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Project Title: Colloid-Facilitated Transport of Radionuclides through the Vadose Zone

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(collaborative project)

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Lead Principal Investigator:

Markus Flury, Department of Crop and Soil Sciences, Washington State University, Pullman, WA 99164, Phone: 509-335-1719, Email: flury@mail.wsu.edu.

Co-Investigators:

James B. Harsh, Department of Crop and Soil Sciences, Washington State University, Pullman, WA 99164, Phone: 509-335-3650, Email: harsh@mail.wsu.edu.

John M. Zachara, Environmental Molecular Science Laboratory, Pacific Northwest National Laboratories, Richland, WA 99352, Phone: 509-376-3254, Email: john.zachara@pnl.gov.

John F. McCarthy, Department of Geology, University of Tennessee, Knoxville, TN 37996, Phone: 865-974-8039, Fax: 865-974-8086, Email: jmccart1@utk.edu.

Peter C. Lichtner, Geoanalysis-Earth and Environmental Sciences, Los Alamos National Laboratory, Los Alamos, NM 87545, Phone: 505-667-3420, Fax: 505-665-8737, Email: lichtner@lanl.gov.

1. Research Objectives:

This project seeks to improve the basic understanding of the role of colloids in facilitating the transport of contaminants in the vadose zone. We focus on three major thrusts: (1) thermodynamic stability and mobility of colloids formed by reactions of sediments with highly alkaline tank waste solutions, (2) colloid-contaminant interactions, and (3) in situ colloid mobilization and colloid-facilitated contaminant transport occurring in both contaminated and uncontaminated Hanford sediments. The specific objectives that will be addressed are:

1. Determine the lability and thermodynamic stability of colloidal materials, which form after reacting Hanford sediments with simulated Hanford Tank Waste.
2. Determine the potential of Hanford sediments for in situ mobilization of colloids for different types of sediments and different leaching scenarios.
3. Characterize the interactions between initially-formed colloids, their dissolution/alteration products, and native colloidal particles with contaminants in

batch experiments under various ionic strength and pH conditions.

4. Evaluate colloid-facilitated radionuclide transport through sediments under different degrees of water saturation in packed and undisturbed sediment columns.
5. Implement colloid-facilitated contaminant transport mechanisms and thermodynamic stability constants into a reactive chemical transport model, and verify model simulations with experimental transport data.

Results of this project will help to understand the fundamental mechanisms of Cs transport under the leaking Hanford tanks, and thus contribute to the long-term clean-up strategies at the Hanford site.

2. Research Progress and Implications:

This report summarizes work after 1.8 years of a 3-year project. The project team has communicated by e-mail and phone conferences. Team members from Washington State University have visited the Pacific Northwest National Laboratory and the Environmental Molecular Science Laboratory several times during the reporting period to conduct research at the national laboratory.

We have completed the studies on reactions of minerals with caustic Hanford tank waste solutions. Systematic studies on the effects of different anions, cations, and the radionuclide Cs-137 were completed and technical manuscripts on these experiments were submitted for publication. The concentration of NaOH and the type of anion played the dominant roles in determining minerals formed. Increasing NaOH concentration and temperature enhanced the formation of feldspathoids; when NaOH concentration was high (e.g., 16 M), stable cancrinite and sodalite formed rapidly. Cancrinite formed in the presence of nitrate or sulfate; sodalite formed in the presence of chloride, carbonate or without added anions. Low concentration of Cs (< 100 mM) did not affect the formation of lepispheric cancrinite and sodalite, whereas only highly crystalline cancrinite formed when Cs concentration was >250mM. The presence of K did not alter but slowed down the formation of cancrinite and sodalite. The presence of divalent cations led to the formation of intermediate or stable silicates, aluminates, hydroxides or even aluminosilicates.

We investigated the incorporation of Cs and the stability of the incorporated Cs in feldspathoids, zeolites, and allophane that may form in the sediments under conditions mimicking Hanford tank leaks. The incorporated Cs was quantified by atomic absorption spectroscopy after digestion in 1 M HCl. Cancrinite, sodalite, LTA zeolite, the 3-D cross-shaped zeolite, and allophane were capable to preferentially incorporate Cs when they form in the alkaline simulants. The internal sites of feldspathoids and zeolites were accessible by ion exchange reactions. Incorporated Cs in sodalite and cancrinite cannot be easily replaced by other cations. This is likely due to the result of the small aperture size of the beta-cage in sodalite the the epsilon-cage in cancrinite. The hydration energy and the size of cations are important in determining if the ions can be replaced by other cations.

Large undisturbed sediments cores were sampled in the ERDF pit between the 200E and 200W tank farms at Hanford in 2003. These cores have been characterized and bottom plates and a sprinkler head for water application for unsaturated flow experiments have been constructed. Several membrane types and porous plates have been tested for potential use as suction devices at the bottom. Stainless steel membranes in combination with nylon meshes were the most suitable materials and the bottom plates have been designed to accommodate these membranes. The cores are being instrumented with tensiometers and TDR sensors, and unsaturated flow experiments will be started in July 2004.

