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4 **Uranium Transport in a Crushed Granodiorite: Experiments and Reactive Transport**
5 **Modeling**
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Abstract

The primary objective of this study was to develop and demonstrate an experimental method to refine and better parameterize process models for reactive contaminant transport in aqueous subsurface environments and to reduce conservatism in such models without attempting to fully describe the geochemical system. Uranium was used as an example of a moderately adsorbing contaminant because of its relevance in geologic disposal of spent nuclear fuel. A fractured granodiorite from the Grimsel Test Site (GTS) in Switzerland was selected because this system has been studied extensively and field experiments have been conducted with radionuclides including uranium. We evaluated the role of pH, porous media size fraction, and flow interruptions on uranium transport. Rock cores drilled from the GTS were shipped to Los Alamos National Laboratory, characterized by x-ray diffraction and optical microscopy, and used in uranium batch sorption and column breakthrough experiments. A synthetic water was prepared that represented the porewater that would be present after groundwater interacts with bentonite backfill material near a nuclear waste package. Uranium was conservatively transported at pH 8.8. Significant adsorption and subsequent desorption was observed at pH ~7, with long desorption tails resulting after switching the column injection solution to uranium-free groundwater. Our experiments were designed to better interrogate this slow desorption behavior. A three-site model predicted sorption rate constants for a pH 7.2 solution with a 75-150 μm granodiorite fraction to be 3.5, 0.012, and 0.012 mL/g-h for the forward reactions and 0.49, 0.0025, and 0.001 h^{-1} for the reverse reactions. Surface site densities were 1.3, 0.042, and 0.042 $\mu\text{mol/g}$ for the first, second, and third sites, respectively. 10-year simulations show that including a slow binding site increases the arrival time of a uranium pulse by ~70%.

Keywords: uranium, granodiorite, reactive transport, desorption, column experiments

1. Introduction

Geologic disposal of nuclear waste is intended to protect humans and the environment from unacceptable levels of radioactive contamination over very long time periods (anywhere from thousands to millions of years). At contaminated environmental sites, it is necessary to predict the fate and transport of contaminants in groundwater over many decades or even hundreds of years to make informed site management decisions. These long timescales impart considerable uncertainty in risk assessment predictions, which are used as the basis for disposal system designs, contaminated site management decisions, and/or regulatory oversight of both of these.

Because of this uncertainty, there is often a tendency to be very conservative in predictive models (i.e., to make pessimistic assumptions and greatly simplify process descriptions). For models of fate and transport of contaminants in groundwater systems, this practice often results in using a simple, conservatively-estimated partition coefficient (K_d value, ml/g) to describe contaminant interactions with geologic media surfaces (Payne et al., 2013; Davis et al., 2005; Morel and Hering, 1993). The opposite extreme is to use a full description of the geochemical system, with all the solid- and solution-phase species and reactions accounted for in a model. An example of the latter is the component additivity (CA) modeling approach, in which contaminant interactions with media surfaces are represented using a weighted average of all the solid-solution reactions in the system (fully described mechanistically) with the abundances of different mineral surfaces in the system being used as weighting factors (Dong and Wan, 2014; Nebelung and Brendler, 2010; Davis et al., 2004; Waite et al., 2000). While in principle this is a

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4 very robust approach, it is inevitably data limited and requires an expensive and time-consuming
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6 characterization effort to succeed. Such expense is not justified for contaminants that interact so
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8 weakly with media surfaces that they can be considered nonreactive in risk assessment
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10 calculations or for those that interact so strongly that risk assessments are insensitive to the
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12 details of their interactions. However, a significant characterization effort may be justified for
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14 contaminants that interact just strongly enough to make their risk/dose calculations highly
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16 sensitive to the details of their adsorption/desorption interactions. The objective of this study is
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18 to demonstrate a practical approach to addressing the characterization of contaminant-media
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20 interactions for contaminants that fall into this latter category while avoiding both the excessive
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22 conservatism of a simplified approach and the detailed and costly characterization that comes
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24 with a full geochemical description of the system.
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31 Uranium is an example of a radionuclide contaminant that has a wide potential range of
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33 adsorption behavior to geologic materials and for which subtle differences in its adsorption
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35 behavior can make significant differences in its estimated risk contribution for nuclear waste
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37 repositories or contaminated sites. It is an element of concern for nuclear waste repository risk
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39 assessments because of its large inventory in spent nuclear fuel, its moderate solubility under
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41 oxidizing conditions, and the long half-lives of its isotopes. Uranium has a complex
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43 geochemistry that results in as much as a two to three order of magnitude range in its effective
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45 adsorption partition coefficient over a pH range from 6.5 to 9, with a strong dependence on
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47 carbonate solution concentrations (Vandenhove et al., 2009; Sheppard et al., 2006; Echevarria et
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49 al., 2001). At neutral pH, uranium adsorbs relatively strongly to many mineral surfaces. At pH
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51 greater than 8 in natural waters of typical alkalinity, its adsorption decreases significantly
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53 because of the tendency for stable neutral and negatively-charged uranyl carbonate (or ternary
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4 uranyl-Ca/Mg-carbonate) complexes to form and dominate uranium solution speciation. These
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6 neutral or negatively-charged complexes resist adsorption onto negatively-charged mineral
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8 surfaces.
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11 This complex geochemical behavior of uranium and the wealth of data available on
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13 uranium geochemistry have prompted some researchers to invoke detailed geochemical
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15 descriptions to predict uranium transport in subsurface environments (Dong and Wan, 2014;
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17 Shang et al., 2014, 2011). Recognition of the difficulties in fully characterizing environmental
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19 systems has also prompted semi-mechanistic approaches such as the Generalized Composite
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21 Surface Complexation Model of Davis and Curtis (2003) and the multi-rate models of Liu et al.
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23 (2009, 2008). In this paper, we introduce a simplified variation of these approaches and
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25 demonstrate an experimental method for parameterizing the modeling approach. We recognize
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27 that our method will require refinements and additional data collection to provide a robust
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29 predictive capability for a contaminant with complex geochemistry like uranium and may serve
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31 as a complementary method to the approaches mentioned above. However, the method
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33 (particularly with future refinements that we recommend later) may be directly suitable for
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35 contaminants with less complex geochemistry and solution speciation behavior than uranium.
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43 We used a crushed granodiorite from the Grimsel Test Site (GTS) in Switzerland as a
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45 model system, which has been used for many years to study nuclear waste disposal concepts and
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47 radionuclide transport processes in crystalline rock (Geckeis et al., 2004; Möri et al., 2003).
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49 Crystalline rock is being considered as a nuclear waste repository host medium in several
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51 countries (Schwartz, 2012; Soler et al., 2011), and it is also being considered for deep borehole
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53 nuclear waste disposal (Bates et al., 2014; Driscoll et al., 2012). An attractive feature of the GTS
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55 is that it has infrastructure in place to conduct field radionuclide transport experiments, and thus
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4 it offers the potential to compare radionuclide transport behavior observed at laboratory and field
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6 scales. We note here that many deep crystalline rock environments have reducing redox
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8 potentials and uranium mobility is known to be much lower in reducing environments than in
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10 oxidizing environments because U(IV) is much less soluble and more adsorptive than U(VI). In
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12 this paper we consider only oxidizing systems in which uranium is likely to remain in the more
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14 mobile U(VI) form. The intent here is not to mimic a specific system but rather to demonstrate
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16 methods that can be applied to any system to obtain a simplified description of contaminant
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18 transport that can be defensibly used in long-term risk assessments.
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24 Two of the most likely scenarios for radionuclide transport in crystalline rock (after being
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26 release from an engineered isolation system) are: (1) rapid advective transport through fractures
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28 in the host rock formation and/or (2) sorption of radionuclides to mobile native colloids or to
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30 colloids produced from engineered barrier materials (Dai et al, 2012; Huber et al., 2011; Liu et
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32 al., 2009; Liu et al., 2008). In order to assess and manage the risk of transport in rock systems
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34 that will be unique to each repository's geographic location, a general methodology would be
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36 helpful. Some of the important steps would be to (1) characterize potential flowpath surfaces,
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38 (2) interrogate radionuclide/geologic material interactions and kinetic rates of those interactions,
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40 and (3) model scenarios ranging from the most conservative (worst case) through more realistic
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42 cases with qualified uncertainties. This approach would provide a tool for decision makers to
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44 incorporate risk, sound science, and the need to eventually make a decision as the risk of doing
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46 nothing (surface storage) begins to exceed the risk of subsurface repository disposal strategies.
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48 This paper will focus on interpretation of batch and column experiments with uranium and pH
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50 changes to help develop methodologies to evaluate the dominant parameters for a more general
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52 assessment tool.
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2. Materials and Methods

