Mine Water Environ (2016) 35:369–380
DOI 10.1007/s10230-015-0376-y

TECHNICAL ARTICLE

Predictive Reactive Transport Modeling at a Proposed Uranium In Situ Recovery Site with a General Data Collection Guide

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Received: 25 February 2015 / Accepted: 14 October 2015 / Published online: 3 November 2015
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Abstract Restoration of uranium in situ recovery (ISR) sites to predevelopment conditions is often very difficult. Future downgradient groundwater geochemistry can be evaluated using reactive transport modeling coupled with appropriate data collection. U.S. regulatory requirements specify that the geochemistry at the aquifer exemption boundary should never be affected, but compliance with this regulation has not been monitored at previous ISR sites. At the Dewey Burdock site near Edgemont, SD, USA, a change in groundwater flow direction created a scenario in which the oxidized side of a U roll-front deposit is downgradient of the ore zone. This increases the potential for future U transport, since conventional understanding of U geochemistry is that the reduced side provides more natural attenuation. Reactive transport modeling using U sorption parameters from batch sorption tests provides a predictive tool for future U transport. Prediction variations were tested using two different samples, considering different reaction assumptions and possible pH measurement errors. The results indicate a large range in U transport predictions, with high sensitivity to sorption parameters due to sample heterogeneity, pH, and the presence or absence of calcite. While the sample data set for these initial predictions was limited, the results highlight the need for additional calibration points and a thorough understanding of rock/water interactions in the downgradient zone. We provide a general data collection guide for steps in evaluating downgradient transport at future U ISR sites. These steps include core sampling in the downgradient and restored zones, along with batch sorption and column testing with restored and background groundwater in contact with the restored zone solid phase. Final reactive transport modeling will rely on high-quality calibration data from batch and column testing (plus any available field testing), but thorough site evaluation will also require appropriate long-term monitoring.

Keywords Geochemical modeling · PHREEQC · Batch sorption

Electronic supplementary material The online version of this article (doi:10.1007/s10230-015-0376-y) contains supplementary material, which is available to authorized users.

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Introduction

Background

Sandstone-hosted U roll-front deposits are found in Tertiary-age sediments throughout the western USA (Hobday and Galloway 1999). These deposits form at the interface between oxidized and reduced sandstones (Supplemental Fig. 1). Generally, the original source for the U is granitic rocks or volcanic ash with U concentrations slightly exceeding crustal abundance. Uranium remains soluble in groundwater in the presence of dissolved oxygen, but the U becomes less soluble when a reduction front is encountered. These redox fronts form down-dip or downgradient of the recharge area (Supplemental Fig. 1). The geochemistry associated with these deposits is complex and

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variable, but overall they contain a mixture of U(VI) minerals on the oxidized side of the front and U(IV) minerals on the reduced side of the front (Harshman 1974). Due to sorption or mineral precipitation reactions, U concentrations within an ore zone may or may not be above drinking water standards. However, groundwater within U roll-front deposits is usually not of drinking water quality, due to high concentrations of U daughter products, mainly radium and radon.

The relatively low-grade U in these deposits and their location in young, near-surface, permeable sandstones make them economically mineable using in situ recovery (ISR). Uranium ISR reverses the process that caused them to be deposited. The process involves the addition of oxygen and carbon dioxide or sodium bicarbonate. Oxygen and complexing agents are added to the groundwater to form a lixiviant, which is circulated through a well field developed around the rolls, oxidizing the U from U(IV) to U(VI) and dissolving it (Fig. 1). The groundwater containing aqueous U (pregnant lixiviant) is pumped to the surface, and the U is removed from solution in ion exchange tanks. The "barren" lixiviant is then re-fortified with oxygen and a complexing agent and recirculated through the ISR well field (Fig. 1). Slightly more water is extracted than injected in order to maintain an inward hydraulic gradient to prevent the movement of the lixiviant into portions of the aquifer not targeted for U recovery. Once U recovery is complete, well fields are generally restored by flushing the recovery zones using either local or treated groundwater. The U ISR zones are then referred to as "restored zones".

Regulatory Requirements and Current Status

The U.S. Environmental Protection Agency (EPA) is tasked under the Safe Drinking Water Act with establishing requirements that protect underground sources of drinking water. Under the Uranium Mill Tailings Radiation Control Act of 1978 (UMTRCA) section 206, EPA is also authorized to develop health and environmental standards for sites where ores are processed for their U content. In 1983 (with updates in 1995), EPA promulgated regulations at Title 40 *Code of Federal Regulations* Part 192, "Health and Environmental Protection Standards for Uranium and Thorium Mill Tailings," in response to the UMTRCA statutory requirements. At that time, U recovery was based almost exclusively on conventional milling, but since then, U recovery in the USA has shifted to U ISR technology. Because of this, the regulations in 40 CFR 192 are not specific to U ISR sites, but they have been applied, based on the Solid Waste Disposal Act (EPA 2011, 2012a). EPA is currently evaluating the 40 CFR 192 regulations for potential amendments that would be specific to U ISR facilities (EPA 2011, 2012a). In a response to a scientific advisory review of the potential amendments (EPA 2012a), the EPA director stated, "We are currently looking at ways in which geochemical modeling can help inform both establishing and implementing new ISL/ISR standards" (EPA 2012b).

Currently, for U ISR to proceed in the USA, the EPA Underground Injection Control (UIC) program must approve an aquifer exemption request submitted by the state UIC program, which permanently exempts the mineable portion of the aquifer as a future source of drinking water under the Safe Drinking Water Act. This exemption recognizes that the presence of U ore makes the groundwater unfit as drinking water. However, private drinking water wells may exist near the aquifer exemption boundaries of proposed ISR sites. Current EPA regulation 40 CFR 144.12 indicates that no impact on groundwater quality can occur beyond the aquifer exemption boundary. In the USA, the Nuclear Regulatory Commission (NRC) or state regulators evaluate final U ISR site closure and any longer-term monitoring requirements. In Texas and Wyoming, past closures of U ISR sites have only required stability monitoring within the restored area for 6 months to 1 year (NRC 2009; EPA 2011). Sites were often closed based on a "class of use" for groundwater (NRC 2009), which meant that the groundwater within the restored zone was not always restored to pre-ISR conditions for all constituents (Hall 2009). For these sites, no long-term impacts on downgradient groundwater quality were evaluated, and no long-term monitoring was required. Consequently, the EPA requirement of no impact on groundwater quality outside of the aquifer exemption boundary cannot currently be evaluated. However, evaluations of the current permitting requirements are beginning to recognize the need for downgradient modeling as a tool for understanding longer-term groundwater geochemistry (EPA 2011, 2012a, b).

