Final Report

Project Title: COLLOID-FACILITATED TRANSPORT OF RADIONUCLIDES THROUGH THE VADOSE ZONE

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Science Category: Research

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1 Research Objective

Implement colloid-facilitated contaminant transport mechanisms and thermodynamic stability constants for colloids into a reactive chemical transport model, and verify model simulations with experimental transport data.

Radioactive and hazardous waste stored in the underground tanks at the Hanford site has leaked or is suspected to have leaked into the vadose zone. Radionuclides, which are normally considered to be strongly sorbed (e.g., Pu and Cs), have been detected at much deeper depth than predicted based on current theories of vadose zone contaminant transport. There is strong indication that contaminants can be transported via colloids. Such colloid-facilitated transport is likely to occur at the Hanford site, where contaminants leaking from the storage tanks are released directly to the vadose zone. At Hanford, the potential for in situ formation of colloids as leaking tank waste enters the vadose zone is high. Tank waste supernatants are known to consist of solutions with high pH, ionic strength, and aluminate concentrations. When such alkaline solutions contact soils and sediments around the tanks, it is likely that soluble silica-rich allophane, feldspathoids, and zeolite-like materials are formed. These negatively-charged colloids are capable of adsorbing or coprecipitating with contaminant cations and moving through soil and sediment matrices. The objectives of this proposed project are to study three major processes responsible for colloid-facilitated transport: (1) formation and mobilization of colloids, (2) association of contaminants with colloidal particles, and (3) co-transport of colloids and contaminants in the vadose zone. We specifically consider chemical and geochemical conditions at the Hanford site. The radionuclide Cs is selected as a model contaminant. Soil or sediment samples representative of the porous material under waste storage tanks will be collected at the Hanford site. Formation of colloids will be studied in batch systems by reacting solutions typical for tank waste with vadose zone materials and with solutions expected at equilibrium with soil material. Colloids will be separated and characterized in terms of size, structure, composition, and surface charge characteristics. The interactions of Cs with colloidal particles isolated from the previous step will be investigated with batch sorption experiments and spectroscopic techniques. Transport and co-transport of colloids and the radionuclide Cs will then be studied with a series of laboratory column experiments using repacked Hanford sand material. Experiments will be carried out under unsaturated, steady-state as well as transient water flow to study the effect of water content on colloid transport. Magnetic Resonance Imaging will be used to visualize colloidal movement inside the porous medium. Sorption

studies and column outflow data will be analyzed with numerical models to elucidate the relevant mechanisms responsible for contaminant sorption as well as colloid and radionuclide transport. Sorption and reaction models will be combined with transport models to quantitatively describe the column experiments. The results of the proposed research will lead to a better understanding of colloid-formation, colloid-contaminant-soil interactions, colloid migration, and colloid-facilitated transport in the vadose zone. The experiments proposed use conditions specific to the Hanford site, and the results are therefore directly applicable to clean-up strategies and procedures for Hanford contamination problems. We expect to provide conclusive evidence under what conditions, if any, colloid-facilitated transport can be expected at the Hanford site, and what the quantitative magnitude of this transport process will be.

2 Research Progress and Implications

The reactive transport model FLOTRAN was used to simulate Cs transport in column experiments conducted at Washington State University. FLOTRAN was applied to column experiments involving simulated tank waste using a 1.4 M NaOH + 3.7 M $NaNO_3$ + 0.125 M $NaAlO_4$ solution to investigate migration of Cs through Hanford sediment columns at temperatures of 22°C and 50°C. The Pitzer model was used for activity coefficient corrections. Shown in Figure 1 are breakthrough curves for Cs^+, Na^+, and NO_3^-. Results indicated a complex behavior of species concentrations eluted from the column. The initial breakthrough of Cs was well reproduced in the calculations using ion exchange coefficients obtained from an independent study (Steefel et al., 2003; Lichtner et al., 2004). One puzzling aspect of the experiments, however, was that nitrate did not behave as a nonreactive tracer as expected and as predicted by the model. The model calculations, however, were based on a fully saturated column rather than an initially dry column. To partially compensate for this, the initial fluid composition was set to the composition of the observed breakthrough concentrations.

2.1 Kinetic Formulation of Ion Exchange

Ion exchange reactions are usually considered to have fast, reversible, reaction kinetics governed by electrostatic attraction. However, when taking place on colloids ion exchange reactions appear to exhibit irreversibility, for example sorption of plutonium on colloids as observed at the Nevada Test Site (Kersting et al., 1999). To account for such irreversibility, a kinetic description of ion exchange rates is needed.