2.1 Porous media

Granodiorite rock cores were collected from borehole CFM 11.002 at the Grimsel Test Site (GTS) in Switzerland and shipped to Los Alamos National Laboratory for processing. Cores were crushed using a percussion mortar, sieved into 75-150, 150-355, and 355-500 μm size fractions, thoroughly rinsed in high-purity water (Millipore, Milli-Q[®], > 18 M Ω cm resistivity), oven dried for 12 hours at 60 °C, and stored in centrifuge tubes until use. Optical microscope (Wild Heerbrugg, M420) microphotographs show that, although the three size fractions of crushed granodiorite used in the following experiments vary in size by a factor of 7, the relative abundance of light and dark grains appears to remain fairly consistent (Fig. 1).

Figure 1. Microphotographs of the three different grain sizes of crushed and sieved Grimsel granodiorite. 500 μm scale bars are shown in the lower right corner of each image.

Rock samples were characterized by quantitative x-ray diffraction (QXRD) analysis and used in batch sorption and column breakthrough experiments (Table 1). The bulk chemical analysis of the unaltered granodiorite and the weathered granodiorite (fracture fill material, or FFM) adjacent to and occupying the fractures was measured by x-ray fluorescence (Table 2).

Table 1. Quantitative X-ray diffraction interpretation (wt%) of Grimsel granodiorite materials.

Sample	Quartz	Plagioclase	K-Feldspar	Mica	Chlorite	Kaolinite	Epidote ^a	Total
75-150 µm	42.9	27.5	4.2	24.9	0.2	0.4	---	101.1
150-355 µm	24.3	43.8	7.8	23.6	0.2	0.2	---	99.9
355-500 µm	15.3	46.4	6.7	30.9	0.2	0.5	---	100.0

^aThere are tiny amounts (probably a few tenths of percent) of epidote.

Table 2. X-ray fluorescence analysis (wt%) of Grimsel materials.

Constituent	Granodiorite bulk	FFM bulk	Detection Limits
fuse ratio	7:1	7:1	7:1
Na ₂ O	4.01	3.15	0.0451
MgO	0.725	4.28	0.0300
Al ₂ O ₃	14.0	14.3	0.0313
SiO ₂	70.9	63.4	0.1507
P ₂ O ₅	0.115	0.124	0.0049
K ₂ O	4.22	4.90	0.0112
CaO	1.90	1.03	0.0084
TiO ₂	0.436	0.491	0.0092
MnO	0.081	0.086	0.0252
Fe ₂ O ₃	3.10	3.83	0.0041
V	29	41	13
Cr	bdl	bdl	10
Co	bdl	bdl	15
Ni	bdl	bdl	5
Cu	bdl	bdl	5
Zn	31	53	5
Ge	bdl	bdl	24
As	bdl	bdl	15
Rb	110	192	4
Sr	135	71	5
Zr	217	236	6
Ba	403	372	19
W	bdl	bdl	43
U	bdl	bdl	4
LOI	0.35	4.28	
total	99.931	99.970	
bdl = below detection limit LOI = loss on ignition			

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4 Although the FFM was not used in the experiments presented here, future work will focus on
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6 FFM because the vast majority of flow is expected to occur in fractures. The granodiorite data is
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8 intended to represent the worst-case scenario for transport, as the FFM is expected to have more
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10 attenuation potential due to its significant weathering and enrichment in clay minerals. The bulk
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12 chemical differences between the FFM and unaltered granodiorite are minor, with significant enrichment
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14 of Mg, minor enrichments of K and Fe, and minor depletions of Si, Na and Ca in the FFM compared to
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16 the granodiorite.
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20 One sample of crushed granodiorite in the 75-150 μm size range was analyzed for surface
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22 area using the BET gas adsorption method with Kr as a sorbent. The specific surface area of this
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24 sample was determined to be 0.142 m^2/g . The specific surface areas of the 150-355 μm and 355-
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26 500 μm granodiorite size fractions were not measured, but FFM samples in these size ranges
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28 were found to be 0.71 and 0.53 times the specific surface area of a 75-150 μm FFM sample.
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30 Assuming these ratios apply to the granodiorite, the specific surface areas of the 150-355 μm and
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32 355-500 μm granodiorite samples would be 0.10 and 0.075 m^2/g , respectively.
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39 2.2 *Synthetic groundwater*

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41 The groundwater used in all experiments was a synthetic Grimsel groundwater (SGGW)
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43 adjusted for additional constituents from the FEBEX bentonite packing material planned to be
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45 used as an engineered barrier to isolate waste packages within a repository. The recipe is given
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47 in Table 3. All solutions were made with high-purity water and analytical-grade reagents.
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51 SGGW in equilibrium with the atmosphere has a pH of 8.8-9.1.
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Table 3. Synthetic Grimsel groundwater recipe.

Compound	g L ⁻¹
Na ₂ SO ₄	0.1440
KCl	0.0048
MgCO ₃	0.0427
NaHCO ₃	0.2733
CaCl ₂	0.0130
H ₄ SiO ₄	0.0341
pH	8.8-9.1

2-(N-morpholino)ethanesulfonic acid (MES) was used to buffer the pH for all experimental solutions below pH 8.9 (6.9 and 7.9 solutions), and a 0.01 M MES solution was found to buffer the SGGW near pH 6.9. MES was selected as a buffer due to effective buffering in the pH 6-8 range while having a low tendency to complex with metal ions (Good et al., 1966), including uranyl ion (U(VI)²⁺). Buffering with inorganic acid/base pairs such as carbonate or phosphate could affect the aqueous speciation and transport behavior of uranium by forming uranyl complexes (carbonate) and possibly uranyl precipitates (phosphate). The use of MES as a buffer for uranium and actinide studies also follows examples set by others (Giammar and Hering, 2001).

2.3 Uranium and tritiated water

The uranium used in all experiments was a combination of ²³³U (Eckert and Ziegler) and natural uranium from a 1 g L⁻¹ ICP-MS standard (SpexCertiPrep). For all uranium solutions, approximately 98% of the uranium (mostly ²³⁸U) was from the ICP-MS standard, and about 2% was ²³³U added to ensure rapid, accurate, and inexpensive quantification by liquid scintillation counting. It was assumed that the ²³³U and ²³⁸U would behave identically with respect to adsorption and speciation in all experiments, as isotopic fractionation is expected to be minimal for sorption reactions without redox and/or precipitation (Ilton et al., 2012; Crançon al., 2010) .

A groundwater concentration of 6.5 μM uranium was used, and this concentration was experimentally verified to be under the solubility limit for the pH range of 6.9 to 9.1. Equilibrium speciation calculations using PHREEQC (Parkhurst and Appelo, 2013) also predicted uranium to be below the solubility limit for all solutions (with the exception of a slight supersaturation with respect to soddyite, $(\text{UO}_2)_2\text{SiO}_4 \cdot 2\text{H}_2\text{O}$, at pH 6.9). Tritium in the form of tritiated water was used as an ideal tracer and co-injected with uranium to provide mean groundwater residence times and to allow for the calculation of dispersivity coefficients in the columns.

