although there were some relatively fast, high-recovery responses (i.e., short circuits) between certain injection–production well combinations. These have the effect of “stealing” flow from other regions within the six patterns, but none were extreme enough to consider making flow rate changes, especially given the potential for unintended consequences on other injection–production flows that such changes could entail. To estimate the swept volume in the six well patterns, a composite breakthrough curve was constructed of all tracers in all producers as a function of the total volume pumped from all producers (Figure A11).

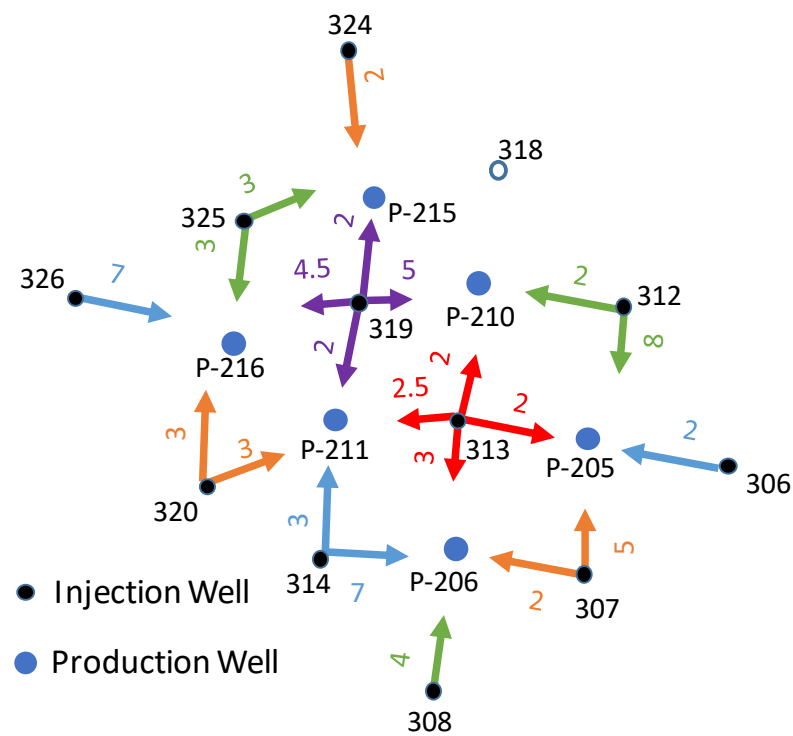


Figure A3. Approximate first-arrival times in days since the start of tracer injection for each of the injector-producer combinations (numbers next to arrows). Well numbers are shown next to dots representing wells. Lengths of arrows have no significance.

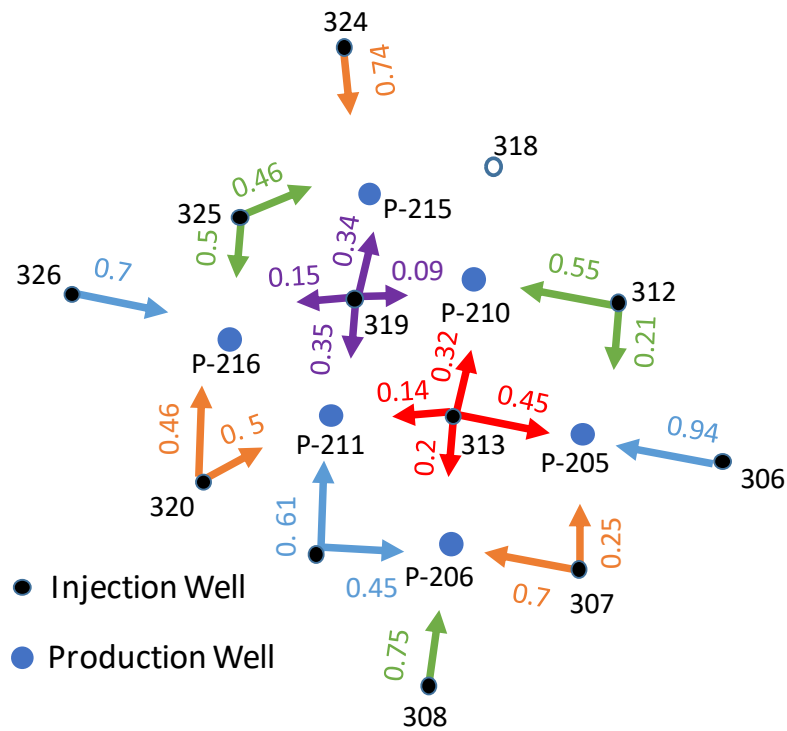


Figure A4. Extrapolated fractional recoveries for each of the injector-producer combinations (numbers next to arrows). Well numbers are shown next to dots representing wells. Lengths of arrows have no significance.

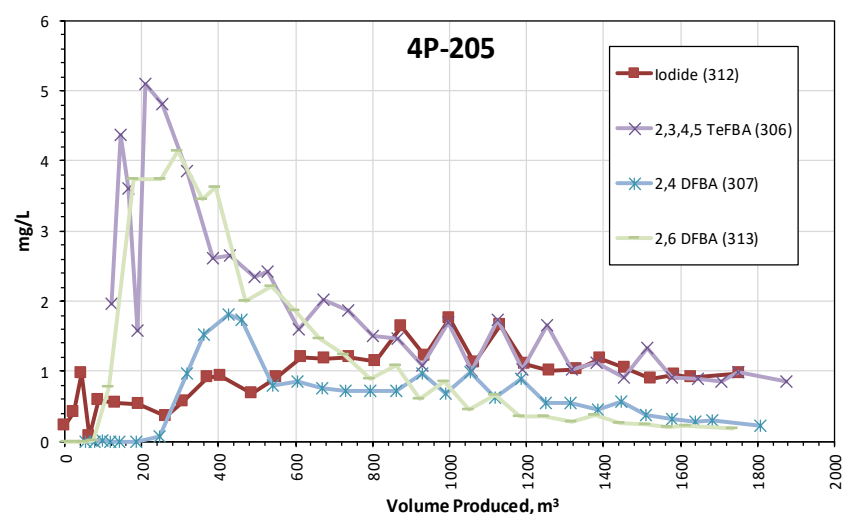


Figure A5. Tracer breakthrough curves as a function of volume produced in well 4P-205. Legend indicates number of the well into which each tracer was injected.

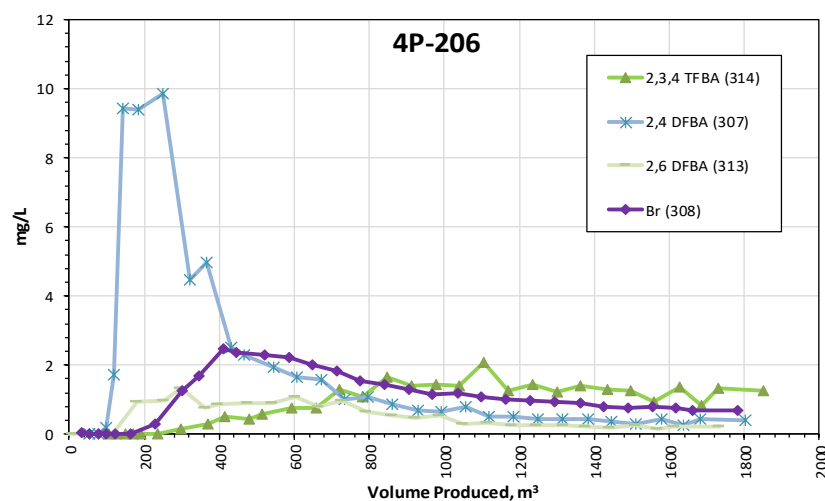


Figure A6. Tracer breakthrough curves as a function of volume produced in well 4P-206. Legend indicates number of the well into which each tracer was injected.

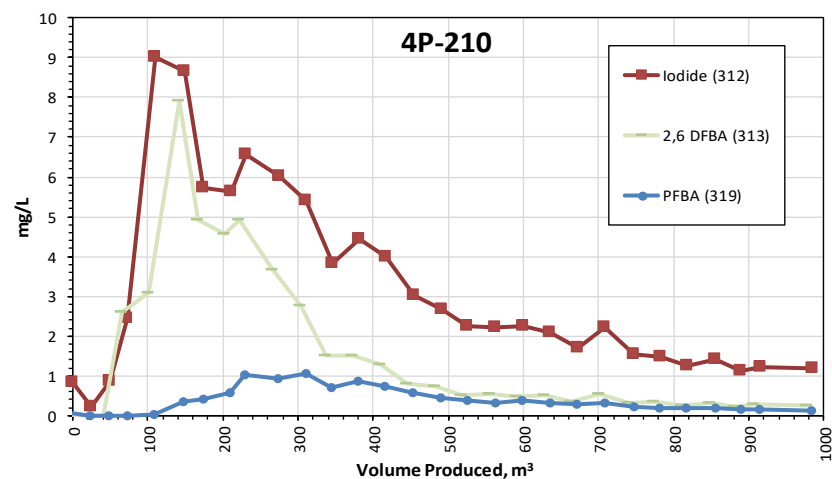


Figure A7. Tracer breakthrough curves as a function of volume produced in well 4P-210. Legend indicates number of the well into which each tracer was injected.

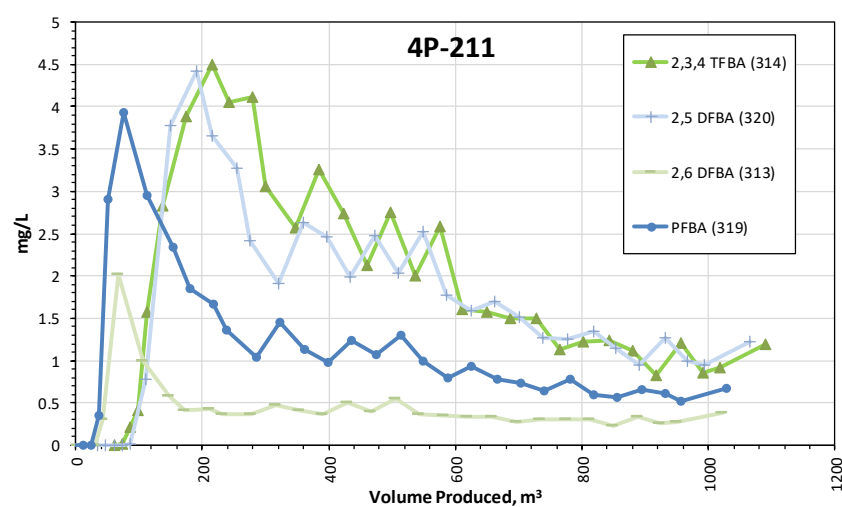


Figure A8. Tracer breakthrough curves as a function of volume produced in well 4P-211. Legend indicates number of the well into which each tracer was injected.

