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Colloid Facilitated Transport in Fractured Rocks: Parameter Estimation and Comparison with Experimental Data

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ABSTRACT

Colloid-facilitated migration of plutonium in fractured rock has been implicated in both field and laboratory studies. Other reactive radionuclides may also experience enhanced mobility due to groundwater colloids. Model prediction of this process is necessary for assessment of contaminant boundaries in systems for which radionuclides are already in the groundwater and for performance assessment of potential repositories for radioactive waste. Therefore, a reactive transport model is developed and parameterized using results from controlled laboratory fracture column experiments.

Silica, montmorillonite and clinoptilolite colloids are used in the experiments along with plutonium and Tritium.. The goal of the numerical model is to identify and parameterize the physical and chemical processes that affect the colloid-facilitated transport of plutonium in the fractures. The parameters used in this model are similar in form to those that might be used in a field-scale transport model.

INTRODUCTION

Some contaminants in groundwater interact strongly with immobile minerals which retard their movement relative to groundwater flow. However, they may also sorb to colloids, suspended particles in the submicometer size range often resulting from weathering of immobile minerals, thus enhancing their mobility.

Radionuclides are a class of contaminants for which colloid-facilitated transport may be of particular significance. Increased interest in understanding colloid-facilitated radionuclide migration followed the discovery of low concentrations of plutonium (Pu) in groundwater significantly further downstream from an underground nuclear test source than would be predicted for aqueous solute transport (1). The plutonium was found with inorganic colloidal particles, suggesting that it was carried by the colloids.

Colloid-facilitated radionuclide migration in groundwater has recently been included in the assessment of the performance of the potential geologic repository at Yucca Mountain, Nevada. One reason why geologic repositories are considered for the disposal of spent nuclear fuel is the strong affinity of many radionuclides to sorb onto immobile minerals. However, the presence of colloids may enhance radionuclide mobility of some component of source releases in the groundwater. This may have an impact on the efficiency of geologic media to act as a natural barrier.

In this study, we develop a reactive transport model for colloid-facilitated plutonium transport in fractures based upon laboratory column experiments that utilize natural colloids, Pu and tritium (^{3}H). Using the column experiments and the numerical model, we seek to identify the physical and chemical processes and parameters that affect colloid-facilitated transport of plutonium transport in fractured rocks.

EXPERIMENTAL SUMMARY

A series of colloid-facilitated plutonium transport experiments were conducted in naturally fractured rock cores. Prior to these experiments, soluble Pu(V) was sorbed onto inorganic montmorillonite and silica colloids, and Pu(IV) was sorbed onto inorganic clinoptilolite colloids. Some of the Pu-

colloid solution was then injected into saturated, fractured rock cores, through which steady water flow (natural water from well U-20WW at NTS, or a synthetic water with the same major ion chemistry) had been established. The colloid mass concentrations in the injection solutions ranged from ~140 to 200 mg/L in all experiments, and Pu concentrations were on the order of 10^{-8} M. The percent of total Pu initially sorbed onto colloids in the feed solutions ranged from 70% for the Cheto-montmorillonite colloids to 90-100% (actually measured at ~90% in batch experiments, but the column results suggest closer to 100%) for the clinoptilolite colloids. In addition, tritiated water was injected with the Pu-colloid solution, thus providing a non-reactive tracer to determine diffusion, dispersion, and fracture aperture size. Figure 1 shows a schematic of the experiments.

Twelve transport experiments involving Pu(V) and Cheto-montmorillonite, Otay-montmorillonite, and silica colloids were conducted in two separate fractured cores from borehole UE-20c at the NTS. The two cores were obtained from within 7 feet of each other in a heavily fractured interval of the Topopah Spring Tuff unit. One core was from 2851 ft below the surface and the other from 2858 ft below the surface. Two transport experiments involving Pu(IV) and clinoptilolite colloids were conducted in two separate fractured cores from boreholes PM1 and PM2. The PM1 core was from 4823 ft below the surface while the PM2 core was from 4177 ft below the surface. The fractured cores were cut perpendicularly to their axes such that the fracture bisected the length of the resulting core section. The cores ranged in length from 12.6 to 21.9 cm, and they all had a diameter of 8.7 cm. For each of the cores from UE-20C, experiments were conducted with high and low flow rates for each of the different colloids: Cheto-montmorillonite, Otay-montmorillonite, and silica with Pu(V). Similarly, high and low flow rate experiments were conducted with clinoptilolite colloids with Pu(IV) for the cores from PM1 and PM2. Thus, for each colloid type, four different experiments with Pu were conducted.

