

FINAL REPORT
U.S. Department of Energy

**COLLOID TRANSPORT AND RETENTION IN FRACTURED
MEDIA**

Principal Investigator: John F. McCarthy
Institution: Oak Ridge National Laboratory

Project Collaborators

L. Liang and David Walker
(Oak Ridge National Laboratory)

Larry D. McKay
(University of Tennessee)

Motomu Ibaraki
(Ohio State University)

and Paul Reimus
(Los Alamos National Laboratory)

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EXECUTIVE SUMMARY

The goal of this project was to identify the chemical and physical factors that control the transport of colloids in fractured materials, and develop a generalized capability to predict colloid attachment and detachment based on hydraulic factors (head, flow rate), physical processes and structure (fracture aperture, matrix porosity), and chemical properties (surface properties of colloids, solution chemistry, and mineralogy of fracture surfaces).

Both aqueous chemistry and physical structure of geologic formations influenced transport. Results of studies at all spatial scales reached consensus on the importance of several key controlling variables: 1) colloid retention is dominated by chemical conditions favoring colloid-wall interactions; 2) even in the presence of conditions favorable to colloid collection, deposited colloids are remobilized over long times and this process contributes substantially to the overall extent of transport; 3) diffusive exchange between water-conducting fractures and finer fractures and pores acts to “buffer” the effects of the major fracture network structure, and reduces predictive uncertainties. Predictive tools were developed that account for fundamental mechanisms of colloid dynamics in fracture geometry, and linked to larger-scale processes in networks of fractures. The results of our study highlight the key role of physical and hydrologic factors, and processes of colloid remobilization that are potentially of even greater importance to colloid transport in the vadose zone than in saturated conditions. We propose that this work be extended to focus on understanding vadose zone transport processes so that they can eventually be linked to the understanding and tools developed in our previous project on transport in saturated groundwater systems.

RESEARCH OBJECTIVES

The goal of this project was to identify the chemical and physical factors that control the transport of colloids in fractured materials, and develop a generalized capability to predict colloid attachment and detachment based on hydraulic factors (head, flow rate), physical processes and structure (fracture aperture, matrix porosity), and chemical properties (surface properties of colloids, solution chemistry, and mineralogy of fracture surfaces).

In this project, we improved our fundamental understanding of the role of physical and chemical features of fractures (fracture aperture, fluid flow velocity and the surface characteristics of fracture walls) on transport of colloids of different sizes, compositions and surface charge using artificial one-dimensional fractures. This information was used to test hypotheses and confirm interpretations arising from colloid transport experiments using intact columns of fractured geological material, and field experiments in fractured formations. The fundamental understanding was used to improve descriptions of colloid transport and retention at multiple scales, including both mechanistic description to evaluate the fundamental forces controlling colloid-fracture interactions, as well as fracture network models to predict the larger-scale expression of these interactions on colloid transport. The models were tested against observed results of transport studies conducted both in simple “artificial fractures” and in intact monoliths of fractured porous media to (1) determine the extent to which laboratory descriptions of colloid transport in fractures were useful to predict behavior in natural systems, (2) identify which parameters postulated to control colloid transport in fractures need to be included in models, and thus which critical system descriptors must be characterized to evaluate the importance of colloid transport at a given lithology.

The column and field studies were conducted in a geological formation (the Conasauga Group) containing a highly fractured and highly weathered shale saprolite. This lithology represented an important and hydrologically interconnected flow path that is widely distributed throughout the southern Appalachians, including the mixed waste disposal trenches at several DOE facilities in Oak Ridge. Comparisons of transport at different depths—corresponding to differences in fracture network characteristics—was critical to general understanding and improved predictions of the role of colloids in contaminant migration because the study determined the interaction between fracture characteristics (fracture spacing, size distribution and wall surface composition) and colloid size and composition. This basic understanding is applicable over a range of lithologies relevant to DOE problems, including fractured lacustrine clay deposits at the Fernald Feed Materials Production Plant (Ohio), as well as fractured basalt at Idaho National Engineering Laboratory and the Hanford Site (Washington). The results of this study is also relevant to colloid and solute transport studies in fractured tuffs from the Nevada Test Site for the DOE Yucca Mountain Site Characterization Project.

