Final Report

Influences of Flow Transients and Porous Medium Heterogeneity on Colloid-Associated Contaminant Transport in the Vadose Zone

Award Numbers: DE-FG07-02ER63492 (Yale) and DE-FG07-02ER63491 (Colorado)

Project ID: 86900

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Summary

Radionuclides, metals, and dense non-aqueous phase liquids have contaminated about six billion cubic meters of soil at Department of Energy (DOE) sites. The subsurface transport of many of these contaminants is facilitated by colloids (i.e., microscopic, waterborne particles). The first step in the transport of contaminants from their sources to off-site surface water and groundwater is migration through the vadose zone. Developing our understanding of the migration of colloids and colloid-associated contaminants through the vadose zone is critical to assessing and controlling the release of contaminants from DOE sites. In this study, we examined the mobilization, transport, and filtration (retention) of mineral colloids and colloid-associated radionuclides within unsaturated porous media. This investigation involved laboratory column experiments designed to identify properties that affect colloid mobilization and retention and pore-scale visualization experiments designed to elucidate mechanisms that govern these colloid-mass transfer processes. The experiments on colloid mobilization and retention were supplemented with experiments on radionuclide transport through porous media and on radionuclide adsorption to mineral colloids. Observations from all of these experiments – the column and visualization experiments with colloids and the experiments with radionuclides – were used to guide the development of mathematical models appropriate for describing colloids and colloid-facilitated radionuclide transport through the vadose zone.

Project Objectives

Our research was guided by an Environmental Management and Science Program (EMSP) goal to improve conceptual and predictive models of contaminant movement in vadose-zone environments. As described in the report *National Roadmap for Vadose-Zone Science and Technology* [*DOE,* 2001], soil-water colloids are capable of adsorbing contaminants, such as radionuclides and metals, and facilitating their migration through the vadose zone and towards groundwater reservoirs. Our research centered on advancing understanding of this phenomenon. In particular, we combined laboratory experimentation with mathematical modeling to

1. elucidate the effects of porewater-flow transients on colloid mobilization in unsaturated porous media;
2. determine the sensitivity of colloid deposition rates to changes in porewater pH and colloid mineralogy;
3. identify mechanisms that govern mineral-colloid mobilization and deposition in unsaturated porous media;
4. develop and test mathematical models appropriate for simulating colloid mobilization, transport, and deposition under both steady-flow and transient-flow conditions;
5. quantify the effects of mineral-grain geometry and surface roughness on colloid-filtration rates;
6. evaluate the influences of colloids on the transport of strontium and cesium (i.e., DOE-contaminants-of-concern) through soils and sediments; and
7. explore the role of porous-medium heterogeneity on colloid transport.

Summary of Project Activities

Column Experiments on Colloid Mobilization and Retention

Colloid mobilization and retention were examined in sand-packed columns that measured 12.7 cm in diameter and 32.8 cm in length. Moisture probes for measuring saturation and tensiometers for measuring capillary pressure were inserted at 7.7, 16.4, and 25.1 cm from the top of the columns. Peristaltic pumps at the inflow (top) and outflow (bottom) ends of the column regulated the sand-pack moisture content and the downward flow or water and colloids through the porous media.

We found that colloids composed of illite and kaolinite exhibited high mobility over a range of moisture contents, although deposition reactions at air-water and solid-water interfaces did affect their transport [*Gao et al.*, 2004]. The filtration of illite colloids was insensitive to changes in porewater pH and was probably dominated by straining within films of water that lined partially saturated pores (Figures 1a – 1c). Kaolinite deposition, on the other hand, increased substantially as porewater pH declined (Figures 1d – 1f), which suggests that its transport is strongly influenced by electrostatic interactions at air-water and solid-water interfaces.

Transients in porewater flow induced rapid mobilization of retained colloids F*Gao et al.*, 2004]. Mineral colloids made of kaolinite were mobilized in concentrations that exceeded

