Column Testing and 1D Reactive Transport Modeling To Evaluate Uranium Plume Persistence Processes

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Abstract

At many U.S. Department of Energy Office of Legacy Management sites, natural flushing was selected as a remedial option for groundwater uranium plumes. However, current data indicate that natural flushing is not occurring as quickly as expected, and solid-phase and aqueous uranium concentrations are persistent.

At the Grand Junction, Colorado, office site, column testing was completed on a core collected below an area where uranium mill tailings have been removed. The total uranium concentration in this core was 13.2 mg/kg, and the column was flushed with laboratory-prepared water with no uranium and chemistry similar to a nearby well. The core was flushed for a total of 74 pore volumes, producing a maximum effluent uranium concentration of 6,110 µg/L at 2.1 pore volumes and a minimum uranium concentration of 36.2 µg/L at the final pore volume. These results indicate complex geochemical reactions at small pore volumes (early time) and a slow uranium release at greater pore volumes (later time). Data indicate the occurrence of nonequilibrium processes that create uranium concentration rebound when column flows are stopped and then restarted. These data confirm the potential for plume persistence, which is occurring at the field scale. One-dimensional reactive transport modeling was completed using PHREEQC (a geochemical model program) and calibrated to the column test data manually and using PEST (inverse modeling calibration routine). Processes of sorption, dual porosity with diffusion, mineral dissolution, dispersion, and cation exchange were evaluated separately and in combination.

The calibration results indicate that sorption and dual porosity are major processes in explaining the column test data. These processes are also supported by fission-track radiography that shows solid-phase uranium residing in less-mobile pore spaces. These procedures provide valuable information on plume persistence and secondary-source processes that may be used to better inform and evaluate remedial strategies, including natural flushing.

Key words: reactive transport modeling, uranium, column testing

Introduction

For several U.S. Department of Energy (DOE) Office of Legacy Management (LM) sites, natural flushing of groundwater uranium plumes to a nearby river was the selected remedy. However, at many of these LM sites, natural flushing has not occurred as quickly as anticipated (Dam et al. 2015) due to persistent uranium in the solid and water phases.

At the Grand Junction, Colorado, office site (fig. 1), the U.S. War Department acquired the property in 1943 for use by the Manhattan Engineer District, which operated a refinery onsite from 1943 to 1946 to concentrate uranium oxide. Beginning in 1953, the U.S. Atomic Energy Commission conducted a research program in a small pilot mill at the site to test experimental uranium-ore-milling techniques, and in 1954, a larger pilot mill was constructed. Approximately 30,000 tons of ore were processed before milling operations ceased in 1958. The milling operations resulted in the contamination of soil and groundwater at the site, and the removal of uranium mill tailings and contaminated soil began in late 1989, with most of the contaminated soil being removed by 1994. Additional small deposits of

contaminated soil and material were removed during remedial action conducted from 1998 through 2014.

The compliance strategy for contaminated groundwater and surface water at the Grand Junction office site is natural flushing with institutional controls. Contaminants in the alluvial aquifer were projected to flush to acceptable levels 50–80 years after remediation was completed. However, continued groundwater monitoring has indicated a uranium plume persistence issue (DOE 2015). To better understand this issue, cores were collected below areas where uranium mill tailings were removed. These cores were analyzed for uranium content, and column testing was completed on these cores to better understand the uranium release amounts, rates, and processes.

This paper uses the data from the core with the highest uranium content, which was the only column completed with analyses of full geochemistry data instead of just having uranium data. These data were used to calibrate a one-dimensional (1D) reactive transport model and evaluate the uranium release processes. Processes of sorption, dual porosity with diffusion, mineral dissolution, dispersion, and cation exchange were evaluated separately and in combination.

Figure 1 *Site location and core collection location.*

Methods

Fission-Track Radiography

Fission-track radiography was done in combination with petrography to determine the association of uranium with aquifer sediments. Commonly, uranium resides in mineral grains that are too small to be positively identified, even using electron beam techniques. However, deductions about mineralogy from petrographic methods and fission-track radiography are often possible. Fission-track radiography involves the irradiation of a uranium-bearing sample with a flux of thermal neutrons that causes induced fission of the highly fissionable ^{235}U isotope. Fission fragments recoiling from the sample surface may be detected by covering a polished thin section with a suitable detector material. The detector material used was muscovite mica. Fission fragments entering the detector cause structural disturbances that can be developed for optical inspection by subsequent etching of the detector with concentrated hydrofluoric acid. The developed fission tracks observed under a microscope reveal sources of uranium in the thin section. Uranium concentrations and locations can be estimated by observing the density of fission tracks and comparing the locations to the original thin section.