METHODS AND RESULTS

Fundamental Description Of Particle Transport In Fractures

Using first principles, models were developed for particle deposition rate on the surface of fractures and results experimentally tested. The model is similar to those originally developed for describing aerosol and aqueous filtration by stationary collectors, but is unique in accounting for the geometry of the collector surface; in this case, infinite planes of two separated by a finite aperture width. Using a particle tracking method, an algorithm has been developed to describe the colloid dynamics in fractures, including consideration of particle diffusion, sedimentation under gravity field, and electrostatic interactions of colloids with fracture walls under infinite plane geometry. A steady state solution is attained. The particle diffusion and collection by walls are most significant, compared to gravitational sedimentation. We have also derived an analytical solution for large Peclet numbers under steady state (expressed in terms of parabolic cylinder functions), and confirmed agreement between this solution and the steady state solution given by the particle-tracking model (Walker and Liang, in review). An experimental system of 1-D parallel-plate artificial fracture with SiO₂-coated fracture walls was used to test and validate the model predictions (McCarthy, Liang and Walker in preparation; Fig. 1). The advanced mechanistically rigorous descriptions of colloid migration under infinite plane geometry will be incorporated in models of colloid transport in water films within partially saturated media.

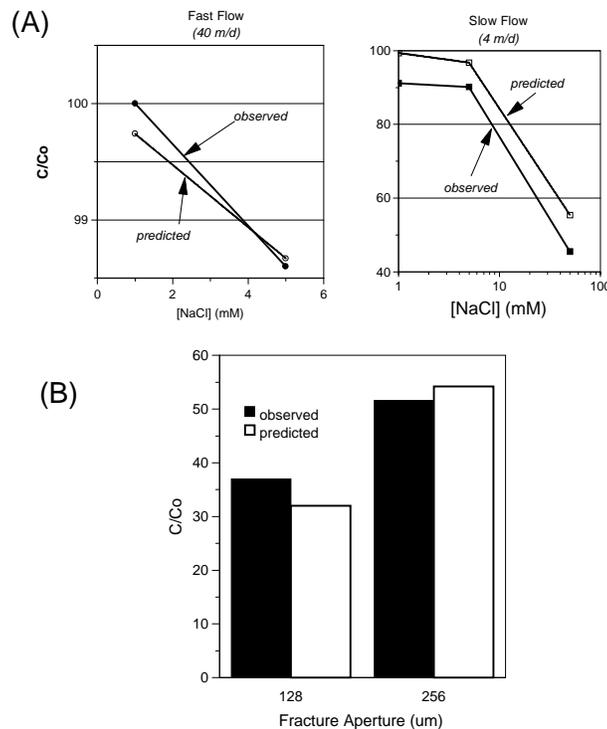
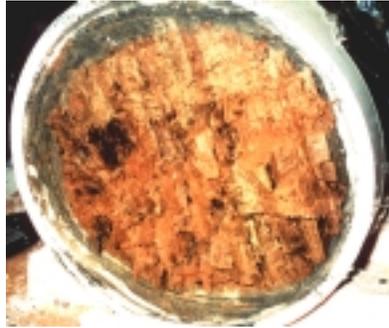


Figure 1. Comparison of analytical model predictions with experimental observations of colloid transport in artificial fracture apparatus. (A) Effect of flow rate and ionic strength on colloid transport through model fractures; (B) Effect of aperture width on colloid transport.