The target pHs of the MES-buffered SGGW were 6.9 and 7.9. Table 4 shows relative abundances of uranium-bearing species in SGGW as predicted by PHREEQC (Parkhurst and Appelo, 2013) using the llnl.dat database (Johnson, 2010) with the addition of uranyl-calcium-carbonate and uranyl-magnesium-carbonate complexation constants from Dong and Brooks (2006).

Table 4. Fractional abundance of uranium-bearing species in SGGW as a function of pH (from PHREEQC).

Constituent	pH 6.9	pH 7.9	pH 8.8
$\text{UO}_2\text{Ca}(\text{CO}_3)_3^{2-}$	0.478	0.562	0.563
$\text{UO}_2\text{Mg}(\text{CO}_3)_3^{2-}$	0.181	0.217	0.230
$\text{UO}_2(\text{CO}_3)_2^{2-}$	0.141	0.0171	0.00261
$\text{UO}_2\text{Ca}_2(\text{CO}_3)_3^0$	0.0868	0.0998	0.0900
$\text{UO}_2(\text{CO}_3)_3^{4-}$	0.0785	0.0943	0.105
$\text{UO}_2(\text{CO}_3)^0$	0.0180	0.00022	---
$\text{UO}_2\text{Mg}_2(\text{CO}_3)_3^0$	0.00790	0.00935	0.00943
$\text{UO}_2(\text{OH})^+$	8.5e-5	1.1e-6	2.4e-8
UO_2^{2+}	2.5e-6	1.9e-9	8.8e-12
SUM	0.9910	0.9993	0.9999

Uranium adsorption partition coefficients (K_d values) for many different minerals have been reported to vary over several orders of magnitude between pH 7 and 9 (Joseph et al., 2013;

Kaplan and Serkiz, 2004; Missana et al., 2004; Mori, 2004; Davis and Curtis, 2003; Echevarria et al, 2001; Waite et al., 1994), with K_d values of essentially zero at pH greater than 9. For a given $p\text{CO}_2$, uranium exhibits much stronger adsorption at pH near 7 because of the greater abundance of positively-charged uranyl species (UO_2^{2+} and $\text{UO}_2(\text{OH})^+$) and less abundance of nonsorbing neutral and negatively-charged uranyl carbonate or uranyl-Ca/Mg-carbonate complexes.

2.4 *Analytical measurements*

Tritium and uranium concentrations were measured by liquid scintillation counting, or LSC (Perkin-Elmer Tri-Carb 2550 or Perkin-Elmer Quantulus), with energy ranges of 0-18.6 keV for tritium and 100-260 keV for uranium. An aliquot of a groundwater sample was weighed, diluted to 6 mL with high-purity water, and poured into a 20 mL polypropylene scintillation vial with 14 mL of liquid scintillation cocktail (PerkinElmer, Ultima Gold™ AB). Samples were counted for two 15 minute increments and the average was used to yield counts per minute per mL or CPM mL^{-1} . The transformed index of an external standard (tSIE) was used to adjust for variable quenching of the samples. pH measurements were made using a pH meter (Orion, Model 290) and a glass pH electrode (Fisher, AccupHast) calibrated with pH 4.01, 7.00 and 9.01 buffers.

2.5 *Batch adsorption experiments*

Batch adsorption experiments were conducted with the 150-355 μm fraction of crushed granodiorite material at pH 6.9 and 8.8. 12 mL of uranium-spiked SGGW (6.5 μM U) and 0.2, 0.5, or 1.0 g of granodiorite were added to 50-mL polypropylene centrifuge tubes. Control experiments without the geologic materials present were conducted at each pH to evaluate

adsorption to container walls. The experimental matrix is summarized in Table 5 and all experiments were conducted in duplicate. The relatively short-duration experiments were conducted mainly to place constraints on adsorption rate constants in the uranium-SGGW-granodiorite system.

Table 5. Batch adsorption experimental matrix.

Material	SGGW pH = 6.9	SGGW pH = 8.8
0.2 g Granodiorite	1, 10, 100, 1000 min	1, 10, 100, 1000 min
0.5 g Granodiorite	1, 10, 100, 1000 min	1, 10, 100, 1000 min
1.0 g Granodiorite	1, 10, 100, 1000 min	1, 10, 100, 1000 min
Control (no rock)	1, 10, 100, 1000 min	1, 10, 100, 1000 min

The centrifuge tubes were vertically positioned on an orbital shaker (VWR Scientific, DS-500) and horizontally oscillated at 180 RPM (Fig. 2).

Figure 2. Image of granodiorite batch adsorption-desorption experimental setup.

The tubes were also manually inverted several times at least once a day to ensure adequate mixing of the media and solution.

1 mL samples were collected after 1, 10, 100, and 1000 minutes and were measured for total uranium concentration. The solution removed for analysis was not replaced. At the end of

the experiments, the pH of the remaining solution in the centrifuge tubes was measured to determine if it had drifted during the experiments. Additional batch experiments were conducted with various column experiment components to evaluate adsorption and to aid in material selection. These components included Tygon[®] tubing (R-3603), polyethylene tubing used for columns, and glass wool used as a fill material at the ends of some columns.

2.6 *Column transport experiments*

Small columns were constructed from 6.5 cm lengths of 1 cm diameter polyethylene tubing. These small columns were devised to allow rapid and economical evaluation of sorption/desorption behavior under flowing conditions (and in duplicate or triplicate). The inside of the ends of the polyethylene columns were tapped to accept threaded polyethylene fittings with hose barbs on one end. Tygon[®] tubing (R-3606) and 3-way polycarbonate stopcocks were used to connect the columns to 60 mL polypropylene syringes (BD Falcon) at the bottom (influent side) of the column. Columns were wet-packed with 5.0 g of material by incrementally adding ~0.25 g of material to a column with solution ponded in the bottom. The columns were tapped to settle grains after sedimentation and to ensure uniform porosity between columns. A small amount of glass wool (~0.04 g) was used at the top and bottom to prevent grains from entering the tubing. Polypropylene syringes containing either uranium-bearing or uranium-free solution were loaded into syringe pumps (KD Scientific, Model 100) that were set to a flow rate of 0.3 mL h⁻¹. Flow was directed upward to help maintain saturation and to minimize the potential for air bubbles collecting in the column. An additional length of Tygon[®] tubing was connected to the barb on the top of the column and directed column effluent to a fraction collector (Gilson, FC-220) filled with 13 × 100 mm polyethylene test tubes. The fraction

collectors were enclosed in an acrylic plastic chamber with an evaporation pan to limit evaporation of samples before analysis (Fig. 3).

Figure 3. Image of column setup with 5 columns running in parallel.

The columns were initially flushed with uranium-free SGGW until the effluent pH stabilized to within 0.1 pH units of the influent solution. The influent solution was then switched to solution containing uranium and tritium. Syringes were refilled several times during the course of the experiments and were eventually changed to uranium- and tritium-free solution to observe desorption behavior in the column. Samples were collected at increments ranging from 90 minutes for early samples to 900 minutes for later samples and sample mass was weighed with a digital balance (Mettler, PL1200) to determine actual flow rates. pH measurements were recorded for all samples from one of the duplicate columns.

The column experimental summary is provided in Table 6. Flow interruptions, flow rate changes, and influent pH changes were introduced to help elucidate uranium adsorption and desorption mechanisms. Three size fractions were used (75-150 μm , 150-355 μm , and 355-500 μm) and were run in triplicate. Actual flow rates in all columns were calculated to be approximately 0.27 mL h⁻¹.

Table 6. Summary of solution chemistry and flow rates changes for column experiments.

