Uranium transport in a crushed granodiorite: Experiments and reactive transport 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 μmol/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%.

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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 (Davis et al., 2005; Morel and Hering, 1993; Payne et al.,

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2013). 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 (Davis et al., 2004; Dong and Wan, 2014; Nebelung and Brendler, 2010; Waite et al., 2000). While in principle this is a very robust approach, it is inevitably data limited and requires an expensive and time-consuming characterization effort to succeed. Such expense is not justified for contaminants that interact so weakly with media surfaces that they can be considered nonreactive in risk assessment calculations or for those that interact so strongly that risk assessments are insensitive to the details of their interactions. However, a significant characterization effort may be justified for contaminants that interact just strongly enough to make their risk/dose calculations highly sensitive to the details of their adsorption/desorption interactions. The objective of this study is to demonstrate a practical approach to addressing the characterization of contaminant-media interactions for contaminants that fall into this latter category while avoiding both the excessive conservatism of a simplified approach and the detailed and costly characterization that comes with a full geochemical description of the system.

Uranium is an example of a radionuclide contaminant that has a wide potential range of adsorption behavior to geologic materials and for which subtle differences in its adsorption behavior can make significant differences in its estimated risk contribution for nuclear waste repositories or contaminated sites. It is an element of concern for nuclear waste repository risk assessments because of its large inventory in spent nuclear fuel, its moderate solubility under oxidizing conditions, and the long half-lives of its isotopes. Uranium has a complex geochemistry that results in as much as a two to three order of magnitude range in its effective adsorption partition coefficient over a pH range from 6.5 to 9, with a strong dependence on carbonate solution concentrations (Echevarria et al., 2001; Sheppard et al., 2006; Vandenhove et al., 2009). At neutral pH, uranium adsorbs relatively strongly to many mineral surfaces. At pH greater than 8 in natural waters of typical alkalinity, its adsorption decreases significantly because of the tendency for stable neutral and negatively-charged uranyl carbonate (or ternary uranyl-Ca/Mg-carbonate) complexes to form and dominate uranium solution speciation. These neutral or negatively-charged complexes resist adsorption onto negatively-charged mineral surfaces.

This complex geochemical behavior of uranium and the wealth of data available on uranium geochemistry have prompted some researchers to invoke detailed geochemical descriptions to predict uranium transport in subsurface environments (Dong and Wan, 2014; Shang et al., 2011, 2014). Recognition of the difficulties in fully characterizing environmental systems has also prompted semi-mechanistic approaches such as the Generalized Composite Surface Complexation Model of Davis and Curtis (2003) and the multi-rate models of Liu et al. (2009, 2008). In this paper, we introduce a simplified variation of these approaches and demonstrate an experimental method for parameterizing the modeling approach. We recognize that our method will require refinements and additional data collection

to provide a robust predictive capability for a contaminant with complex geochemistry like uranium and may serve as a complementary method to the approaches mentioned above. However, the method (particularly with future refinements that we recommend later) may be directly suitable for contaminants with less complex geochemistry and solution speciation behavior than uranium.

We used a crushed granodiorite from the Grimsel Test Site (GTS) in Switzerland as a model system, which has been used for many years to study nuclear waste disposal concepts and radionuclide transport processes in crystalline rock (Geckeis et al., 2004; Möri et al., 2003). Crystalline rock is being considered as a nuclear waste repository host medium in several countries (Schwartz, 2012; Soler et al., 2011), and it is also being considered for deep borehole nuclear waste disposal (Bates et al., 2014; Driscoll et al., 2012). An attractive feature of the GTS is that it has infrastructure in place to conduct field radionuclide transport experiments, and thus it offers the potential to compare radionuclide transport behavior observed at laboratory and field scales. We note here that many deep crystalline rock environments have reducing redox potentials and uranium mobility is known to be much lower in reducing environments than in oxidizing environments because U(IV) is much less soluble and more adsorptive than U(VI). In this paper we consider only oxidizing systems in which uranium is likely to remain in the more mobile U(VI) form. The intent here is not to mimic a specific system but rather to demonstrate methods that can be applied to any system to obtain a simplified description of contaminant transport that can be defensibly used in long-term risk assessments.

Two of the most likely scenarios for radionuclide transport in crystalline rock (after being release from an engineered isolation system) are: (1) rapid advective transport through fractures in the host rock formation and/or (2) sorption of radionuclides to mobile native colloids or to colloids produced from engineered barrier materials (Dai et al, 2012; Huber et al., 2011; Liu et al., 2008, 2009). In order to assess and manage the risk of transport in rock systems that will be unique to each repository's geographic location, a general methodology would be helpful. Some of the important steps would be to (1) characterize potential flowpath surfaces, (2) interrogate radionuclide/geologic material interactions and kinetic rates of those interactions, and (3) model scenarios ranging from the most conservative (worst case) through more realistic cases with qualified uncertainties. This approach would provide a tool for decision makers to incorporate risk, sound science, and the need to eventually make a decision as the risk of doing nothing (surface storage) begins to exceed the risk of subsurface repository disposal strategies. This paper will focus on interpretation of batch and column experiments with uranium and pH changes to help develop methodologies to evaluate the dominant parameters for a more general assessment tool.

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.