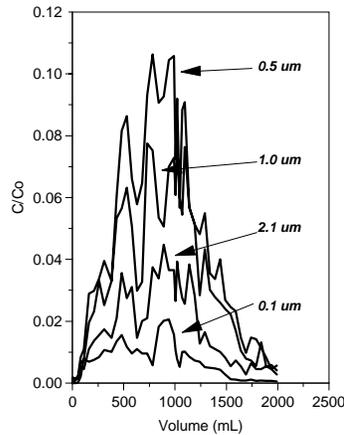
Colloid Transport In Intact Geological Columns

Colloid tracer experiments using undisturbed monoliths of fractured saprolite under water-saturated conditions investigated the influence of particle diameter and the ionic strength and cation valence of the groundwater solution. There was an optimum size of 0.5 to 1.0 μm for transport of the latex microspheres tracers. Loss of the smaller-than-optimum particles was attributed to the more rapid diffusion of the smaller particles, leading to more collisions with, and retention by, the fracture walls. This was confirmed by dismantling of the core and mapping of distribution of the microspheres using petrographic thin sections and epifluorescent microscopy to visualize the fluorescent colloids. In experiments using aqueous solutions containing different ionic strengths of monovalent (Na^+) and divalent (Ca^{2+}) cations, colloid retention increased as ionic strength increased, with far greater retention with the divalent cations (Fig. 2).

(A) Cross-section of the undisturbed monolith of fractured Dismal Gap formation saprolite



(B) Typical Colloid Breakthrough Curve



(C) Effect of Ionic Strength and Composition on Colloid Transport

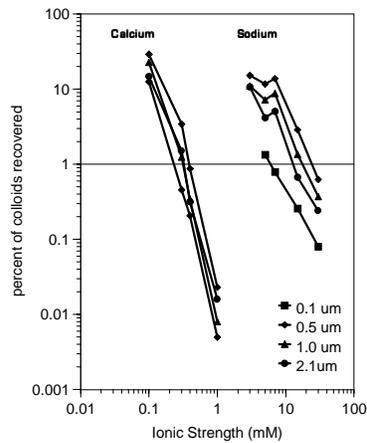


Figure 2. Colloid transport in undisturbed monoliths of saturated fractured saprolite from the Dismal Gap formation (Oak Ridge National Laboratory)

Field-Scale Colloid Tracer Migration

Two series of field tracer experiments were completed. In the first experiment was conducted at a radionuclide-contaminated DOE site at which groundwater contained near-saturated levels of CaCO_3 . Colloid transport was very limited (Fig. 3), consistent with the effects of high Ca levels observed in the column studies. However, colloids retained by the formation could be mobilized by experimental manipulation of ionic strength that increased the concentration of colloids by two orders of magnitude within a few days. Hypotheses concerning the effects of water chemistry and fracture network characteristics were tested at the second experimental site. The ionic strength of the groundwater at the second site was less than half that at the first site; furthermore, colloids were injected into wells screened in two contrasting lithologies: a highly weathered saprolite similar to the intact column (characterized by a dense network of small fractures), and an underlying rubbly, weathered bedrock (characterized by larger, more widely-spaced fractures). Data (Fig. 3) revealed 1) there is considerably greater mobility of colloids at the second site compared to the first site, consistent with the lower ionic strength, and 2) that there are very significant differences in the rate and extent of colloid transport in the two lithologies, with much greater retention of small colloids in the densely-fractured upper zone. These results are consistent with the ionic strength studies at the column scale (above), and with predictions from the fracture network model (below).

