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Research article

Reactive transport of uranium in fractured crystalline rock: Upscaling in time and distance

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ABSTRACT

Batch adsorption and breakthrough column experiments were conducted to evaluate uranium transport through altered material that fills fractures in a granite rock system at the Grimsel Test Site in Switzerland at pH 6.9 and 7.9. The role of adsorption and desorption kinetics was evaluated with reactive transport modeling by comparing one-, two-, and three-site models. Emphasis was placed on describing long desorption tails that are important for upscaling in time and distance. The effect of increasing pH in injection solutions was also evaluated. For pH 6.9, a three-site model with forward rate constants between 0.07 and 0.8 ml g^{-1} h^{-1}, reverse rate constants between 0.001 and 0.06 h^{-1}, and site densities of 1.3, 0.104, and 0.026 μmol g^{-1} for 'weak/fast', 'strong/slow', and 'very strong/very slow' sites provided the best fits. For pH 7.9, a three-site model with forward rate constants between 0.05 and 0.8 mL g^{-1} h^{-1}, reverse rate constants between 0.001 and 0.6 h^{-1}, and site densities of 1.3, 0.039, and 0.013 μmol g^{-1} for a 'weak/fast', 'strong/slow', and 'very strong/very slow' sites provided the best fits. Column retardation coefficients (R_d) were 80 for pH 6.9 and 10.3 for pH 7.9. Model parameters determined from the batch and column experiments were used in 50 year large-scale simulations for continuous and pulse injections and indicated that a three-site model is necessary at pH 6.9, although a K_d-type equilibrium partition model with one-site was adequate for large scale predictions at pH 7.9. Batch experiments were useful for predicting early breakthrough times in the columns while column experiments helped differentiate the relative importance of sorption sites and desorption rate constants on transport.

1. Introduction

Providing reliable predictions for risk assessments of nuclear waste repository designs is a challenge due to difficulties in upscaling in time and distance. Our work focuses on refining an experimental and reactive transport modeling approach for describing and parameterizing upscaled radionuclide transport in a more robust and less conservative manner than a simple K_d-type equilibrium partitioning model without resorting to a full geochemical description of the rock-water-radionuclide system. K_d-type models are often overly conservative and do not take full credit for all the retardation processes that may be occurring in a given system (Davis et al., 2005; Morel and Hering, 1993; Payne et al., 2013) – this can lead to overly conservative repository system designs that are prohibitively expensive. Detailed geochemical models typically account for a large number of reactions but still often miss key site-specific reactions slow reaction rates leading to marginal predictive improvements. The motivation for this work is that each unique system must be investigated for site-specific behaviors, including processes such as slow desorption kinetics and bond-aging phenomena often not accounted for in geochemical models (Boukhalfa et al., 2013; Davis et al., 2004; Dong and Wan, 2014; Mohanty et al., 2014; Nebelung and Brendler, 2010; Waite et al., 2000). While detailed geochemical descriptions remain useful (e.g., Liu et al., 2008), we suggest using a focused set of initial experiments to identify key processes that may require more detailed investigation and also to provide reasonable semi-empirical descriptions of radionuclide transport processes that can be used in performance assessment calculations. These calculations, in turn, can be used to evaluate the need for more detailed process descriptions on a risk-informed basis.

We demonstrate a cost-effective approach of accounting for radionuclide retardation processes in performance assessments, particularly for moderately-adsorbing radionuclides for which risk

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estimates can be sensitive to assumptions and uncertainties associated with adsorption and desorption processes. The approach involves conducting breakthrough experiments in small columns that require minimal amounts of geologic materials, with emphasis on interrogating and parameterizing long-term desorption behavior that can strongly influence large-scale transport behavior. Preliminary experiments (Dittrich and Reimus, 2015; Wang et al., 2013b; Wang et al., 2014b) were expanded upon to incorporate longer desorption periods and tighter control of pH conditions to improve efforts in upscaling to the longer time scales needed for repository design and reliable risk assessments.

Uranium is likely to be an important radionuclide in risk or dose calculations for most geologic repository systems for unreprocessed spent nuclear fuel due to its large inventory and relatively weak adsorption in many geochemical environments. 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 (Davis and Curtis, 2003; Echevarria et al., 2001; Joseph et al., 2013; Waite et al., 1994), with essentially zero K_d at pH of 9 or higher. For a given pCO_2, U exhibits much stronger adsorption at the low end of this pH range because of the greater abundance of positively-charged uranyl species (UO_2^{2+} and $UO_2(OH)^+$) and the lesser abundance of nonsorbing neutral and negatively-charged uranyl carbonate or uranyl-Ca/Mg-carbonate complexes at neutral pH (Dittrich and Reimus, 2015).