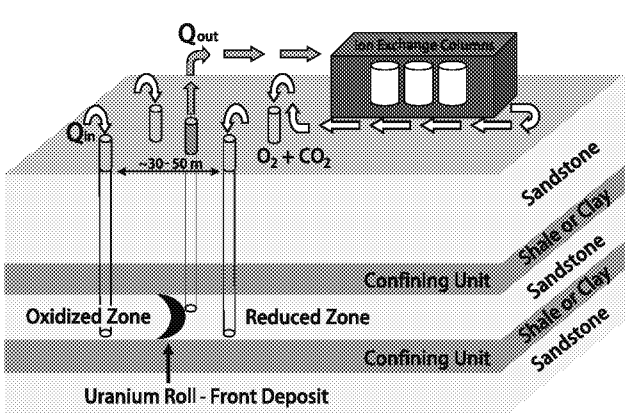

Fig. 1 Generic uranium ISR process

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Reactive Transport Modeling

Given the lack of long-term monitoring data at past ISR sites, and the difficulty of restoring ISR zones to pre-mining conditions (Borch et al. 2012; Hall 2009), predictive reactive transport modeling is an important tool to address stakeholder concerns and satisfy regulatory requirements. Attenuation of metal contaminants in groundwater has often been addressed using simple retardation approaches (Bethke and Brady 2000). However, reactive transport modeling incorporates important geochemical complexities that are required for more accurate transport prediction (Bethke and Brady 2000; Curtis et al. 2009). These added geochemical complexities are beginning to be recognized as especially important at ISR sites (EPA 2011, 2012b). This paper focuses on the appropriate use of and data requirements for predictive reactive transport modeling in addressing possible long-term geochemical changes in aquifers downgradient of ISR sites. Reactive transport modeling related to the proposed Dewey Burdock U ISR site near Edgemont, South Dakota, USA (Fig. 2) provides an example. While the modeling is very site specific, additional data needs were identified and appropriate approaches are provided that should be applicable to other U ISR sites. To give a more consistent methodology across U ISR sites, a general data collection guide is provided that will help guide the collection of the data necessary for input into more accurate reactive transport modeling. In addition, these approaches are generally applicable to most sites with potential downgradient metal transport in groundwater.

Dewey Burdock Study Site

Initial Data

The initial groundwater data requirements for the permitting of any proposed U ISR site generally include: (1) baseline groundwater quality, (2) groundwater flow directions, and (3) aquifer hydraulic conductivities. These data come from company monitoring well installations and subsequent sampling (groundwater quality and hydraulic head measurements). Several aquifer tests might be performed to determine hydraulic conductivities and measure the integrity of confining units. These data are basic first-step information in understanding the site hydrogeology. Such information for the Dewey Burdock site was provided in license/permit applications to the NRC and EPA (Powertech 2008, 2009 and, respectively) and the final NRC Supplemental Environmental Impact Statement (NRC 2014).

In addition to understanding the basic hydrogeologic conditions at an ISR site, multiple drilling locations are used to define the U roll-front and the associated ore zone. Currently, USA regulatory requirements do not specifically

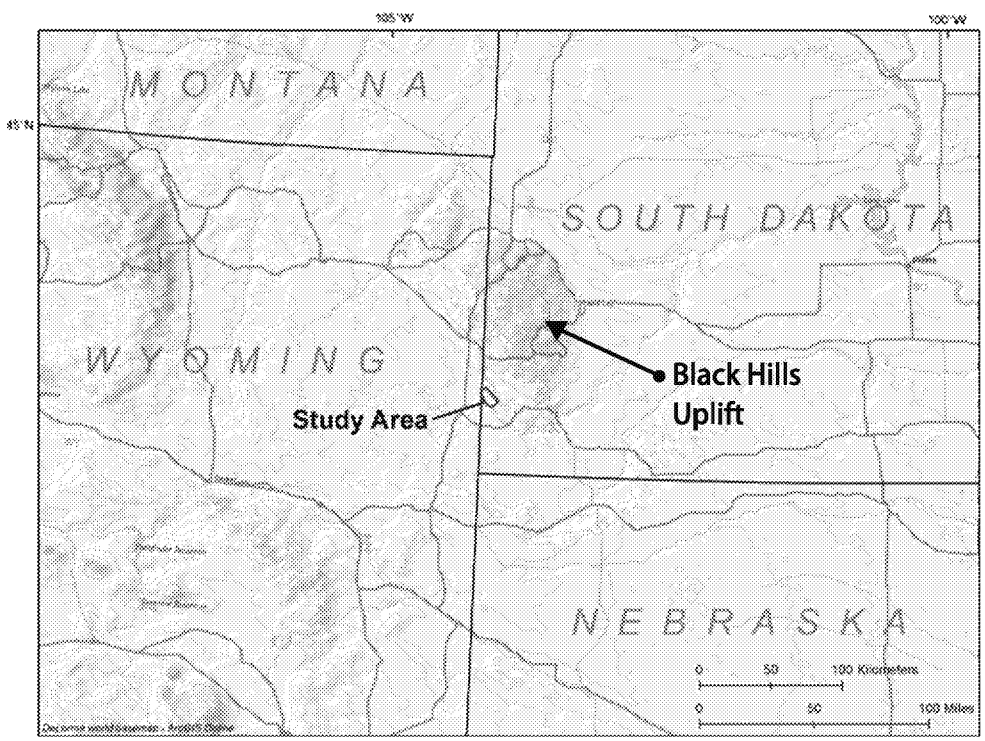

Fig. 2 Dewey Burdock site location

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require the collection of rock core during the permit process. At the Dewey Burdock site, the overall locations of the U roll-front deposit, oxidized zones, and reduced zones were mapped using exploration holes with geophysical logging. Logging allowed for the identification of geologic units and the location of uranium ore zones with gamma logs. In addition, a few confirmation core holes were drilled. The mining company used these cores for ore zone confirmation and ore recovery testing. The remaining, unpreserved core (stored in typical rock core boxes) was also analyzed for additional mineralogical characterization (Johnson et al. 2013). Several oxidized core zones were also analyzed for Fe content and U sorption testing (Johnson et al. 2016). The U sorption parameters, specifically site densities and equilibrium constants, from Johnson et al. (2016) were used as input data in the reactive transport modeling. While the core from the Dewey Burdock site was not directly downgradient of the proposed recovery zones, it provides proxy core information for likely geochemical conditions within the oxidized zone. Some reduced zone core material was also available and was analyzed for sulfur, carbon, and metal content (Johnson et al. 2013). However, the reduced zone core was not kept anoxic, so it was not considered reliable material for laboratory determination of U sorption and precipitation potential for use in reactive transport modeling.

Evaluation of Downgradient Oxidized Zone

The natural condition for a U roll-front is for U to be sorbed or precipitated in the reduction front due to the presence of organic carbon or pyrite, or both. At a currently forming roll front (Supplemental Fig. 1), groundwater U concentrations in the oxygenated side should be higher than in the reduced side. At the Dewey Burdock site, the groundwater flow direction during U roll-front formation was likely toward the southeast, based on the shape of the redox boundary (Fig. 3) and the direction of the C-shape of the ore zone in geophysical logs (Frank Lichnovsky, personal communication). However, the current groundwater flow direction is now rotated 90 degrees, with groundwater flow toward the southwest (Fig. 3), based on monitoring well data (Powertech 2008, 2009). The exact cause for the change in groundwater flow direction is unknown, but is likely due to faulting during uplift of the Black Hills (Fig. 2). Much of the current groundwater is depleted in oxygen, even in the oxidized zone (Johnson 2012), because oxygen is depleted in the surrounding, upgradient reduced zone. Uranium concentrations in groundwater across the site, including the ore zone, are low because of this oxygen depletion, which reduces U solubility. However, U daughter products, such as radium and radon, are well above drinking water standards within the ore zone (Powertech 2008).