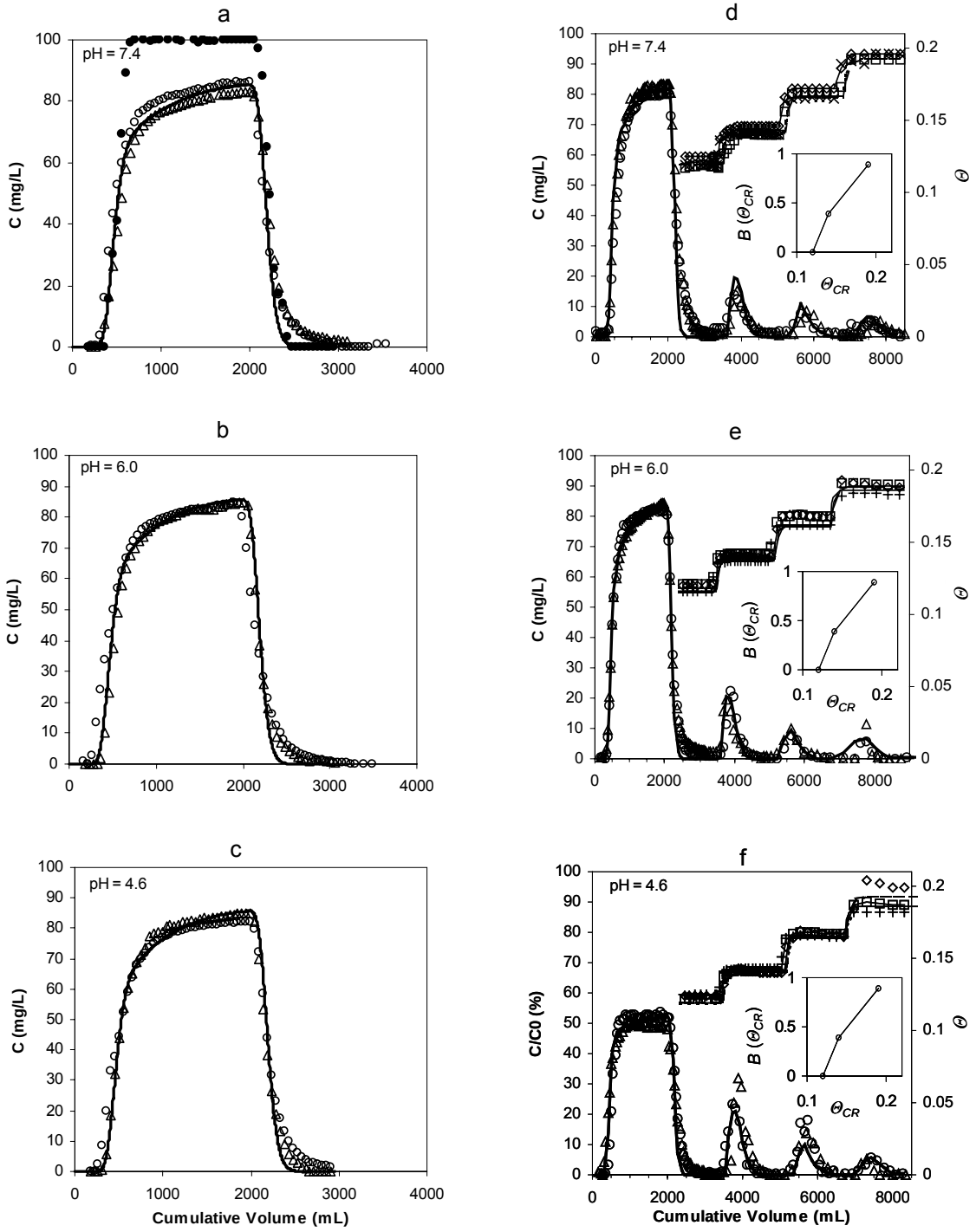

Figure 1. Model-calculated effluent concentrations (lines) and those measured in duplicate experiments (open circles and triangles) with (a – c) illite and (d – f) and kaolinite. Experiments with illite were run under steady-flow conditions, while the experiments with kaolinite involved a steady-flow period (0 – 2,500 mL) followed by transient-flow periods in which column inflow and outflow rates were increased in a step-wise fashion (2,500 – 8,500 mL). The filled circles in (a) denote the breakthrough curve for bromide. The diamonds, squares, and pluses in (d – f) delineate moisture contents measured at 7.7, 16.4, and 25.1 cm from the top of the column, respectively, while the associated lines represent moisture contents computed by solving the Richards' equation. The insets in (d – f) show the optimal cumulative densities for Θ_{CR}. See *Gao et al*. [2004] for further explanation.

20 mg L^{-1} during column experiments conducted under transient-flow conditions typical of rainfall-induced infiltration events (Figures 1d – 1f). In these experiments, the mass of colloids mobilized during imbibition (wetting) of the porous medium was closely linked to the magnitude of the moisture-content increase, and the rate of colloid release scaled linearly with porewater velocity. We quantified this colloid-mobilization with a model that incorporated a simple parameterization scheme to distribute the colloid-release response over a range of moisture contents [*Gao et al.*, 2004].

Colloids were not only mobilized during imbibition, but also during porous-medium drainage (Figure 2). We discovered that moving air-water interfaces associated with a downward propagating drying front scoured kaolinite colloids from surfaces of the porous medium [*Saiers et al.*, 2003]. The efficiency of the air-water interfaces in scavenging immobile colloids varied directly with drying-front velocity and inversely with porewater ionic strength. A model that approximated the porous medium as a bundle of capillary tubes and that coupled pressure-head changes to rates of air-water interface movement reproduced the time-series data on effluent kaolinite concentrations measured during column drainage [*Saiers et al.*, 2003].

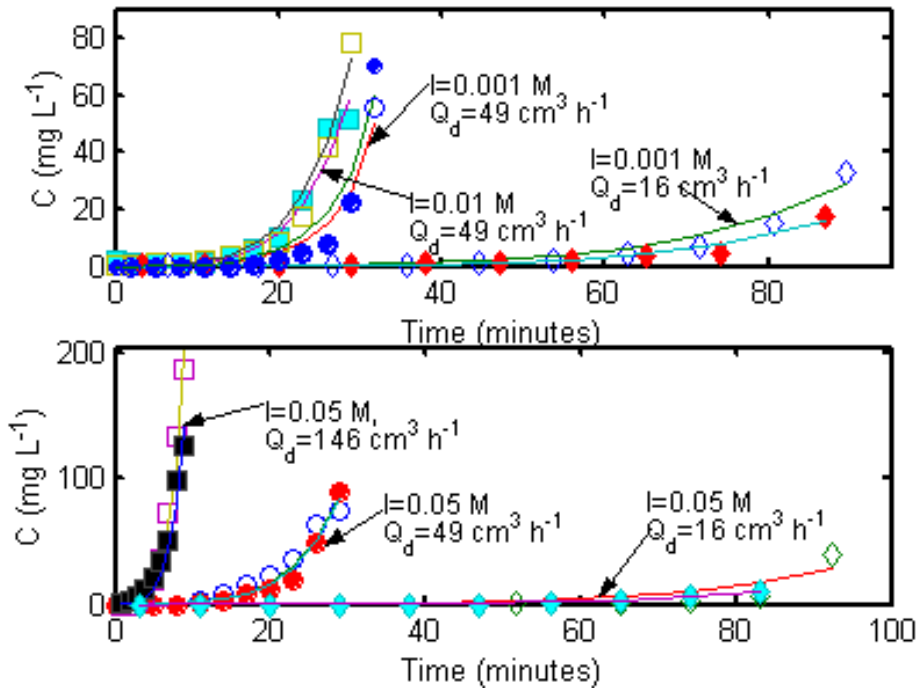

Figure 2. Measured (symbols) and modeled (lines) concentrations of kaolinite colloids mobilized during drainage of quartz sand packs. Kaolinite colloids were deposited on the sand within water-saturated columns and then mobilized from the sand as the drying front moved through the sand during column drainage. The experiments are distinguished on the basis of ionic strength (I) and the volumetric discharge measured during drainage of the sand pack (Q_d). Time equals zero minutes at the onset of drainage. See Saiers et al. [2003] for additional details.