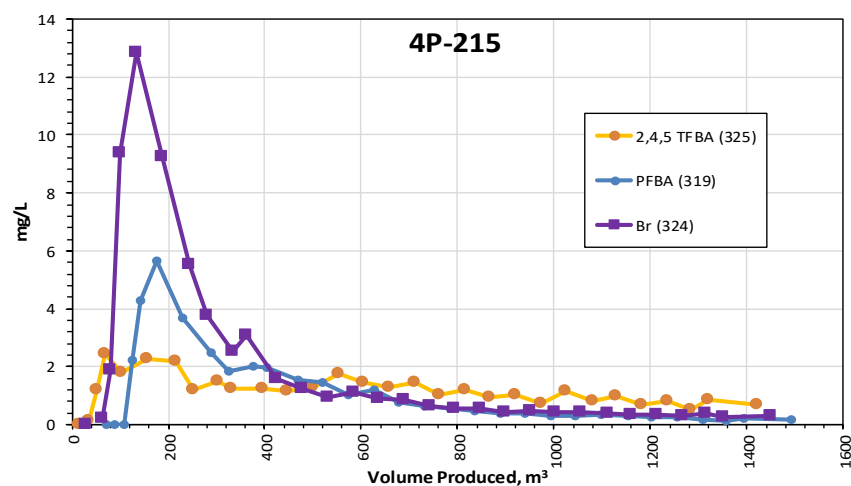


Figure A9. Tracer breakthrough curves as a function of volume produced in well 4P-215. Legend indicates number of the well into which each tracer was injected.

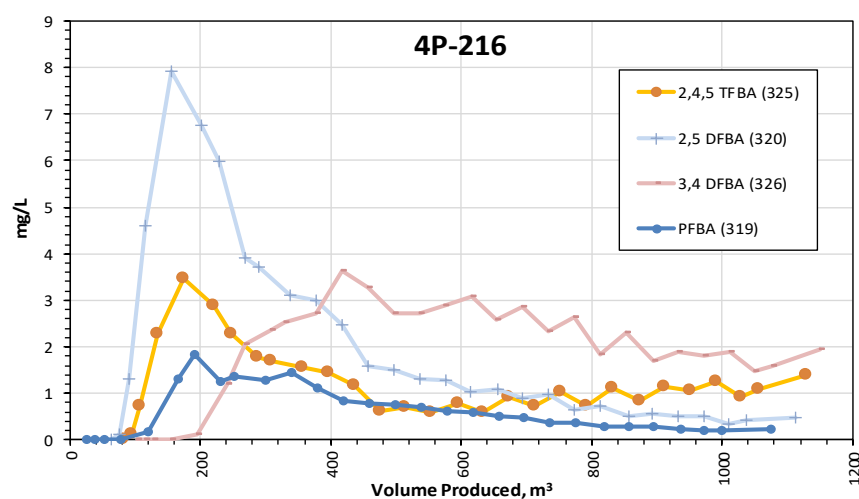


Figure A10. Tracer breakthrough curves as a function of volume produced in well 4P-216. Legend indicates number of the well into which each tracer was injected.

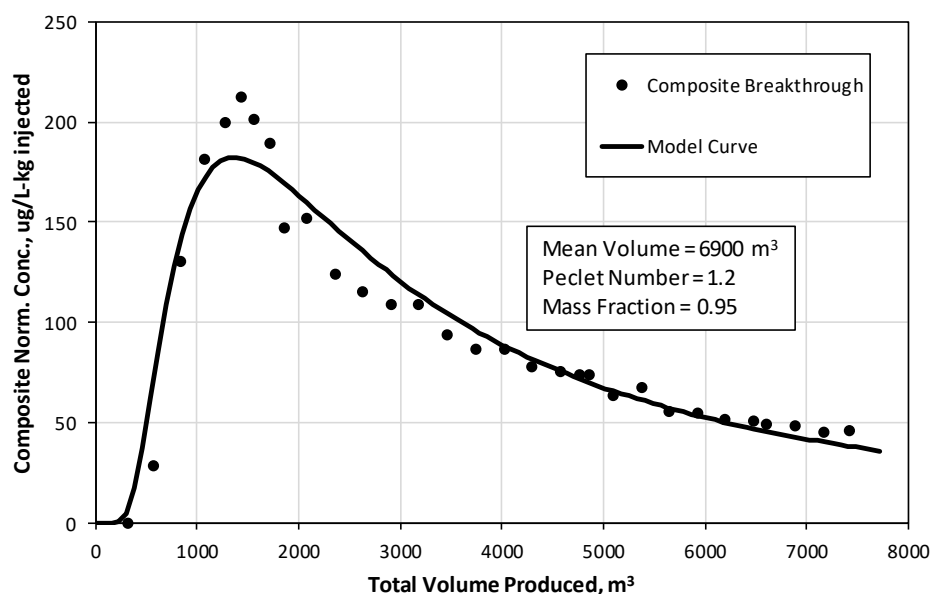


Figure A11. Calculated composite-normalized tracer breakthrough curve for all six well patterns and the results of a RELAP model fit to the data (best-matching parameters listed in box).

Such a composite breakthrough curve is obtained by summing the flow-weighted mass-normalized tracer concentrations in each producer at each total volume produced and dividing the result by the number of injectors (for an overall mass normalization). Mathematically, at any given total volume produced, this result is given by:

$$C(V_{t,i}) = \sum_{p=1}^6 \left[\frac{(V_{p,i} - V_{p,i-1})}{(V_{t,i} - V_{t,i-1})} \sum_{h=1}^{11} \frac{(C_{p,h,i} + C_{p,h,i-1})}{2 M_h} \right] / 11 \quad (\text{A3})$$

where, $C(V_{t,i})$ = composite-normalized tracer concentration as a function of total volume produced from all producers after time increment i (i.e., $V_{t,i}$), $\mu\text{g/L-kg}$ injected, $V_{p,i}$, $V_{p,i-1}$ = volume produced from producer p at time increments i and $i - 1$, L, $V_{t,i}$, $V_{t,i-1}$ = total volume produced from all producers at time increments i and $i - 1$, L, $C_{p,h,i}$, $C_{p,h,i-1}$ = concentration of tracer injected into injector h in producer p at time increments i and $i - 1$, $\mu\text{g/L}$, and M_h = mass of tracer injected into injector h , kg.

Figure A11 shows the composite tracer breakthrough curve, and it also shows a fit to the curve using the RELAP (Reactive transport LAPlace transform inversion) model (Appendix A of [53]). Briefly, RELAP uses the advection-dispersion equation to fit a tracer dataset using a mean residence time (or mean volume), a Peclet number, and a mass fraction participating in the test as adjustable parameters to match the data. The resulting best-fitting parameters are listed in Figure A11, and they indicate that 95% of the total injected tracer mass would have ultimately been recovered if the test had run long enough. Additionally, the estimated volume swept by tracers (i.e., the mean volume) was approximately 6900 m^3 . The small Peclet number of 1.2 indicates that there was a large amount of tracer dispersion (Peclet number is the ratio of travel distance to longitudinal dispersivity, L/α). Qualitatively, this large amount of dispersion is reflected in the long tail and the relatively large mean volume relative to the volume associated with the peak concentration. These breakthrough curve features likely reflect the “flaring” of tracers at the edges of the six patterns, which is a result of some of the tracer mass that was injected into wells at the outer periphery of the patterns initially moving away from the producers, only to eventually (and very slowly) be drawn back into one of the producers. These circuitous flow pathways give rise to the long tail and large amount of dispersion, and they could also “strand” some tracer mass, resulting in the estimation of incomplete recovery.

For comparison, the geometrically calculated volume of water within all six patterns assuming a porosity of 25% and an ore-zone thickness in each well equal to the screened interval length (and not counting any flare outside of the patterns) is approximately 7600 m^3 . Another estimate of swept volume can be obtained from the following equation applied to each of the individual tracer

breakthrough curves (after performing a log-linear extrapolation), and then summing the volume associated with each breakthrough curve:

$$V_{swept} = R\mu_{vol} \quad (A4)$$

where, V_{swept} = swept volume, m^3 , R = extrapolated tracer recovery, $\mu_{vol} = \frac{\int_0^\infty C(V)VdV}{\int_0^\infty C(V)dV} - \frac{V_{pulse}}{2}$ (i.e., first moment of extrapolated breakthrough curve), m^3 , $C(V)$ = normalized tracer concentration as a function of volume injected into the injection well at a given production well, and V_{pulse} = volume of injection pulse, m^3 .

This estimate yields a swept volume of approximately 7400 m^3 , and it is probably a bit more rigorous than the RELAP analysis of the composited breakthrough curve (Figure A11) because the latter involves a model fit that assumes classical advection-dispersion behavior, whereas the former does not require any such assumption. However, the two estimates are in good agreement, and the RELAP-derived estimate is used here because it can be directly applied to the amendments test, where only a composite breakthrough curve was obtained because tracers were not separately injected into different injectors.

The analyses of the single-well push-pull dithionite tests in HH 15-16 yielded an estimate of the volume of water treated per mole of dithionite that was independent of the uranium concentration in the water and equal to about 500 L/mole or 0.5 m^3 /mole in both push-pull tests [22,23]. If this value is applied to the swept volume estimate of the six well patterns in HH 4-11, the estimated number of moles of dithionite needed to treat all the water swept in the patterns is $(6900 m^3)/(0.5 m^3/mole) = 13,800$ moles of dithionite. At 174 g/mole, this amounts to about 2400 kg of sodium dithionite, and considering a 90% product purity, approximately 2700 kg of impure product would be needed. To err on the high side (given uncertainties in the swept volume estimate and allowing for the potential that a dithionite injection may alter flow pathways and thus alter the swept volume), it was decided to purchase and inject 8400 kg of 90% pure product into the six HH 4-11 well patterns. This is about 3.1 times the calculated amount necessary to treat the swept water volume in the six patterns.

Appendix C. Supporting Information for Implementation of the Amendment Test

Table A7. Masses of chemicals added to each batch of dithionite amendment solution.