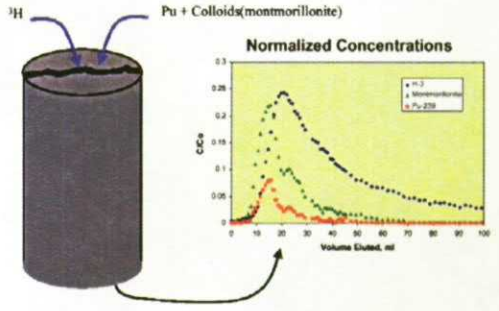

Figure 1. Schematic of laboratory experiments. Example results shown for experiment conducted with montmorillonite colloids.

CONCEPTUAL MODEL

The chemical and physical processes controlling plutonium mobility in the experimental columns include (1) plutonium aqueous speciation; (2) plutonium sorption and desorption on colloids; (3) filtration of colloids on the fracture walls; (4) solute diffusion into the matrix; and (5) surface complexation and ion exchange of plutonium with fracture minerals and matrix minerals (see Figure 2). The five processes function competitively with each other; the first two increasing the mobility of plutonium, the latter three reducing mobility. Additionally, the fracture aperture affects the fluid velocity for a given flow rate and the proximity of solutes in the fracture to the fracture wall where diffusion into the matrix, sorption of solutes to fracture minerals, and filtration of colloids occurs.

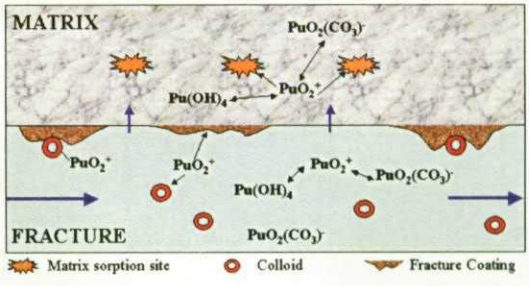

Figure 2. Schematic of conceptual model for plutonium and colloid transport in fractures

NUMERICAL MODEL

The tritium breakthrough curves obtained for UE-20C columns 2851 and 2858 (referred to from here on as 2851 and 2858) were interpreted using

the computer model RELAP (2) and the PM1 and PM2 breakthrough curves were interpreted using the computer model FEHM (3,4). These simulations yield estimates of effective half apertures, matrix diffusion coefficients, and solute dispersivity parameters. These parameters are then used directly in estimating the reactive transport parameters.

We simulate the colloid-facilitated plutonium transport column experiments with a discrete fracture model using FEHM. The model utilizes a computational grid normal to the fracture to capture both the fracture and matrix and the chemical and physical processes described in the conceptual model (Figure 2). In the fractures, advective transport, first-order kinetic Pu sorption onto colloids, equilibrium Pu sorption onto fracture minerals, and first-order kinetic colloid filtration all affect Pu migration. In the matrix, the dominant processes affecting Pu mobility are diffusion and equilibrium sorption onto matrix minerals.

The experiments are modeled using a 2-D x-, y-grid. The first column in the grid represents the fracture and its width is set to the fracture aperture, which is obtained from the model fits to the tritium data. The remaining columns represent the matrix and are finely spaced to capture matrix diffusion. Along the length of the model, the grid is evenly discretized at a fine enough resolution to minimize numerical errors. Each column requires a unique grid with the column's dimensions, aperture, flow rate, input concentrations of plutonium and colloid, diffusion coefficient, and dispersivity. Parameters for sorption of Pu onto silica colloids should be the same regardless of which column is used. Likewise, sorption parameters for Pu onto fracture minerals and matrix minerals for a specific column should be the same regardless of flow rate and which colloids are involved in the particular experiment.

Automatic parameter estimation is used to find model parameters that lead to the best matches between simulated and observed concentration breakthrough curves. Thus, the goal of parameter estimation is to reduce the difference between observed and simulated results by adjusting the model parameters. In this study, we couple the PEST (Parameter ESTimation) software package (5) with the reactive transport model, described above.

In a parameter estimation simulation, PEST runs FEHM as many times as necessary to determine the optimal set of parameters. PEST uses the Gauss-Marquardt-Levenberg algorithm (GML) to adjust the FEHM parameters while reducing an objective function. In this case the objective function is the sum of the squared residuals (SSR) where the residual is the difference in the observed and simulated concentrations. By comparing parameter changes with objective function improvement achieved with each iteration, PEST determines how and if to proceed with additional optimization iterations.

RESULTS

The simulations seek to identify the optimal set of transport parameters for multiple experiments in which the same type of colloid was used. Therefore, four different parameter estimation simulations were conducted for each of the four different colloids. In each parameter simulation set, results for two flow rates on two different columns, hence a total of four results, are used. For each of these sets of simulations, six model parameters are estimated. They include 1) forward rate of Pu sorption onto the colloid, 2) reverse rate of Pu desorption off of the colloid, 3) matrix sorption Kd in the first column, 4) fracture sorption Kd in the first column, 5) matrix sorption Kd in the second column, and 6) fracture sorption Kd in the second column. Figure 3 shows the reactions and which parameters are being fit.