Column Test

The air-dried core sample was sieved to a particle size of less than 2 mm diameter and used to fill an Omnifit glass chromatographic column that was 21.3 cm long by 2.5 cm wide with a volume of about 30 mL. Care was taken to obtain a representative sample by mixing the sample and minimizing particle size/density bias. Sediment was placed in the column in approximately 1 cm lifts with gentle tapping between lifts.

The column was leached with laboratory-prepared water that matched the composition of groundwater collected from a nearby well. A peristaltic pump with nylon tubing was used to pump the synthetic well water through the column from bottom to top at a flow rate of approximately 0.15 mL/min. The synthetic well water was kept in a collapsible plastic container to minimize exposure to air. The number of flushing pore volumes (PVs) was determined by multiplying the flow rate by the length of time required to fill the column with synthetic well water. A fraction collector was used to collect column effluent in glass test tubes. Outflow water was collected for analysis at approximately every 0.85 pore volumes, and the flow was stopped at every 25 pore volumes (referred to as stop flow). The core was flushed for a total of 74 pore volumes, and the test period was 23 days. Column effluent was analyzed for alkalinity, pH, Ca, Na, Mg, K, Mn, Fe, Cl, NO_3, SO_4, and total organic carbon.

PHREEQC Modeling

The column test data was analyzed using the geochemical modeling program PHREEQC (Parkhurst and Appelo 2013) as a 1D reactive transport model. PHREEQC modeling used a 1D column with 20 cells for a cell length of 0.01065 m and used the inflow water chemistry of the lab-prepared water (tab. 1). Unfortunately, the column was run continuously without any equilibration time, so the simulations with PHREEQC used the first water sample at 0.83 PV (tab. 1) to simulate initial conditions, with equilibration of the water phase onto the solid phase. In PHREEQC, this equilibration is necessary for simulating uranium sorption and for use in cation exchange. This equilibration creates the initial amount of uranium sorbed onto the solid phase based on the sorption parameters and adds the full complement of cations onto the solid phase for subsequent cation exchange. Initial modeling only considered the first 25 pore volumes, and calibration was done manually with an emphasis on matching uranium. A sequential order of processes was simulated to avoid adding too much complexity in one step. Processes of sorption, dual porosity with diffusion, mineral dissolution, dispersion, and cation exchange were evaluated separately and in combination. Sorption was simulated using the generic surface complexation model of Davis et al. (2004) with calibration proceeding through the use of varying sorption equilibrium constants and surface site densities. Dual porosity was simulated using a single diffusion exchange factor between mobile and immobile cells built into the 1D transport code of PHREEQC. The PHREEQC database was updated to use the ternary complexes of uranyl and carbonate with alkaline-earth metals (Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}) from Dong and Brooks (2006) and new uranium thermodynamic data from Guillaumont et al. (2003). Final calibration used the inverse modeling techniques of PEST (Doherty 2005) for every analyzed pore volume and all measured analytes.

Table 1 Chemistry of a few select analytes for the column inflow water and the first water sample that was used for assumed column equilibration in the reactive transport model.

Analyte	Inflow Water	Equilibrated Water at 0.83 PV
pH	7.0	7.6
Alkalinity as $CaCO_3$ (mg/L)	313	101
Calcium (mg/L)	192	530
Sulfate (mg/L)	918	4,180
Uranium (µg/L)	0.0	2,000