Pore-Scale Visualization Experiments

We developed pore-scale visualization techniques to test our inferences on mechanisms that govern colloid retention and mobilization in the column experiments [*Gao et al.*, 2006]. In these experiments, a transparent flow cell packed with a thin layer of unsaturated sand was placed on a stage of an inverted microscope to permit direct observation of retention and mobilization.

Multiple mechanisms contributed to colloid retention in the visualization experiments [*Gao et al.*, 2006]. Insular air bubbles scavenged colloids, which is consistent with results of experiments conducted with etched micromodels [*Wan and Wilson*, 1994; *Sirivithayapakorn and Keller*, 2003]. Colloids also were retained within thin films of water that stretched between pendular rings of unsaturated pores (Figure 3a) – results that confirm previous speculation of the significance of film straining in influencing colloid mobility [*Wan and Tokunaga*, 1997; *Lenhart and Saiers*, 2002; *Saiers and Lenhart*, 2003]. Colloids were effectively immobilized upon entry and subsequent storage within zones of stagnant water (Figure 3b). This concept of stagnant-water zones has long been used to account for the storage of solutes, but, with very few exceptions [*Gamerdinger and Kaplan*, 2001; *Cherrey et al.*, 2003], has been ignored in descriptions of colloid transport and, prior to our work, no confirmatory evidence for stagnant-water storage of colloids existed.

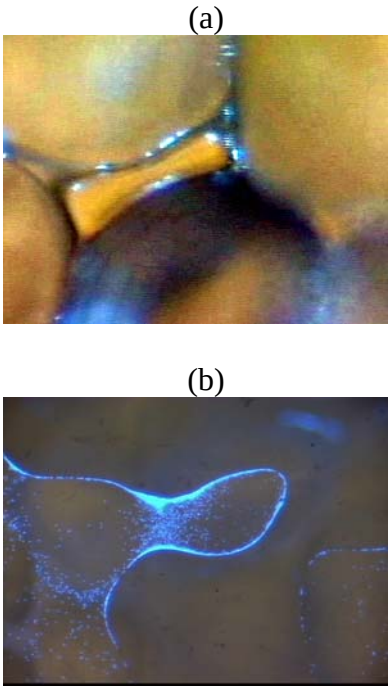

Figure 3. Pore-scale visualization of colloid immobilization: (a) colloids retained within thin films and pendular rings of a partially saturated pore (air occupies the center of the pore) and (b) colloids stored within stagnant-water regions that branch off from mobile-water regions (note colloid accumulation along perimeter of stagnant water zone at air-water boundary) (*Gao et al.*, 2006).

The visualization experiments were especially useful in yielding insight into the mechanism that control colloid mobilization [*Gao et al.*, 2006]. During transient porewater flow, characterized by temporal increases in moisture content, two mechanisms dominated the mobilization response. Film-strained colloids were released as the films were abruptly eliminated when partially saturated pores filled spontaneously with water. Porous-medium imbibition also promoted the release of colloids held within stagnant-water zones as water invaded air-filled regions of the porous medium and fragmented stagnant-water zones reconnected to areas of bulk fluid flow. The increases in flow rate that accompanied the moisture-content increases during the transient-flow experiments did not shear detectable quantities of colloids from the surfaces of the sand grains or insular air bubbles. Knowledge gained from these experiments is being used to refine the structure of our mathematical models that account for coupled transient porewater flow, colloid mobilization, and transport. This work is being conducted as part of our current EMSP award (DE-FG02-06ER64188).

Pore-Scale Modeling: Influences of Mineral-Grain Shape and Roughness on Colloid Filtration

Even in our well-controlled laboratory systems, the porous medium is non-ideal, consisting of non-spherical mineral grains with considerable surface roughness. Published theoretical descriptions of colloid filtration, which were developed for water-saturated systems, are not designed to account for these non-idealities. One aspect of our research was devoted to modifying colloid-filtration theory to account for non-idealities associated with real geologic materials [*Saiers and Ryan*, 2005]. Through statistical analysis of pore-scale simulations of laminar flow and convective-diffusive transport, we have quantified how colloid-filtration rates (i.e., the single-collector contact efficiency) vary with porewater velocity, colloid size, and measurable indices that quantify mineral-grain shape and surface roughness (Figure 4). Our published results are appropriate for water-saturated systems. We are currently extending this analysis to account for complexities associated with water-unsaturated porous media. We believe this work will facilitate a shift from empirical descriptions of colloid deposition in the vadose zone to one in which colloid deposition can be predicted on the basis of measurable system properties.