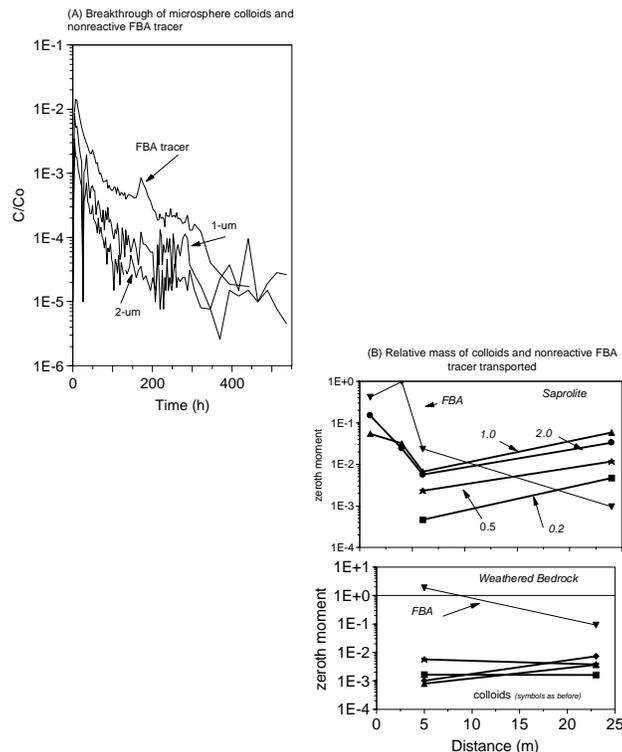


Fig. 3. Field-scale transport of different sizes of carboxylate-modified latex microspheres through water-saturated fractured formations. (A) Breakthrough of microspheres over a 3-m flow path of fractured saprolite. Note that colloids were injected for a 4-h period, yet deposited colloids continued to be released from the formation over extended times. (B) The relative mass of colloids (zeroth moment) of colloids injected into two lithologies at the same location.

Fracture Network Models of Colloid Transport

Numerical simulations of colloid transport in discretely fractured porous media investigated the importance of diffusion into fine porosity as well as the retention and remobilization of colloids. The processes accounted for by the finite element code, COLDIFF, include advective-dispersive transport of colloids, filtration and mobilization of colloidal particles in both fractures and porous media, and diffusive interactions of colloids between the fractures and porous media. Results demonstrated the importance of the porosity of the matrix and colloid retention. Simulations successfully reproduced observed transport data in saprolite monoliths (Fig. 4), and highlighted the tailing caused by remobilization of colloids after the source was removed. Field-scale simulations indicated that diffusive transfer of colloids to fine porosity and colloid retention and remobilization on fracture walls were dominant processes affecting the long-term colloid concentration and migration distance. In environments where porosity is relatively high and colloids are able to diffuse from the fractures, the properties of the porous matrix were more important than those of the fracture network. Because the properties of the fracture network are more difficult to know with certainty relative to those of the porous matrix, predictive uncertainties associated with colloid transport in discretely fractured porous media may be reduced.