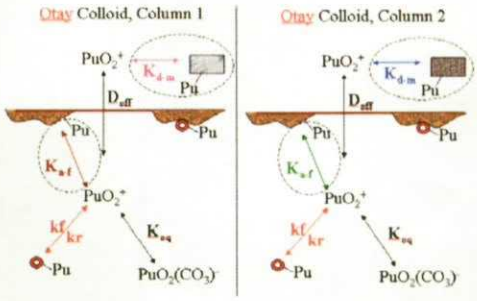

Figure 3. Schematic comparing plutonium transport in the presence of the same colloid type in two different columns. Plutonium-colloid reaction parameters expected to be the same whereas sorption parameters to fracture and matrix minerals expected to differ between the two columns.

The first-order kinetic model parameters for attachment and detachment of colloids to fracture surfaces generally provides very good matches between simulated and observed colloid breakthrough data. Holding the colloid

attachment and detachment parameters fixed, PEST simulations are conducted to estimate the parameters for plutonium sorption to colloids and immobile minerals.

The Cheto-montmorillonite experiments are matched very well for all four experiments (See Figures 4 and 5). In contrast, there are substantial differences in the plutonium breakthrough data between the two columns when silica colloids were used (see Figures 6 and 7). The peaks for both high- and low-flow experiments are substantially larger for column 2858 than 2851. Thus the parameter estimation process is challenged to come up with one set of kinetic parameters for plutonium sorption on silica colloids for all experiments yet different matrix and fracture Kds for the two different columns. The resulting fit is a compromise that over predicts the peaks in one set of experiments and under predicts them in the others, minimizing the objective function for the set of four experiments. Fits to the Otay-montmorillonite colloid experiments capture the trends reasonably well, but again show the compromises associated with fitting four experiments with one set of parameters (see Figures 8 and 9). The clinoptilolite colloid experiments yield the greatest mass of plutonium in the effluent (see Figures 10 and 11). The desorption rate of plutonium from clinoptilolite colloids is much smaller than for the other colloids. In fact, the parameter estimation process evolved such that it identified the maximum desorption rate to be so small that no substantial desorption could occur. In other words, the best match between model and experimental results involves no desorption of plutonium over the length and time scales associated with the experimental columns.

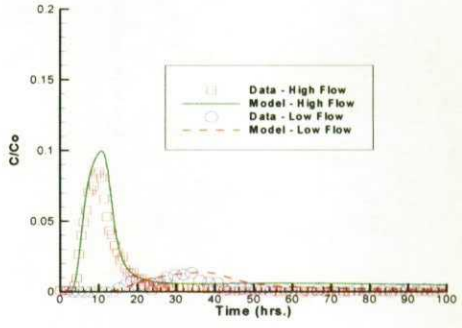

Figure 4. Pu breakthrough curves: Cheto-montmorillonite experiment, column 2851, high and low flow rates.

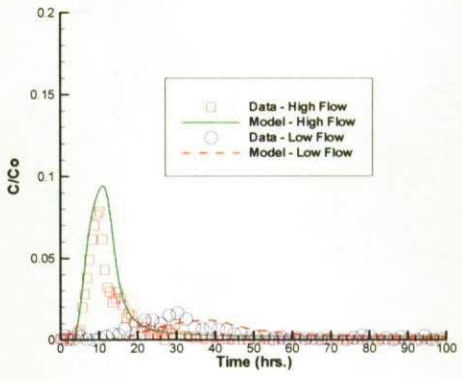

Figure 5. Pu breakthrough curves: Cheto-montmorillonite experiment, column 2858, high and low flow rates.

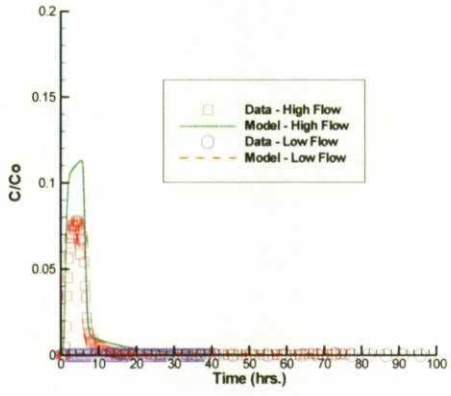

Figure 6. Pu breakthrough curves: silica experiment, column 2851, high and low flow rates.

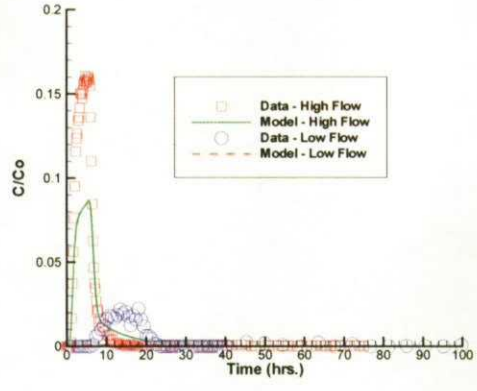

Figure 7. Pu breakthrough curves: silica experiment, column 2858, high and low flow rates.