The U ore zones surround the redox boundary, and the black dots in Fig. 3 are previous drill-hole locations completed for ore identification. The change in groundwater flow conditions at Dewey Burdock created a situation in which the oxidized solid-phase is downgradient of the ore zone for a large portion of the site (Fig. 3). To the authors' knowledge, a change in groundwater flow direction through geologic time at ISR sites is not unusual, but a full 90° difference is unique. In the oxidized zone, core data indicate a lack of pyrite and organic carbon, with the oxidized Fe occurring either as amorphous iron oxyhydroxide or as hematite. Up to 1 wt% hematite was detected in x-ray diffraction analyses (Johnson et al. 2013). The resulting reddish Fe within the core is very apparent (Fig. 3). In general, U is expected to be less mobile in reducing zones due to the greater potential for U precipitation and sorption than in the oxidized zone based on the mineralogy, as this is the controlling mechanism for the original formation of the U deposit. This potential for higher U mobility in the oxidized zone is the reason for focusing on this area with reactive transport modeling, as the oxidized zone poses a greater concern for meeting regulatory compliance (no change in groundwater quality at the aquifer exemption boundary). However, at a larger scale, post-ISR groundwater will eventually encounter the reducing zone along the southwestern side of the oxidized zone (Fig. 3).

Reactive Transport Modeling

Methods and Model Setup

The model area was designed to simulate the restored ISR zone (yellow box in Fig. 3), which was initially the U ore zone/roll front (Supplemental Fig. 1; Fig. 1) with subsequent downgradient groundwater transport (transparent yellow box in Fig. 3). Reactive transport modeling used a 1-D column with PHREEQC (Parkhurst and Appelo 2013) to create the 1-D model domain shown in Fig. 4 to represent the 2-D area shown in Fig. 3. Groundwater flow is from left to right in Fig. 4 and in all of the subsequent graphs. PHREEQC models flow velocity by specifying the cell size and a number of cell-to-cell shifts with time. At the Dewey Burdock site, calculated groundwater flow velocities were 1.86 m/year (6.1 ft/year) in the upper unit and 2.23 m/year (7.3 ft/year) in the lower unit (Petrotek 2012). Modeling used an upper-bound estimate on groundwater flow velocity of 5 m/year (16.4 ft/year) to simulate maximum transport conditions. For convenience, each cell was specified as 5 m (16.4 ft) in length, with a cell-to-cell shift each year. For initial simplicity, no dispersion was added to any of the simulations.

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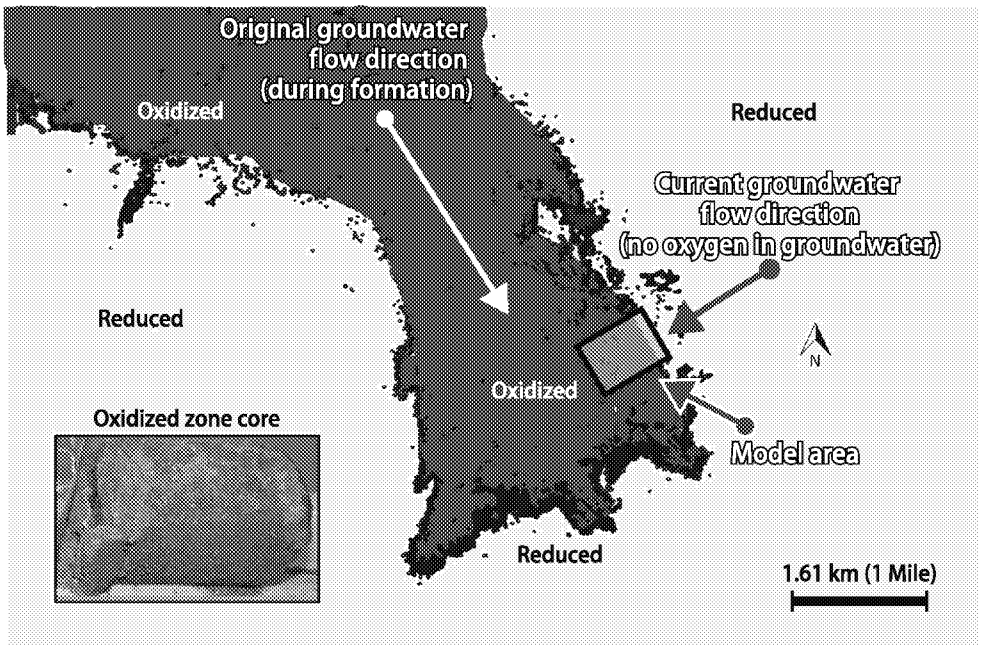

Fig. 3 Oxidized zone map with past groundwater flow direction, current groundwater flow direction, model area (ISR zone area in *box with yellow fill* and downgradient area in *box with transparent fill*) and inserted photograph of an oxidized core sample. Base map courtesy of Powertech (USA) Inc. and Frank Lichnovsky

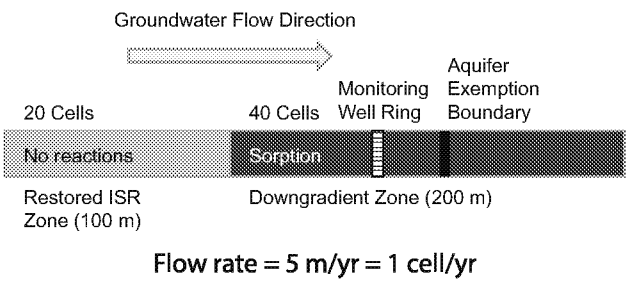

Fig. 4 1D model domain. Cell size is 5 m. The distances from the end of the restored ISR zone to the monitoring well ring and the aquifer exemption boundary are 61 and 97.6 m, respectively. Sorption parameters use best-fit calibration data from Johnson et al. (2016), and simulations do not include any dispersion. Incoming background groundwater (*left side*) and downgradient zone use well 684 water with no uranium. Restored ISR zone uses well 684 water with the addition of 0.2 mg/L of dissolved uranium

The actual "flare area," where groundwater moves away from each injection well, is unknown but was assumed to be 61 m (200 ft), or half the distance from an injection well to the nearest monitoring well. The actual flare area will depend on the final well spacing design and necessary injection rates. The assumed total length of the restored ISR zone was meant to include the injection and production well area, plus the flare area. The resulting distance from the end of the restored zone to the monitoring well ring was 61 m (200 ft), with a total proposed distance of 122 m (400 ft) from the nearest injection wells (Powertech 2008). Given the uncertainties in the actual flare area and the actual distance across the whole ISR production zone, 100 m is a convenient distance for the width of the restored area, with approximately another 100 m to the aquifer exemption boundary, which is proposed to be 36.6 m (120 ft) beyond the monitoring well ring (Powertech 2008). An additional 100 m distance was added to the 1-D model domain to allow for longer-term downgradient transport. The number of cells, dimensions, overall model domain, and locations of the monitoring well ring and aquifer exemption boundary are summarized in Fig. 4. While these dimensions were specified to have distances in the 1-D simulations that were similar to those at the proposed Dewey Burdock ISR site, dimensional changes can be easily adjusted for different site conditions.