Batch	Na ₂ S ₂ O ₄ , kg ⁽¹⁾	Na ₂ SO ₃ , kg	Na ₂ S, kg ⁽²⁾
1	539	522	78
2	539	499	78
3	539	499	0
4	539	499	0
5	539	0	0
6	539	0	0
7	539	45	0
8	539	0	0
9	539	0	0
10	539	0	0
11	539	45	0
12	539	0	0
13	539	23	0
14 ⁽³⁾	404	34	0

⁽¹⁾ Assumes bulk sodium dithionite was 90 wt.% Na₂S₂O₄, with the balance being Na₂CO₃ and Na₂S₂O₅. ⁽²⁾ Note that the original target Na₂S mass in the first two batches was 113 kg, but only 78 kg was actually added because the Na₂S was only 70% pure (the remaining 30% was mostly waters of hydration). However, even this less-than-intended mass of Na₂S resulted in an excessively high pH and the formation of the black precipitate that caused serious problems. ⁽³⁾ 25% of the last batch was assumed to remain in the feed tank heel.

Table A8. Starting/stopping times and rates/volumes of dithionite injection into main injection flow. Different-shaded regions indicate 3 different time periods during which injection was approximately continuous for batches 1–3, batch 4, and batches 5–14, respectively.

Start Time	End Time	Flow Rate, gpm	Volume, gal ⁽¹⁾	Batches
3 April 2018 16:45	4 April 2018 4:00	2.2	1500	1
4 April 2018 8:50	4 April 2018 9:50	2.2	130	1
4 April 2018 10:40	5 April 2018 16:30	1.8	3300	2, 3
6 April 2018 12:50	6 April 2018 18:04	5.3	1650	4
9 April 2018 10:30	9 April 2018 20:35	6.5	3930	5, 6
9 April 2018 20:35	10 April 2018 9:25	3.1	2390	7, 8
10 April 2018 13:45	10 April 2018 20:03	8	3025	9, 10
10 April 2018 20:03	11 April 2018 9:00	3	2330	10, 11
11 April 2018 9:40	11 April 2018 21:30	8	5680	12, 13, 14

⁽¹⁾ Volumes are approximate.

Table A9. Target flow rates during and after the sodium acetate injection (wells not listed had no flow—only two patterns were operated).

Well	Flow Rate, gpm
4P-205	11
4P-206	11
4I-306	2.75
4I-307	5.5
4I-308	2.75
4I-312	2.75
4I-313	5.5
4I-314	2.75

Table A10. Times and flow rates of sodium acetate injection.

Start Time	End Time	Flow Rate, gpm	Volume, gal ⁽¹⁾	Batches
21 May 2018 15:30	23 May 2018 6:20	1–2.5	3000	1–2
23 May 2018 10:35	24 May 2018 7:15	1–5	3000	3–4

⁽¹⁾ Volumes are approximate.



Figure A12. Photo showing 1600-gal mixing tank (black) and 2500-gal feed tank (white) outside of HH 4-11. The arched pipe between the tanks was used to transfer amendment batches from the mixing tank to the feed tank. The feed tank is plumbed directly into HH 4-11 for injections (HH 4-11 is to the right of this photo).

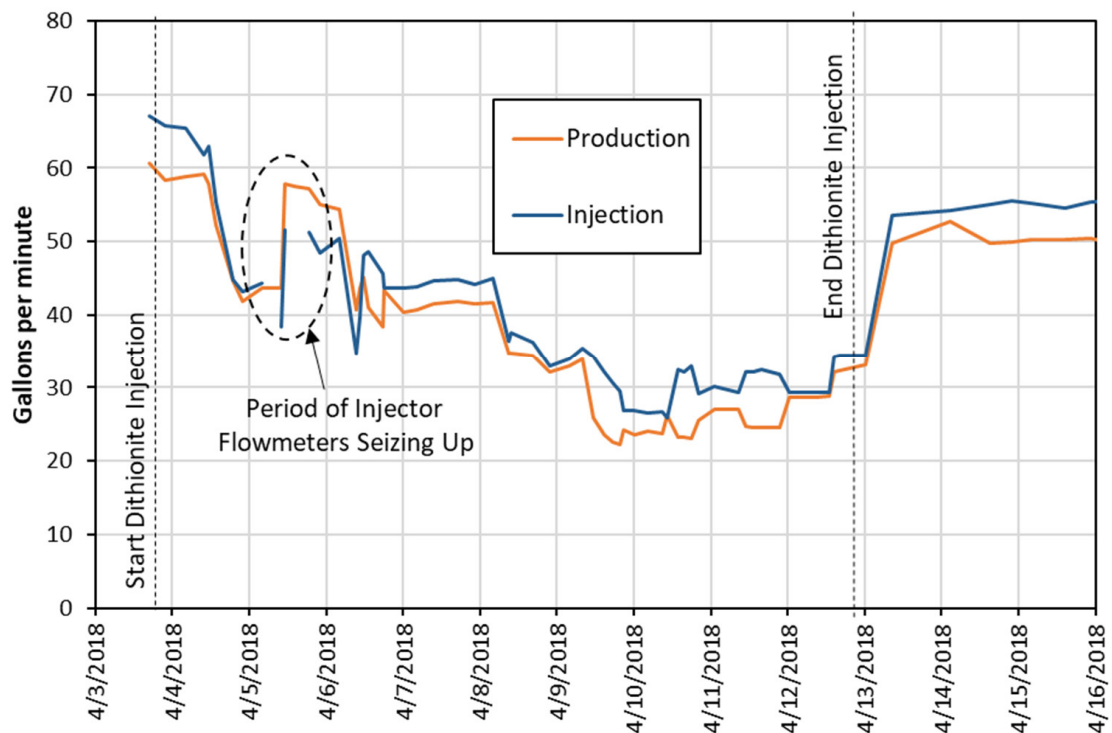


Figure A13. Combined production and injection flows in the six well patterns during and immediately after the dithionite injection. Black precipitate caused injection well flowmeters to seize up and malfunction on 5 April 2018.

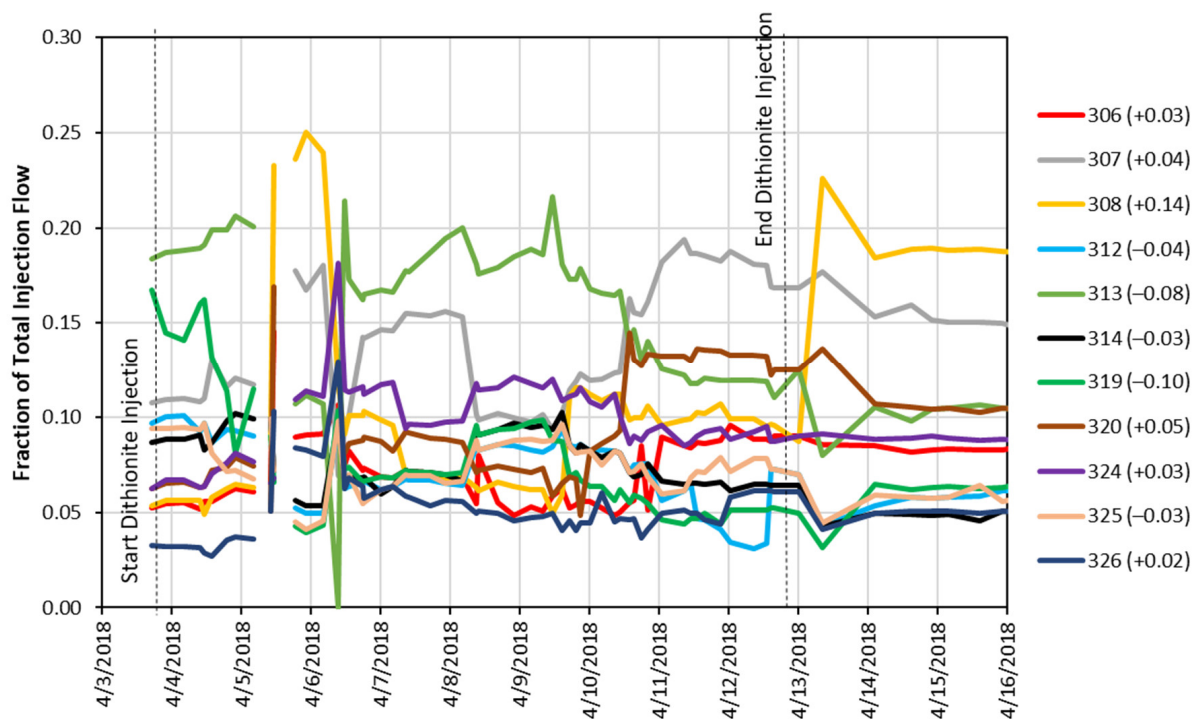


Figure A14. Fractions of total injection flow going into each injection well during the same time period as in Figure A13. Values in parentheses are the changes in fraction of flow for each well from the start of the test (when flows were balanced) to when flows were stabilized at the end of the dithionite injection.

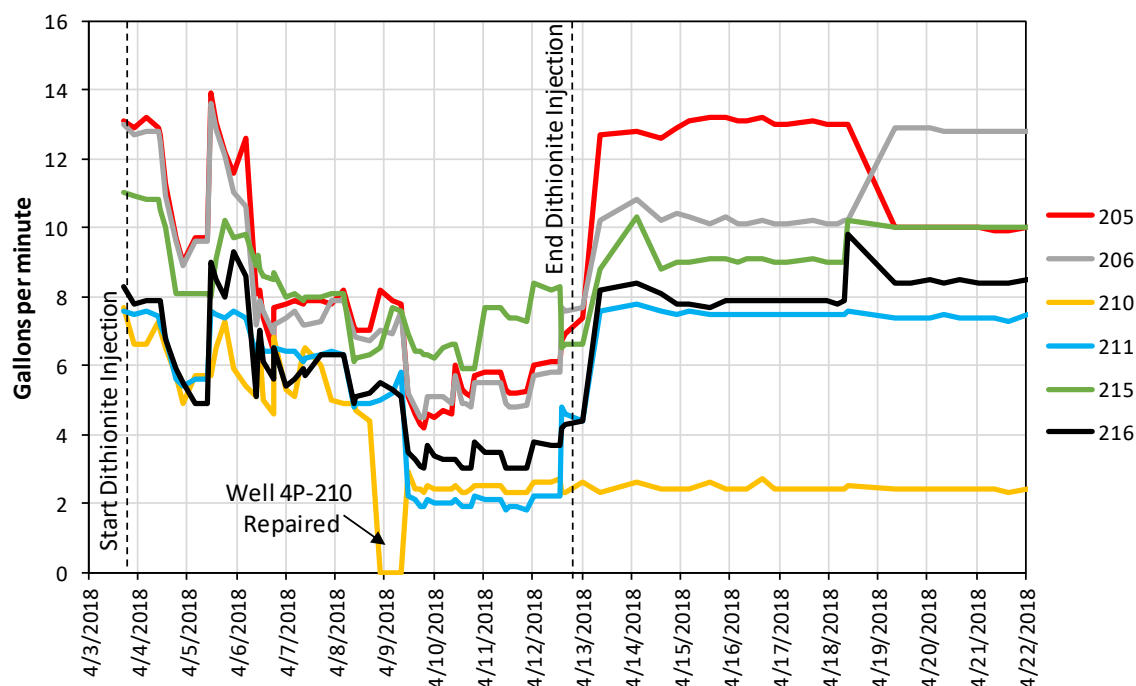


Figure A15. Production well flows during and for some time after dithionite injection.