Conditions	Approximate Start Time, hr	Approximate Start Volume, mL
Inject 6.5 mM U at pH 7.2	0	0
Inject U-free SGGW, pH 6.7	340	90
30-day Flow Interruption	575 (1290 end)	160
7-hr Flow Interruption	1380	185
4-day Flow Interruption	1425 (1520 end)	200
Double Flow Rate (approx.)	1650	240
Halve Flow Rate and pH to 7.2	1770	295
pH to 8.8	1900	330

2.7 Interpretive modeling

The batch and column experiments were interpreted using a multi-site/multi-rate reaction modeling approach where each different type of site could be assigned different adsorption and desorption rate constants and different surface site densities. Separate Fortran programs were used for modeling the two different types of experiments, although the equations used to model the adsorption and desorption reactions in each program were identical. The governing equations in the batch experiment model were:

$$\frac{\partial s_i}{\partial t} = k_{fi}c \left(1 - \frac{s_i}{s_{mi}}\right) - k_{ri}s_i \quad (\text{Eq. 1})$$

$$\frac{\partial c}{\partial t} = \frac{M}{V} \left[-\sum_i k_{fi}c \left(1 - \frac{s_i}{s_{mi}}\right) + \sum_i k_{ri}s_i \right] \quad (\text{Eq. 2})$$

where, c = concentration in aqueous phase, mol mL⁻¹

s_i = concentration on surface sorption site i , mol g⁻¹

t = time, h

k_{fi} = adsorption rate constant for sorption site i, mL g⁻¹ h⁻¹

k_{ri} = desorption rate constant for site i, h⁻¹

s_{mi} = surface site density (maximum adsorption capacity) for sorption site i, mol g⁻¹

M = mass of solids, g

V = volume of solution, mL

The governing equations for the column transport model were Eq. 1 plus the following equation for the mobile aqueous phase:

$$\frac{\partial c}{\partial t} - v \frac{\partial c}{\partial x} + D \frac{\partial^2 c}{\partial x^2} + \frac{\rho_B}{\phi} \left[-\sum_i k_{fi} c \left(1 - \frac{s_i}{s_{mi}} \right) + \sum_i k_{ri} s \right] \quad (\text{Eq. 3})$$

where, v = flow velocity, cm h⁻¹

D = dispersion coefficient, cm² h⁻¹

ρ_B = bulk density of solids, g cm⁻³

ϕ = porosity

In addition to solving equations (1) and (2), the batch model allowed the volume of solution in the reactor to be changed at specified times to account for sampling losses. Equations (1) and (2) were solved using a 4th-order Runge-Kutta algorithm.

The column model solved equations (1) and (3) simultaneously using an implicit finite difference algorithm. The model allowed for varying injection functions to be specified at the column entrance ($x = 0$). It also allowed for flow rate changes and changes to the reaction parameters k_{fi} , k_{ri} , and s_{mi} at multiple times during a simulation. Changes to the reaction parameters could be specified when the pH of the injection solution was changed or when a transition was made from injecting uranium-spiked water to uranium-free water (to simulate adsorption-desorption hysteresis). The changes to reaction parameters were propagated through the columns in the same manner as a conservative tracer.

Our modeling approach was to try to simultaneously match the combined data from both the batch and column experiments using a single set of reaction parameters and a minimal

number of sorption site types. By matching both the batch and column data, the reaction parameters were more highly constrained than if the data from only one type of experiment were matched. The goal was to use only as many site types as necessary to achieve a reasonable qualitative match to the data. An automated parameter estimation algorithm, such as PEST (Doherty, 2010, 2009), was not employed to obtain the matches to the data. It was considered more important to match subtle data features containing only a few observations even if it meant a poorer match to features containing many data points that would have dominated a least-squares or other minimization exercise.

3. Results

3.1. *Batch sorption experiments*

The pH 8.8 batch adsorption experiments indicated no measurable adsorption of uranium to the granodiorite. Figure 4 shows the data from the pH 6.9 batch adsorption experiments along with model curves that represent simultaneous matches to both the batch and column breakthrough data. The solid model curves of Figure 4 were generated using the rate constants and site densities that provided good matches to the initial pH 7.2 portion of the breakthrough curves in the column experiments using the 150-355 μm granodiorite sizefraction (the same size fraction as in the batch experiments). The pH 7.2 parameters from the column experiments (first set of parameters in Table 7 of Section 3.3) were used instead of the pH 6.7 parameters because the pH in the batch experiments drifted upward from a starting pH of 6.9 to final pHs of 7.25, 7.49, and 7.83 in the experiments with 0.2 g, 0.5 g, and 1.0 g of granodiorite, respectively (the batch control experiments drifted up to pH 7.06).

Figure 4. Granodiorite batch sorption data and model results for experiments with a starting pH of 6.9. Data points are averages of two observations and are corrected for interactions observed in control experiments. The solid curves were obtained using adsorption and desorption rate constants of 2.5 ml/g-hr and 0.25 hr⁻¹, respectively, for the first adsorption site (approximately the same as for the first site at a pH of 7.2 in the column experiments). The dashed curves (labeled “model (2)”) were obtained using the same adsorption rate constant but with desorption rate constants of 0.15 hr⁻¹ for the 0.2-g experiments and 0.43 hr⁻¹ for the 1.0-g experiments.

The dashed curves of Figure 4 correspond to improved fits to the 0.2 and 1.0 g data sets after adjusting the desorption rate constant of the first sorption site. The desorption rate constant for the 0.2 g experiments was decreased from 0.25 to 0.15 hr⁻¹ and the desorption rate constant for the 1.0 g experiments was increased from 0.25 to 0.43 hr⁻¹. These adjustments were considered justified because uranium is known to adsorb more strongly at lower pHs in the pH range from 6 to 8 (Vandenhove et al., 2009). Given that the final pH was lowest in the 0.2 g experiments, it is reasonable that the desorption rate constant would be smallest in the 0.2 g experiments. We note that the trend of less uranium adsorption per unit mass of solids as the solids mass increased in the batch experiments is the opposite of what is expected for a nonlinear adsorption isotherm, which has frequently been observed for uranium on various mineral

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4 surfaces (Arnold et al., 2011; Dean, 2010; Davis, 2001; Kohler and Davis, 2001; Kohler et al.,
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6 1996; Waite et al., 1994). We attribute this trend to the tendency for uranium to adsorb more
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8 strongly at the lower pHs of the experiments with lower solid-to-solution ratios. We likely
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10 would have seen the expected trend if the pH had been constant in all the experiments.
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14 The adsorption rate constants were kept the same for all experiments (2.5 ml/g-hr), so a
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16 smaller desorption rate constant translates to a greater effective partition coefficient ($K_d = k_f/k_r$),
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18 and a larger desorption rate constant translates to a smaller effective partition coefficient. The
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20 model curves were not sensitive to the rate constants and surface densities of the second and
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22 third sites because the batch experiments were too short to observe the contribution of these
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24 slower sites. In effect, the batch experiments were useful for helping constrain the adsorption
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26 and desorption rate constants of only the first site in the column experiments. The surface
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28 coverage of uranium at the end of the 0.2-g batch experiments was calculated to be 0.78
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30 $\mu\text{moles}/\text{m}^2$, which is about 40% of the total uranium sorption site density of 1.92 $\mu\text{moles}/\text{m}^2$ for
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32 silicate surfaces used by Davis and Curtis (2003), whereas the surface coverages in the 0.5-g and
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34 1.0-g batch experiments were calculated to be 0.39 and 0.23 $\mu\text{moles}/\text{m}^2$, respectively.
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41 The solutions were predicted by PHREEQC calculations predicted the solutions to be
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43 slightly supersaturated with respect to amorphous SiO_2 and soddyite $((\text{UO}_2)_2\text{SiO}_4 \cdot 2\text{H}_2\text{O})$ at pH
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45 6.9, suggesting that there could have been some uranium sorption and/or precipitation during the
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47 batch experiments. However, the 6.5 μM uranium stock solution stored in a Teflon[®] bottle and
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49 buffered to pH 6.9 remained stable with respect to uranium concentrations for periods much
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51 longer than the batch experiments.
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3.2. Material interactions experiments

The pH 7.2 granodiorite column experiments were a challenge to interpret because of significant interactions between uranium and some of the column materials. Some simple batch experiments were conducted to screen for the uranium interactions with system components and to allow for quantification and correction (Fig. 5).