As groundwater in each cell moves to the next cell, the water interacts with the solid phase specified in the next cell. To simulate these reactions, the PHREEQC database was modified to include the calcium/magnesium uranyl carbonate complexes reported by Dong and Brooks (2006) and recently updated U thermodynamics (Guillaumont et al. 2003). The full database is provided with the supplemental material in Johnson et al. (2016). For the base case simulations, no reactions were simulated in the restored ISR zone, and the downgradient zone included only sorption reactions (Fig. 4). Incoming groundwater at the left side of the 1-D column used data from well 684 from another ore zone (Johnson 2012) within the same formation as "background" groundwater, since the proposed model domain did not have any true background groundwater quality data. Because of the lack of oxygen, exploration holes that were converted to monitoring wells in and around the ore zone (upgradient and downgradient) have very similar groundwater quality, along with low

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dissolved U concentrations (Johnson 2012). They are therefore reasonable proxies for typical background groundwater. For simplicity, no U was included in the background groundwater data included in the simulations. The background groundwater was also used as the initial groundwater in the downgradient zone (Fig. 4). The final groundwater quality in the restored ISR zone is unknown since this is a proposed ISR site. Based on the authors' discussions with U recovery companies, 0.2 mg/L of dissolved U was added to the background groundwater to represent a reasonable restored-zone groundwater quality.

Sorption batch tests were completed to provide information on downgradient sorption away from the restored ISR zone. The methods and final sorption parameters for three core samples are provided in Johnson et al. (2016), which provides total bulk U sorption parameters (site densities and equilibrium constants) that are independent of U sorption on individual mineral assemblages. Core sample identification numbers are the same as those used in several previous studies (Johnson 2012; Johnson et al. 2013, 2016; Powertech 2008, 2009). The final sorption parameters from Johnson et al. (2016) used the generalized composite surface complexation approach of Davis et al. (2004), which was used directly in the 1-D PHREEQC simulations. Since these simulations only represent the oxidized zone, U was considered to remain soluble, and U precipitation reactions were not evaluated. We recognize that three samples are not sufficient for adequate predictions; the resulting simulations are only meant to assist in process understanding and to provide an appropriate method for reactive transport modeling and future data collection.

Base Case Simulations

Predictive reactive transport simulations are shown for samples 11-14C-4 and 11-16C-2 along the 1-D column (Fig. 5a, c) and at the monitoring well ring for 300 years (Fig. 5b, d). The monitoring well ring is at the 161 m distance in the 1-D column. As discussed in Johnson et al. (2016), sample 11-16C-2 had a higher sorption capacity than 11-14C-4, providing dramatically different predictions. Simulation plots from sample 11-14C-5 are not provided because the sorption capacity of that sample at the 0.2 mg/L U concentration is essentially the same as 11-14C-4 (Johnson et al. 2016). However, sample 11-14C-5 would provide greater sorption capacity than 11-14C-4 at

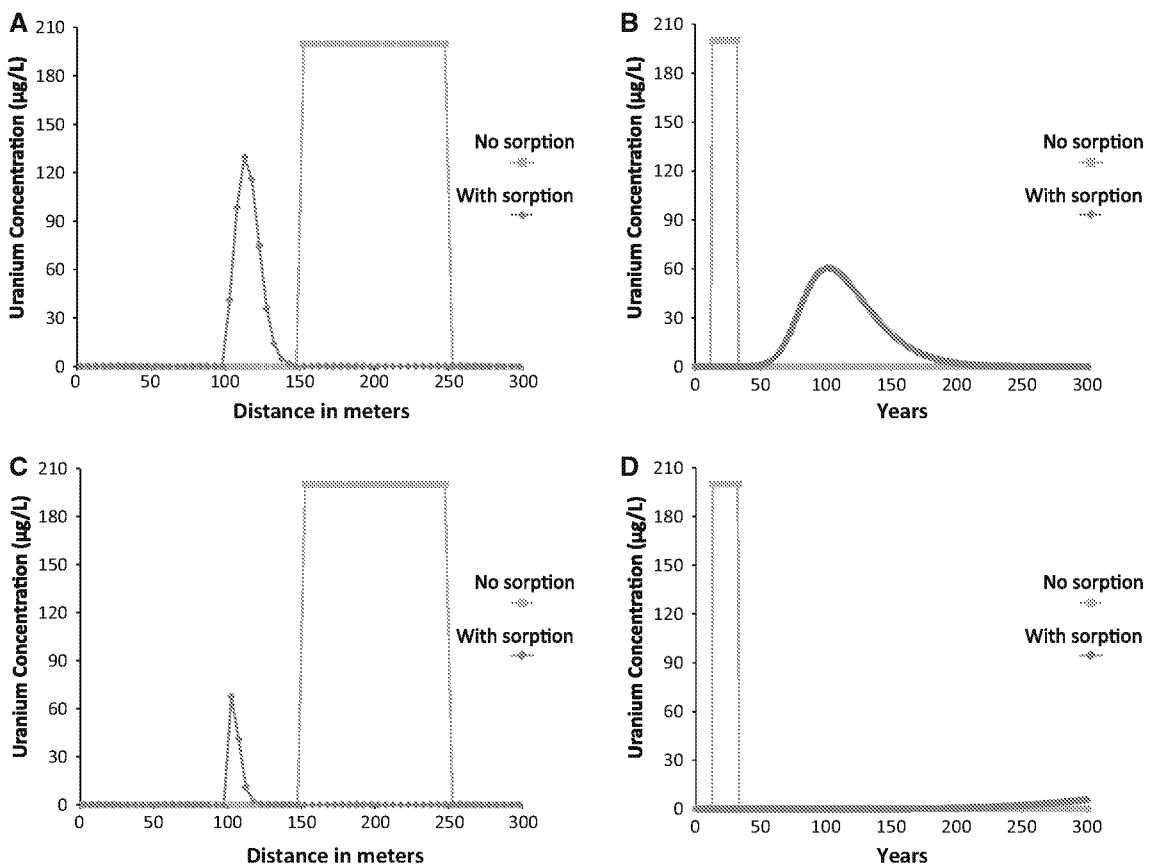

Fig. 5 Sample 11-14C-4, 1D column at 30 years (**a**) and at monitoring well ring (**b**). Sample 11-16C-2, 1D column at 30 years (**c**) and at monitoring well ring (**d**)

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higher U concentrations, as the sorption curves for the two samples are not the same at higher U concentrations (Johnson et al. 2016).

In Fig. 5, the red line and square symbols indicate the transport of the 0.2 mg/L U left in the restored zone without any sorption (conservative transport). The blue line with diamond symbols represents U transport using the sorption parameters determined from the sorption batch tests in Johnson et al. (2016). At 30 years, much of the U is still very close to the end of the restored zone (at 100 m, Fig. 5a, c). This occurs because equilibrium sorption from the restored ISR zone groundwater with 0.2 mg/L U has added U onto the aquifer solids. At 30 years, the conservatively-transported restored zone water is at 150–250 m, and the equilibration of the background groundwater with the U-loaded solids in the 100–150 m distance creates the U concentrations seen in Fig. 5a, c. Through time at the monitoring well ring, the mass of U in the groundwater is spread out due to continual sorption/desorption, and the maximum peak concentration is reduced (Fig. 5b). If dispersion is added, this peak spreads out even more, and peak concentrations are lower. For simplicity in comparing changes due to geochemical differences, dispersion was not added to any of the presented U transport predictions. For sample 11-16C-2, with stronger sorption, U was not detected at the monitoring well ring until after approximately 225 years due to continual sorption/desorption processes that retard U mobility.