2.1.1 Ion Exchange Reactions

The simplest approach to developing a kinetic formulation of ion exchange is to assume simple reaction kinetics in which the rate is equal to the difference between the forward and backward rates with concentrations raised to powers of the reaction stoichiometric coefficients. This form of the rate law, however, is not unique (with the exception of monovalent exchange) and depends on the stoichometry used to write the exchange reaction. As long as the rate law is consistent with the equilibrium state of the reaction, the correctness of the form of the rate law cannot be ascertained

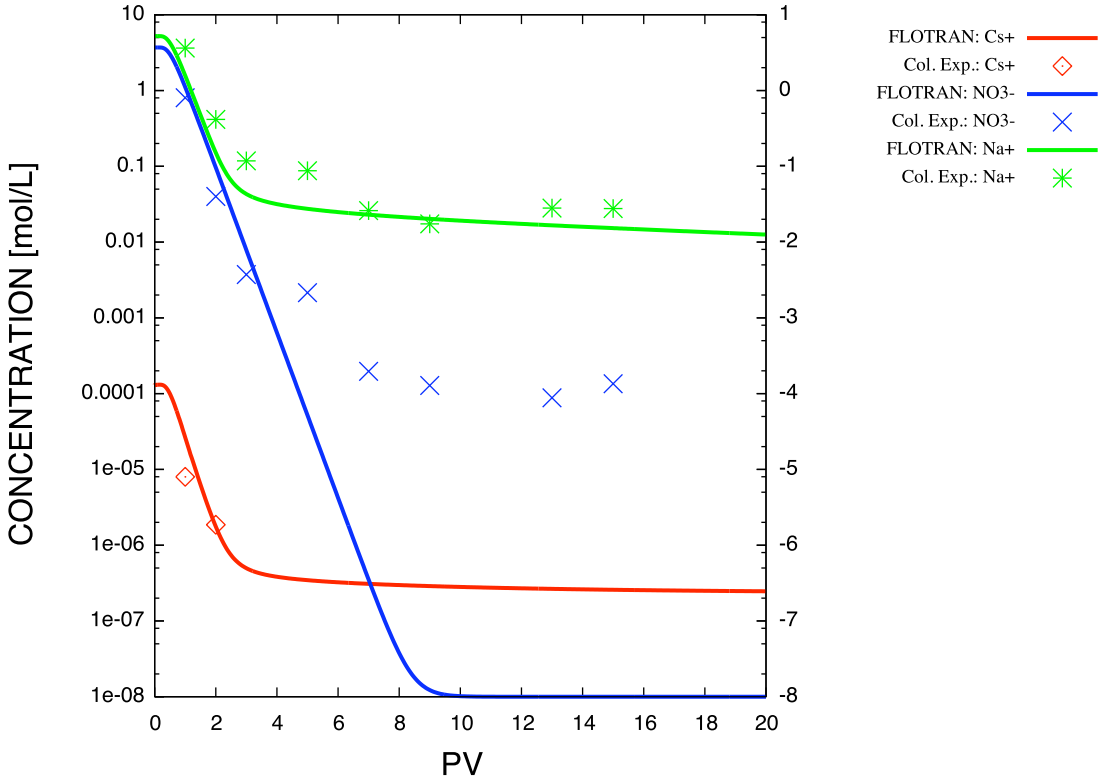

Figure 1. Breakthrough curves for Cs^+, Na^+, and NO_3^- plotted as a function of eluted pore volumes and compared with column data.

without further experiment effort. In particular, the form of the rate law cannot be deduced from the reaction stoichiometry alone, but requires additional experimental data as is well known from the theory of kinetics (e.g. Frost and Pearson, 1963). However, rate laws which violate conservation of charge can be eliminated even though they may reproduce the correct equilibrium state.