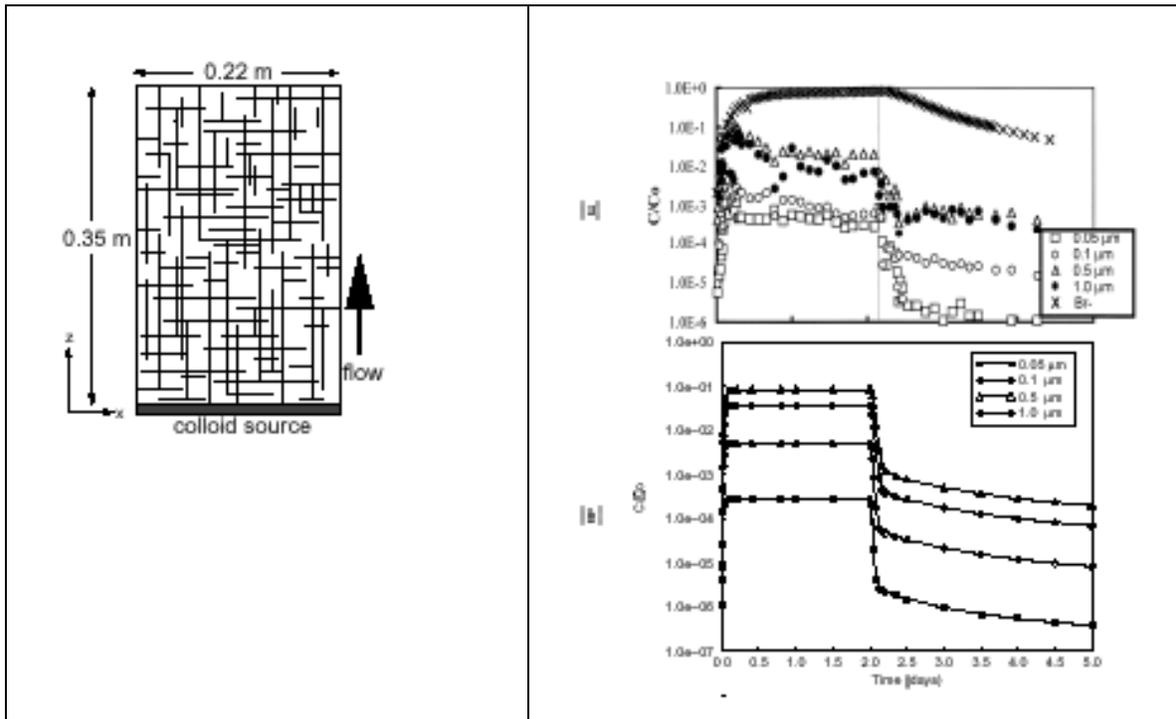


Fig. 4. Comparison of observed data and network model simulation of colloid transport through an undisturbed monolith of Dismal Gap saprolite. The top panel is the representation of the experimental core for the network model. The graphs show the relative concentration ratios (C/C_0) for the laboratory core-scale experiment (from Cumbie and McKay 1999), and the results of the numerical simulation performed using COLDIFF.

RELEVANCE, IMPACT, AND TECHNOLOGY TRANSFER

Assessment of current problems, evaluating long-term risks to the environment and human health, and engineering of cost-effective remedial options all require that the mechanisms of contaminant transport be properly described. This project has created tools to predict the rate and extent of colloid transport, and thus the impact on radionuclide transport. Alternately, the new knowledge and predictive tools can be applied to develop new strategies to enhance introduction of nutrients, electron donors or acceptors or other treatments into contaminated formations for stimulate in-situ remediation. Understanding the processes by which colloids move in the subsurface will leads to predictions that will improve risk assessment, optimize remedial options, and create opportunities for new approaches to cost-effective in-situ remediation.

The scientific knowledge acquired in this project focused on critical DOE environmental management problems. The project demonstrated that both aqueous chemistry and physical structure of geologic formations influence transport. Results of studies at all spatial scales reached consensus on the importance of several key controlling variables: 1) not unexpectedly, colloid retention is dominated by chemical conditions favoring colloid-wall interactions; 2) even in the presence of conditions favorable to colloid collection, deposited colloids are remobilized over long times and this process contributes substantially to the overall extent of transport; 3) diffusive exchange between water-conducting fractures and finer fractures and pores acts to “buffer” the effects of the major fracture network structure, and reduces predictive uncertainties. Predictive tools were developed that account for fundamental mechanisms of colloid dynamics in fracture geometry, and linked to larger-scale processes in networks of fractures.

A specific application of this new understanding to a DOE problem arose from the use of a DOE-relevant field site for the column and field transport studies. The rates and extent of colloid and water movement was determined in fractured porous media at Waste Area Group 5 of the Oak Ridge National Laboratory and at a site in Bear Creek Valley near waste disposal areas of the Oak Ridge Y-12 Plant. The data are directly relevant to assessments of risk from the migration of transuranic radionuclides, and in evaluation of remedial options.

Although a great deal more remains to be learned about colloid transport in water-saturated media, the results of our study highlight the key role of physical and hydrologic factors, and processes of colloid remobilization that are potentially of even greater importance to colloid transport in the vadose zone than in saturated conditions.