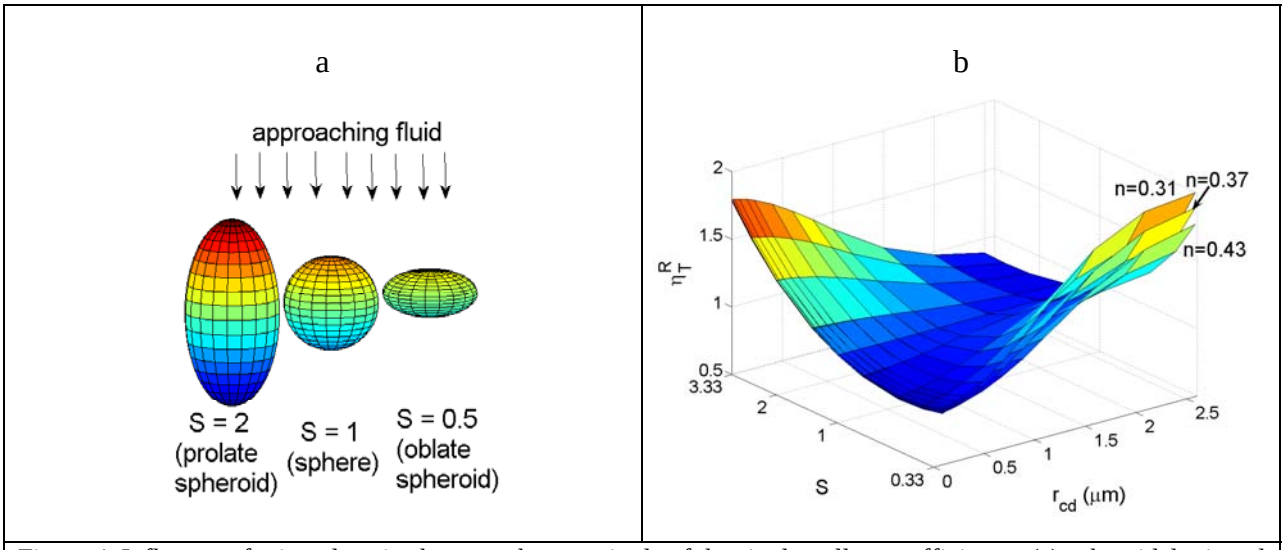

Figure 4. Influence of mineral-grain shape on the magnitude of the single-collector efficiency. (a) spheroidal mineral grains characterized by the shape index *S*, which expresses the ratio of the length of the semi-axis oriented parallel to the flow direction of the approaching fluid to the length of the semi-axes oriented normal to the approaching flow. (b) effects of mineral-grain shape (*S*) and colloid radius (r_{cd}) on the magnitude of η_T^R. η_T^R is a measure of the deviation in the single-collector contact efficiency (η_T) caused as a spherical collector changes shape, but its grain size remains constant. The three η_T^R-*S*-r_{cd} response surfaces are distinguished on the basis of porosity (*n*). See Saiers and Ryan [2005] for additional details.

Colloid Transport Through Structured, Heterogeneous Porous Media

As a part of this project, we initiated a study of the influences of structured heterogeneities on the migration of mineral colloids [*Gao et al.*, In prep.]. This involved measuring the movement of kaolinite particles through columns constructed by embedding a tubule of coarse-grained sand within a matrix of fine-grained sand. Analysis of measurements made during

experiments conducted under water-saturated conditions indicated that advective-dispersive colloid transport occurred in both the coarse-grained tubule and surrounding fine-grained matrix and that colloid exchange between these two mobile-water domains was small. In experiments in which the column was placed under tension, the fine-grained matrix remained nearly water saturated and served as the primary conduit for colloid transport, while the moisture content and pore-water velocities within the coarse-grained tubule were comparatively low. Under unsaturated conditions, colloids were held at air-water interfaces along the boundary between the fine-grained matrix and unsaturated coarse-grained tubule indicating that the coarse-grained tubule served as a sink for colloids. These findings suggest that zones of high intrinsic permeability, such as macropores, root channels, and fractures, may serve as preferential colloid-transport pathways in water-saturated porous media, but may contribute little to colloid mobility under a wide range of conditions in vadose-zone environments.

Desorption Kinetics and Colloid-Facilitated Transport of Cations: Flow-Through Column Study

One of the key criteria for facilitated transport is that desorption of the contaminants from the colloids is slow relative to the transport time. Only if desorption is slow can colloids carry contaminants ahead of a contaminant plume [*Ryan and Elimelech*, 1996; *Roy and Dzombak*, 1998]. While this criterion is well known [*Vilks et al.*, 1993], its importance had only been inferred from field evidence and models [*Roy and Dzombak*, 1998]. To test this criterion, we examined the facilitated transport of Cs^+ and Sr^{2+} by illite colloids in saturated flow-through columns containing quartz sand [*Turner et al.*, under review (a)]. To model the transport of the cations and colloids, we adapted the Saiers and Hornberger [1999] model of colloid-facilitated transport to account for second-order cation adsorption to and desorption from the quartz, second-order cation adsorption to and desorption from "fast" and "slow" sites on the illite colloids, and second-order colloid deposition to and release from the quartz. The column results and model simulations revealed that strontium desorption from the illite colloids was indeed about three times faster than that for cesium, and that cesium desorption was slow relative to the rate of transport (Figure 5, cesium; Figure 6, strontium). Sensitivity analysis showed that the cation adsorption capacity of the quartz sand was a critical parameter for modeling the transport results. The fast and slow sites on the illite colloids behaved like planar and frayed edge sites typically identified for cesium adsorption to illite. The amount of cesium adsorbed to the slow, or frayed edge, sites was similar to the frayed edge site density of illite estimated by other researchers.