Two equivalent forms of ion exchange reactions for the purposes of equilibrium calculations are in common use. One form is given by

$$\frac{1}{z_{j_0}}\mathcal{A}_{j_0} + \frac{1}{z_j}\left(X_m\right)_{z_j}\mathcal{A}_j \;\rightleftharpoons\; \frac{1}{z_j}\mathcal{A}_j + \frac{1}{z_{j_0}}\left(X_m\right)_{z_{j_0}}\mathcal{A}_{j_0}, \tag{1a}$$

and the other by

$$z_j\mathcal{A}_{j_0} + z_{j_0}\left(X_m\right)_{z_j}\mathcal{A}_j \;\rightleftharpoons\; z_{j_0}\mathcal{A}_j + z_j\left(X_m\right)_{z_{j_0}}\mathcal{A}_{j_0}, \tag{1b}$$

obtained by multiplying the former reaction by the product $z_{j_0}z_j$. The quantities z_{j_0} and z_j denote the valencies of cations $\mathcal{A}_{j_0}$ and $\mathcal{A}_j$, with reference cation denoted by the subscript j_0 and the subscript $j \neq j_0$ represents all other cations. Species $\left(X_m\right)_{z_j}\mathcal{A}_j$ indicates sorption of the jth cation associated with the mth mineral on the surface exchange site X_m. Only in the case of monovalent exchange ($z_{j_0} = z_j = 1$) are the two forms identical. The respective mass action equations are given by

$$K_{j_0 j} \;=\; \left(\frac{X_{j_0}^m}{a_{j_0}}\right)^{1/z_{j_0}} \left(\frac{a_j}{X_j^m}\right)^{1/z_j}, \tag{2a}$$

and

$$\widetilde{K}_{j_0 j} \;=\; \left(\frac{X^m_{j_0}}{a_{j_0}}\right)^{z_j} \left(\frac{a_j}{X^m_j}\right)^{z_{j_0}}, \tag{2b}$$

where, using the Gaines-Thomas convention, the equivalent fractions X^m_k are defined by

$$X^m_k = \frac{z_k S^m_k}{\sum_l z_l S^m_l} = \frac{z_k}{\omega_m} S^m_k, \quad \sum X^m_k = 1, \tag{3}$$

with ω_m the site concentration associated with the mth mineral defined by

$$\omega_m = \sum_k z_k S^m_k. \tag{4}$$

The site concentration ω_m is related to $\mathcal{Q}_m$, the cation exchange capacity (CEC) with units mol/kg, associated with the mth mineral, by the expression

$$\omega_m = \varphi_m \rho_m \, \mathcal{Q}_m, \tag{5}$$

with mineral density ρ_m and volume fraction φ_m.

Typically, an average exchange capacity $\mathcal{Q}$ is defined for the bulk rock, related to the contribution from individual minerals $\mathcal{Q}_m$ by the summation

$$\mathcal{Q} \;=\; \sum_m \chi_m \mathcal{Q}_m, \tag{6}$$

where χ_m denotes the mass fraction of the mth mineral given by

$$\chi_m \;=\; \frac{\varphi_m \rho_m}{\sum_{m'} \varphi_{m'} \rho_{m'}}. \tag{7}$$

The average site concentration ω is related to $\mathcal{Q}$ by the expression

$$\omega = (1-\varphi)\rho_s \mathcal{Q}, \tag{8}$$

with porosity φ and solid density ρ_s given by

$$\rho_s \;=\; \frac{1}{1-\varphi} \sum_m \varphi_m \rho_m, \tag{9}$$

and

$$1-\varphi \;=\; \sum_m \varphi_m. \tag{10}$$

The average site concentration ω is related to the mineral site concentrations ω_m by the sum

$$\omega \;=\; \sum_m \omega_m, \tag{11}$$

where the bulk site concentration averaged over different minerals making up the rock aggregate satisfies

$$\omega = \sum_j z_j S_j, \tag{12}$$

with the total site concentration S_j equal to

$$S_j \;=\; \sum_m S_j^m. \tag{13}$$

For equi-valent exchange $(z_j = z)$, an explicit expression exists for the sorbed concentrations given by

$$S_j^m \;=\; \frac{\omega_m}{z}\frac{k_j^m C_j}{\sum k_l^m C_l}, \tag{14}$$

where C_k denotes the kth cation concentration. This expression follows directly from the mass action equations and conservation of exchange sites. Note that the bulk sorbed concentration does not have the same form as the individual mineral contributions unless the selectivity coefficients k_j^m are the same for each mineral, in which case

$$S_j \;=\; \frac{\omega}{z}\frac{k_j C_j}{\sum k_l C_l}. \tag{15}$$

2.1.2 Kinetic Rate Laws

The kinetic reaction rate for reaction (1a) has the following form

$$I_{j_0 i}^m \;=\; k_{j_0 j}^{mf} a_{j_0}^{1/z_{j_0}} \left(X_j^m\right)^{1/z_j} - k_{j_0 j}^{mb} a_j^{1/z_j} \left(X_j^m\right)^{1/z_{j_0}}, \tag{16a}$$