Figure 5. Uranium interactions with granodiorite column components in batch experiments (144 hrs, 10 ml solution). Note: Polyfiber was not used in columns.

Column experiments conducted at pH 8.8 and shown in Figure 6 indicate no measurable adsorption or retardation of uranium to either the granodiorite or to the materials used in these experiments (i.e., polyethylene columns and Tygon[®] tubing, R-3606).

Figure 6. ^3HHO and uranium breakthrough curves from a granodiorite column experiment at pH 8.8.

Results of the column system control experiments and model matches to the data are shown in Figure 7.

Figure 7. Tritium and uranium breakthrough curves in control columns at pH 7.2. Model parameters from red model curves were used to construct injection functions in granodiorite column experiments.

The model results of the control experiments with empty columns were used to simulate the injection pulse in the granodiorite experiments after accounting for the sorption effects of the other system components. To approximate the injection pulses in the granodiorite columns

(which had longer injection pulses and less dispersion than the empty control columns), the attenuation parameters from the model fits in Figure 7 were used to predict the injection pulses.

Additional experiments (not shown here) were conducted to evaluate the influence of column components at pH 7.9 and also to better quantify the effects of the glass wool on uranium transport at pH 7.2 (Dittrich et al., 2014; Dittrich and Reimus, 2013; Reimus and Dittrich, 2013). The pH 7.9 experiments included separate systems with either Tygon[®] or Teflon[®] tubing with polyethylene columns. It was apparent that there was less attenuation of uranium in the Tygon[®]/PE control system at pH 7.2, although attenuation was still significant enough to have to account for it. There was no attenuation of uranium relative to tritium in the Teflon[®]/PE columns, suggesting that interactions with the PE columns at pH 7.9 are minimal and the observed uranium attenuation in the Tygon[®]/PE system is from interactions with the Tygon[®] tubing.

3.3. Column experiments

The data from the column experiments using the 75-150 μm , 150-355 μm , and 355-500 μm size fraction of granodiorite are shown in Figure 8 overlaid with model simulations and simulated uranium injection functions that take into account uranium attenuation in the tubing and other column system components. Reaction parameters resulting in the model curves are listed in Table 7.

Figure 8. Tritium and uranium breakthrough curve data and model simulations for granodiorite size fractions of 75-150 μm (top), 150-355 μm (middle), and 355-500 μm (bottom).

Table 7. Reaction model parameters yielding matches to granodiorite column transport data shown in Figure 8. In all cases, first number is for Site 1, second number is Site for 2, and the third number is for Site 3. *Italic text* indicates values that were varied for different size fractions.

75-150 μm material	k_f, mL/g-hr	k_r, hr⁻¹	S_m, $\mu\text{mol/g}$
pH 7.2 adsorption	3.5, 0.012, 0.012	(0.49/0.42) ^a , 0.0025, 0.001	1.3, 0.042, 0.042
pH 6.7 desorption	3.5, 0.012, 0.012	0.077, 0.0001, 0.0001	1.3, 0.042, 0.042
pH 7.2 desorption	3.5, 0.012, 0.012	0.21, 0.0025, 0.001	1.3, 0.042, 0.042
pH 8.8 desorption	1.0, 0.5, 0.2	3.0, 1.0, 0.01	1.3, 0.042, 0.042
150-355 μm material	k_f, mL/g-hr	k_r, hr⁻¹	S_m, $\mu\text{mol/g}$
pH 7.2 adsorption	2.5, 0.0095, 0.0095	(0.46/0.42/0.35) ^a , 0.0025, 0.001	1.3, 0.042, 0.042
pH 6.7 desorption	2.5, 0.0095, 0.0095	0.077, 0.0001, 0.0001	1.3, 0.042, 0.042
pH 7.2 desorption	2.5, 0.0095, 0.0095	(0.21/0.14) ^a , 0.0025, 0.001	1.3, 0.042, 0.042
pH 8.8 desorption	1.0, 0.5, 0.2	3.0, 1.0, 0.01	1.3, 0.042, 0.042
355-500 μm material	k_f, mL/g-hr	k_r, hr⁻¹	S_m, $\mu\text{mol/g}$
pH 7.2 adsorption	1.3, 0.0075, 0.0075	0.42, 0.0025, 0.001	1.3, 0.042, 0.042
pH 6.7 desorption	1.3, 0.0075, 0.0075	0.077, 0.0001, 0.0001	1.3, 0.042, 0.042
pH 7.2 desorption	1.3, 0.0075, 0.0075	0.42, 0.0025, 0.001	1.3, 0.042, 0.042
pH 8.8 desorption	1.0, 0.5, 0.2	3.0, 1.0, 0.01	1.3, 0.042, 0.042

^aSlashes and parentheses indicate where different desorption rate constants were used for different columns packed with the same size fraction (first site only)

Figure 9 shows the pH and flow rate as a function of volume eluted in one of the 75-150 μm size fraction granodiorite columns.

Figure 9. pH and flow rate history during column experiments (measured in a column containing 75-150 μm size fraction).

4. Discussion

4.1 Reaction parameters

The reaction parameters of Table 7 are in excellent agreement for a given sieve size fraction, reflecting the high reproducibility of the experiments. Furthermore, the adsorption rate constants of the dominant sorption site (Site 1 in Table 7) scale almost exactly with the deduced specific surface areas of the granodiorite size fractions mentioned at the end of Section 2.1. The adsorption rate constants for Site 1 are 3.5, 2.5 and 1.8 mL/g-hr for the 75-150 μm , 150-355 μm , and 355-500 μm size fractions, respectively, and have the same ratio of values as the specific surface areas of 0.14, 0.10, and 0.075 m^2/g for these size fractions. The adsorption rate constants for Sites 2 and 3 in Table 7 also have similar ratios, although they are not exactly the same as the ratios of the specific surface areas. Slight differences in reaction parameters for the replicate columns were allowed in recognition that there were potentially minor differences in the porosities and the material heterogeneity in the columns. Davis and Curtis (2003) used a maximum uranium sorption site density of 1.92 $\mu\text{moles}/\text{m}^2$ on silicate surfaces based on the recommendations of Davis and Kent (1990). In our modeling we assumed ~ 1.3 $\mu\text{moles}/\text{g}$ as a maximum surface site density, which implies a specific surface area of ~ 0.68 m^2/g (i.e., $1.3/1.92$) to be in agreement with the value used by Davis and Curtis (2003).