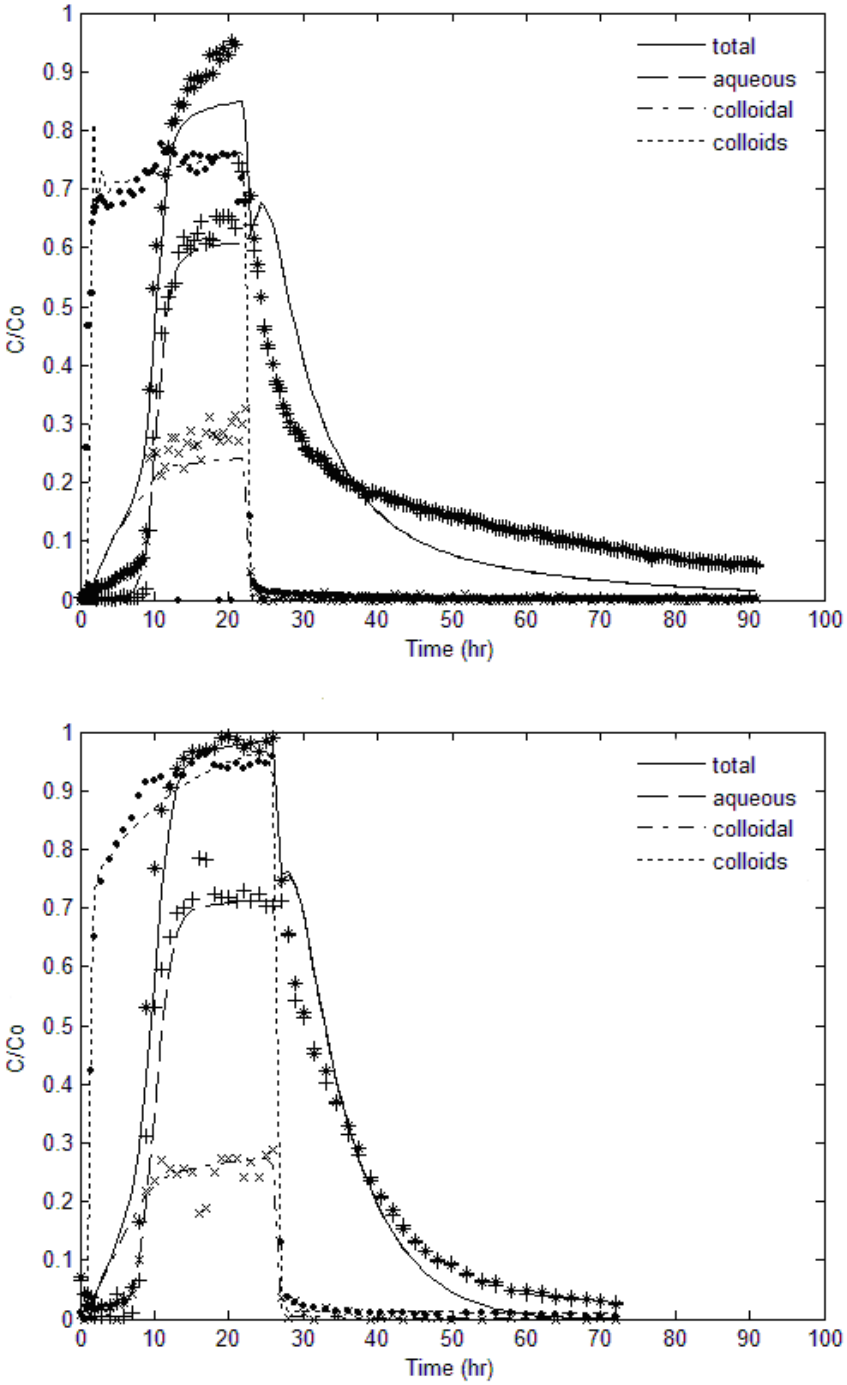

Figure 5. Experimental data and model fits for colloid-facilitated cesium transport in quartz sand at 0.1 mM ionic strength (above) and 2.0 mM ionic strength (below). The total cesium concentration in the injection solution is 7.5×10^{-7} M and the illite colloid concentration is 100 mg L^{-1}. Symbols: total cesium (*), aqueous (dissolved) cesium (+), colloidal cesium (×), and illite colloids (•). Model fits are shown by the series of lines in the legend.