To evaluate the influence of calcite and possible errors in pH measurements, the following sections add slight differences to the base case simulations. These additional simulations provide sensitivity analysis that bound the range of reasonable U transport predictions. Such analyses should always be included as an integral part of any reactive transport modeling.

Simulations with Calcite Equilibrium

To evaluate the influence of reaction assumptions, the simulations discussed above and shown in Fig. 5 were redone with calcite equilibrium throughout the column. In the original simulations, the groundwater saturation index was −0.14, or slightly undersaturated. This saturation index is well within potential analytical error. While the addition of calcite equilibrium is a small change in the groundwater chemistry, the predictive model is quite different (Fig. 6). In Fig. 6, the original simulations (with sorption, blue line, diamond symbol) and the conservative U transport (no sorption, red line, square symbol) are the same as shown in Fig. 5. The additional simulation with calcite equilibrium (with calcite equilibrium, green line, triangle symbol) shows an increase in U mobility. This increased mobility is due to a decrease in sorption because of the additional amount of calcium uranyl carbonate complexes in solution created by a slight increase in calcite dissolution. These complexes keep U in solution, similar to the U ISR process.

Simulations with pH Change Throughout the Column

To test prediction sensitivity with possible analytical error, the base case simulation for sample 11-14C-4 (Fig. 5a, b) was redone with a 5 % increase and decrease in the measured pH (Fig. 7a, b, and Fig. 7c, d, respectively). The pH change was applied to the groundwater throughout the column and for any incoming background groundwater. The 5 % increase in pH changed the pH from 6.78 to 7.12; the 5 % decrease lowered the pH to 6.44. The results (Fig. 7) indicate that these slight changes in pH dramatically influenced U mobility. In the PHREEQC output, the higher pH increased the amount of calcium uranyl carbonate complexes in solution and decreased the amount of uranyl ion on the sorption surface, both of which increased U mobility. The reverse was true for the pH decrease. Further examination of the output indicates that the pH change strongly influenced the amount of dissolved uranyl ion due to a change in the distribution of U complexes.

Simulations with Different pH Changes in the Restored and Background Zones

Given the pH sensitivity shown in Fig. 7 and discussed above, a final simulation was done using a lower pH in the restored zone (pH 6) and a 5 % increase in pH for the background groundwater. The results at 30 years (Fig. 8a, note different scale from previous graphs) show a zone with U concentrations that exceed the original 0.2 mg/L U concentration. The U spike still reaches a peak of 0.225 mg/L at the monitoring well ring (Fig. 8b, note different scale) between about 40 and 75 years. These U concentrations are due to increased U sorption from the lower pH in the restored zone, which is later desorbed by the higher pH background groundwater. Because of the large amount of sorbed U, the desorption influence creates higher U concentrations in the groundwater than the original concentrations left in the restored zone.

The simulations for Fig. 8a, b did not include calcite equilibrium; Fig. 8c, d show the results when equilibration with calcite is assumed throughout the column. These simulations are probably more realistic, since at least some calcite is often present in many aquifers; the cores in the Burdock area contain 0.15 % calcite by weight (Johnson et al. 2013). These simulations show that U is more mobile in the restored zone water with a lower pH (Fig. 8c, d,

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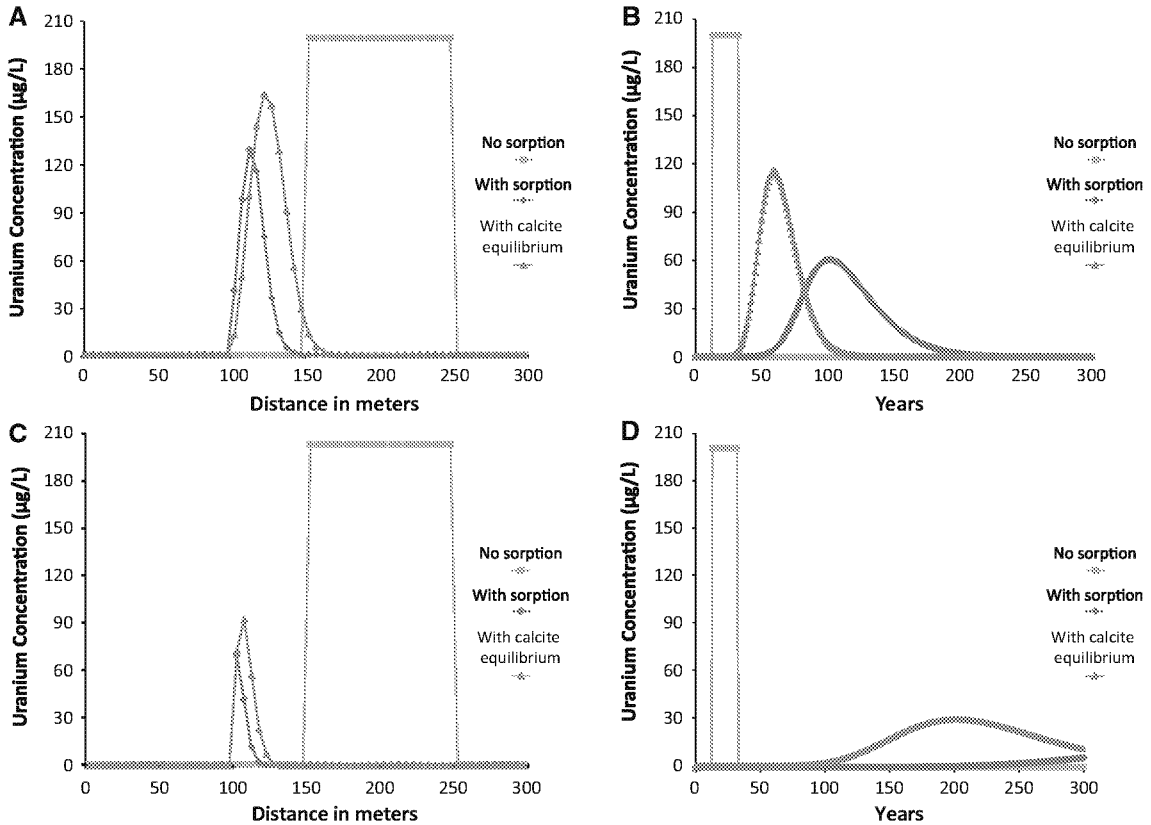

Fig. 6 Sample 11-14C-4, 1D column at 30 years (**a**) and at monitoring well ring (**b**) with sorption and calcite equilibrium. Sample 11-16C-2, 1D column at 30 years (**c**) and at monitoring well ring (**d**) with sorption and calcite equilibrium. Original simulations from Fig. 5 are indicated

curve underneath the no-sorption curve), since more calcite dissolves, creating more U complexes in solution. When the background groundwater with a 5 % pH increase equilibrates, calcite precipitates, and so there are fewer dissolved U complexes. As background groundwater moves into the column, a new sorption curve is established (Fig. 8c, d, curve not underneath the no-sorption curve). The addition of calcite in this case demonstrates the need for quantitative mineralogy in the restored and the downgradient zone in addition to understanding the groundwater geochemistry.