The adsorption and desorption rate constants of the first adsorption site (i.e., the site with the fastest rates and the largest site density) were not well constrained by the column experiments. The model fits were relatively insensitive to these rate constants provided that the ratio of the constants was fixed and that the rate constants exceeded some lower threshold value below which earlier-than-observed uranium breakthrough was predicted. The short-duration batch adsorption experiments (Fig. 4) helped constrain the adsorption rate constant to be

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4 approximately 2.5 mL/g-hr (much faster or slower rate constants would result in a poor match to
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6 the batch data). Several points are worth discussing with respect to the best-fitting reaction
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8 parameters of Table 7 and the uranium breakthrough curves of Figure 8. Although the
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10 parameters of Table 7 provide good matches to the column data sets, they should not necessarily
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12 be considered unique. There were some correlations noted between the parameters for a given
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14 site; for instance, similar results could be obtained by increasing the surface site density and
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16 decreasing the adsorption rate constant for a site (particularly for sites that have relatively small
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18 surface densities) while keeping the desorption rate constant approximately the same for that site.
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20 Davis and Curtis (2003) found a similar negative correlation between site densities and
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22 equilibrium constants for surface complexation reactions in their modeling efforts, which did not
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24 consider reaction kinetics. Also, the desorption rate constants of the second and third sites at pH
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26 6.7 were not well constrained; these rate constants could be varied over a relatively large range
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28 from zero to 0.0003 hr^{-1} without having much effect on the model curves. In effect, these rate
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30 constants could not be distinguished from zero. The range of reaction parameters resulting in
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32 reasonable fits to the pH 7.2 column data was better constrained than for the pH 6.7 data.
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42 *4.2 Deductions about uranium adsorption and desorption processes from column experiments*

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44 It is reasonable to question whether three different adsorption sites are really necessary to
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46 explain the column transport data, particularly since the last two sites have small surface
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48 densities and differ only in their desorption rate constants at pHs higher than 6.7. Figure 10
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50 shows the results of sequentially fitting the data sets from one of the 75-150 μm granodiorite
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52 column experiments (column 8) with one, two, and three adsorption sites. The results of this
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54 sequential fitting exercise for other column experiments were very similar and are not shown.
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59 The model parameters corresponding to the fits of Figure 10 are listed in Table 8.
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Figure 10. Model simulations and uranium data from one experiment (column 8) comparing a one-site, two-site, and three-site model.

Table 8. Model parameters yielding matches to the column 8 data using a one-site, two-site, and three-site model. For each model, the first number is for Site 1, second number is for Site 2, and third number is for Site 3.

One-site model	k_f , mL/g-hr	k_r , hr ⁻¹	S_m , μ mol/g
pH 7.2 adsorption	3.5	0.35	1.3
pH 6.7 desorption	3.5	0.07	1.3
pH 7.2 desorption	3.5	0.35	1.3
pH 8.8 desorption	1.0	3.0	1.3
Two-site model	k_f , mL/g-hr	k_r , hr ⁻¹	S_m , μ mol/g
pH 7.2 adsorption	2.5, 0.021	0.46, 0.0025	1.3, 0.084
pH 6.7 desorption	7.3, 0.021	0.22, 0.0001	1.3, 0.084
pH 7.2 desorption	2.5, 0.021	0.46, 0.0025	1.3, 0.084
pH 8.8 desorption	1.0, 0.2	3.0, 0.02	1.3, 0.084
Three-site model	k_f , mL/g-hr	k_r , hr ⁻¹	S_m , μ mol/g
pH 7.2 adsorption	1.3, 0.0075, 0.0075	0.42, 0.0025, 0.001	1.3, 0.042, 0.042
pH 6.7 desorption	1.3, 0.0075, 0.0075	0.077, 0.0001, 0.0001	1.3, 0.042, 0.042
pH 7.2 desorption	1.3, 0.0075, 0.0075	0.42, 0.0025, 0.001	1.3, 0.042, 0.042
pH 8.8 desorption	1.0, 0.5, 0.2	3.0, 1.0, 0.01	1.3, 0.042, 0.042

It is apparent that the ability of the model to fit the data is significantly improved by increasing the number of adsorption sites from one to two. A one-site model is not capable of

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4 matching the leveling-off of concentrations at C/C_0 values less than 1 during the uranium
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6 injection phase of the experiments or the slow desorption behavior observed later in the
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8 experiments. The incremental improvement of a three-site model over a two-site model is much
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10 more subtle, with an obvious improvement only during the late portion of the experiment where
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12 the pH was raised from 6.7 to 7.2. Here, the addition of a third site with a somewhat slower
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14 desorption rate constant than the second site provides a better fit to this small portion of the
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19 experiment.
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21 Of particular interest for risk assessments over long time and distance scales is the
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23 sensitivity of the model fits to the slow desorption rate constants of the second and third sorption
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25 sites, as long-term model predictions are significantly affected by subtle differences in slow
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27 desorption rates. Figure 11 compares the three-site model curve of Figure 10 with a curve
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29 generated using the same parameters, except that the desorption rate constant of the third
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31 sorption site was set to zero. It is apparent that changing the desorption rate constant of the third
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33 site to zero had little overall effect on the model curve, which suggests that the column
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35 experiments were not conducted in a manner that would allow them to very accurately
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37 interrogate slow desorption rates at pH 7.2. The implications of this result are discussed in
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43 Section 4.3.
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Figure 11. Uranium breakthrough column data (column 8) and model simulations comparing the three-site model with the desorption rate constants from Table 8 (black line) and the desorption rate constant of the third site set equal to zero (red line).

4.3 Effect of geochemical and flow transients (e.g., pH, flow rate, flow interruptions)

For the model to capture the abrupt drop in uranium concentrations immediately after the transition from injection of uranium-bearing water to uranium-free water, the desorption rate constant for all sorption sites had to be decreased significantly at the time of the transition. As Figure 9 shows, this abrupt decrease corresponded to a drop in pH from about 7.2 to 6.7, and given that uranium partitioning to solids is predicted to increase with such a pH change, the decrease in the desorption rate constants is reasonable. Increasing the adsorption rate constants would have a similar effect, but decreasing the desorption rate constants was more logical because the uranium was already adsorbed to the solids at the time of the pH change. The ability to capture the concentration drop with the model was most sensitive to the desorption rate constant of the first site, with the model being relatively insensitive to the second and third desorption rate constants. The effective partition coefficient for any given site is equal to the ratio of the adsorption to desorption rate constants (i.e., $K_{di} = k_{fi}/k_{ri}$), so the changes in Table 7