Results

Fission-track radiography (fig. 2) indicates that uranium is co-located with iron oxide cements between quartz grains. Thus, it is likely that the iron oxide cements represent less-mobile pore spaces with a higher iron content that can likely sorb more uranium onto the solid phase. As such, this is direct evidence before starting any modeling efforts that dual porosity issues should be evaluated (fig. 2).
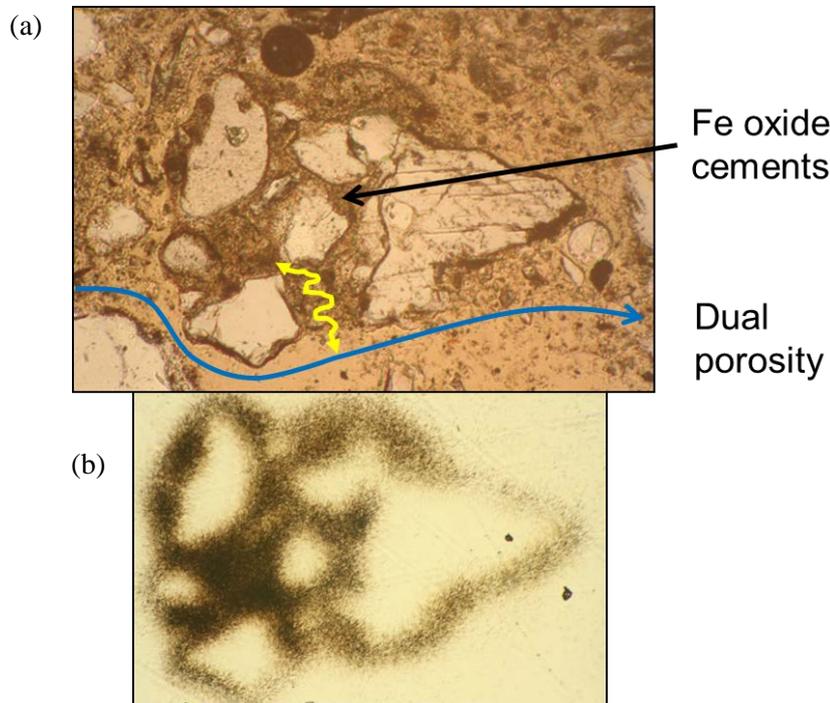

Figure 2 *Fission-track radiography with transmitted light image (a) and fission-track image (b) at the same location in one thin section. A greater density of fission tracks indicates more uranium.*

The total uranium concentration in this core was 13.2 mg/kg compared to background values of less than 1 mg/kg. The maximum effluent uranium concentration of 6,110 µg/L occurred at 2.1 pore volumes (fig. 3), and a minimum uranium concentration of 36.2 µg/L occurred at the final pore volume.

Initial modeling evaluated the uranium concentration from the first 25 pore volumes (fig. 3). Sorption was the first process evaluated (fig. 3a) followed by dual porosity (fig. 3b). Using sorption alone provides a relatively good fit to the measured data (fig. 3a) but could not fit the concentration tailing at PVs 5 through 25. The use of dual porosity seems like a reasonable process, but the use of dual porosity alone does not provide a good fit to the initial uranium concentration spike and subsequent tailing effect (fig. 3b). However, the combination of using sorption and dual porosity in PHREEQC does provide a relative good fit to the measured uranium data (fig. 4) and is logical based on the fission-track radiography results with uranium sorption on iron oxides in less-mobile pore spaces.

Additional processes included the addition of gypsum dissolution and dispersion. The addition of gypsum dissolution provides a better uranium peak (fig. 5a) likely due to added uranium mobility provided by an increasing amount of calcium in solution and, thus, the creation of calcium uranyl complexes (Dong and Brooks 2006). The presence of gypsum in the core material is inferred based on the loss of both calcium and sulfate at 60 PVs along with gypsum being undersaturated in the inflow water but at saturation in the effluent. However, no direct mineralogic data has yet been measured (such as x-ray diffraction). The addition of dispersion provides an additional improvement in the calibration by smoothing out the initial uranium concentration peak (fig. 5b). Saturation indices for uranium minerals were evaluated, but no evidence of possible uranium mineral precipitation was indicated. Thus, mineral dissolution/precipitation for uranium minerals was not included.

Manual calibration could have stopped with the inclusion of sorption, dual porosity, gypsum dissolution, and dispersion, but cation exchange processes were also added (fig. 6), given the presence of clays identified from thin-section petrography. The addition of cation exchange processes provided the best calibration fit that could be achieved using manual calibration techniques (fig. 6).