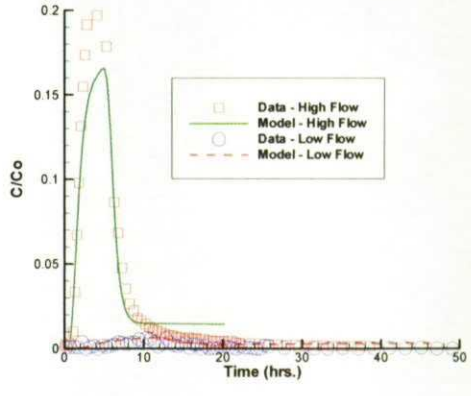

Figure 8. Pu breakthrough curves: Otay-montmorillonite experiment, column 2851, high and low flow rates.

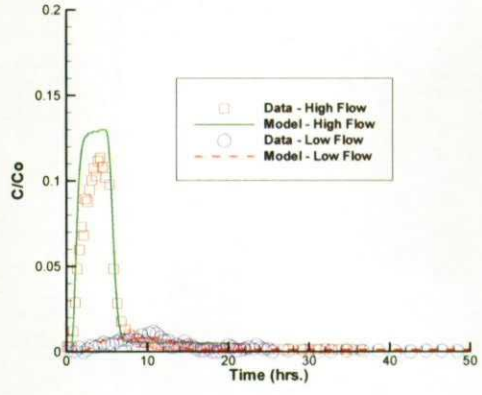

Figure 9. Pu breakthrough curves: Otay-montmorillonite experiment, column 2858, high and low flow rates.

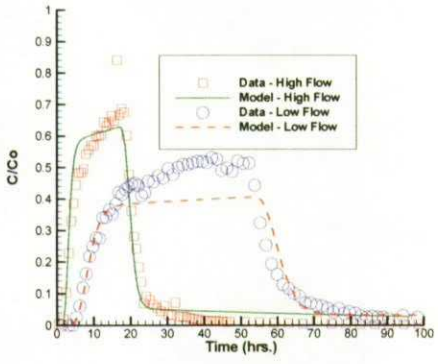

Figure 10. Pu breakthrough curves: clinoptilolite experiment, column PM1, high and low flow rates.

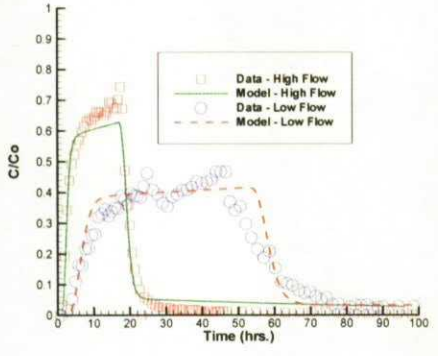

Figure 11. Pu breakthrough curves: clinoptilolite experiment, column PM2, high and low flow rates.

SUMMARY

The reactive transport model uses empirical parameters (e.g. Kd and k_f) that describe sorption and desorption of plutonium on colloids and immobile minerals as well as colloid attachment and detachment from fracture walls. Thus, the parameters used in this model are similar in form to those that might be used in a field-scale transport model. Specific findings associated with this study are:

1. Simulations using parameters fit by RELAP and FEHM lead to good matches between model and experimental results.

2. We have used automatic parameter estimation and results from multiple column experiments to simultaneously estimate the transport parameters for sorption and desorption kinetics of plutonium on four different types of colloids.

3. The parameter estimation simulations also yield sorption parameters for plutonium to immobile minerals in the four different columns considered.

4. The desorption rate of plutonium off of colloids is the most sensitive parameter. Small changes in this parameter lead to large changes in model results. This is not surprising due to the experimental design in which colloids are effectively doped with plutonium prior to injection in the columns. Thus desorption off of the colloids governs the mass of plutonium transported by colloids.

5. No free aqueous plutonium exits the columns. Thus, over the time and space scales of the experiments, the sorption to immobile minerals must be great enough to effectively remove all free plutonium from aqueous solution.

6. Zeolite colloids have the smallest desorption rate, suggesting that they would support the greatest travel distances and times of Pu.

7. Zeolite colloid experiments provide little information on sorption rate to colloid or to the fracture and matrix minerals because all plutonium that originates on the colloids breaks through on the colloids.

8. Other less sorptive colloids (Silica and Clay) appear to facilitate plutonium transport only for small residence times, but they do provide information on matrix and fracture sorptive properties.

ACKNOWLEDGEMENTS

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