Our current effort has focused on U transport in a saturated, fractured crystalline rock system, using the Grimsel Test Site (GTS) in Switzerland as a source of geologic materials due to extensive field and laboratory experimentation and characterization (Geckeis et al., 2004; Möri et al., 2003). We have lowered the pH of the site-specific groundwater to be more consistent with other crystalline rock systems and to provide greater amounts of U adsorption (U sorption is negligible at ambient GTS pH of ~9). We also conducted our experiments under oxidizing conditions to avoid redox processes that would further complicate U transport behavior, although we recognize that many deep crystalline rock environments are inherently reducing and such redox processes may ultimately need to be considered for a redox-sensitive element like U (Huber et al., 2011). The Grimsel granodiorite system was chosen for this study for several reasons: (1) it is representative of a generic crystalline rock repository, (2) field transport experiments with U and other radionuclides are being conducted at the site, and (3) the Los Alamos National Laboratory is involved in a formal collaboration with the Colloid Formation and Migration project at the GTS.

2. Materials and methods

2.1. Groundwater and uranium

The groundwater used in all experiments was a synthetic Grimsel groundwater (SGGW) made by adding $NaSO_4$, KCl, $MgCO_3$, $NaHCO_3$, $CaCl_2$, and H_4SiO_4 to high purity water with the exact recipe provided in Supplemental Materials (Table A1). The SGGW represents the water chemistry in the shear zone at the GTS (Huber et al., 2011; Missana et al., 2004) with additional Mg and carbonate that would be contributed from an engineered barrier consisting of FEBEX bentonite (ENRESA, 1998). The SGGW has a pH range of 8.8–9.1, which was lowered to pH 6.9 and 7.9 with N-morpholinoethanesulfonic acid (MES) and remained stable for at least 6 months (Wang et al., 2014a, 2013b). These pH values allowed for comparison with similar experiments conducted at the GTS.

A 6.5 μM U solution was made by spiking SGGW with a combination of ^{233}U (Eckert and Ziegler) and natural uranium (Spex-CertiPrep, ICP-MS standard). Uranium-bearing species in SGGW were calculated using PHREEQC (Parkhurst and Appelo, 2013) and the llnl.dat database (Johnson, 2010) with the addition of uranyl-calcium-carbonate and uranyl-magnesium-carbonate complexation constants from Dong and Brooks (2006) and are shown in Table A2. Tritium was co-injected with U in all column experiments as a conservative tracer to provide a means to quantify residence times and dispersivity in the columns. This low concentration of U was selected to model a small concentration of mobile U after attenuation from transport through an engineered barrier and to ensure U chemical stability in the SGGW.

2.2. Fracture fill material

Fracture fill material (also known as FFM or fault gouge) from a highly altered fracture in a granite/granodiorite formation was collected during coring operations at the GTS. Samples (<1 μm to 15 cm pieces) were shipped to Los Alamos National Laboratory and all pieces less than 1 cm in size were combined and crushed, sorted, and rinsed in high-purity water to removal all fines. The 150–355 μm size fraction was used in all experiments. Quantitative x-ray diffraction (QXRD) mineralogy shows that the FFM is 34% albite, 31% biotite, 16% muscovite, 13% quartz, 5% microcline, and 1% or less of smectite and calcite. Previous publications have shown that the material used represents the surfaces of the fractures at the GTS well and these details and SEM images are shown in Dittrich et al. (2015a, 2015b). Bulk chemical analysis by x-ray florescence (XRF) has also been previously reported (Dittrich and Reimus, 2015). Surface area was 0.23 $m^2\ g^{-1}$ as measured by krypton-BET (Micromeritics Analytical Services).

2.3. Analytical measurements

Radionuclide concentrations were measured by liquid scintillation counting, or LSC (Perkin Elmer Tri-Carb 2550) for 30 min with Ultima Gold AB (Packard) liquid scintillation cocktail with energy ranges of 0–20 keV for tritium and 100–260 keV for U. pH measurements were made using a pH meter (Orion Model 290) and a glass pH electrode (Fisher AccupHast).

2.4. Column transport experiments

Column transport experiments were conducted by injecting pH-adjusted SGGW spiked with U and tritium with upward flow through 6 cm long Teflon® mini-columns filled with 5.0 g of FFM. All experiments were conducted in duplicate. Tubing, syringes, and fittings were made of Teflon® to reduce sorption artifacts and a 75 μm PEEK screen retained material in the columns. Construction details are provided elsewhere (Dittrich et al., 2015c; Dittrich and Reimus, 2014). Teflon® syringes (Torviq, TS-50, 50 mL) with syringe pumps (KD Scientific, Model 100) set to 0.3 mL h^{-1} were used to eliminate interactions between U and the syringes, which have been observed in column experiments with polypropylene syringes (Kersting et al., 2012). 3-way stopcocks allowed for refilling syringes and switching solutions while minimizing flow and pressure disturbances. Effluent samples were collected in an enclosed fraction collector (Gilson, FC-220) filled with 13 × 100 mm polystyrene test tubes (Figure A1).

Control experiments with empty columns were conducted to identify potential interactions between U and flow system materials. The columns were initially flushed with U-free SGGW for 7 days to ensure the effluent pH stabilized within 0.1 pH unit of U solutions. The influent solution was then switched to SGGW containing U and tritium.

The actual flow rate through the columns (~0.28 mL h^{-1}) was determined by weighing test tubes before and after sample collection. U and tritium activity were measured in every sample.