PEST, a parameter estimation software package, was used for the final simulation over the whole column test period, including the stop flows at 25 PVs. This simulation used sorption, dual porosity, gypsum dissolution, dispersion, and cation exchange processes. PEST varied all the input parameters associated with each process and created a very good fit to the uranium concentration data (fig. 7). The inset in Figure 7 highlights the stop flow data at 25 and 50 PVs, which provides evidence for nonequilibrium processes and the need for the dual porosity factor. Without the use of dual porosity, equilibrium sorption does not simulate the uranium rebound when flow is stopped. The model results did not fit the uranium peak for the second stop flow as well as for the rest of the data (inset in fig. 7), and the reason for this is unclear. Likewise, it is unclear if the column flow rate of 561 m/year compared to actual groundwater flow rates of 0.91 to 1.5 m/year has created nonequilibrium conditions during the stop flow tests that may or may not occur under field conditions.
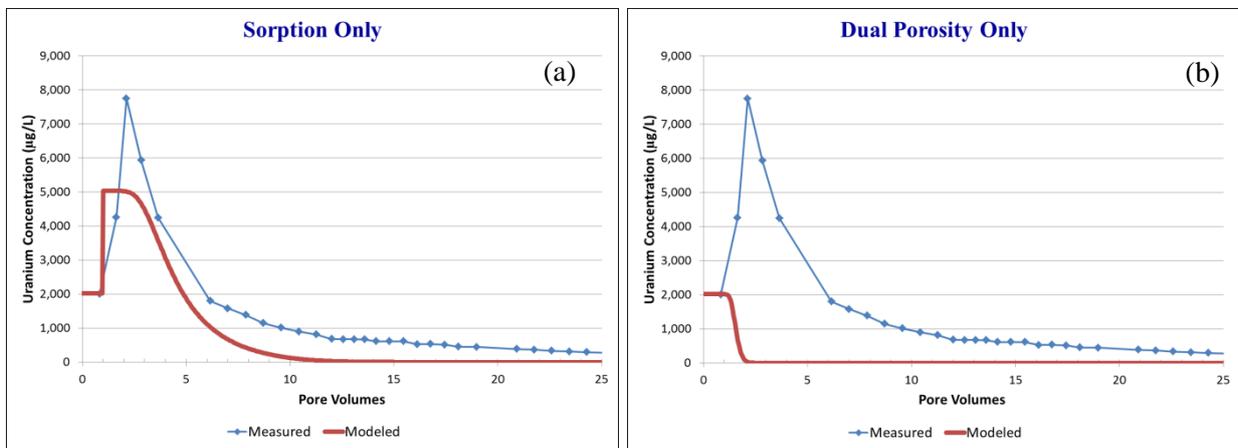

Figure 3 Measured uranium concentrations compared to modeled results for the addition of sorption only (a) and dual porosity only (b).
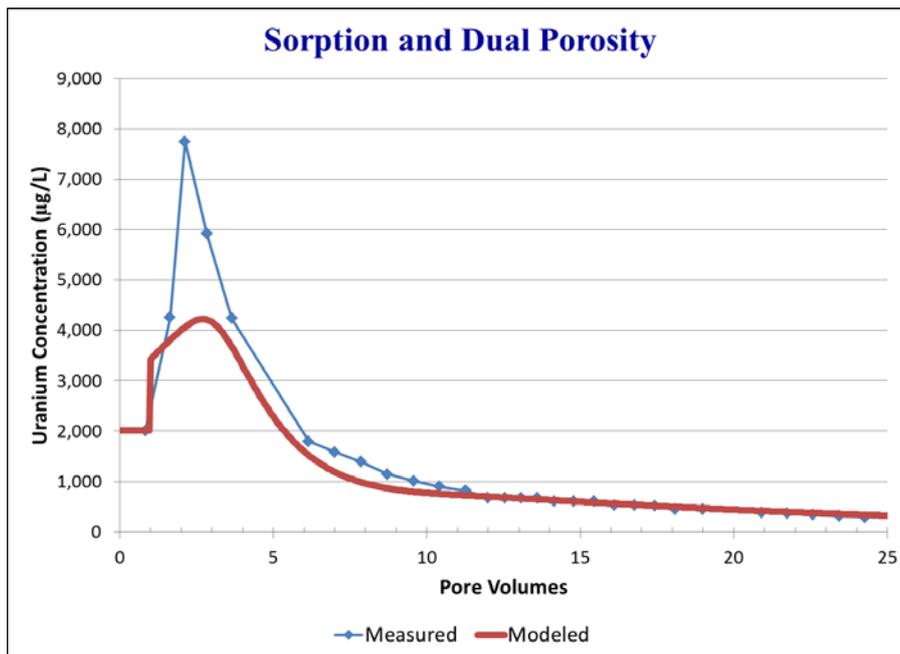