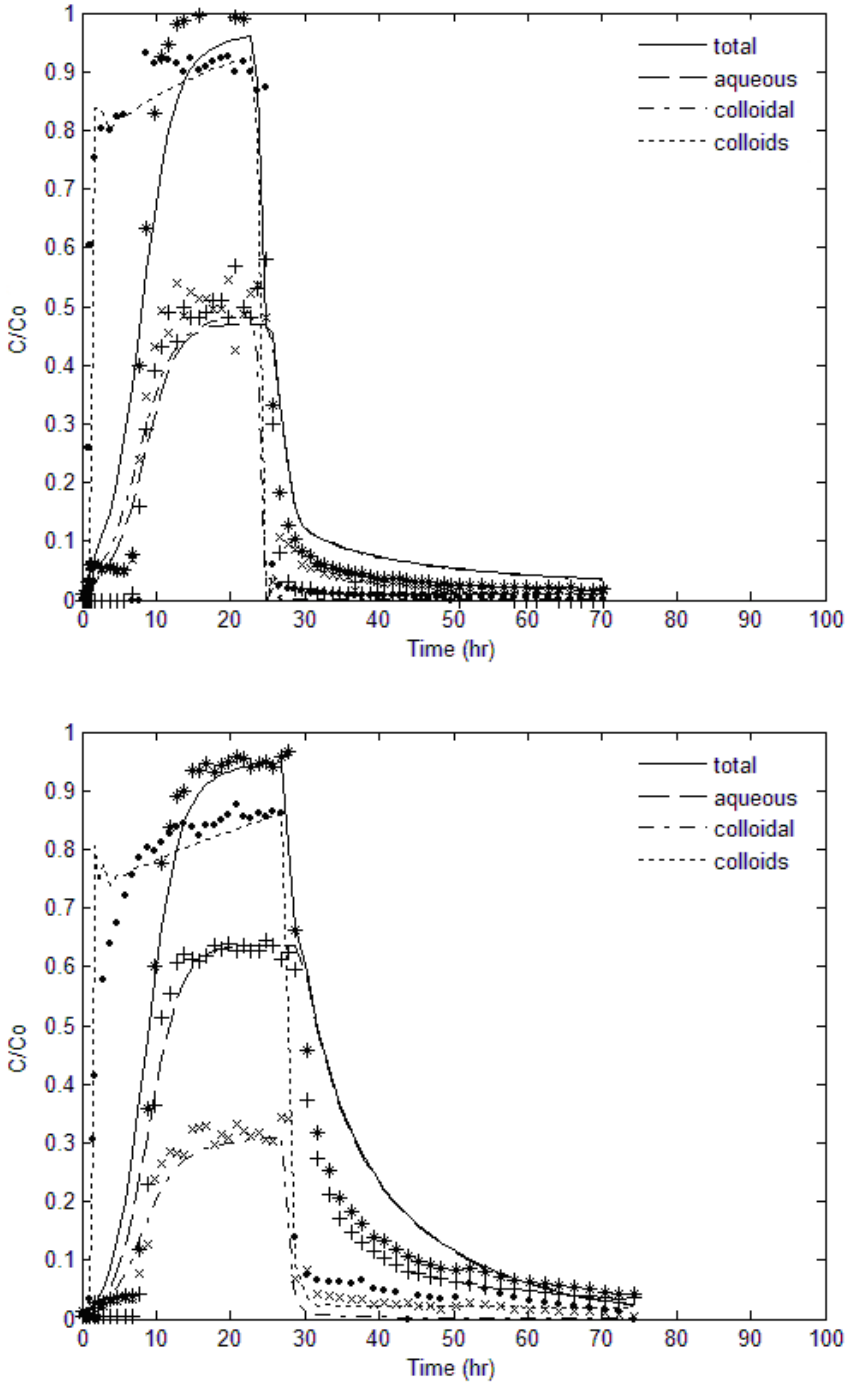

Figure 6. Experimental data and model fits for colloid-facilitated strontium transport in quartz sand at 0.1 mM ionic strength (above) and 2.0 mM ionic strength (below). The total strontium concentration in the injection solution is 7.5×10^{-6} M and the illite colloid concentration is 100 mg L^{-1}. Symbols: total strontium (*), aqueous (dissolved) strontium (+), colloidal strontium (×), and illite colloids (•). Model fits are shown by the series of lines in the legend.

Desorption Kinetics and Colloid-Facilitated Transport of Cations: Recirculating Column Study

Slow desorption of cesium from illite was particularly evident at nanomolar cation concentrations in a recirculating column (*Turner et al.*, in review (b)). The recirculating column was designed to examine the kinetics of cation adsorption/desorption to illite colloids and quartz sand in a way that could not be done in simple batch experiments. Equilibrated suspensions of cesium, strontium, and illite colloids were recirculated through saturated columns of 15 and 30 cm length containing quartz sand. The experiments simulated resident times of 31 to145 h and transport distances of 8.6 to 40.7 m by recirculating the cation/illite suspension through the column 57 to 135 times.

Both cesium and strontium displayed desorption kinetics that indicate two types of adsorption sites on the illite. For strontium, about three-quarters of the desorption from the illite colloids occurred rapidly over the first 6 h, and about one-quarter of the desorption occurred slowly (Figure 7). The initial fast desorption was about 400 times faster than the slow desorption. For the cesium, desorption from the illite colloids occurred rapidly for about three-fifths of the cesium (Figure 8). The other two-fifths of the cesium sites accumulated cesium over time.

We surmised that some of the cesium initially desorbed from the illite colloids was adsorbed to the quartz, and later desorbed from the quartz and accumulated on high-affinity frayed edge sites on the illite colloids. This accumulation significantly increased the importance of colloid-facilitated transport for cesium by illite colloids.

Colloid-Facilitated Cation Transport Experiments in Unsaturated Porous Media

The cation desorption kinetics parameters are now being used to evaluate cesium and strontium transport in unsaturated columns of homogeneous and physically heterogeneous quartz sand. Initial experiments will focus on the examining the differences between saturated and unsaturated colloid-facilitated transport by conducting experiments similar to those reported above for saturated porous media in unsaturated porous media of varying moisture contents. The results of these experiments will be modeled by combining models of colloid transport in unsaturated porous media (*Lenhart and Saiers*, 2002) and colloid-facilitated cation transport (*Turner et al.*, in review (a)). Other experiments will determine the effects of physical heterogeneity in unsaturated porous media. A macropore will be simulated by constructing a column containing a thin cylinder of coarse-grained sand in a matrix of fine-grained sand. We will complete these experiments concurrently with the experiments for the current EMSP grant.

