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

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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:

- Determine the lability and thermodynamic stability of colloidal materials, which form after reacting Hanford sediments with simulated Hanford Tank Waste.
- Determine the potential of Hanford sediments for in situ mobilization of colloids for different types of sediments and different leaching scenarios.
- 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.
- Evaluate colloid-facilitated radionuclide transport through sediments under different degrees

of water saturation in packed and undisturbed sediment columns.

- 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 0.8 years of a 3-year project. The project team has met at several occasions. John McCarthy visited Washington State University in March 2003, Markus Flury traveled to Los Alamos to meet with Peter Lichtner in April 2003, and Markus Flury and John Zachara attended the EMSP PI meeting in Richland in May, 2003.

Given that there is a wide range of chemical compositions of Hanford Tank Waste, we have studied mineral formation and transformation by systematically varying anion composition and OH concentrations of simulated tank solutions in presence and absence of Cs. The feldspathoids and zeolite formed in the presence of Cs were analyzed with X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), and solid state NMR. The presence of Cs in the simulant solutions did not affect the types of minerals formed in 1 M NaOH solutions until the Cs concentration was greater than 0.1 M, a concentration that is not likely to occur in the sediment underlying the Hanford tanks. Elemental mapping indicated that incorporated Cs was homogeneously distributed in cancrinite and sodalite. High concentrations of Cs promoted the formation of highly crystalline cancrinite in hexagonal bar shape. The presence of Cs in solutions precluded the influence anions have shown in the non-cesium system. The presence of chloride anion was favorable for the formation of pure sodalite in a non-cesium solution, yet no sodalite has been found in the precipitates formed at high Cs concentration (0.5 M).

Adsorption experiments indicated that Cs could access the internal parts of LTA, cancrinite and sodalite, but the diffusion appeared more difficult than that of Na and K. Cesium exchange in cancrinite and sodalite caused structural disordering of the minerals as reflected by the XRD patterns. Incorporated and sorbed Cs showed 40 ppm chemical shifts on the ^{133}Cs NMR patterns of LTA, indicating different chemical environments. Similar shifts were observed on cancrinite and sodalite lepispheres. We speculate that the adsorbed cesium was located in the larger cages of LTA zeolite, while the incorporated cesium is present in the smaller cages. Cesium could not migrate from one cage type to the other due to the large size of cesium ions. For the same reason, incorporated Cs could be easily replaced by other ions (e.g. Ca or K). Incorporating or adsorbing Cs did not distinctly shift the peak position or split the peak of ^{23}Na NMR. This can be the result of the high motion of Na ions and water molecules inside the cages or channels which averages out the chemical environment of the ions.

Hanford sediments were sampled in the ERDF pit between the 200E and 200W tank farms at Hanford. In two sampling campaigns in April and May 2003, we sampled three large undisturbed soil cores. The core sediments represent the two major sediment facies occurring in the Hanford formation: a coarse-pebbly sand and a finer-textured sand. The cores will be used for unsaturated

transport experiments and are being prepared in the laboratory for setup. We are currently testing different porous materials as candidates to control the lower boundary conditions of the cores. Stainless steel membranes and fiberglass wicks seem to be the most promising materials so far, and detailed tests are conducted to examine colloid transmission through these materials. As soon as these tests are completed, we will finalize the column design and ship two of the columns to Tennessee, where John McCarthy will conduct the unsaturated transport experiments with the cores. One core will stay at Washington State University as backup. During the sampling at Hanford, plenty of disturbed sediment materials, and few smaller undisturbed cores were sampled for mineralogical and hydrological characterization of the sediments. This characterization work is currently ongoing.

Colloid stability work, both in terms of mineral stability as well as colloid suspension stability, has been initiated. Native colloids isolated from Hanford sediments, colloids isolated after reaction of Hanford sediments with simulated tank waste, and reference clay minerals are tested for colloidal stability using three different methods: (1) batch flocculation series, (2) photon correlation spectroscopy, and (3) column mobilization experiments. Critical coagulation concentrations (CCC) are being determined for different electrolytes and sodium adsorption ratios (SAR). These studies will show whether colloids at Hanford can form stable suspensions in the pore water and how long suspensions stay stable.

Saturated and unsaturated colloid and colloid-facilitated Cs transport experiments have been carried out under different degree of Cs loading on colloids. Experiments were done with ^{137}Cs and we are using ^{22}Na to determine Cs-Na selectivities in our columns. Results indicate the Cs movement can be facilitated by colloidal particles, but the quantitative amount of Cs that is moving with colloids is relatively small. Cesium is effectively stripped off from colloidal particles when colloids move through uncontaminated Hanford sediments, thereby limiting the amount of Cs that can be transported via colloids. Colloid mobility decreases with decreasing water saturation of the sediments. Nevertheless, at water saturations representative for natural Hanford sediments, a fraction of colloids remained mobile, indicating that colloidal movement and transport are possible in the Hanford vadose zone.

Colloid-facilitated transport mechanisms are being incorporated into a geochemical transport code (FLOTTRAN) and tested with the experimental data on colloid-facilitated Cs transport from the laboratory columns. FLOTTRAN has been compared with analytical solutions of a two-region model (CXTFIT), and is currently adapted to include colloid-facilitated contaminant transport.

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, 2003 to June, 2004.
Colloid stability:	June, 2003 to June, 2004.
Contaminant-colloid interactions:	November, 2003 to August, 2005.
Membrane test sand setup of large columns:	June, 2003 to August, 2003.
Shipment of large cores to Tennessee:	September 2003.
Undisturbed core experiments in Tennessee:	September, 2003 to September, 2005.

Colloid-facilitated transport experiments:	September, 2003 to September, 2005.
Sediment characterization:	September, 2003 to February, 2004.
FLOTRAN modeling:	June, 2003 to September, 2005.

4. Information Access:

A WEB site has been established 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 are in preparation.