Figure 4 Measured uranium concentrations compared to modeled results for the use of sorption and dual porosity together.
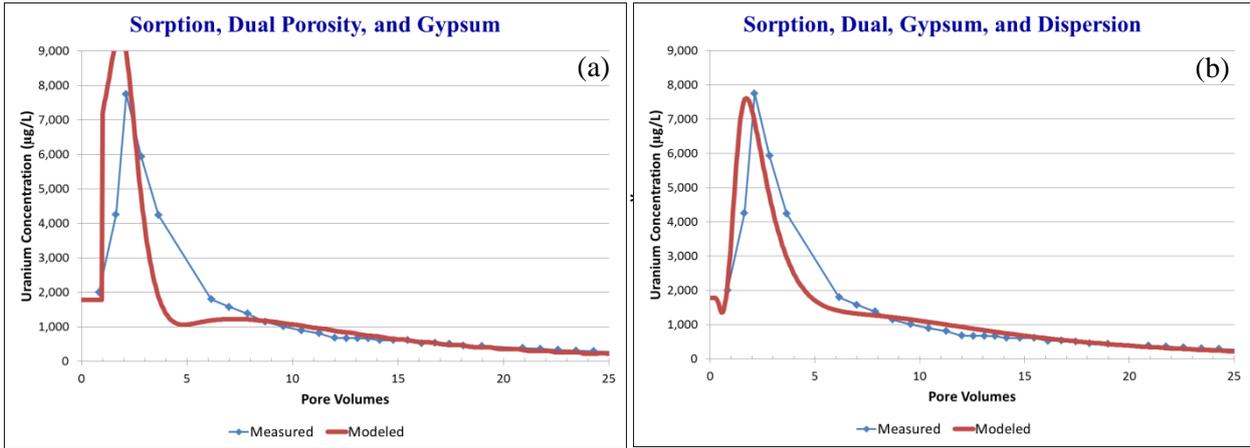
Figure 5 *Measured uranium concentrations compared to modeled results for the use of sorption, dual porosity, and gypsum dissolution (a) and with the addition of dispersion (b).*
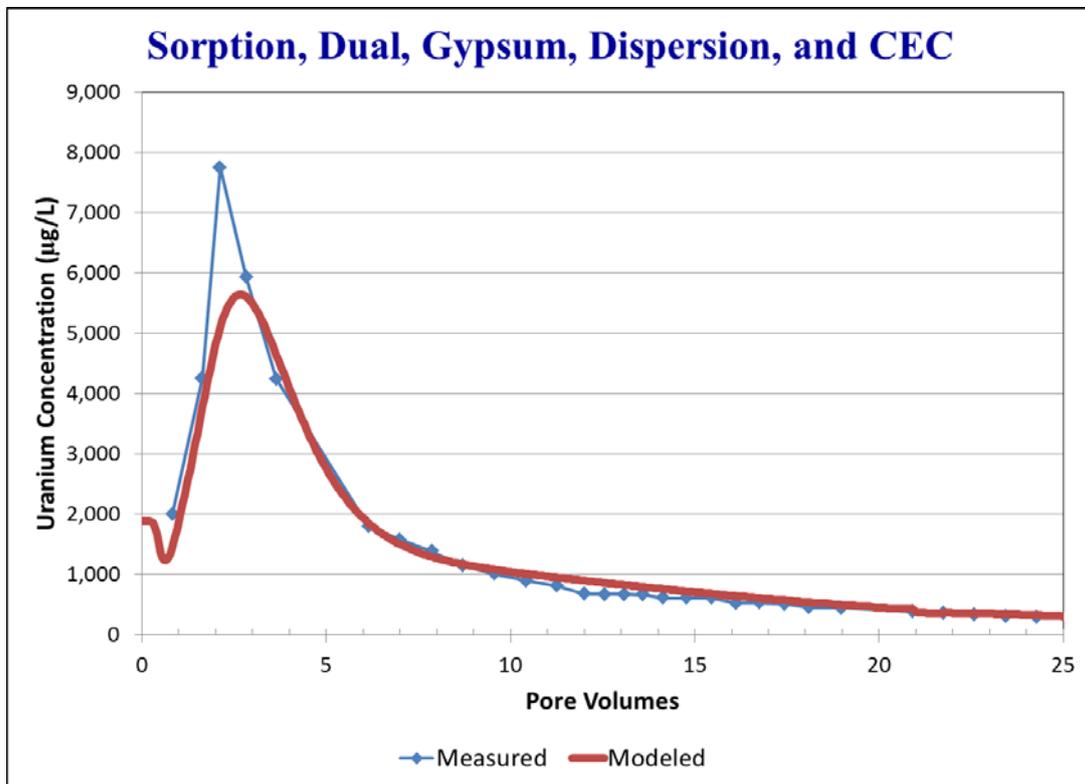

Figure 6 *Measured uranium concentrations compared to modeled results for the use of sorption, dual porosity, dispersion, and cation exchange capacity (CEC). Final best-fit manual calibration.*