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4 suggest an increase in the partition coefficient by a factor of 5 to 6 (for the first site) when
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6 switching from pH 7.2 to pH 6.7. This change is reasonable for uranium partitioning as a
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8 function of pH at constant $p\text{CO}_2$ on various mineral surfaces (e.g., uranium sorption to
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10 ferrihydrite at $p\text{CO}_2 = 0.01$ atm, Davis and Curtis, 2003, Fig. 5.1).
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14 We note that the transition from uranium-bearing to uranium-free solutions frequently
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16 resulted in a short spike in uranium concentrations at the time of the transition. We attribute this
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18 to a pressure/flow transient during the syringe change-out that likely resulted in some uranium
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20 mobilization., possibly from the tubing surfaces rather than the geologic media. There was also a
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22 small pH spike that was observed during the transition (at ~100 ml in Figure 9), which could also
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24 have caused a spike in uranium concentrations.
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28 Increases in pH late in the column experiments clearly promoted uranium desorption. It
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30 was interesting, however, that the best-fitting desorption rate constant for the first site was lower
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32 after the pH was raised from 6.7 to 7.2 than it was during the initial pH 7.2 portion of the
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34 experiment, suggesting some adsorption/desorption hysteresis. Also, the increase to pH 8.8 did
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36 not result in extremely rapid or complete desorption of the uranium, which might be expected
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38 based on the fact that no uranium adsorption was observed in either the batch or column
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40 experiments conducted at pH 8.8. These results suggest that uranium that adsorbed at lower pHs
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42 or that was exposed to lower pHs while adsorbed to the granodiorite surfaces was more resistant
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44 to desorption after the pH was increased than it would have been if the pH had always remained
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46 at the higher pH. Mass recovery calculations indicated that the amount of uranium remaining in
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48 the columns after extended periods of flow at pH 8.8 for the 75-150 μm , 150-355 μm , and 355-
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50 500 μm size fraction columns were 22%, 22%, and 16%, respectively. These recoveries cannot
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52 be unequivocally attributed to the geologic materials because of the observed interactions of
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4 uranium with the system components (about 20% of the uranium injected into the columns was
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6 assumed to be held up by the column system components based on the results of the
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8 blank/control column experiments). However, we note that there was complete recovery of
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10 uranium in the pH 8.8 column experiments (Fig. 6) using the same column components as in the
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12 lower pH experiments. If the incomplete recovery was due to adsorption to the system
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14 components, this adsorption must have occurred at the lower pH and not been reversible when
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16 the pH was increased.
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21 Flow interruptions and flow rate changes had relatively minor effects on the uranium
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23 concentrations. The exception was the 30-day flow interruption, which resulted in a significant
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25 increase in concentration that the model did not predict. When flow was re-established, it is very
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27 possible that the first water collected had artificially high uranium concentrations because of re-
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29 dissolution of precipitated uranium in the tubing. The model predicted that the long flow
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31 interruption would actually result in a decrease in uranium concentration rather than an increase,
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33 and the slight dip in uranium concentrations observed after the initial spike is consistent with this
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35 prediction. The two subsequent flow interruptions and the increase in the flow rate did not result
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37 in significant shifts in uranium concentrations, also consistent with model predictions. The
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39 reason for this behavior is that the equilibrium partitioning in the columns was shifted to greater
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41 uranium partitioning to the solids after the pH decrease. In effect, the release of uranium was
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43 dictated by a sharp increase in the ability of the granodiorite to adsorb uranium, and in particular,
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45 the ability of the sites with the fastest sorption/desorption kinetics in the column to adsorb
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47 uranium (i.e., the first site). The drop in pH effectively caused the first (fastest) site type to
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49 rapidly transition from being nearly completely loaded with uranium at pH 7.2 to being
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51 significantly under-loaded at pH 6.7. The lower, steady concentrations in the long tail after the
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4 transition essentially reflect this new partitioning, rather than a true desorption rate. In other
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6 words, they reflect a desorption rate only of the most abundant and fastest site, not of the slower
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8 sites.
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11 Changes in flow rates or flow interruptions of various durations can be useful for
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13 interrogating slow desorption kinetics, particularly when implemented well into the tail of a
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15 column breakthrough experiment. The magnitude of an increase in concentration after a flow
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17 interruption or after a decrease in flow rate can provide information on desorption kinetics,
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19 although it can also indicate an influence of diffusion and/or adsorption-desorption behavior in
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21 secondary porosity in the column (Liu et al., 2013, 2008). The magnitude of the concentration
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23 decrease after a flow rate increase can provide the same information. These generalizations hold
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25 true only if the contaminant is not effectively in equilibrium with the fastest sorption sites on the
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27 solids in the column. This was not strictly the case for uranium at pH 6.7 in the columns because
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29 of the shift in equilibrium partitioning to favor stronger partitioning to all sites when the pH was
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31 dropped from 7.2 to 6.7. The lack of any significant increase or decrease in concentration after a
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33 flow interruption or flow rate change suggests that adsorption and desorption rates were
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35 approximately equal at the time of the flow transients (and there were no dual-porosity effects).
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37 The slight decrease in concentrations after the first long flow interruption (ignoring the spike that
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39 probably resulted from dry-out of the column tubing) indicates that adsorption rates were slightly
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41 greater than desorption rates at the time of this interruption, which reflects that there were still
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43 plenty of unoccupied sorption sites in the column at the lower pH. The fact that concentrations
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45 did not change much with the flow interruptions and flow rate changes, particularly the late ones,
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47 also suggests that there was very little diffusive mass transfer between primary and secondary
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porosity in the system. Consequently, the model assumed only single-porosity transport behavior.

4.4 Implications for large-scale reactive transport predictions

Despite the shortcomings and lessons learned in our experiments, we believe that the small column procedure holds great promise for being able to interrogate the slow desorption rates that can be a significant source of uncertainty in large-scale performance assessment calculations. To illustrate the sensitivity of large-scale reactive transport predictions to slow desorption rates, Figure 12 shows the results of some large-scale predictive simulations using the pH 7.2 parameters determined for the largest granodiorite size fraction in the column experiments. These simulations were conducted using the same three-site model that was used to match the column data. It was assumed that there was a one-year groundwater travel time from the source to the point of compliance (not unusual for a fractured crystalline rock system). The uranium source was either a continuous input concentration (solid curves) or a 10-year constant-concentration pulse (dashed curves), with the input concentrations being the same as those used in the batch and column experiments (6.5 μM). The black curves correspond to model predictions using the exact parameters given in Table 7 for the largest size fraction and the red curves correspond to model predictions using these same parameters except that the desorption rate constant of the third site was decreased by one order of magnitude.

Figure 12. Large-scale model predictions for continuous and 10-year pulse inputs using reaction parameters for the three-site model (black curves) and for the three-site model with the desorption rate constant of the third site decreased by one order of magnitude (red curves). Groundwater travel time is one year.

These different desorption rate constants for the third site cannot be readily distinguished from the current column experiment data, and it would be very difficult to interrogate either of these rate constants in batch sorption/desorption experiments given the predominance of the first adsorption site. However, it should be possible to interrogate these rate constants and distinguish between them in more carefully-designed column experiments (i.e., experiments implementing the suggested improvements in section 4.5).

Figure 12 shows that for a continuous input, the arrival of uranium at the compliance point is delayed by about 30% (~8 years) for the slower desorption rate constant (of the third site) relative to the faster desorption rate constant. The difference between the desorption rate constants is more striking in the case of the pulse input (dashed curves), where the delay in arrival time for the slower rate constant is about 70% (~17 years) relative to the faster desorption rate constant. In addition, the peak uranium concentration is over 3 times lower in the case of the slower desorption rate constant. The reason for the greater impact on the pulse input is that the

small fraction of slow sites exerts a greater influence when the total inventory of uranium transporting through the system is smaller, as is the case for the 10-year pulse compared to the continuous input. With a continuous input, the slow sites fill up rather quickly after the leading edge of the “plume” passes by, which results in these sites no longer exerting much influence on transport. With a pulse input, a greater fraction of the slow sites remain unoccupied as the plume passes by, so these sites continue to have an effect on transport.

The slow sites can also have a greater impact on reactive transport when the source has a smaller concentration. Figure 13 shows the results of four continuous-input simulations, with two being identical to those of Figure 12, and two having an order-of-magnitude lower input concentration than was assumed in the simulations of Figure 12. It is apparent that (1) for the same rate constant, there is greater uranium attenuation at the lower input concentration, and (2) the difference between the curves associated with the slower and faster desorption rate constants is much greater at the lower input concentration. The explanation for these results is the same as for the pulse input versus the continuous input at the higher concentration. The total inventory of

Figure 13. Large-scale model predictions for continuous inputs of two different concentrations using the reaction parameters for the three-site model and for the three-site model with the desorption rate constant of the third site decreased by one order of magnitude. Input concentrations are 6.5 mM (hi) and 0.65 mM (low). Groundwater travel time is one year.

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4 uranium is much smaller in the case of the lower input concentration, so the slow sites do not fill
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6 up as rapidly and exert a greater influence on reactive transport at the lower concentration.
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9 These simulations illustrate how important even a relatively small number of sites having
10 slow desorption rates can be for predictions of large-scale reactive transport. Our experimental
11 method is intended to interrogate the rate constants of these relatively sparse slow sites, which
12 are very difficult to interrogate using batch experimental methods. We recognize that the current
13 set of experiments was not optimal for this interrogation; hence the suggested improvements of
14 Section .5. However, among the positive attributes of our column experiments was the use of
15 uranium concentrations approaching the solubility limit and the extended periods of time that
16 uranium was injected into the columns at these concentrations. These strategies maximized the
17 loading of uranium onto the granodiorite and increased the probability that significant amounts
18 of uranium would adsorb to the slower sites that we were targeting for interrogation. The
19 estimated loading of the uranium onto the granodiorite in the columns was in the range of 0.6 to
20 1.0 $\mu\text{M}/\text{m}^2$, depending on the size fraction (higher loadings on larger size fractions), allowing for
21 some uncertainty in the fraction adsorbed to granodiorite versus system components. These
22 loadings are generally higher than in the batch experiments. In effect, this approach increased
23 the desorption signal that could be observed from the slow sites after uranium concentrations
24 were decreased.
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49 *4.5 Integrating the method with other approaches for describing contaminant transport*