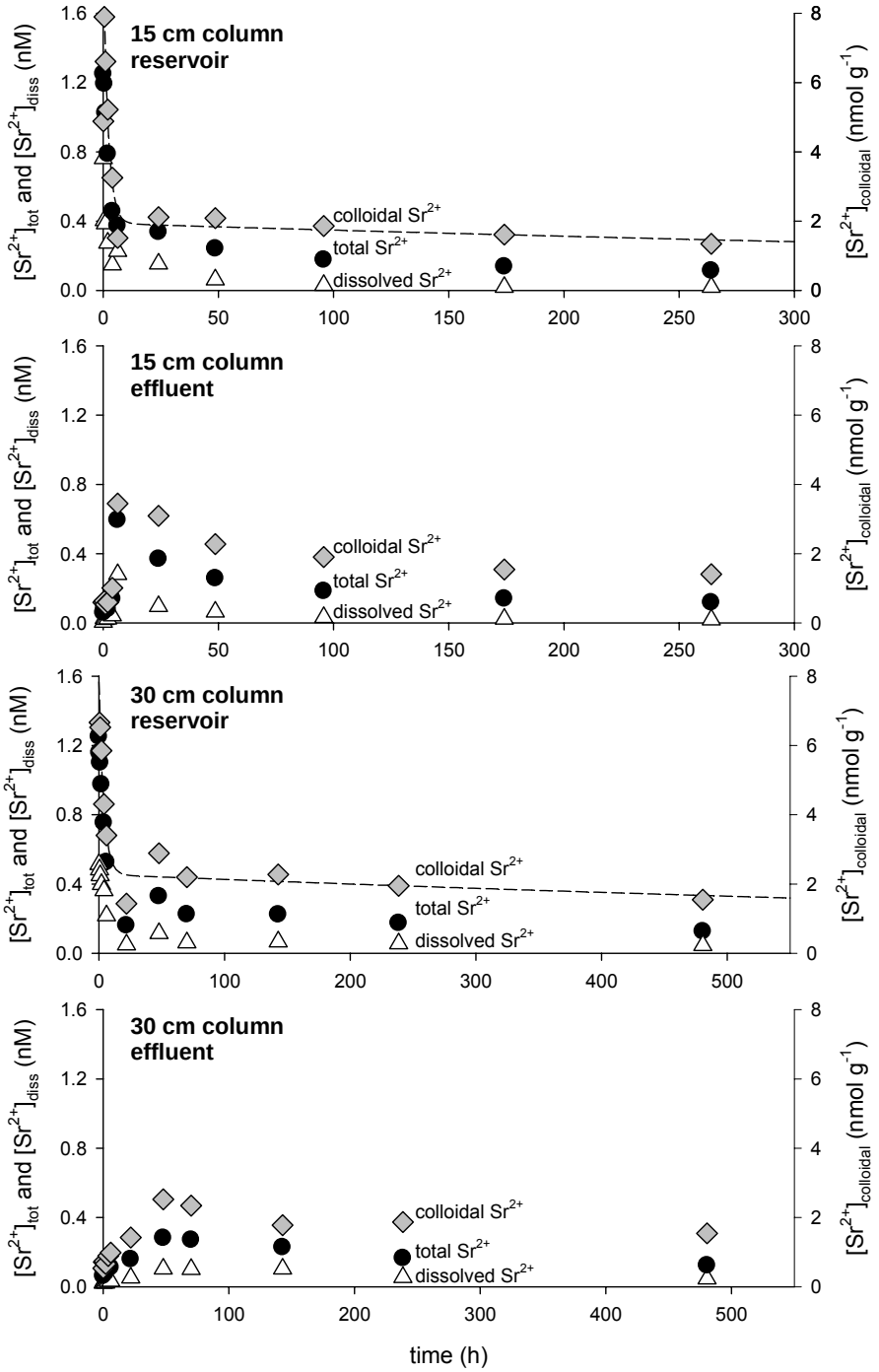

Figure 7. Concentration of total ($[Sr^{2+}]_{tot}$), dissolved ($[Sr^{2+}]_{diss}$), and colloidal ($[Sr^{2+}]_{colloidal}$]) strontium as a function of time in the recirculating column experiments. Colloidal strontium concentration on right axis. Breakthroughs for the 15 cm column (two upper graphs, reservoir and effluent samples) and the 30 cm column (two lower graphs, reservoir and effluent samples). Dashed curves show the fit of the two-site kinetic model to the colloidal strontium data in the reservoir.

