

**Project ID:** 70135

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

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**Number of Graduate Students and Post-Doctorates actively involved in the project:**

3 Graduate Students and 1 Post-Doctorate.

**Research Objectives:**

This project seeks to improve the basic understanding of colloid and colloid-facilitated transport of Cs in the vadose zone. The specific objectives are:

- Determine the structure, composition, and surface charge characteristics of colloidal particles formed under conditions similar to those occurring during leakage of waste typical of Hanford tank supernatants into soils and sediments surrounding the tanks.
- Characterize the mutual interactions between colloids, contaminant, and soil matrix in batch experiments under various ionic strength and pH conditions. We will investigate the nature of the solid-liquid interactions and the kinetics of the reactions.
- Evaluate mobility of colloids through soil under different degrees of water saturation and solution chemistry (ionic strength and pH).
- Determine the potential of colloids to act as carriers to transport the contaminant through the vadose zone and verify the results through comparison with field samples collected under leaking tanks.

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.

**Research Progress and Implications:**

This report summarizes work after 3 years of a 3-year project. We are currently in the last phase of a one-year no-cost extension. For the last phase of the project, we have hired a new postdoctoral scientist, Gang Chen, with a PhD degree in Civil and Environmental Engineering.

We have continued our work on colloid formation during reactions of Hanford Tank Waste solutions with Hanford sediments. Characterization of contaminated sediments below Hanford tank

farms has shown that sediments in contact with tank liquors have been altered mineralogically, but not to the extent observed in laboratory batch experiments. It was hypothesized that the lower liquid-to-solid ratio in the field condition was responsible for the different findings between contaminated sediments and laboratory experiments. To test this hypothesis, we have initiated batch reaction experiments with liquid-to-solid ratios representative for Hanford tank leaks.

Four simulant tank waste (STW) solutions, which are high in NaOH (1.4 and 2.8 mol/kg), NaNO<sub>3</sub> (3.7 mol/kg) and NaAlO<sub>2</sub> (0.125 and 0.25 mol/kg), were prepared and reacted with reference kaolinite KGa-1 and KGa-2 at 50 and 80 °C for up to two months. The structure and morphology of the resulting products were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), and Fourier transform infrared (FTIR) spectroscopy. The products were also examined for cation exchange and Cs<sup>+</sup> sorption as a function of ionic strength and types of cations in the background solutions. Cancrinite and sodalite were the only new minerals observed in all of the conditions tested in this experiment. Two major chemical processes were involved in the reactions: dissolution of kaolinite and precipitation of cancrinite and sodalite. Increasing NaOH concentration and temperature, and decreasing NaAlO<sub>2</sub> concentration increased the transformation rate. Both cancrinite and sodalite appeared stable thermodynamically under the experimental conditions. The newly formed feldspathoids were vulnerable to acid attack and pronounced dissolution occurred at pH below 5.5. Cancrinite and sodalite can incorporate NaNO<sub>3</sub> ion pairs in their cages or channels. Sodium in cancrinite and sodalite was readily exchangeable by K<sup>+</sup>, but less easily by Cs<sup>+</sup> or Ca<sup>2+</sup>. The feldspathoid products sorb nearly an order of magnitude more Cs<sup>+</sup> than the unaltered kaolinite. The cesium adsorption is reduced by competing cations in the background solutions. At low ionic strength (0.01 M NaNO<sub>3</sub> or 0.005 M Ca(NO<sub>3</sub>)<sub>2</sub>), Ca<sup>2+</sup> was more competitive than Na<sup>+</sup>. When the concentration of the background solution was increased 10 times, Na<sup>+</sup> was more competitive than Ca<sup>2+</sup>.

A series of saturated column experiments were conducted to investigate effects of colloids on Cs transport in two types of porous media (Hanford sediment characteristic of 2:1 clay minerals and silica Ottawa sand). The colloids used were obtained by reacting Hanford sediment with simulated tank waste solutions. Because of the highly non-linear nature of Cs sorption found in batch experiments, we used two different concentrations of Cs (7.5x10<sup>-5</sup> M and 1.4x10<sup>-8</sup> M) for the transport experiments. The presence of colloids facilitated the transport of Cs through both Hanford sediment and silica sand via association of Cs with mobile colloidal particles. Due to the non-linearity of the Cs sorption, the colloid-facilitated Cs transport was more pronounced at the low Cs concentration (1.4x10<sup>-8</sup> M) than at the high concentration (7.5x10<sup>-5</sup> M) when expressed relative to the inflow Cs concentration. In absence of colloids, no Cs moved through the 10-cm long columns during the experiment within about 20 pore volumes, except for the high Cs concentration in the silica sand where a complete Cs breakthrough was obtained. Also, it was found that colloid-associated Cs could be partially stripped off from colloids during the transport. The stripping effect was controlled by both Cs concentration and sorption capacity of the transport matrix.

We have completed colloid transport experiments under steady-state conditions with varying water saturations. A column system was developed with which we could control volumetric water contents with accuracy better than 0.01 effective saturation and the water potentials to better than 0.06 cm-H<sub>2</sub>O. Inflow and outflow boundary conditions had to be meticulously controlled to ensure uniformity of water contents and water potentials inside the column. Colloid breakthrough curves were determined under a series of water contents ranging from 0.2 to 1.0 effective saturation. Results showed that colloids are mobile under water saturations typical for Hanford sediments, but the amount of colloids transported decreased with decreasing water saturation of the sediments.

Modeling efforts have indicated that water flow is best described with a mobile-immobile water concept, implying that a portion of the pore water is not contributing to flow.

### **Planned Activities:**

In the final months of the project will finalize the last Hanford liquor-sediment reactions and repeat some experiments needed to finalize scientific manuscripts. In addition, we will work on the final report of the project.

### **Time Line:**

Reaction of Hanford sediments with tank solutions:	June, 2003 to September, 2003.
Repetition of selected experiments:	June, 2003 to August, 2003.
Chemical modeling of batch reactions:	June, 2003 to August, 2003.
Writing of technical manuscripts and final report:	June, 2003 to September, 2003.

### **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>. Results so far have been published in or submitted to several scientific journals:

Flury, M., J.B. Mathison, and J.B. Harsh, In situ mobilization of colloids and transport of cesium in Hanford sediments, *Environ. Sci. Technol.*, 36, 5335-5341, 2002.

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.*, (in press), 2003.

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

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.*, (submitted), 2003.

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.*, (submitted), 2003.

Two more manuscripts on (1) colloid formation and mineral alterations and (2) colloid-facilitated Cs transport are in preparation.