Key Findings

These simulations demonstrate the high sensitivity in the predictions of U transport to very subtle changes in groundwater geochemistry, specifically pH and calcite equilibrium. However, based on the predictive differences in Fig. 5 for the two different samples, heterogeneity in the aquifer is also a very important issue, independent of any modeling assumptions. The next sections discuss additional data needs and provide an overall data collection guide. These sections provide guidance for reducing large predictive ranges with the most appropriate and more accurate data. However, predictive differences based on overall heterogeneity will still remain.

Additional Data Needs

For this study, only three proxy core samples were available from the southern portion of the U roll front. More thorough reactive transport modeling would require actual downgradient core from multiple intervals. Sample intervals should be selected based on the downhole geology. In addition, because of the limited number of calibration points for the batch sorption tests, the sorption parameters could not all be independently estimated (Johnson et al. 2016). Additional calibration points could include additional U concentrations and additional geochemical conditions, such as changing pH, alkalinity, calcium, and carbon dioxide concentrations, similar to the procedures of Davis et al. (2004). In addition to providing increased confidence in the calibration efforts, the additional data could confirm the sensitivity of the U mobility with changing geochemistry.

Batch sorption tests provide adequate information for equilibrium conditions (Johnson et al. 2016), but column

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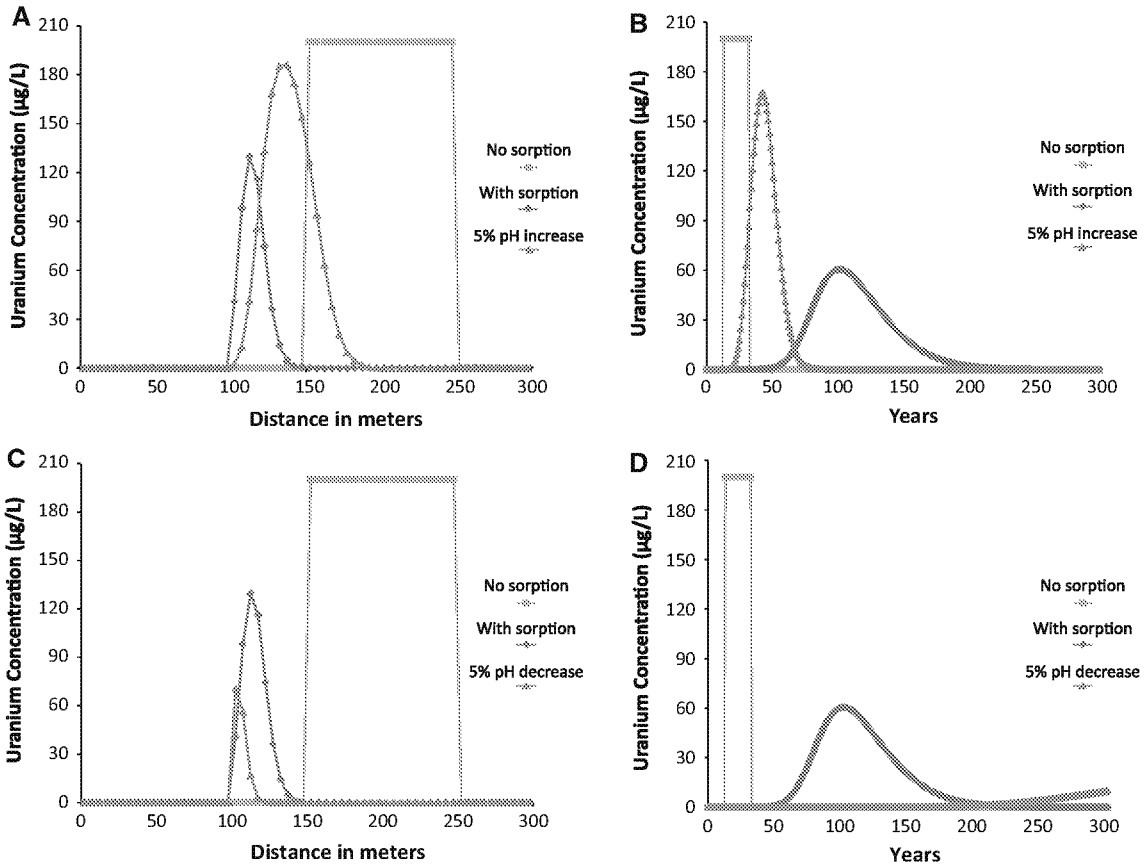

Fig. 7 Sample 11-14C-4, with sorption and a 5 % increase in groundwater pH, 1D column at 30 years (**a**) and at monitoring well ring (**b**). Sample 11-14C-4, with sorption and a 5 % decrease in groundwater pH, 1D column at 30 years (**c**) and at monitoring well ring (**d**). Original simulations from Fig. 5a, b are indicated

studies can provide more realistic groundwater flow scenarios, where the addition of kinetic rates and rate-limited sorption might be necessary. Column tests can provide additional calibration data for reactive transport simulations beyond the equilibrium batch tests. Column tests should also include variations in U concentrations along with changing pH, alkalinity, and concentrations of calcium and carbon dioxide. Such tests can provide data for sensitivities in U mobility with changes in geochemistry. Whether or not column tests could provide all of the necessary U sorption parameters without batch tests is an area for additional research.

The best calibration for reactive transport models at U ISR sites would be a pilot field study. Injection of post-restoration water into the downgradient zone would provide the most realistic information on U mobility. However, such a test would risk the loss of some of the injection water. A more likely scenario is an injection of post-restoration water from a restored ISR well field into a newly developed well field after the aquifer exemption has been approved. Presuming the new well field has not been turned on, any field test with injection, withdrawal, or natural flow testing of post-restoration water will be overprinted once the well field is activated.

Given the high sensitivity of reactive transport modeling results to pH, very accurate background and post-restoration groundwater geochemistry are required. Variations in space and time for these waters should be thoroughly evaluated, in addition to an evaluation of potential analytical errors. Although not tested in this work, the evolution of background groundwater as it flows into the restored zone should also be evaluated; this is referred to in the next section as "evolved background groundwater". Over time, as the background groundwater flows into the restored ISR zone, the geochemistry of the background groundwater may change, depending on the final mineralogy of the restored ISR zone.