Appendix D. Supporting Information for Amendment Test Results

Appendix D.1. Qualitative Evaluation of Amendment Distribution/Sweep through the Test Well Patterns

No nonreactive/conservative tracers were introduced with the sodium dithionite because the plan was to execute the amendment test with the same well pattern flow balance as in the fall 2017 pre-amendment tracer test, so the flow distribution was expected to be the same during the dithionite test as during the tracer test. However, because of the the plugging/back-pressure problems encountered during the dithionite injection (Section 2.3.1), it clearly would have been beneficial to have used at least one conservative tracer that was uniformly added to all injection batches to allow an assessment of how much the flow distribution changed as a result of these plugging problems. It was originally thought that it may be possible to use total cation charge or total anion charge as a proxy for a conservative tracer. This works quite well in cases where there are no reactions other than anion or cation exchange (which conserves both negative and positive charges). However, the negative charge associated with dithionite does not behave conservatively because the dithionite reacts to form an assortment of products, some of which remain immobilized on aquifer sediments until they become oxidized to more mobile anionic species. Since local charge balance must always be maintained in solution, any nonconservative transport behavior of anion charge will necessarily result in nonconservative transport behavior of cation charge (i.e., cations must also become partially immobilized).

The nonconservative transport behavior of the positive and negative charges associated with dithionite injections are readily apparent in Figures A16 and A17. These show the normalized breakthrough curves of the conservative tracer bromide, and of the positive and negative charges when the dithionite injection solutions were “pulled back” in the two HH 15-16 dithionite push-pull tests. In both tests, the peak-normalized concentrations of the positive and negative charges were less than half that of the bromide tracer. This implies that a considerable amount of the injected charge was effectively immobilized or retarded when the injection solution was pumped back. However, the positive and negative charges reached higher normalized concentrations than bromide within a few days of pumping, and they continued to tail above background concentrations for the rest of the test, indicating that the dithionite reaction products were slowly being oxidized, resulting in mobilization and recovery of the charge(s).

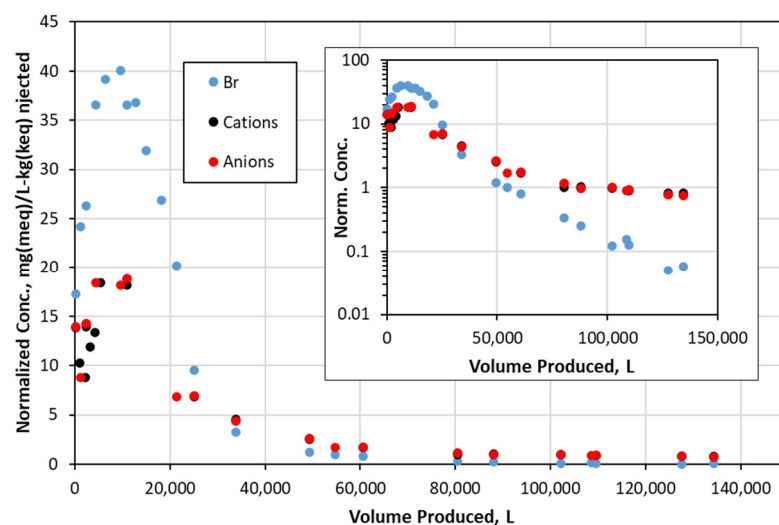


Figure A16. Normalized concentrations of bromide, cation charge, and anion charge as a function of volume produced in the dithionite push-pull test in well 15P-308. Inset plot shows log concentrations.

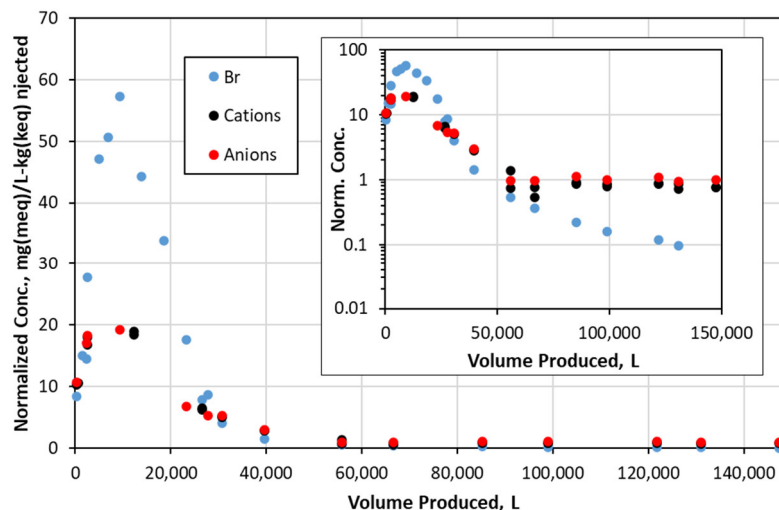


Figure A17. Normalized concentrations of bromide, cation charge, and anion charge as a function of volume produced in the dithionite push-pull test in well 15P-315. Inset plot shows log concentrations.

To perform a qualitative assessment of flow distribution/sweep through the six well patterns during and after the dithionite injection, a composite-normalized breakthrough curve of cation charge ($\mu\text{eq/L per keq injected}$) as a function of total volume produced from the six production wells up until the time of the acetate injection was constructed in a manner similar to the composite tracer breakthrough curve in the pre-amendment tracer test (i.e., using Equation (A3)). In this case, the total cation charge was approximated by the sum of Na^+ , Ca^{2+} , and Mg^{2+} charge (in excess of the background charge), as K^+ charge was small and did not change significantly, and no other cations contributed significant charge until Fe^{2+} concentrations increased significantly by the end of the test.

The following approach was then taken to perform a qualitative comparison of the swept volumes and Peclet numbers in the dithionite and tracer tests. To begin, a first-order reversible reaction in a small amount of secondary porosity (porosity that is not flowing but is accessible by diffusion out of flowing porosity) was added to the RELAP model [53], corresponding to the best fit to the composite tracer breakthrough curve to effectively lower the peak concentration by about a factor of two and extend the tail of the curve. These adjustments are roughly consistent with the observed differences between the bromide and cation curves shown in Figures A16 and A17, and the resulting adjusted curve is shown along with the tracer data and the best-fitting curve in Figure A18. Next, using the model parameters for the adjusted curve, the composite-normalized cation concentrations after the dithionite injection were forward-predicted assuming that the dithionite injection occurred over the three separate time periods that are reflected by the different-shaded rows in Table A8

(RELAP can account for injections of different durations spread out over different times). The contribution from each of the three separate injections was summed to obtain an overall predicted breakthrough curve. The only parameter adjusted to improve the match to the cation data was the mass fraction participating in the test, which was also used as the recirculation factor (i.e., it was assumed that the same mass fraction was “flared-off” each time the produced water was recirculated into the injection wells). If this approach did not result in a reasonable match to the data, then the mean volume and Peclet number would also be adjusted to improve the match.

Figure A19 shows the results of this exercise with a mass fraction and recirculation factor of 0.86. It is apparent that the match to the observed composite breakthrough curve is quite good, which implies that the composite mean swept volume and Peclet number after the dithionite injection were nearly the same as in the earlier tracer test despite all the plugging problems and the lack of flow balance in the dithionite test. It is inferred that the main impact of the plugging problems and the lack of flow balance is that approximately 10% more mass was “flared” out of capture zones of the production wells with each pass through the closed-loop flow system than would have occurred under the ideally balanced flow conditions of the tracer test (86% recovery vs. 95% in the tracer test). This analysis is not highly rigorous, and the results would change somewhat if the assumed cation retardation was different from what is reflected in Figure A18.

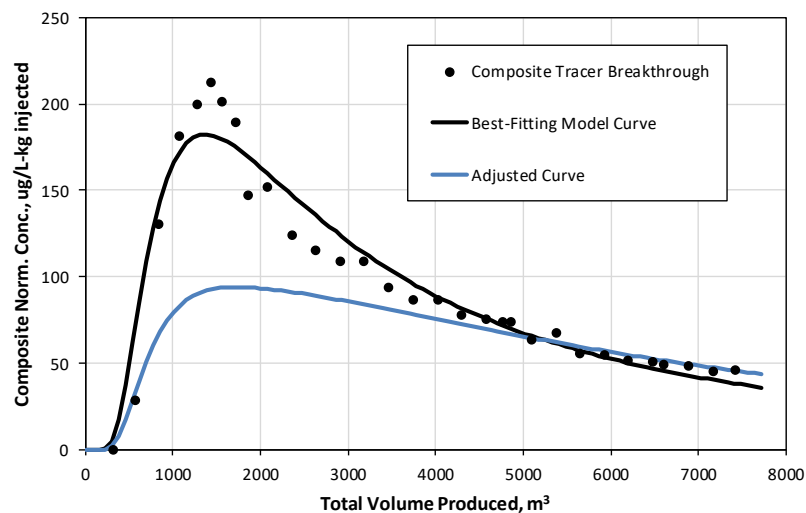


Figure A18. Best RELAP model fit to the composite tracer breakthrough curve in the fall 2017 test and adjusted model fit to account for nonconservative transport behavior of cations and anions (as observed in HH 15-16 dithionite push-pull tests).

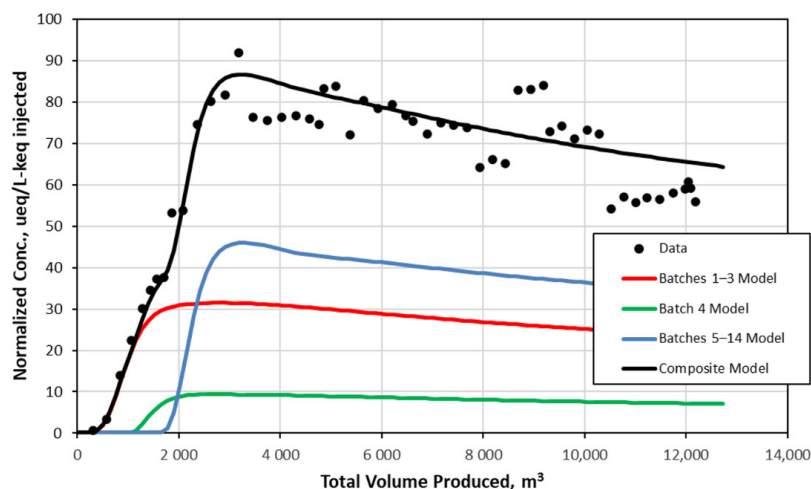


Figure A19. Forward prediction of composite-normalized cation charge breakthrough curve up until the acetate injection in the amendments test using the model parameters associated with the adjusted model curve of Figure A18 and applying a recirculation factor of 0.86. Colored lines show contributions from each of the 3 “separate” injections highlighted in Table A8.