and for reaction (1b) the form

$$\widetilde{I}_{j_0 j}^m \;=\; \widetilde{k}_{j_0 j}^{mf} a_{j_0}^{z_j} \left(X_j^m\right)^{z_{j_0}} - \widetilde{k}_{j_0 j}^{mb} a_i^{z_{j_0}} \left(X_{j_0}^m\right)^{z_j}. \tag{16b}$$

where $k_{j_0 j}^{mf}$, $k_{j_0 j}^{mb}$, $\widetilde{k}_{j_0 j}^{mf}$, and $\widetilde{k}_{j_0 j}^{mb}$ denote the forward and backward rate constants associated with the mth mineral, respectively. Although the reaction rates $I_{j_0 j}$ and $\widetilde{I}_{j_0 j}$ corresponding to reactions (1a) and (1b) are not simply related, the equilibrium constants for the corresponding reactions are related by the expression

$$\widetilde{K}_{j_0 j}^m \;=\; \left(K_{j_0 j}^m\right)^{z_{j_0} z_j}. \tag{17}$$

The ratio of the forward and backward rate constants are equal to the equilibrium constants according to

$$K_{j_0 j}^m \;=\; \frac{k_{j_0 j}^{mf}}{k_{j_0 j}^{mb}}, \tag{18}$$

and similarly for $\widetilde{K}_{j_0 j}^m$.

Another form of the kinetic rate law analogous to transition state theory is to write the reaction rate as

$$I_{j_0 j}^m \;=\; -k_{j_0 j}^{mb} \mathcal{P}_{j_0 j}^m \left(1 - K_{j_0 j}^m Q_{j_0 i}^m\right), \tag{19}$$

where the prefactor $\mathcal{P}_{j_0 j}^m$ and ion activity product $Q_{j_0 j}^m$ are defined by

$$\mathcal{P}_{j_0 j}^m \;=\; a_j^{z_{j_0}} \left(X_{j_0}^m\right)^{z_j}, \tag{20}$$

and

$$Q^m_{j_0 j} \;=\; \frac{a_{j_0}^{1/z_{j_0}} \left(X^m_j\right)^{1/z_i}}{a_j^{1/z_i} \left(X^m_j\right)^{1/z_{j_0}}}. \tag{21}$$

Equilibrium holds if $K^m_{j_0 j} Q^m_{j_0 j} = 1$. In this form the rate is equivalent to Eqn.(16a). However, setting $\mathcal{P}^m_{j_0 j}$ equal to a constant or some other form dictated by experiment, leads to alternative rate laws with the identical equilibrium state.

2.1.3 Multicomponent Mass Conservation Relations Involving Colloids

Mass conservation equations for a multicomponent system involving colloid-facilitated transport and including homogeneous aqueous reactions, mineral precipitation and dissolution, and ion exchange reactions with the form given in (1a) using cation $\mathcal{A}_{j_0}$ as reference cation are given by

$$\frac{\partial}{\partial t}\varphi\Psi_{j_0} + \boldsymbol{\nabla}\cdot\left(\boldsymbol{q}\Psi_{j_0} - \varphi D\boldsymbol{\nabla}\Psi_{j_0}\right) = -\frac{1}{z_{j_0}}\sum_{j\neq j_0,\,m} I^m_{j_0 j} - \frac{1}{z_{j_0}}\sum_{j\neq j_0,\,c} I^c_{j_0 j} - \sum_m \nu_{j_0 m} I_m, \tag{22a}$$

$$\frac{\partial}{\partial t}\varphi\Psi_{j} + \boldsymbol{\nabla}\cdot\left(\boldsymbol{q}\Psi_{j} - \varphi D\boldsymbol{\nabla}\Psi_{j}\right) = \frac{1}{z_{j}}\sum_m I^m_{j_0 j} + \frac{1}{z_{j}}\sum_c I^c_{j_0 j} - \sum_m \nu_{jm} I_m, \tag{22b}$$

for aqueous primary species. The sums over indices m and c run over all minerals and colloids present in the system. Individual primary species concentrations are denoted by C_j and the total concentration Ψ_j is defined by

$$\Psi_j \;=\; C_j + \sum_i \nu_{ji} C_i, \tag{23}$$

where the sum is over secondary species with concentrations C_i related by the mass action relations