General Data Collection Guide

In this data collection guide for reactive transport modeling at U ISR sites, it is assumed that thorough overall site characterization has already been completed, including

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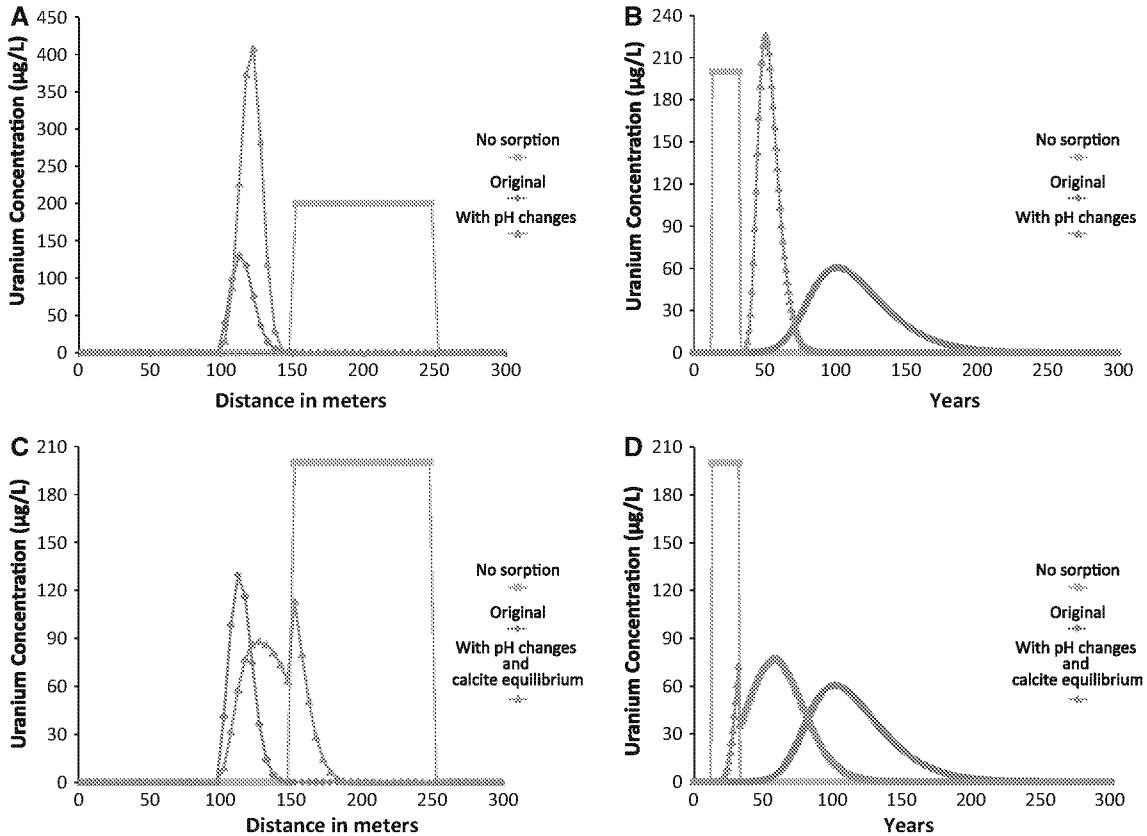

Fig. 8 Sample 11-14C-4, with a pH of 6 in the restored zone and a 5 % increase in background groundwater pH, 1D column at 30 years (**a**) and at monitoring well ring (**b**). Sample 11-14C-4, with a pH of 6 in the restored zone and a 5 % increase in background groundwater pH and downgradient calcite equilibrium, 1D column at 30 years (**c**) and at monitoring well ring (**d**). Original simulations from Fig. 5a, b are indicated (curves labeled "No sorption" and "Original")

overall site geology and hydrogeology, ore locations, groundwater flow directions and velocities, and other relevant parameters. Specific modeling codes are not specified, but the use of the latest thermodynamic data for U speciation is necessary (Johnson and Tutu 2013). In order to proceed with reactive transport modeling (step 7 below), additional characterization data should include core analyses (steps 1–3) and sorption testing (steps 4–6), as listed below:

1. Collect representative downgradient core at multiple intervals with depth to characterize quantitative mineralogy (especially important for calcite).
2. Collect representative core in the restored zone at multiple intervals with depth to characterize quantitative mineralogy (especially important for calcite).
3. Contact the restored zone core in a column with background groundwater to produce an evolved background groundwater in the restored zone.
4. Conduct batch sorption and column tests using the downgradient core with the final restoration groundwater, evolved background groundwater, and background groundwater to determine sorption parameters and possible mineral dissolution/precipitation reactions.
5. In the batch and column tests, use variable U concentrations and geochemical conditions that bracket the observed variations in field data in and around the restored well field.
6. Conduct field pilot tests with restored groundwater, if possible.
7. Conduct reactive transport modeling with parameters and information derived from steps 1–6.

Addition of an evolved background groundwater is necessary to confirm whether the newly restored zone solid-phase geochemistry will change the chemistry of the incoming background groundwater. For the Dewey Burdock modeling, these data were not available, since no ISR has occurred. While step 1 can be completed before U ISR begins, steps 2 through 6 all require the collection of restored zone core and restored zone groundwater, which can only be done after restoration is completed. The reactive transport modeling (step 7) could be initiated and

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conceptually set up before U ISR begins, but requires final restoration data for completion.

Batch sorption tests are adequate for equilibrium sorption parameters, but kinetic rates or dual domain conditions have to be evaluated using column tests. In addition, column tests will likely improve transport modeling parameters that influence long-term concentration tailing. Temporarily stopping the flow in the column tests to evaluate concentration rebound is critical to evaluate whether the column is in equilibrium with the injection fluid. Field pilot tests would provide the best input parameters for reactive transport modeling, but they may not be feasible due to regulatory requirements and cost.

All of the above steps relate to providing adequate calibration data for rock/water interactions in a post-ISR scenario. Understanding the mineralogy of the restored and downgradient zones is a key element in providing the appropriate groundwater interactions with a sequence consisting of: (1) restored zone groundwater, (2) evolved background groundwater within the restored zone, and (3) background groundwater. This sequence represents a time-series of groundwater interaction within the restored zone, which may have a different solid-phase geochemistry than the initial U ore zone due to the ISR process, as upgradient groundwater flows through the restored zone and into the downgradient zone. As seen from the Dewey Burdock site simulations, understanding the geochemistry of the water and solid phases in all of these zones under various conditions is necessary. Appropriate laboratory testing using batch sorption and column tests can provide the calibration data needed for predictive reactive transport models and the bounding information on parameter sensitivities.

While the focus of this paper has been on the oxidized zone of a U roll-front formation, these procedures are just as applicable for evaluation of the reduced side. If a reducing zone is being evaluated, sampling and testing should be done in anoxic conditions with a focus on the amount of available reductants (e.g. organic carbon and pyrite), and the potential for U removal under reducing conditions should also be evaluated. Examination of mineral dissolution/precipitation reactions will require solid-phase analyses of the post-batch and post-column test material to identify U concentration reductions related to sorption or mineral precipitation.

Reactive transport modeling predictions (1-D/2-D/3-D) can be done using appropriate interactions with the known mineralogy and calibrated sorption parameters from batch and column testing. Additional interactions could include reactions such as mineral dissolution and precipitation, cation exchange, and redox changes. The inclusion of these additional reactions will need to be assessed from the quantitative mineralogy. Batch and column test results may confirm the need for additional reactions, but also may not provide direct evidence for them. Final selection of the modeling code, number of dimensions, and combinations and locations of rock/water interactions will be site specific and based on available data and analytical results. Most of the effort in such evaluations is spent getting appropriate model input parameters. Since no contaminant plume exists (and may never exist), the reactive transport modeling efforts are purely forward simulations with no additional calibration data being available until longer-term monitoring occurs.

Any modeling efforts should continually evaluate predictive ranges based on analytical uncertainties, natural heterogeneity (solid and water), and calibration uncertainties. These uncertainties can be reduced as additional data become available. In addition, changes in overall rock/water interactions and updates to the conceptual model should be a continual process as additional data are gained. For example, as with the Dewey Burdock simulations, the final geochemistry of groundwater in the restored zone is unknown. However, if reactive transport models have been completed for preliminary predictions, the true geochemistry of the restored groundwater can be entered, and transport simulations can be repeated. This allows continuous assessment of restoration progress, including evaluations of reasonable end points for restoration that will meet compliance at the aquifer exemption boundary. Longer term, such modeling efforts will be an iterative process between modeling and data collection. Modeling results can assist in designing an appropriate monitoring network, and the data from such monitoring can be fed back into subsequent model updates.