Additionally, it is possible that cations making a second or third pass through the closed-loop system may experience less retardation than the first time through (possibly no retardation) because they are no longer being injected with the dithionite that was assumed to be the cause of the retardation. Despite these uncertainties, it is concluded that the plugging problems and lack of flow balance during the dithionite injection did not have a large impact on the overall swept volume or flow distribution in the six patterns, although the problems did cause about 10% additional “flare-off” of injected solutions than would have been observed under balanced flow conditions.

Appendix D.2. Other Supporting Information for Amendment Test Results, including Concentration Trends in Production Wells 4P-206, -211, and -215

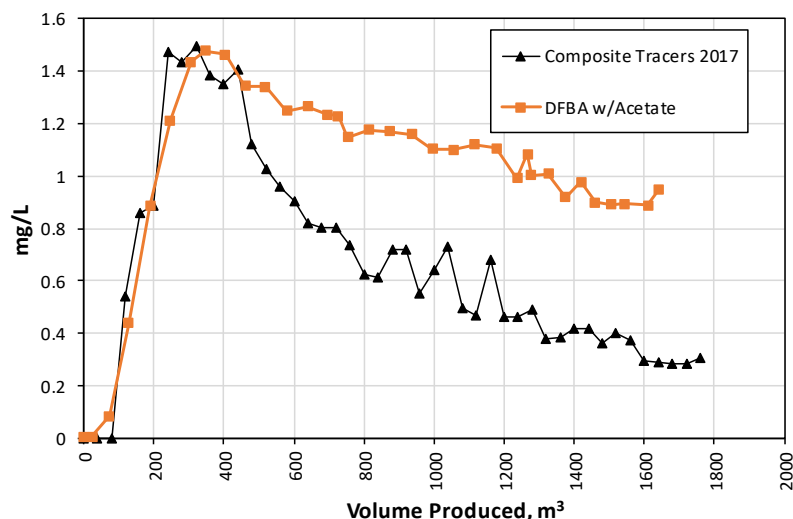


Figure A20. Breakthrough curves of tracers in well 4P-205 in fall 2017 and of difluorobenzoate after the acetate addition. Note that fall 2017 tracer concentrations are the sum of the 4 tracers arriving in 4P-205 divided by 6 (the number of injection wells used in the acetate test). The higher tail of the DFBA w/acetate curve is attributed to the recirculation of the tracer in the amendment test, whereas the tracers were diverted to a surface facility and not recirculated in the 2017 tracer test.

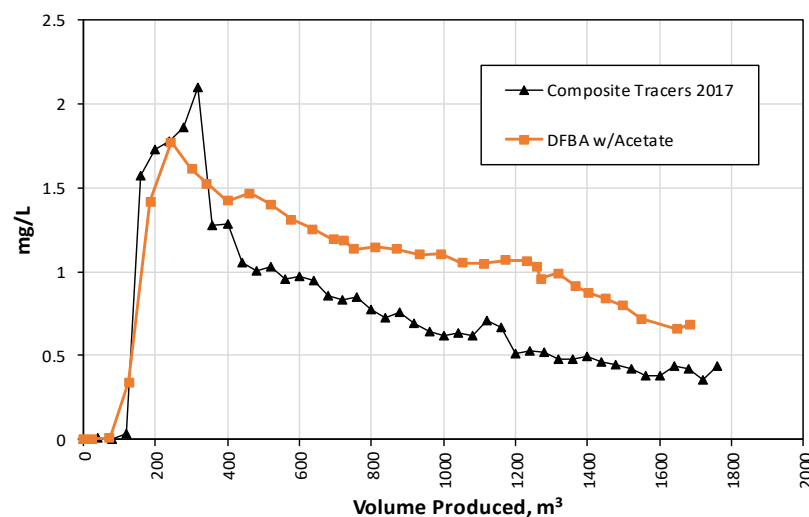
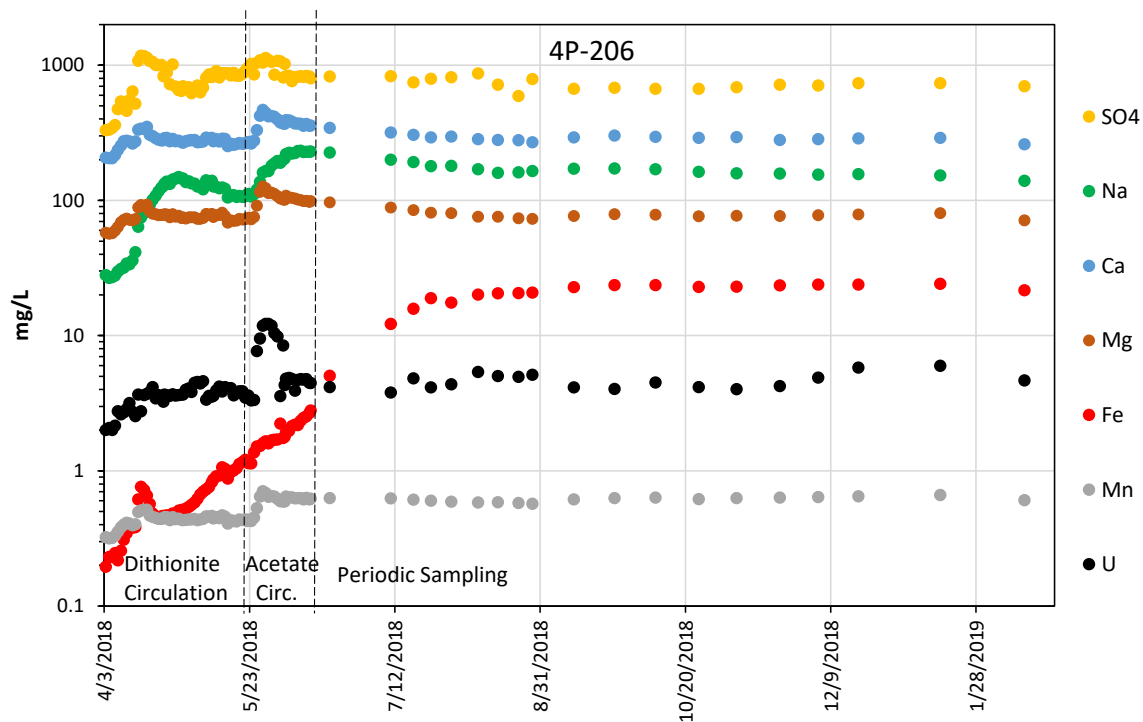
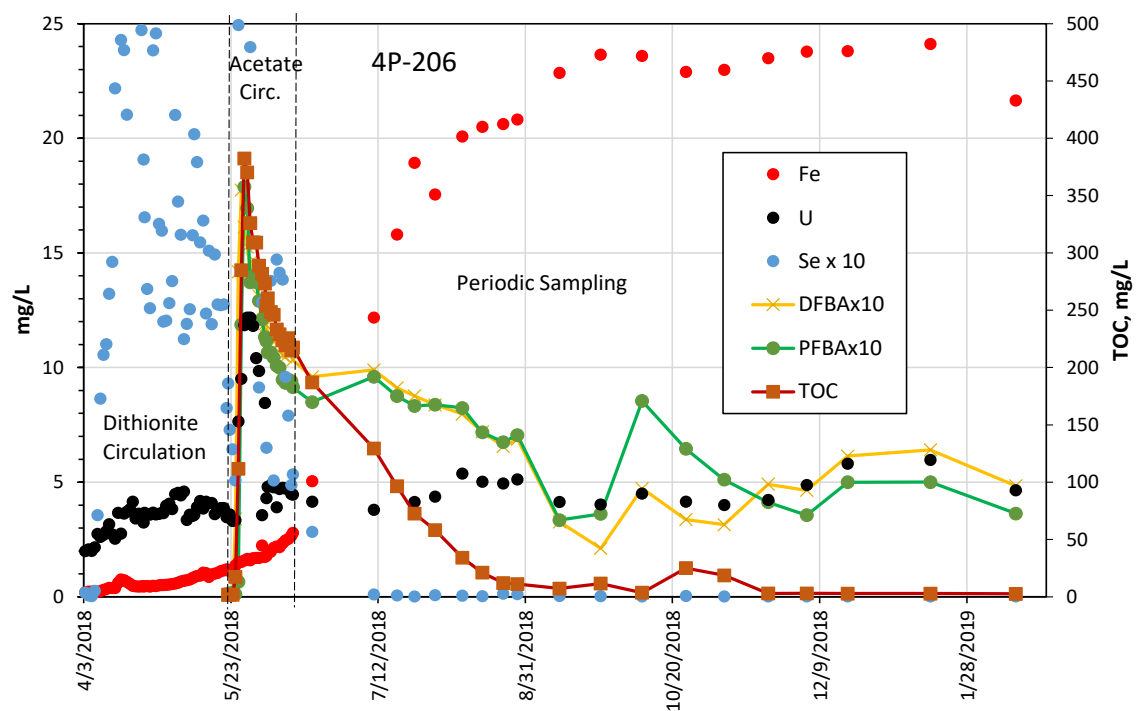


Figure A21. Breakthrough curves of tracers in well 4P-206 in fall 2017 and of difluorobenzoate after the acetate addition. Note that fall 2017 tracer concentrations are the sum of the 4 tracers arriving in 4P-206 divided by 6 (the number of injection wells used in the acetate test). The higher tail of the DFBA w/acetate curve is attributed to the recirculation of the tracer in the amendment test, whereas the tracers were diverted to a surface facility and not recirculated in the 2017 tracer test.

