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

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1. Introduction

Many contaminants in groundwater strongly interact with the immobile porous matrix, which retards their movement relative to groundwater flow. Colloidal particles, which are often present in groundwater, have a relatively small size and large specific surface area which makes it possible for them to also adsorb pollutants. The sorption of tracers to colloids may enhance their mobility in groundwater, relative to the case where colloids are not present. A class of pollutants for which colloid-facilitated transport may be of particular significance are radioactive isotopes. A major reason for why geologic repositories are considered suitable for the disposal of spent nuclear fuel is the strong affinity of many radionuclides to adsorb onto the porous matrix. Therefore, radionuclides accidentally released, would be contained in the geological media by adsorption or filtration until sufficient decay takes place. However, the presence of colloids may enhance radionuclide mobility in the groundwater, and reduce the efficiency of geologic media to act as a natural barrier.

Wider interest in understanding colloid-facilitated contaminant migration on the field-scale, followed the discovery of plutonium in a deep aquifer at the Nevada test site, significantly further downstream than had been predicted based on its sorption properties and the mean groundwater flow (Kersting et al., 1999). The plutonium was found with inorganic colloidal particles, suggesting that it was carried by the colloids at approximately the groundwater velocity. A similar observation was made in a shallow aquifer for plutonium and americium at Los Alamos National Laboratory (Penrose et al., 1990). Although more recently different mechanisms have been proposed to explain the findings at Los Alamos (Marty et al., 1997).

Most of the studies in the literature are hypothetical and do not directly compare the numerical models to colloid-faciliated transport column experiments. In this study, we compare a reactive transport model to colloid-facilitated plutonium transport experiments conducted by Reimus et al. (2001). Using automatic parameter estimation, multiple experimental breakthrough curves are used simultaneously to fit parameters that control plutonium and colloid migration.

2. Work Description

Experimental Summary

A series of colloid-facilitated Plutonium transport experiments in naturally fractured rock cores were conducted by Reimus et al. (2001). In those experiments, soluble Pu(V) was sorbed onto inorganic montmorillonite and silica colloids. In addition, Pu(IV) was sorbed onto inorganic clinoptilolite colloids. Some of the Pu-colloid solution was injected into saturated, fractured rock cores, through which steady water flow had been established. The percent of total Pu in the feed solutions ranged from 70% for the Cheto-montmorillonite colloids to 100% for the zeolite colloids. In addition, tritiated water was injected with the Pu-colloid solution, thus providing a non-reactive tracer for comparison. Figure 1 shows a schematic of the experiments. The experimental results are used to develop parameters for the colloid-facilitated plutonium transport model discussed in the next section.

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. The five processes function competitively with each other; the first two increasing the mobility of plutonium, the later 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.

3. 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 simulations were conducted for each of the four different colloids: Cheto-montmorillonite, silica, Otay-montmorillonite, and clinoptilolite colloids. In each simulation, 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 to the first column, 4) fracture sorption Kd to the first column, 5) matrix sorption Kd to the second column, and 6) fracture sorption Kd to the second column.

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. We have chosen not to invoke more complicated models because it adds additional parameters, for which extrapolating to larger time and space scales may not be straightforward. Again, we seek to model this system with the minimum set of equations necessary to capture to governing processes as observed in the breakthrough curves. Holding the colloid filtration parameters described above as fixed in the parameter estimation simulations, 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. In contrast, there are substantial differences in the plutonium breakthrough data between the two columns when silica colloids were used Fits to the Otay-montmorillonite colloid experiments capture the trends and show the compromises associated with fitting four experiments with one set of data. The clinoptilolite colloid experiments yield the greatest mass of plutonium in the effluent. As identified during parameter estimation, the desorption rate of plutonium from this colloid is much smaller than for the other colloids. In fact, the parameter estimation process evolved such that it identified the maximum desorption rate before 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.

4. Conclusions and Discussion

The reactive transport model for which the parameters are fit does not seek to identify the specific mechanistic reactions that occur at the molecular scale. Rather, the model uses empirical parameters that describe the integrated retardation that occurs in the fracture and the sorption and desorption of plutonium on colloids. 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. Previous parameters estimated by Reimus (2001) for diffusion, dispersion and kinetic colloid filtration in his experiments are readily incorporated into the FEHM model used in this study. Simulations using those parameters lead to good matches between model and experimental results

2. Extending upon Reimus' approach, 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 greatest travel distance 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.

5. References

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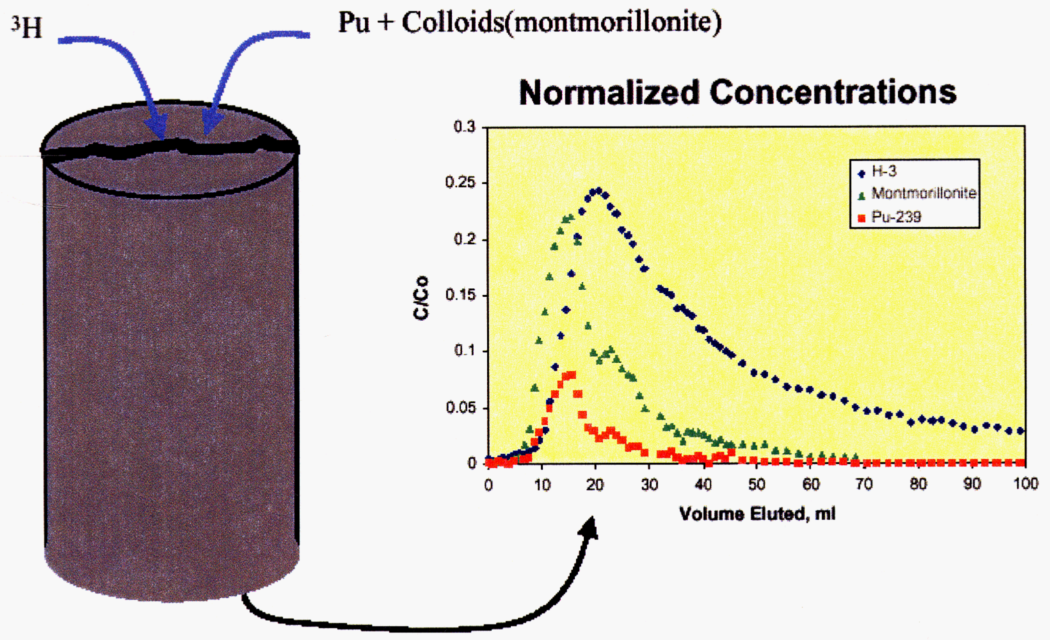

Figure 1. Schematic of laboratory experiments. Example results shown for experiment conducted with montmorillonite colloids. Data for experiments provided in Reimus et al. (2001).