Future Work

Future plans include additional use of PEST with each individual process to better quantify the goodness of fit (measured data minus modeled data) for each process. These processes will be evaluated separately and in combination, similar to what was presented for the manual calibration procedures. This will provide a more quantitative evaluation of the importance of each process. In addition, the large amount of calibration data in the concentration tail will be evaluated for weighting and whether or not this large amount of data biases the automated model calibration when using PEST.
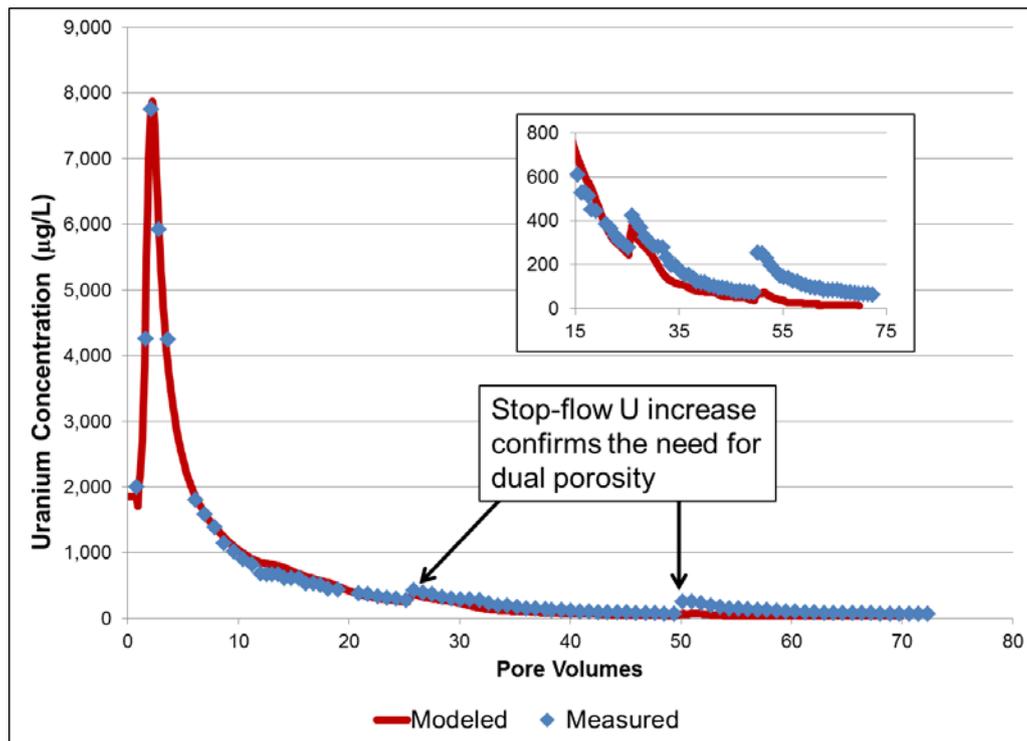
Figure 7 *Measured uranium concentrations compared to modeled results for the use of sorption, dual porosity, gypsum dissolution, dispersion, and cation exchange capacity calibrated using PEST.*

Lessons Learned

Lessons learned that will be considered in future column studies include:

(1) Allowance for column equilibration between the water and solid phase.

(2) Evaluation of slower flow rates with start/stop flows to test nonequilibrium conditions.

(3) More frequent sampling at early pore volumes and less frequent sampling at later pore volumes.

(4) Adding direct confirmation of gypsum occurrence.

Conclusions

Column test data confirm a long tailing process for uranium release from the solid phase, similar to plume persistence issues that are seen at the field scale. Reactive transport modeling provides a useful tool for evaluating the amount, rate, and processes that control uranium release from the solid phase to the column effluent water. Manual calibration results indicate that sorption and dual porosity are major processes in explaining the column test data. These processes are also supported by fission-track radiography that shows solid-phase uranium residing in less-mobile pore spaces created by iron oxide cements. Gypsum dissolution, dispersion, and cation exchange help improve the calibration but visually do not appear to be as important as sorption and dual porosity. Future work will evaluate the importance of each process more quantitatively, along with testing whether or not the weighting of data at greater pore volumes where the long concentration tail that occurs creates bias in the model calibration. All of these procedures provide valuable information on plume persistence and secondary-source processes that may be used to better inform site decision making and evaluate possible remedial strategies, including natural flushing.

Acknowledgements

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