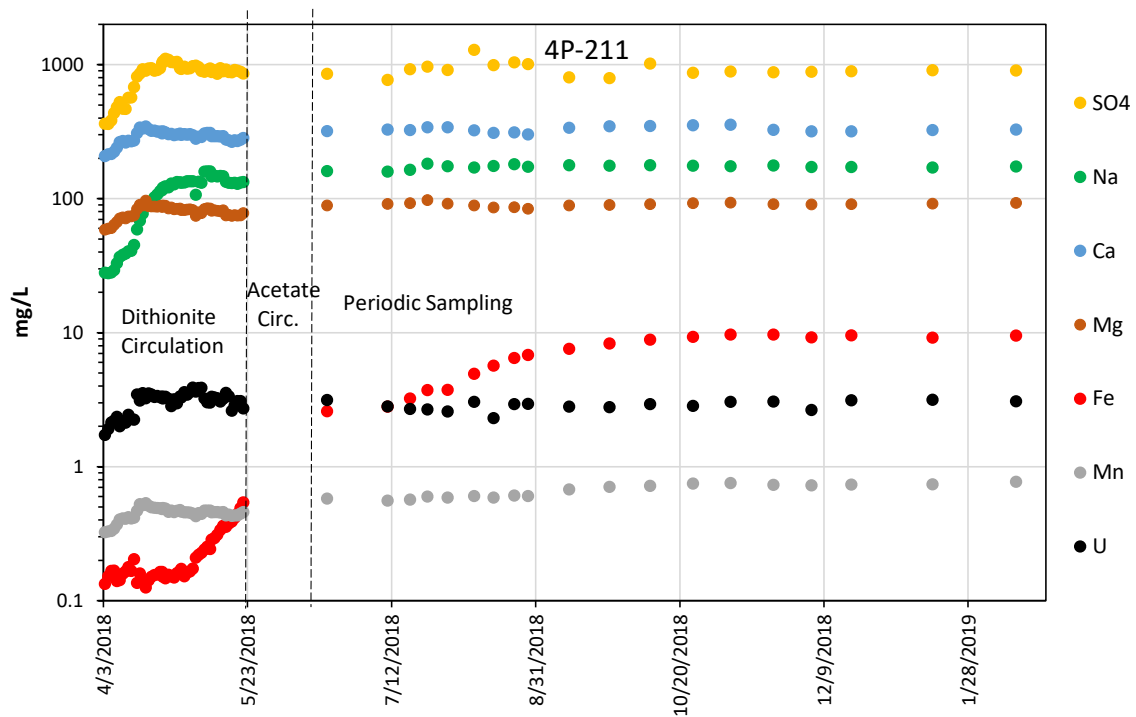


(A)

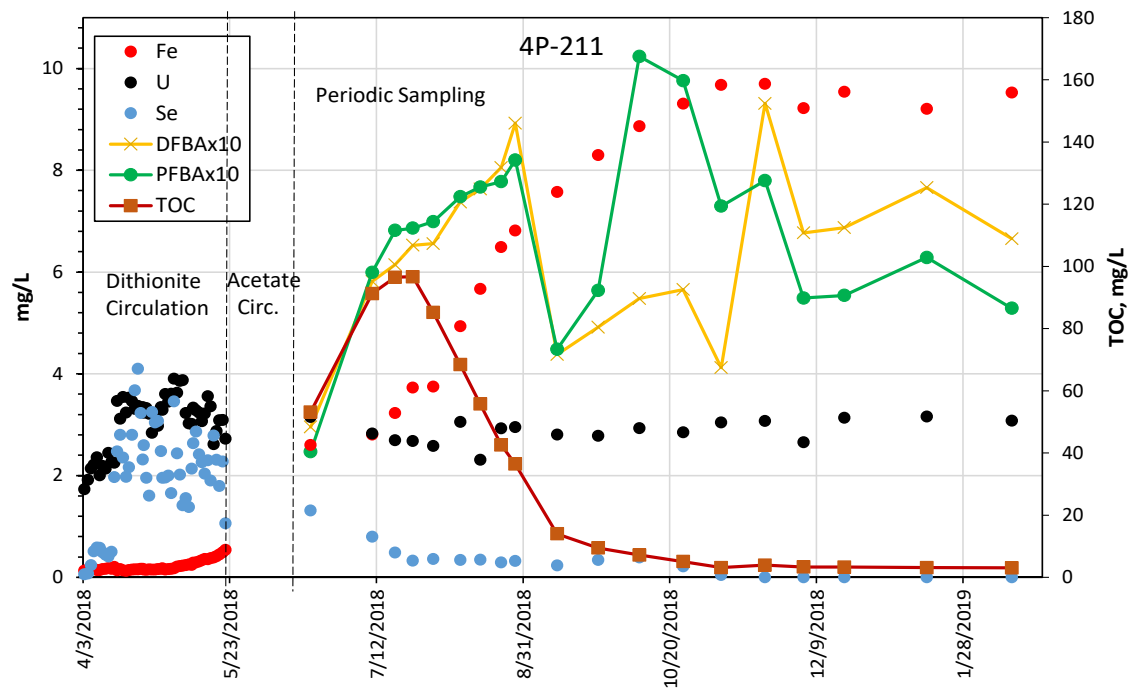


(B)

Figure A22. (A) Concentration histories of several key constituents in production well 4P-206 during the amendment test. (B) Concentration histories of redox-sensitive constituents (Fe(II), U, Se), TOC (as acetate surrogate), and tracers. Note that Se, difluorobenzoate (DFBA), and pentafluorobenzoate (PFBA) concentrations are multiplied by 10.

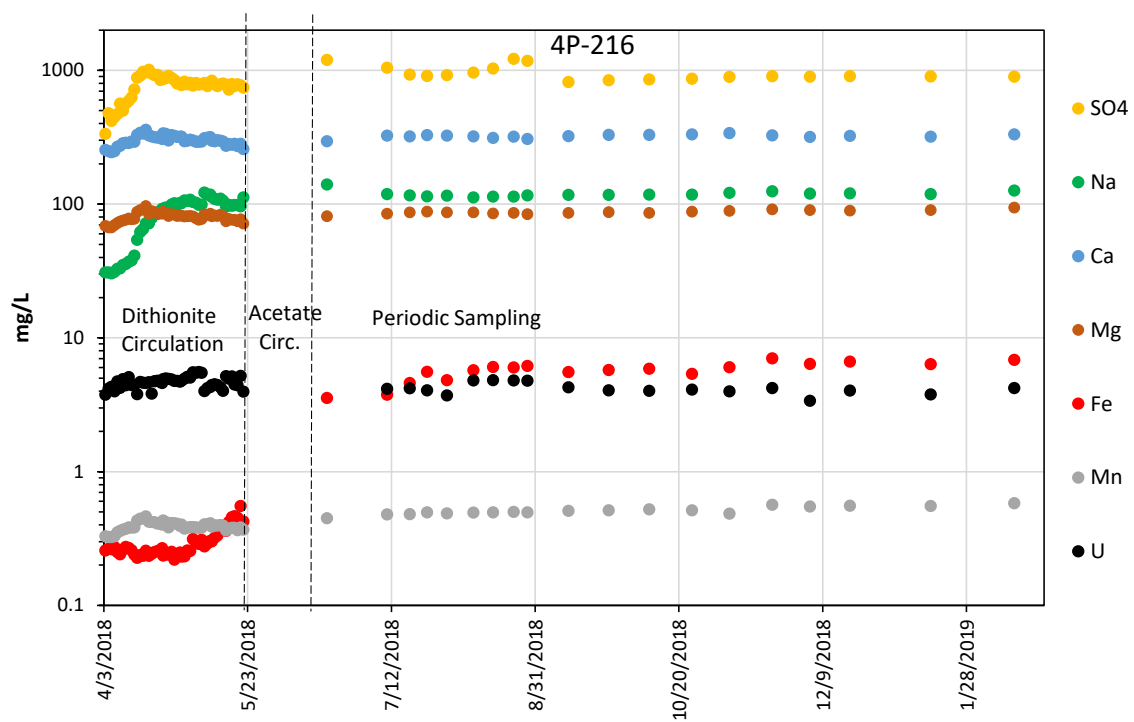


(A)

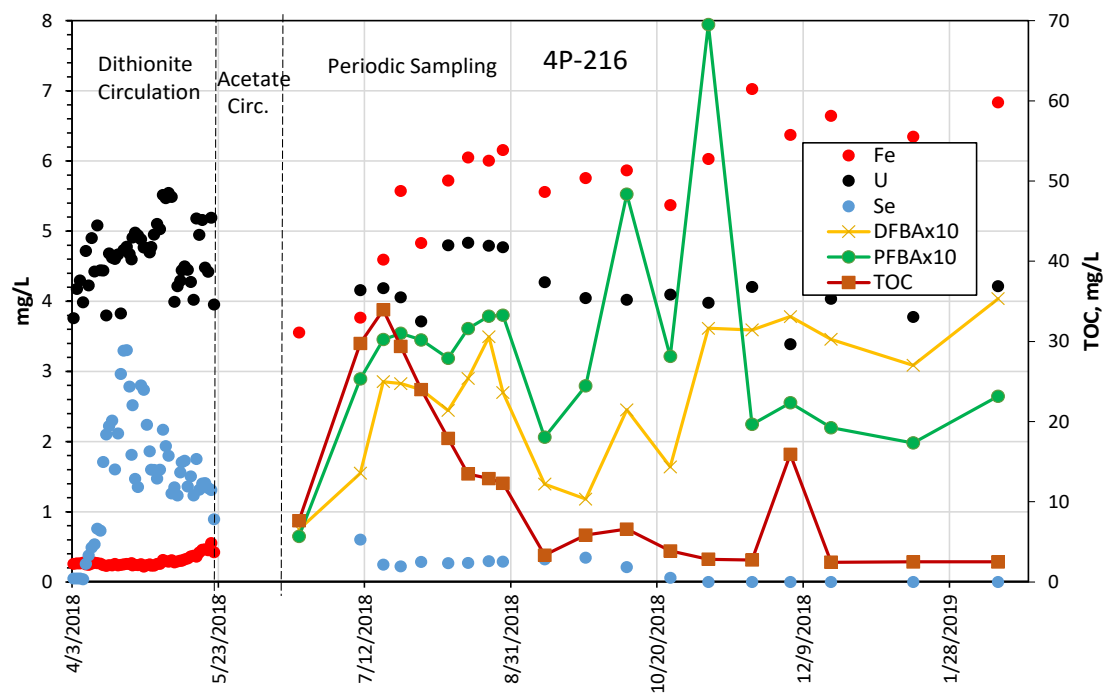


(B)

Figure A23. (A) Concentration histories of several key constituents in production well 4P-211 during the amendment test. (B) Concentration histories of redox-sensitive constituents (Fe(II), U, Se), TOC (as acetate surrogate), and tracers. Note that difluorobenzoate (DFBA) and pentafluorobenzoate (PFBA) concentrations are multiplied by 10.