We experimentally determined colloid stability of natural colloids extracted from vadose zone sediments. Colloid stability was assessed with three different methods: the batch turbidity method, column mobilization experiments, and dynamic light scattering. Critical coagulation concentrations (CCC) were determined for pure Na and pure Ca electrolyte solutions, as well for mimicked Hanford vadose zone pore waters with varying sodium adsorption ratio (SAR). Critical coagulation concentrations obtained from the batch turbidity method were sensitive to initial colloid mass concentrations, settling time, and CCC criteria. The CCC values determined from dynamic light scattering were lower than those determined from the batch turbidity method. The CCC was strongly affected by the SAR and the absolute electrolyte concentrations. For conditions at the Hanford site, our results suggest that colloids likely will form stable suspensions in the vadose zone pore water.

Colloid transport experiments were conducted under steady-state water flow conditions with effective water saturations ranging from 0.56 to 1.0. Under saturated conditions, no colloids were removed from the liquid phase during transport, while under unsaturated conditions colloids were removed from the mobile water region. Colloid removal increased with decreasing system saturation. Under constant chemical conditions, colloids captured within the column could quantitatively be recovered in the column outflow by re-saturating the column after each unsaturated-flow breakthrough. Through microscopic observations in a glass micromodel containing suspended air bubbles, we found that colloids did not adhere to the liquid-gas interface. Using the extended DLVO theory, free energies of Lifshitz-van der Waals, electrostatic and Lewis acid/base interactions between colloids, sediments and the liquid-gas interface were calculated based on their independently determined surface thermodynamic properties. Experimental results and surface thermodynamic calculations support the hypothesis that colloids were retained near the liquid-gas-solid interface.

The reactive transport model FLOTRAN was used to simulate cesium transport of the column experiments. Discrepancies observed between the experiments and the numerical model indicated that kinetic limitations may be present in the ion exchange reactions and that the local equilibrium assumption adopted by FLOTRAN may not be valid. FLOTRAN currently does not simulate kinetic ion exchange reactions. New code was written to enable FLOTRAN to model kinetic ion exchange reactions. A major restructuring of the code was

required since the global implicit scheme utilized by FLOTRAN only solved the aqueous species transport equations in a coupled manner. In order to simulate kinetic ion exchange, the sorbed species needed to be solved simultaneously with the aqueous component equations. In addition, a kinetic reaction subroutine was written to calculate the reaction term for kinetic ion exchange equations. This new version of FLOTRAN is currently being tested. Once verified, we will attempt to fit the colloid-facilitated Cs transport experiments using this new kinetic ion exchange capability.

3. Planned Activities:

Besides the continued experimental work, a major effort will be devoted to data analysis and manuscript preparation. The major future activities and their time lines are listed below:

Thermodynamic mineral stability:	June, 2004 to September, 2005.
Colloid stability:	June, 2004 to September, 2004.
Contaminant-colloid interactions:	June, 2004 to August, 2005.
Undisturbed core experiments in Washington:	July, 2004 to September, 2005.
Undisturbed core experiments in Tennessee:	August, 2004 to September, 2005.
Colloid-facilitated transport experiments:	June, 2004 to September, 2005.
Eu and Am sorption experiments:	June, 2004 to September, 2005.
FLOTRAN modeling:	June, 2004 to September, 2005.
Final report:	June, 2005 to September, 2005.

4. Information Access:

A WEB site is maintained for reporting and dissemination of research results. The WEB site can be accessed through the home page of Markus Flury at <http://akasha.wsu.edu>. Several scientific manuscripts of the work done so far have been published or submitted for publication and others are in preparation. The published manuscripts are all available in electronic form as PDF files at <http://akasha.wsu.edu>. The following manuscripts have been published during the reporting period:

Flury, M., S. Czigany, G. Chen, and J.B. Harsh, Cesium migration in saturated silica sand and Hanford sediments as impacted by ionic strength, *J. Contam. Hydrol.*, 71, 111-126, 2004.

Zhuang, J., Y. Jin, and M. Flury, Comparison of natural colloid and kaolinite transport in porous media, *Vadose Zone J.*, 3, 395-402, 2004.

Zhao, H., Y. Deng, J.B. Harsh, M. Flury, and J. Boyle, Alteration of kaolinite to cancrinite and sodalite by simulated Hanford Tank Wastes and its impact on cesium retention, *Clays Clay Miner.*, 52,1-13, 2004.

Flury, M., J.B. Harsh, and J.B. Mathison, Miscible displacement of salinity fronts: Implications for colloid mobilization, *Water Resour. Res.*, 39, 1373,

doi:10.1029/2003WR002491, 2003.

Zhuang, J., M. Flury, and Y. Jin, Colloid-facilitated Cs transport through water-saturated Hanford sediment and Ottawa sand, *Environ. Sci. Technol.*, 37, 4905-4911, 2003.

Cherrey, K.D., M. Flury, and J.B. Harsh, Nitrate and colloid transport through coarse Hanford sediments under steady-state, variably-saturated flow, *Water Resour. Res.*, 39, 1165, doi:10.1029/2002WR001944, 2003.