Conclusions

Current regulations in the USA specifically state that downgradient groundwater quality should not be influenced by U ISR sites. However, long-term downgradient monitoring has not been required at past ISR sites. Reactive transport modeling for the proposed Dewey Burdock U ISR site shows that sorption processes can provide significant natural U attenuation, even in oxidized bedrock. However, uncertainties due to heterogeneity, analytical error, and calibration error can produce large predictive ranges for U transport. Given these sensitivities, accurate solid-phase and groundwater geochemistry data are necessary. In addition, batch and column tests with multiple U concentrations and variations in geochemical conditions can provide added calibration points to potentially decrease the reactive transport prediction uncertainty.

A data collection guide to provide a more consistent method for reactive transport modeling and a more standard approach to evaluate downgradient transport at U ISR

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sites was developed. The data collection guide focuses on thorough solid- and water-phase measurements to understand rock/water interactions and provide appropriate input parameters for reactive transport modeling. This information can be used during restoration to assess whether restoration targets can adequately protect downgradient groundwater and whether any proposed alternate concentration limits are reasonable.

While reactive transport modeling uncertainties can be reduced by careful evaluation of modeling assumptions, analytical errors, and calibration uncertainties, aquifer heterogeneities are difficult to fully determine in three dimensions. Therefore, a reactive transport model will never fully represent reality; an appropriate level of future downgradient monitoring will be required. Reactive transport modeling provides predictive concentration ranges with distance that can be used to improve the design of monitoring networks. In turn, these monitoring networks can be used iteratively with the modeling, adding calibration data through time to improve the modeling and reduce uncertainties.

Acknowledgments Funding for this work was provided by the U.S. Department of Energy Office of Legacy Management. Additional funding was provided by the University of Witwatersrand, South Africa. We also thank Dr. James Stone (South Dakota School of Mines and Technology), the journal editors and two anonymous journal reviewers for additional comments that helped improve this manuscript.

References

Bethke CM, Brady PV (2000) How the K_d approach undermines ground water cleanup. Ground Water 38(3):435–443

Borch T, Roche N, Johnson TE (2012) Determination of contaminant levels and remediation efficacy in groundwater at a former in situ recovery uranium mine. J Environ Monit 14(7):1814–1823

Curtis GP, Kohler M, Davis JA (2009) Comparing approaches for simulating the reactive transport of U(VI) in ground water. Mine Water Environ 28:84–93

Davis JD, Meece DE, Kohler M, Curtis GP (2004) Approaches to surface complexation modeling of uranium(VI) adsorption on aquifer sediments. Geochim Cosmochim Acta 68(18):3621–3641

Dong W, Brooks SC (2006) Determination of the formation constants of ternary complexes of uranyl and carbonate with alkaline earth metals (Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}) using anion exchange method. Environ Sci Technol 40:4689–4695

EPA (2011) Considerations related to post-closure monitoring of uranium in situ leach/in situ recovery (ISL/ISR) sites, draft technical report. US Environmental Protection Agency (EPA). http://www.epa.gov/radiation/docs/tenorm/post-closure-monitoring.pdf

EPA (2012a) Advisory review of considerations related to post-closure monitoring of uranium in situ leach/in situ recovery (ISL/ISR) sites, draft technical report. US EPA. http://yosemite.epa.gov/sab/sabproduct.nsf/964968D9229863A0852579A7006EC71A/$File/EPA-SAB-12-005-unsigned.pdf

EPA (2012b) Response to advisory review of considerations related to post-closure monitoring of uranium in situ leach/in situ recovery (ISL/ISR) sites, draft technical report. http://yosemite.epa.gov/sab/sabproduct.nsf/0/964968d9229863a0852579a7006ec71a/$FILE/EPA-SAB-12-005_Response_06-12-2012.pdf

Guillaumont R, Fanghanel T, Fuger J, Grenthe I, Neck V, Palmer D, Rand MH (2003) Update on the chemical thermodynamics of uranium, neptunium, plutonium, americium and technetium. Elsevier, Amsterdam

Hall SM (2009) Groundwater restoration at uranium in situ recovery mines, south Texas coastal plain. USGS OFR 2009-1143. http://pubs.usgs.gov/of/2009/1143/

Harshman EN (1974) Distribution of elements in some roll-type uranium deposits. Proc, Symp on the Formation of Uranium Ore Deposits, Athens, Greece, IAEA-SM-183/4, pp 169–183

Hobday DK, Galloway WE (1999) Groundwater processes and sedimentary uranium deposits. Hydrogeol J 7:127–138

Johnson RH (2012) Geochemical data from groundwater at the proposed Dewey Burdock uranium in situ recovery mine, Edgemont, South Dakota. USGS OFR 2012-1070. http://pubs.usgs.gov/of/2012/1070/

Johnson RH, Tutu H (2013) Reactive transport modeling at uranium in situ recovery sites: uncertainties in uranium sorption on iron hydroxides. In: Brown A, Figueroa L, Wolkersdorfer C (eds), Reliable mine water technology, vol I, pp 377–383. http://www.imwa.info/docs/imwa_2013/IMWA2013_Johnson_417.pdf

Johnson RH, Diehl SF, Benzel WM (2013) Solid-phase data from cores at the proposed Dewey Burdock uranium in situ recovery mine near Edgemont, South Dakota. USGS OFR 2013-1093. http://pubs.usgs.gov/of/2013/1093/

Johnson RH, Truax R, Lankford D, Stone J (2016) Sorption testing and generalized composite surface complexation models for the determination of uranium sorption parameters at a proposed uranium in situ recovery site, Mine Water Environ (in this issue)

NRC (2009) Generic environmental impact statement for in situ leach uranium milling facilities. US Nuclear Regulatory Commission, NUREG-1910, vols 1 and 2

NRC (2014) Environmental impact statement for the Dewey-Burdock project in Custer and Fall River counties, South Dakota, Supplement to the generic environmental impact statement for in situ leach uranium milling facilities. US Nuclear Regulatory Commission, NUREG-1910, final report. http://pbadupws.nrc.gov/docs/ML1402/ML14029A406.html

Parkhurst DL, Appelo CAJ (2013) Description of input and examples for PHREEQC vers 3. A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. USGS techniques and methods. http://pubs.usgs.gov/tm/06/a43/

Petrotek (2012) Numerical modeling of hydrogeologic conditions, Dewey-Burdock project, South Dakota, Powertech Dewey-Burodock project Fall River and Custer Counties, SD. http://pbadupws.nrc.gov/docs/ML1206/ML12062A096.pdf

Powertech (2008) Dewey-Burock project class III underground injection control permit application to the US EPA Region 8, updated January 2013. http://www2.epa.gov/region8/underground-injection-control and ftp://epa.gov/r8/DeweyBurdock/DBApplication.pdf

Powertech (2009) Dewey-Burdock project, application for NRC uranium recovery license Fall River and Custer counties, South Dakota. http://pbadupws.nrc.gov/docs/ML0928/ML092870160.html

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