(A)



(B)

Figure A24. (A) Concentration histories of several key constituents in production well 4P-216 during the amendment test. (B) Concentration histories of redox-sensitive constituents (Fe(II), U, Se), TOC (as acetate surrogate), and tracers. Note that difluorobenzoate (DFBA) and pentafluorobenzoate (PFBA) concentrations are multiplied by 10.

Appendix E. Supporting Geochemical Model Calculations

Appendix E.1. Eh-pH Diagrams Showing Stability Fields for U, Fe, Se, and S under SRH-Relevant Water Chemistry Conditions

Geochemist's Workbench [51] was used to generate Eh-pH diagrams for selenium, iron, uranium, and sulfur, assuming a simplified water chemistry that roughly approximated the water chemistry at the start of the field amendment test. For each element, two diagrams were generated: one at the low end of the element range of concentrations observed during the amendment test, and the other at the high end of the range of concentrations. The diagrams are shown in Figures A25–A32. The CRUNCHFLOW geochemical database [54] supplemented with additional reactions for aqueous U chemistry [43] and uranyl ternary complexes [8,44] was used for the calculations.

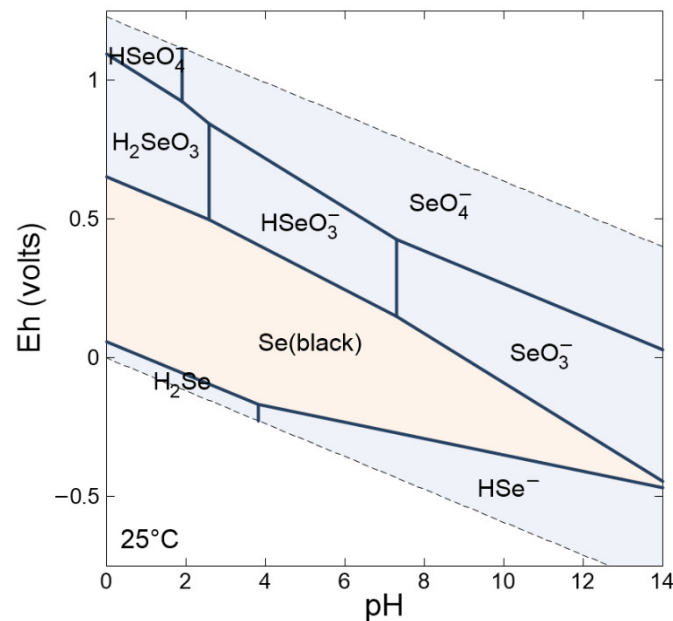


Figure A25. Low selenium 0.1 mg/L, Ca 5 mM (200 mg/L), bicarbonate 7 mM (427 mg/L), sulfate 4 mM (384 mg/L), and chloride 2 mM (71 mg/L).

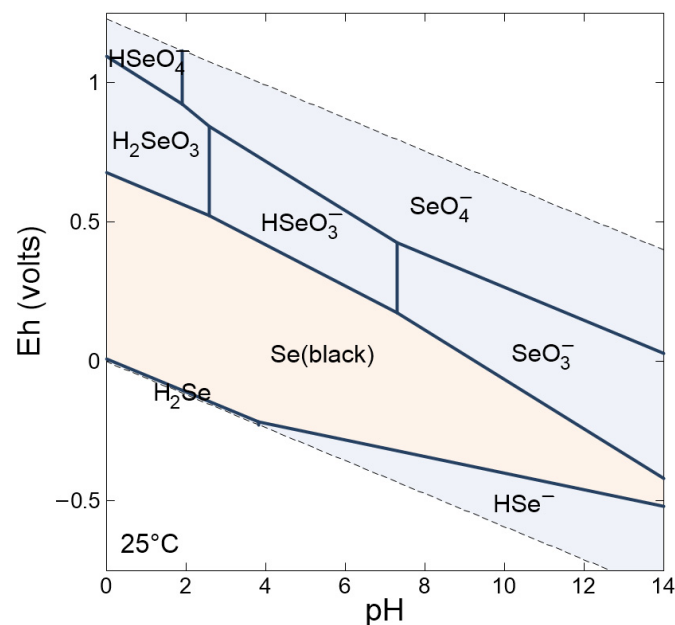


Figure A26. High selenium 5 mg/L, Ca 5 mM (200 mg/L), bicarbonate 7 mM (427 mg/L), sulfate 4 mM (384 mg/L), and chloride 2 mM (71 mg/L).

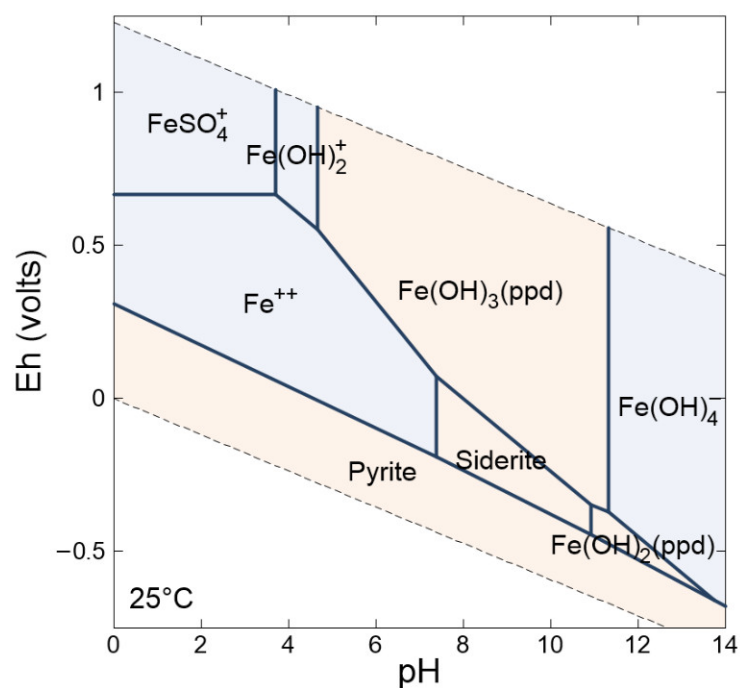


Figure A27. Low iron 0.2 mg/L, Ca 5 mM (200 mg/L), bicarbonate 7 mM (427 mg/L), sulfate 4 mM (384 mg/L), and chloride 2 mM (71 mg/L).

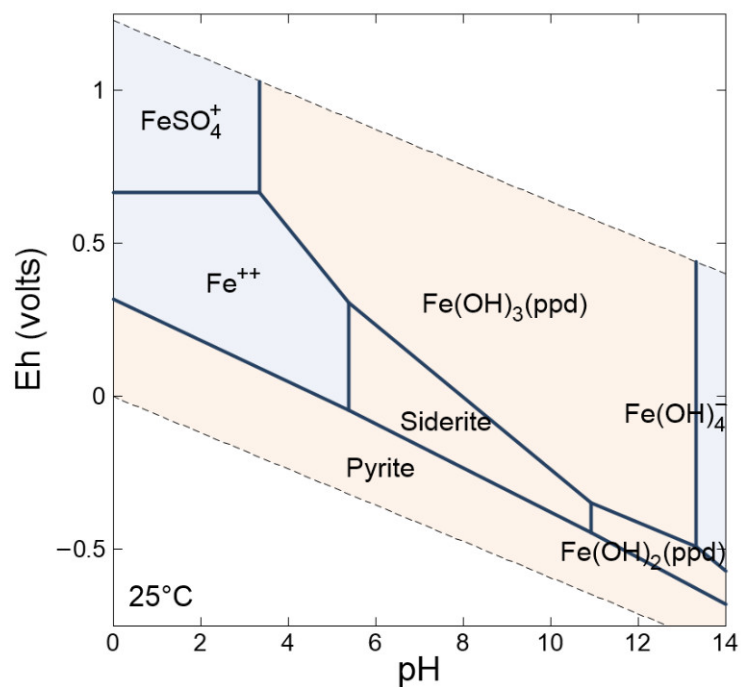


Figure A28. High iron 20 mg/L, Ca 5 mM (200 mg/L), bicarbonate 7 mM (427 mg/L), sulfate 4 mM (384 mg/L), and chloride 2 mM (71 mg/L).

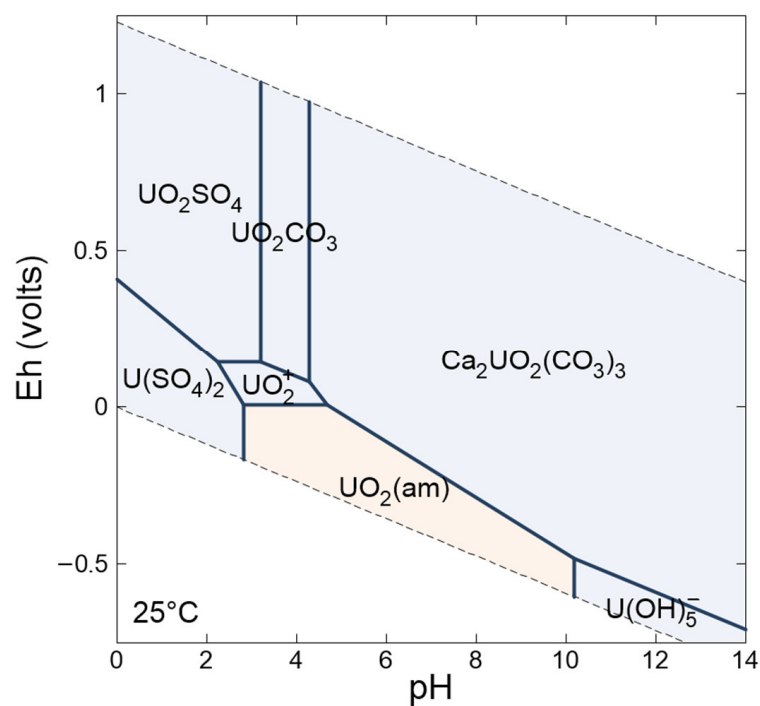


Figure A29. Low uranium 1 mg/L, Ca 5 mM (200 mg/L), bicarbonate 7 mM (427 mg/L), sulfate 4 mM (384 mg/L), and chloride 2 mM (71 mg/L).