Work on this project also helped to focus the efforts of several university researchers on DOE/EM problems. Researchers from the University of Tennessee and The Ohio State University, who had not previously conducted research on DOE-related problems, are continuing research in areas that will be of benefit to understanding environmental

remediation. Furthermore, six students trained within this project have moved onto careers in environmental research with a strong understanding of the unique problems faced by DOE/EM.

PROJECT PRODUCTIVITY

The project accomplished its goals on schedule and within budget. The project successfully addressed the original hypotheses, but gained new insights that were not originally envisioned. For examples, while the original objectives and hypotheses focused on the factors controlling ‘sticking’ of colloids to surfaces, we discovered the previously underestimated importance of detachment in field time scales... Our results demonstrated that slow, long-term detachment processes seems to dominate transport at the field scale.

PERSONNEL SUPPORTED

| Institution | Faculty or Research Staff | Post doctoral or post masters | Students |
|--------------------------------|--------------------------------------|---|-----------------------------------|
| Oak Ridge National Laboratory | J. McCarthy L. Liang D. Walker | | |
| University of Tennessee | L. D. McKay S. D. Driese | W. E. Sanford P. L. Stafford J Palmer | D. Cumbie K. Howard D. Haun |
| Ohio State University | M. Ibaraki | | J. Oswald |
| Los Alamos National Laboratory | P. Riemus | | |

PUBLICATIONS

The results of this research was communicated in several theses and open-literature, peer-reviewed publications, including:

Cumbie, D.H., and L.D. McKay, Influence of diameter on particle transport in a fractured shale saprolite, J. Contam. Hydrol., 31(1-2), pp. 2-20, 1999.

Haun, D. D. B. 1998. Influence of ionic strength and cation valence on transport of colloid-sized microspheres in fractured shale saprolite. MS. Thesis, University of Tennessee, Knoxville, Tennessee.

Cumbie, D.H. 1997. Influence of diameter on particle transport in a fractured shale saprolite, MS. Thesis, University of Tennessee, Knoxville, Tennessee.

Howard, K. H. 1998. Influence of pH on the behavior of fluorobenzoic acids as groundwater tracers. MS. Thesis, University of Tennessee, Knoxville, Tennessee.

Oswald, J. Migration of colloids in discretely-fractured porous media: Effect of matrix diffusion. Ph. D. Thesis. Ohio State University, Columbus, Ohio.

McCarthy, J. F., K. M. Howard and L. D. McKay. 2000. Influence of pH on the behavior of fluorobenzoic acids as groundwater tracers. *J. Environ. Qual.* 29:1806-1813.

Oswald, J. and M. Ibaraki. 2001. Migration of colloids in discretely-fractured porous media: Effect of matrix diffusion. *J. Contam. Hydrol.* (in press).

INTERACTIONS

Results of this research were presented at the EMSP national workshops, to local DOE EM offices, and to national and international meetings, including

McCarthy, J. F. Colloid transport in subsurface environments. Symposium on Colloidal and Interfacial Phenomena, 217th National Meeting of the American Chemical Society, Anaheim CA, March 1999.

McCarthy, J. F. Colloid migration and retention in fractured media. Fractured Rock Science and EMSP Site Specific Integration Workshop. Idaho National Environmental Engineering Laboratory, Idaho Falls, ID, October 1998.

Oswald, J. and M. Ibaraki. Colloid transport in a two-dimensional fracture network model. Spring Meeting of the American Geophysical Union, Boston, MA, May, 1998.

Haun, D., L.D. McKay, and J.F. McCarthy. The role of electrostatic attachment on particle transport in fractured shale saprolite. Conference on mass transport in fractured aquifers and aquitards, University of Copenhagen, Denmark, May 14-16, 1998.

Cumbie, D.H., and L.D. McKay, Laboratory investigations of the influence of particle diameter on transport of latex microspheres in fractured shale saprolite, abstract presented at Fall Meeting of AGU, San Francisco, CA, December 1996. *Winner of Outstanding Student Paper Award.*

McKay, L.D., D.H. Cumbie, and A.D. Harton, Factors influencing colloid transport in fractured shale saprolite, abstract presented at Annual Meeting of the Geological Society of America, Salt Lake City, UT, October 1997.