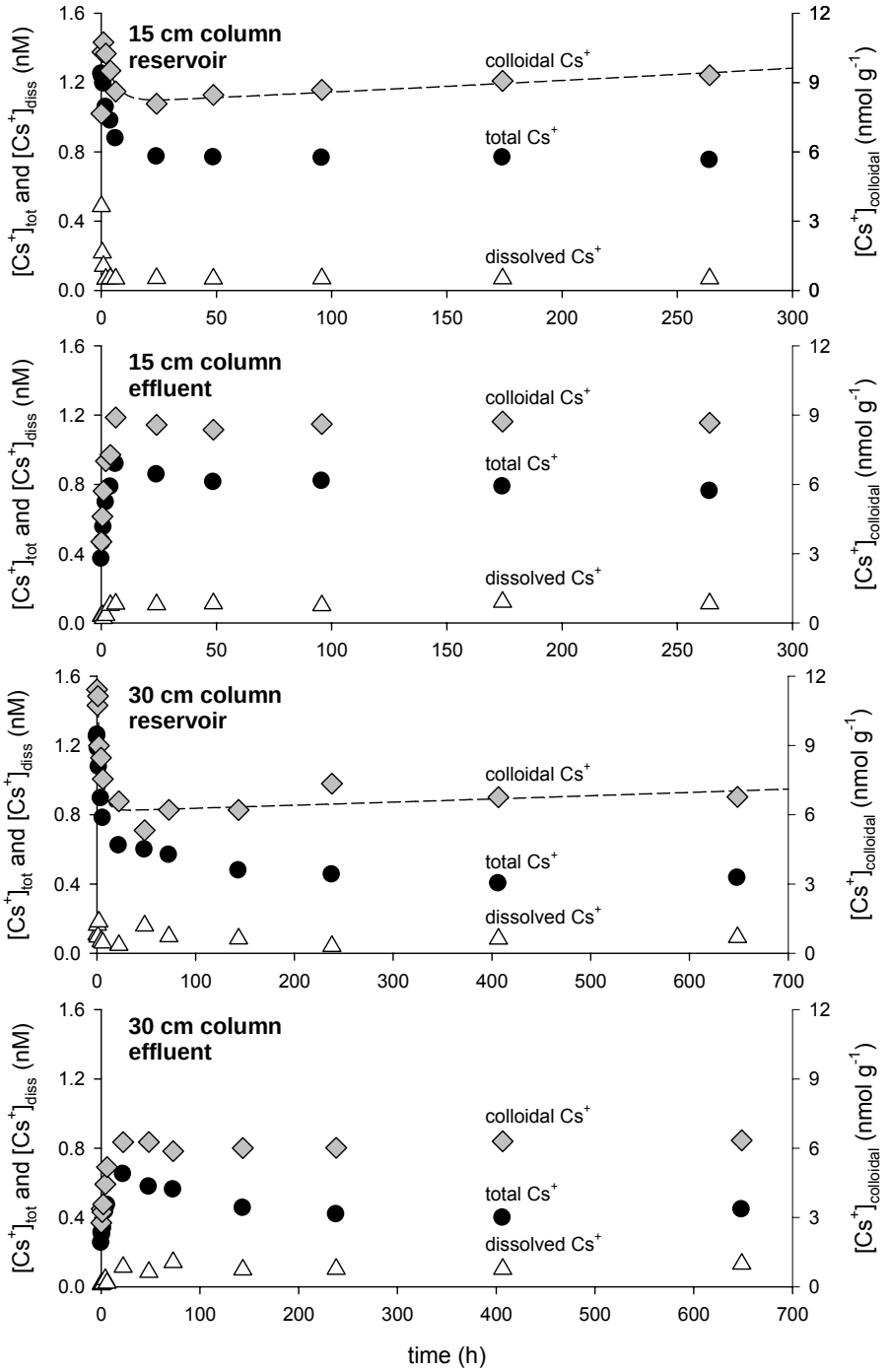

Figure 8. Concentration of total ($[Cs^+]_{tot}$), dissolved ($[Cs^+]_{diss}$), and colloidal ($[Cs^+]_{colloidal}$]) cesium as a function of time in the recirculating column experiments. Colloidal cesium concentration on right axis. Breakthroughs for the 15 cm column (two upper graphs, reservoir and effluent samples) and the 30 cm column (two lower graphs, reservoir and effluent samples). Dashed curves show the fit of the two-site kinetic model to the colloidal cesium data in the reservoir.

Research Products: Peer-Reviewed Publications and Conference Presentations

Findings from this research have been reported in eight manuscripts that have been published or submitted for publication (Box 1). We also have presented our research at numerous scientific conferences in the U.S. and Europe (Box 2).

Box 1. Peer-reviewed papers attributed to the current Yale and University of Colorado EMSP grants: published, in review, and in preparation.

DeNovio, N.M., J.E. Saiers, and J.N. Ryan, 2004. Colloid movement in unsaturated porous media: Recent advances and future directions. *Vadose Zone Journal*, 3: 338-351.

Gao, B., J.E. Saiers, and J.N. Ryan, 2004. Deposition and mobilization of clay colloids in unsaturated porous media. *Water Resources Research*, 40(8), W08602, doi: 10.1029/2004WR003189.

Gao, B. J. E. Saiers, and J.N. Ryan. 2006. Pore-scale mechanisms of colloid deposition and mobilization during steady and transient flow through unsaturated granular media. *Water Resources Research,* 42, W01410, doi: 10.1029/2005WR004233.

Gao, B. J. E. Saiers, and J.N. Ryan. In prep. Transport of clay colloids in unsaturated, heterogeneous porous media. Submitted to *Journal of Contaminant Hydrology*.

Saiers, J.E., G.M. Hornberger, D.B. Gower, and J.S. Herman, 2003. The role of moving air-water interfaces in colloid mobilization within the vadose zone. *Geophysical Research Letters*, 30(21), 2083, doi: 10.1029/2003GL018418.

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Turner, N. B., J.N. Ryan, and J.E. Saiers. In review (a). The effect of desorption kinetics on colloid-facilitated transport of contaminants: Cesium, strontium, illite colloids, and a saturated quartz porous medium. In review at *Water Resources Research*.

Turner, N. B., J.N. Ryan, and J.E. Saiers. In review (b). Kinetics of cesium and strontium desorption from illite colloids in recirculating column of quartz sand. In review at *Environmental Science and Technology*.

Box 2. Presentations of research attributed to the current Yale and University of Colorado EMSP grant.

DeNovio N.M. and Ryan J.N., 2004. Effect of simulated rainfall on the facilitated transport of metals in unsaturated soil cores from a flood plain contaminated by mine wastes. Presented at the *Fall Meeting of the American Geophysical Union*, San Francisco, California, December 2004.

Gao, B. and J.E. Saiers, 2004. Influence of pH on deposition and mobilization of clay colloids in unsaturated porous media. *Proceedings of the 78th ACS Colloid and Surface Science Symposium*, New Haven, CT, June 20 – June 23, 2004.

Ryan J.N., Turner N.B., and Saiers J.E., 2006. Colloids, contaminants, and surface chemistry: Effect of desorption kinetics on the facilitated transport of cesium and strontium by illite colloids. To be presented at the *2006 Meeting of the American Institute of Chemical Engineering*, San Francisco, CA, November 12-17, 2006.

Ryan J.N., Turner N.B., and Saiers J.E., 2006. Colloid-facilitated transport of contaminants in porous media: Using cesium, strontium, and illite to illustrate the role of desorption kinetics. To be presented at the *Geological Society of America Meeting*, Philadelphia, PA, October, 2006.

Saiers, J.E., Gao, B., Xu, S., and Ryan, J.N. 2005. Colloid mobilization and deposition in unsaturated porous media. *Geological Society of America Meeting*, Salt Lake City, UT, October 16-19, 2005 (Invited).

Saiers, J.E., B. Gao, and J.N. Ryan, 2005. Colloid deposition and mobilization mechanisms in unsaturated porous media during steady and transient flow. Presented at the *General Assembly of the European Geosciences Union*, Vienna, Austria, April 25 - April 29, 2005 (Invited).

Saiers, J.E., B. Gao, and J.N. Ryan, 2004a. Visualization of colloid deposition and mobilization during unsteady and steady porewater flow through unsaturated porous media. *Fall Meeting of the American Geophysical Union.* San Francisco, CA, December 13 - December 17, 2004 (Invited).

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Turner, N. B., J.N. Ryan, and J.E. Saiers. In review (b). Kinetics of cesium and strontium desorption from illite colloids in recirculating column of quartz sand. In review at *Environmental Science and Technology*.

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