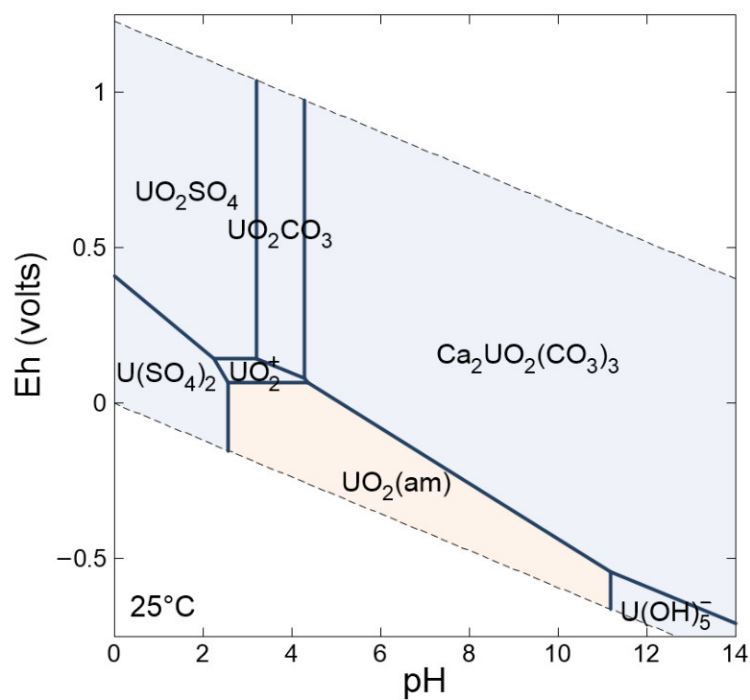


Figure A30. High uranium 10 mg/L, Ca 5 mM (200 mg/L), bicarbonate 7 mM (427 mg/L), sulfate 4 mM (384 mg/L), and chloride 2 mM (71 mg/L).

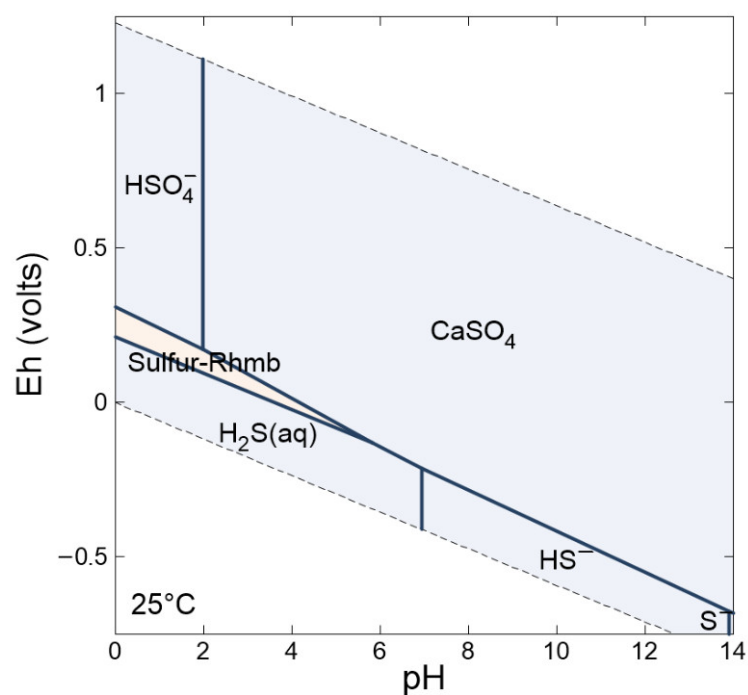


Figure A31. Low sulfur 150 mg/L, Ca 5 mM (200 mg/L), bicarbonate 7 mM (427 mg/L), sulfate 4 mM (384 mg/L), and chloride 2 mM (71 mg/L).

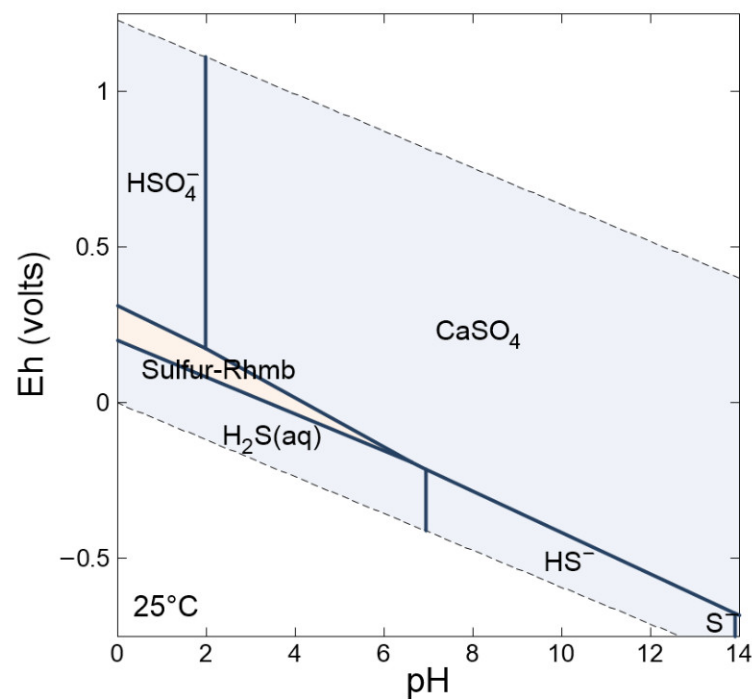


Figure A32. High sulfur 1500 mg/L, Ca 5 mM (200 mg/L), bicarbonate 7 mM (427 mg/L), sulfate 4 mM (384 mg/L), and chloride 2 mM (71 mg/L).

Appendix E.2. Redox Transition Potentials for Se, Fe, U, and S for Specific SRH Water Chemistries, including during the Field Amendment Test

The PHREEQC geochemical model [42] was used to calculate the electrochemical potentials (Eh values) at which oxidation state transitions were predicted to occur for selenium, iron, uranium, and sulfur in water chemistries representative of various stages of the multi-well amendments test and of general relevance to the SRH site. The calculations used the minteq.v4 database supplemented with additional reactions for aqueous U chemistry [43] and uranyl ternary complexes [8,44]. The calculations did not allow for sorption to solid phases, but the following phases were allowed to precipitate if they became supersaturated: amorphous Se(0), FeSe, amorphous UO_2 , ferrihydrite ($\text{Fe}(\text{OH})_3$), amorphous FeS, mackinawite (FeS), siderite (FeCO_3), and gypsum (CaSO_4 hydrate). The results are shown in Table A11, listed in order from highest transition Eh to lowest (with higher implying a reduction that will occur before the couple listed below in the table). The assumed water chemistries for each of the waters of Table A11 are listed in Table A12. The dominant predicted species or phases at each of the transitions are not provided here, but they are generally consistent with the Eh-pH diagrams of Appendix E.1 at the relevant pHs, although there were a few differences that were not considered important and were assumed to be a result of minor differences in the geochemical models and databases used. The approximate measured Eh values (corrected from ORP measurements with the Ag/AgCl electrode) for each of the waters listed in Tables A11 and A12 are provided in the last row of Table A11 (the values for background water, post-mining water, and post-reverse osmosis water are based on measurements performed previously at SRH that were not part of this study).

The results of Table A11 show that the Fe(III)/Fe(II) redox couple is consistently at a higher Eh than the U(VI)/U(IV) redox couple, which supports the statements in Sections 3 and 4 of the paper that Fe(III) must be reduced before significant reduction of U(VI) is likely to occur. The results also show that the measured Eh values in the production wells after the dithionite and acetate injections were sufficiently low to reduce Se(VI), Se(IV), and Fe(III), but not low enough to reduce U(VI), which is consistent with observations during the test. Finally, the results show why there was no apparent sulfate reduction during the test: sulfate is not predicted to reduce until after U(VI) starts reducing.

We note that the absolute Eh values in Table A11 are probably not as important as the differences between the Eh values of the adjacent redox couples. We also note that absolute Eh values for any couple tend to be higher at lower pH, which is a consequence of the downward slopes of the lines from left to right on the Eh-pH diagrams of Appendix E.1. Ideally, one would like to adjust the water chemistry during restoration such that the transition Eh of the U(VI)/U(IV) couple is higher than that of the Fe(III)/Fe(II) couple, but it is apparent that this does not occur for any of the water chemistries of Tables A11 and A12. The takeaway message is that the geochemical calculations predict that it will be extremely difficult to achieve U(VI) reduction at SRH until most Fe(III) is reduced.

Table A11. Calculated Eh values at which oxidized and reduced species have equal concentrations in the different water chemistries of Table A12. Approximate measured Eh of each water (corrected from ORP measurements with the Ag/AgCl electrode) is listed in the last row.

Species	Background Water *	Post-Mining Water *	Pre-Amendment Water *	Post-Dithionite Water *	Post-Acetate Water *	Post-RO Water *
Se(VI)/Se(IV)	384	532	519	518	548	513
Se(IV)/Se(0)	79	218	203	220	241	192
Fe(III)/Fe(II)	−70	222	183	192	173	196
U(VI)/U(IV)	−169	−93	−112	−119	−70	−52
S(VI)/S(−2)	−283	−160	−173	−173	−152	−179
Measured water Eh (approx.)	−20	300+	340	180	50	300+

* See Table A12 for water chemistries. Post-RO water approximates ore-zone water after typical reverse osmosis treatment at SRH (slightly more dilute in total dissolved solids than background water). Calculations were performed using PHREEQC [42] with the minteq.v4 database supplemented with additional reactions for aqueous U chemistry [43] and uranyl ternary complexes [8,44].

Table A12. Water chemistries assumed for the PHREEQC calculations of Tables 2 and A11.

Element/ Species	Background Water	Post-Mining Water	Pre-Amendment Water	Post-Dithionite Water *	Post-Acetate Water *	Post-RO Water *
Cl [−]	4.2	132	64	75	75	15
SO ₄ ^{2−}	72	600	390	1000	1000	94
HCO ₃ [−]	182	720	400	520	450	100
Acetate	NA	NA	NA	NA	300	NA
Na	20	44	27	150	200	7
Ca	51	355	208	350	350	50
Mg	13	96	56	85	100	13
K	5.9	17	12	18	20	3
U	0.05	20	2	4	10	2
Fe	0.1	0.5	0.5	0.8	10	0.1
Se	0.05	0.1	0.1	1.5	1	0.05
pH	8	6.2	6.4	6.4	6.1	6.5

* HCO₃[−] concentrations were adjusted to achieve charge balance for the post-dithionite and post-acetate waters, as alkalinity could not be effectively measured in the field. There was likely some sulfite also present in these waters. Post-RO water approximates ore-zone water after typical reverse osmosis treatment at SRH (slightly more dilute in total dissolved solids as background water).

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