$$C_i \;=\; \gamma_i^{-1} K_i \prod_j \left(\gamma_j C_j\right)^{\nu_{ji}}, \tag{24}$$

to primary species concentratins C_j. Quantities K_i, $\gamma_{j,i}$, ν_{ji} denote the equilibrium constant, activity coefficients for primary and secondary species, and stoichiometric reaction coefficients. Mineral reaction rates I_m have the form

$$I_m \;=\; -k_m a_m\big(1 - K_m Q_m\big), \tag{25}$$

motivated by transition state theory with equilibrium constant K_m and ion activity product Q_m, Sorbed concentrations for minerals and colloids obey the conservation equations

$$\frac{\partial S^m_{j_0}}{\partial t} = \frac{1}{z_{j_0}}\sum_{j\neq j_0} I^m_{j_0 j}, \tag{26a}$$

$$\frac{\partial S^m_{j}}{\partial t} = -\frac{1}{z_{j}} I^m_{j_0 j}, \tag{26b}$$

for minerals, and

$$\frac{\partial S^c_{j_0}}{\partial t} + \boldsymbol{\nabla}\cdot\left(\boldsymbol{q}_c S^c_{j_0}\right) = \frac{1}{z_{j_0}}\sum_{j\neq j_0} I^c_{j_0 j}, \tag{27a}$$

$$\frac{\partial S^c_{j}}{\partial t} + \boldsymbol{\nabla}\cdot\left(\boldsymbol{q}_c S^c_{j}\right) = -\frac{1}{z_{j}} I^c_{j_0 j}, \tag{27b}$$

for colloids labeled with superscript c, where the colloid velocity $\boldsymbol{q}_c$ may be different from the fluid velocity $\boldsymbol{q}$.

Similar expressions hold for the exchange reactions of the form of reactions (1b) but with different stoichiometric exchange coefficients

$$\frac{\partial}{\partial t}\varphi\Psi_{j_0} + \boldsymbol{\nabla}\cdot\Big(\boldsymbol{q}\Psi_{j_0} - \varphi D\boldsymbol{\nabla}\Psi_{j_0}\Big) = -\sum_{i\neq j_0,\,m} z_j \widetilde{I}^m_{j_0 j} - \sum_m \nu_{j_0 m} I_m, \tag{28a}$$

$$\frac{\partial}{\partial t}\varphi\Psi_{j} + \boldsymbol{\nabla}\cdot\Big(\boldsymbol{q}\Psi_{j} - \varphi D\boldsymbol{\nabla}\Psi_{j}\Big) = z_{j_0}\sum_m \widetilde{I}^m_{j_0 j} - \sum_m \nu_{im} I_m, \tag{28b}$$

with sorbed concentrations for minerals

$$\frac{\partial S^m_{j_0}}{\partial t} = \sum_{i\neq j_0} z_j \widetilde{I}^m_{j_0 j}, \tag{29a}$$

$$\frac{\partial S^m_{j}}{\partial t} = -z_{j_0} \widetilde{I}^m_{j_0 j}. \tag{29b}$$

and colloids

$$\frac{\partial S^c_{j_0}}{\partial t} + \boldsymbol{\nabla}\cdot\big(\boldsymbol{q}_c S^c_{j_0}\big) = \sum_{i\neq j_0} z_j \widetilde{I}^c_{j_0 j}, \tag{30a}$$

$$\frac{\partial S^c_{j}}{\partial t} + \boldsymbol{\nabla}\cdot\big(\boldsymbol{q}_c S^c_{j}\big) = -z_{j_0} \widetilde{I}^c_{j_0 j}. \tag{30b}$$

Eliminating the exchange rates from the primary species equations gives the following partial differential equation for primary species concentrations

$$\frac{\partial}{\partial t}\Big(\varphi\Psi_j + \sum_m S^m_j + \sum_c S^c_j\Big) + \boldsymbol{\nabla}\cdot\Big(\boldsymbol{q}\Psi_j + \sum_c \boldsymbol{q}_c S^c_j - \varphi D\boldsymbol{\nabla}\Psi_j\Big) \;=\; -\sum_m \nu_{jm} I_m. \tag{31}$$

This equation is valid for all exchangeable cations and for both forms of the exchange reactions.