TRANSITIONS

The scope of this project was basic understanding that would be applicable to EM problems. Our objectives did not involve a technology, technique, or process improvement. The new understanding of the role of colloids in contaminant transport has clearly had an impact on design and implementation of remedial actions. At ORNL, a remedial decision was made to remove transuranic waste containers buried in unlined trenches because results of this research documented rapid colloid-facilitated transport of the actinides through the fractured saprolite. Likewise, at most other DOE sites, issues of contaminant transport, and of remedial options, have begun to explicitly incorporate consideration of colloid-facilitated transport. Publications and presentations of the PI and co-PIs have been instrumental in raising awareness of this issue, and have thus been instrumental to improvements in DOE's approaches to environmental restoration

PATENTS

None

FUTURE WORK

A proposal for follow-on work was submitted to EMSP, but was not funded. That project proposed to address the goals of the Environmental Management (EM) Science Program (EMSP) that seeks innovative basic research to benefit cleanup technologies for contaminated environments. The project specifically addressed the Science and Technology needs for the emerging critical element of the Environmental Management program in sustainable long-term stewardship. The goal of this research was to improve capabilities to predict radionuclide transport through the vadose zone by incorporating coupled hydrologic and geochemical processes in descriptions of colloid-facilitated contaminant transport at DOE sites in both granular and fractured lithologies. Like our previous EMSP project, the emphasis of this work would be on understanding transport in natural—as opposed to model—systems. The work was to extend insights on colloid transport derived in that project to address critical transport pathways of radioactive waste from near-surface environments through the vadose zone, and thence along groundwater flow paths to human and environmental receptors. Objectives addressed key knowledge gaps of direct relevance to DOE vadose zone problems:

- Demonstrate that heterogeneous flow processes are essential to realistically describing and predicting the colloid and radionuclide transport in the vadose zone.
- Develop and test relationships to predict the depth, velocity and magnitude of the downward colloid and radionuclide migration as a function of the duration, frequency and intensity of recharge.
- Establish the impacts of altered recharge on the rates and extent of transport of colloids and colloid-bound radionuclides. Determine the consequences of current and

future practices in enhancing or further limiting colloid-facilitated radionuclide transport.

The proposed work has three tasks that a) employ state-of-science approaches to evaluate interactions between hydrologic and interfacial processes by simultaneously observing in two-dimensional flow models through light transmission techniques and high-resolution measurements of x-ray absorption and fluorescence; b) determine field-relevant, long-term unsaturated flow and transport experiments using undisturbed monoliths from contrasting geologic formations: granular sediments from the Hanford formation, and fractured porous media from Oak Ridge; and c) innovative models that can simulate complex nonuniform flow processes common in natural soil systems, as well as describe mechanistic descriptions of colloid interactions with surfaces that were developed and tested in our previous EMSP project.

The overall research products would be 1) knowledge and information on previously unexplored areas of radionuclide transport in natural heterogeneous systems that will support EM's mandate to develop and deploy effective technologies for sustained long-term stewardship of contaminated DOE sites, and 2) an improved predictive tool for assessing the transport rate and fate of sparingly soluble radionuclides such as ^{137}Cs and transuranic (TRU) radionuclides.

The work directly supported EM's goal of cost-effective, long-term stewardship by providing a unified mechanistic understanding and quantitative relationships between water flux and the rate, depth and magnitude of colloid transport. Results would provide a scientifically defensible basis for decisions about the fate of deeply distributed radioactive waste, engineering criteria for improved, cost-effective implementation of hydrologic controls to prevent radionuclide transport, and would be expected to lead to inexpensive monitoring and surveillance methods based on remote measurements of water contents to assure continuing contaminant immobilization.