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51 The multi-site, multi-rate reactive transport modeling approach that we used here is well
52 suited to fitting the data from column experiments that are designed to interrogate slow
53 adsorption/desorption sites. This method should be quite robust for developing large-scale
54 reactive transport process models for contaminants exhibiting adsorption/desorption behavior
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4 that is not strongly dependent on solution chemistry, such as simple cations that do not form
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6 strong solution complexes and interact with surfaces primarily by cation exchange.
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9 To be completely useful for large-scale predictions of a contaminant like uranium, which
10
11 has a strong dependence on solution parameters that may be spatially and temporally variable,
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13 the method should involve experiments conducted over the expected range of solution conditions
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15 to ensure rate constants can be determined as a function of these conditions. It is important to
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17 carefully control and measure the solution conditions in each experiment so that one is not
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19 misled by behavior that might be attributed to subtle changes in the conditions. We suspect that
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21 some of the minor upward and downward trends in uranium concentrations when the pH was
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23 held at 6.7 in our column experiments might have been caused by subtle changes in alkalinity,
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25 which we were not strictly controlling.
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31 Davis and Curtis (2003) incorporated generic surface complexation reactions into their
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33 modeling approach and used a geochemical speciation model to deduce multiple uranium surface
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35 complexation reactions of varying strength (i.e., varying magnitudes of equilibrium constants)
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37 that were most likely to be responsible for the behavior they observed under numerous sets of
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39 solution conditions in batch experiments. This allowed them to develop a single model with a
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41 minimal number of adjustable parameters without accounting for specific uranium-mineral
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43 surface complexation reactions. This model could predict uranium adsorption over a relatively
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45 wide range of solution conditions. However, they were unable to obtain good constraints on rate
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47 constants from their batch experiments, and their forward predictions of column experiments
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49 using a local-equilibrium modeling approach (i.e., fast reaction kinetics relative to transport
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51 rates) did not match the tails in the column experiments very well. Our approach sacrifices some
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53 of the mechanistic basis of their approach to obtain better constraints on rate constants of
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4 relatively sparse sites, which, as we have shown (Section 4.3), can have a significant impact on
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6 large-scale transport predictions. There is no fundamental reason why we couldn't adopt an
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8 interpretive modeling approach for the column experiments that incorporates detailed
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10 geochemical speciation AND allows adsorption and desorption reactions to be described by rate
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12 expressions rather than equilibrium expressions. We believe that this is a reasonable next step in
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14 advancing our method and integrating it better with methods such as that used by Davis and
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16 Curtis (2003) and adopted/modified more recently by others (Liu et al., 2009, 2008) while
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18 keeping the model as simple as possible so that it can be readily incorporated into larger-scale
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20 risk assessment models.
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26 The small size of the columns used in our experiments makes it possible to conduct
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28 numerous experiments, including duplicates, under different flow and geochemical conditions
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30 without great expense. However, column experiments are still fundamentally more complex to
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32 conduct than batch experiments, so it will always be possible to evaluate more solution variables
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34 for a fixed amount of resources using batch experiments. We believe a good approach is to
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36 balance the use of batch experiments to evaluate equilibrium partitioning and to constrain rapid
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38 adsorption and desorption rates with column experiments to interrogate the sparser, slower
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40 adsorption sites that have a significant impact on large-scale reactive transport predictions.
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46 *4.6 Lessons learned and suggested improvements to the experimental method*

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49 We consider the experiments and interpretations described in this paper to be an attempt
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51 at demonstrating an improved method for parameterizing reactive transport process models that
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53 can be used in risk assessments for predicting contaminant transport over long time and distance
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55 scales. As an initial attempt, there were a number of lessons learned and improvements that
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57 could be made in future applications of the method. First, it would be preferable to use
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4 experimental systems consisting of materials that have little or no interaction with the
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6 contaminant of interest, if possible. The interactions of uranium with the Tygon[®] tubing and
7
8 other system components at the lower pHs in our experiments introduced uncertainty into the
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10 model interpretations and reactive transport parameter estimates. However, we showed that
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12 control experiments allowed these interactions to be reasonably well quantified so that they
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14 could be accounted for in the experiment interpretations (by correcting the injection functions).
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16 It is recommended that future applications of the small column method involve batch control
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18 experiments to screen for undesirable interactions and blank columns to allow any unavoidable
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20 interactions to be quantitatively accounted for.
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26 A second improvement to the method would be to conduct experiments in which the solution
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28 conditions are held constant for much longer time periods when desorption is being observed.
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30 This would allow interrogation of slower desorption rate constants than those deduced in this set
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32 of experiments. It may be preferable to keep the solution conditions constant until the
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34 contaminant concentration drops to detection limits. This strategy would maximize the
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36 interrogation of slow desorption rates. Another approach would be to conduct batch adsorption-
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38 desorption experiments with desorption starting after different periods of adsorption so that the
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40 influence of adsorption time on desorption kinetics can be investigated. These types of
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42 experiments would be ideal for evaluating so-called “bond-aging” effects (Kaplan and Serkiz,
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44 2004).
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51 When mass balance calculations indicate that a significant amount of contaminant is still
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53 adsorbed in the columns, the best approach may be to keep the solution conditions constant until
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55 contaminant concentrations approach detection limits and then change the solution conditions to
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57 promote additional desorption.
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4 Conducting the flow interruptions and changing the flow rate during the long tail at pH
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7 6.7 was also not optimal in our experiment because at that time uranium was being released from
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9 the solids in the column(s) at a rate that was dictated primarily by the equilibrium partitioning
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11 between the solution and the fastest adsorption site on the solids rather than by desorption rates.
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13 The flow interruptions and rate changes would have been much more effective in placing
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15 constraints on slow desorption rate constants if they had been conducted when uranium
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17 concentrations were decreasing (rather than constant), which generally occurs when uranium
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19 release is controlled by desorption rates.
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26 **5. Conclusions**

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28 The results of the column experiments highlight the extreme sensitivity of uranium
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30 adsorption and reactive transport behavior to solution pH and alkalinity at near-neutral pH
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32 (alkalinity via its dependence on pH under atmospheric conditions). This sensitivity is well
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34 known (Davis and Curtis, 2003; Waite et al., 1994) and is a result of the dependence of uranium
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36 solution speciation on pH and alkalinity, which results in dramatic shifts between positive,
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38 negative and neutrally charged uranium species over narrow ranges of solution chemistry.
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40 Adsorption is much stronger in almost any mineral system when there is a greater abundance of
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42 positively charged solution species (predominantly UO_2^{2+}) provided the pH is high enough that
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44 the mineral surfaces have a net negative surface charge. The granodiorite system is clearly no
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46 exception.
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53 We conclude that at neutral pH and the natural alkalinity of the Grimsel ground water,
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55 uranium will be significantly retarded by adsorption in the Grimsel Test Site granodiorite system.
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57 At pH 7.2, the effective uranium partition coefficient, or K_d value, is at least 4 to 8 mL/g, and at
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pH 6.7 it is 5 to 6 times larger. These values are considered lower limits because they do not account for the impact of slow sites, which were not optimally interrogated in our experiments. The calculations of the preceding section demonstrated how the effective K_d values could be much larger over longer time and distance scales if slow sites are taken into account, particularly if uranium concentrations are lower than in our experiments.

At the natural pH of the Grimsel system, which is around 9.0, uranium retardation appears to be negligible under oxidizing conditions. However, our experiments did suggest that there is some potential for non-negligible retardation of uranium at pH 8.8 based on the observation that the uranium that was adsorbed at lower pHs did not all rapidly desorb when the pH was raised to 8.8. Desorption K_d values deduced from our experiments at pH 8.8 were 0.3 to 0.5 mL/g for the first and second adsorption sites, respectively, and about 20 mL/g for a relatively sparse but much stronger/slower third site.

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