It follows that for both formulations charge is conserved. Multiplying Eqn.(31) by the valence of the jth species and summing over all species gives

$$\Big(\frac{\partial}{\partial t}\varphi + \boldsymbol{\nabla}\cdot\boldsymbol{q} - \varphi D\boldsymbol{\nabla}\Big)\sum_j z_j\Psi_j \;=\; 0. \tag{32}$$

This is a consequence of neutrality of minerals ($\sum_j z_j\nu_{jm}=0$), and conservation of exchange sites according to the result

$$\frac{\partial \omega_m}{\partial t} \;=\; \frac{\partial \omega_c}{\partial t} \;=\; 0. \tag{33}$$

implying that the cation exchange capacity of the porous medium is constant. The surface area for sorption is related to mineral abundances which may change over time and space due to precipitation/dissolution reactions.

It should be noted that for the often employed rate equation of the form

$$I_j \;=\; -k_j\big(S_j - K^D_j\Psi_j\big), \tag{34}$$

with rate constant k_j and where K_j^D denotes the distribution coefficient, which yields the correct relation between sorbed and aqueous concentrations at equilibrium ($S_j = K_j^D \Psi_j$), this rate law does *not* conserve charge. Presently, there does not exist sufficient data to determine the correct form of the kinetic rate law for ion exchange (or surface complexation) reactions on colloids or mineral surfaces.

2.2 Retardation

It follows from the primary species transport equations that for approximately constant distribution coefficients giving the ratio of sorbed to aqueous concentrations for mineral and colloid sorption, that the migration of each cation is retarded by the factor $\mathcal{R}_j$ defined as

$$\mathcal{R}_j \;=\; \frac{1 + \sum_m K_j^m + \sum_c K_j^c}{1 + \sum_c f_c K_j^c}, \tag{35}$$

where $f_c = q_c/q$, and distribution coefficients K_j^m and K_j^c for minerals and colloids, respectively, are defined by

$$K_j^m \;=\; \frac{1}{\varphi \Psi_j} S_j^m, \tag{36}$$

and

$$K_j^c \;=\; \frac{1}{\varphi \Psi_j} S_j^c. \tag{37}$$

For $f_c = 1$, $\mathcal{R}_j$ simplifies to

$$\mathcal{R}_j \;=\; 1 + \frac{\sum_m K_j^m}{1 + \sum_c K_j^c}. \tag{38}$$

Thus according to this latter expression, for $\sum_c K_j^c \gg \sum_m K_j^m \gg 1$, colloids effectively eliminate retardation. However, for sorption on colloids to effectively compete with mineral surfaces, generally requires high colloid concentrations (Honeyman and Ranville, 2002).

2.3 Numerical Implementation

An initial attempt to modify FLOTRAN (Lichtner, 2001) to implement sorption kinetics did not succeed because of major restructuring of the code that was required. The global implicit scheme utilized by FLOTRAN only solved the aqueous primary species transport equations in a coupled manner, whereas to simulate kinetic ion exchange, sorbed species needed to be solved simultaneously with the aqueous primary species equations. A new approach is currently being implemented which requires only minor modifications to the existing code, achieved by storing the existing residual and Jacobian arrays into new arrays that are dimensioned to include the sorbed species.

2.4 References

Frost A.A., and R.G. Pearson (1963) *Kinetics and Mechanism: A Study of Homogeneous Chemical Reactions*, John Wiley & Sons, 2nd Edition, pp 405.

Honeyman, B. D.; Ranville, J. F. (2002) Colloid properties and their effects on radionuclide transport through soils and groundwater. In Geochemistry of Soil Radionuclides; Zhang, P.-C., Brady, P. V., Eds.; SSSA Special Publication 59; Soil Science Society of America: Madison, WI; pp 131–163.

Kersting, A.B., D.W. Efurd, D.L. Finnegan, D.J. Rokop, D.K. Smith, and J.L. Thompson (1999) Migration of plutonium in groundwater at the Nevada Test Site, Nature, 397: 56–59.

Lichtner, P. C., S. Yabusaki, K. Pruess, and C. I. Steefel (2004) Role of competitive cation exchange on chromatographic displacement of cesium in the vadose zone beneath the Hanford S/SX tank farm, Vadose Zone J., 3, 203–219.

Steefel, C. I., S. Carroll, P. Zhao, and S. Roberts (2003) Cesium migration in Hanford sediment: a multisite cation exchange model based on laboratory experiments, J. Contam. Hydrol., 67, 219–246.

3 Information Access

Publications:

Chen, G., M. Flury, J. B. Harsh, and P. C. Lichtner, Colloid-facilitated transport of cesium in variably-saturated Hanford sediments, Environ. Sci. Technol., 39, 3435–3442, 2005.