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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 2.5 years of a 3-year project.

Our Postdoc, Hongting Zhao, has accepted a position at Sandia National Laboratory in October 2001, and we have consequently recruited another Postdoc. We have been able to recruit an excellent new Postdoc, Youjun Deng; however, the recruitment has taken some time and caused some time delay in the project. We anticipate that we will apply for a no-cost extension and continue the work for the duration of the time delay.

The research activities have focused on two major thrust areas: (1) reactions of simulated Hanford waste tank solutions with Hanford sediments, and (2) transport of colloidal particles and cesium through Hanford sediment matrices. In each of these thrust areas, we have conducted a series of experiments under various chemicals and physical conditions.

Three types of sediments from the Hanford formation were reacted with a series of simulated Hanford Waste Tank Solutions. These solutions comprised of a series of treatments with (a) increasing NaOH concentrations: (1) deionized water, (2) 0.1 M NaOH, 3.7 nM $Al(NO_3)_3$, (3) 0.5 M NaOH, 3.7 nM $Al(NO_3)_3$, (3) 1.4 m NaOH, 3.7 m $NaNO_3$ and 0.125 m $NaAl(OH)_4$, (4) 1.4 m NaOH, 3.7 m $NaNO_3$, and 0.26 m $NaAlO_2$, (5) 2.8 m NaOH, 3.7 m $NaNO_3$, 0.13 m $NaAlO_2$, and 50 mg/L $CsNO_3$, and (b) increasing aluminate cocentrations: (1) deionized water, (2) 1 m NaOH, 2 m $NaNO_3$, 0.05 m $NaAlO_4$, (3) 1 m NaOH, 2 m $NaNO_3$, 0.125 m $NaAlO_4$, and (4) 1 m NaOH, 2 m $NaNO_3$, 0.25 m $NaAlO_4$. Reactions were carried out at 25 and 50^{o}C. Colloidal particles (<2μm) were collected from these batch reactors after 1, 10, 25, and 50 days. The supernatant solutions were titrated to pH 8, whereby colloidal particles precipitated out of solution. We examined the mineralogical and physicochemical properties of the colloids using microelectrophoresis, x-ray diffraction (XRD), TEM/SEM, NMR, FT-IR, and determined the solution composition (Si, Al, and pH). To provide fundamental knowledge of colloid formation under mineralogically more controlled conditions, pure minerals (kaolinite, montmorillonite, mica, quartz) were reacted with the simulated tank solutions, and the colloidal products were isolated and characterized. Quartz and biotite particles were hand-picked from the sediments and reacted with the simulated tank solutions in absence and presence of Cs.

Sediment reactions were also carried out in flow-through reactors, were simulated tank waste was pumped through sediment columns at 25 and 50^{o}C. Outflow was collected in fractions and has been analyzed for colloid and elemental composition. We are currently also analyzing the sediments for alterations and shifts in mineralogy and particle size distributions. The flow-through reactors will then be compared to the batch systems.

Aluminum concentration in the supernatant solution of the batch reactors decreased with time while Si concentration increased with time, indicating release of Si from the native minerals and precipitation of new solid phases. Alterations in both mineralogical and chemical properties of the Hanford sediment colloids were found. The x-ray diffraction patterns indicated that the < 2 μm fraction initially consisted of quartz and three major layered aluminosilicates, namely chlorite, kaolinite and illite. Some minerals dissolved and others were altered. New mineral phases precipitated. In summary, three different types of colloidal material were formed after reacting Hanford sediments with simulated tank solutions: (1) altered native aluminosilicate minerals, (2) new precipitates during batch reactions, and (3) silica particles that are precipitated after titration of the supernatant solutions.

Electrophoretic mobility measurements showed that the unreacted sediments had negative mobility throughout the pH range studied (3 to 11); however, after reaction with tank solutions, the electrophoretic behavior changed considerably. A point of zero charge was observed around pH 6 to 7. Above pH 7, the colloids are negatively charged, suggesting that they are forming a relatively stable suspension and that they are electrostatically interacting with cations, such as Cs. Colloidal stability was measured with photon correlation spectroscopy and UV/VIS absorption measurements.

Reactions of simulated tank waste solutions with pure minerals showed that kaolinite was almost completely dissolved and the feldspathoids cancrinite and sodalite were formed. The feldspathoid products sorb nearly an order of magnitude more Cs than the unaltered kaolinite; however, Na and Ca strongly competed for sorption sites. At low concentration (0.01 mol_c/L) Ca was more competitive than Na, but at higher concentration (0.1 mol_c/L), Na was more competitive than Ca and displaced most of the Cs.

Sorption studies of Cs on reacted sediments and colloids formed show different sorption affinities for different minerals and colloids from Hanford sediments. Colloids formed after reactions of sediments with simulated tank solutions had less sorption affinity for Cs than the native, unaltered, colloidal particles, possibly due to the dissolution of clay minerals. We determined Cs ad- and desorption kinetics as well as the Cs capacity of the colloids.

Given that reacted sediments contain a mixture of different minerals in the colloidal size fraction, we have also synthesized pure sodalite and cancrinite to obtain reference XRD, NMR, and FTIR data. For the synthesis we have varied the chemical conditions mimicking a wide range of OH concentrations representative for Hanford tank waste solutions. Minerals were examined so far with SEM and TEM, and we will continue with NMR and FTIR characterization.

Several different column experiments with colloids and cesium have been conducted under saturated and unsaturated conditions. The long-term experiment on *in situ* colloid mobilization from Hanford sediments in combination with Cs transport has been completed and a technical manuscript describing this study has been submitted for review. The results of this study have shown that a large fraction of colloidal material was mobilized from the Hanford sediments when a Hanford tank leak was simulated. Mobilized colloids consisted mainly of quartz, mica, illite, kaolinite, and chlorite. Mobilized colloids carried a fraction of the cesium along. While transport of solution phase cesium in 1 M $NaNO_3$ tank waste was much faster than in 1 mM $NaNO_3$ pore water, cesium that was attached to colloids moved almost unretarded through the sediments. Cesium attached to mobilized colloids was likely associated with high affinity sorption sites on micas and illites. We have initiated a series of mobilization experiments with systematically varying ionic strength of the infiltrating solutions, and concurrently measure hydraulic conductivities during colloid mobilization.

Systematic tests with solutions of different ionic strengths were conducted to investigate Cs and colloid transport in different sediment matrices. Cesium as well as colloid transport was strongly affected by the ionic strength of the aqueous phase. While Cs transport is enhanced by increased ionic strength, colloid transport is limited under high ionic strength. The column tests were compared with the results of the batch sorption experiments and the two types of experiments were found to provide consistent and comparable data, sorption parameters from batch and column studies agreed well with each other. We have studied colloid transport in variably saturated Hanford sediments, and developed an experimental system that allows control of water saturations in 10% saturation increments. Colloid transport experiments were conducted with *in situ* colloids from Hanford sediments and with colloids formed by reacting Hanford sediments with simulated tank waste as described above. Colloids were found to be mobile, but irreversible attachment increased with decreasing water saturation.

Planned Activities:

We will finalize the synthesis and characterization of cancrinite/sodalite/zeolite using pure solutions described above. Cesium-137 will be included in the synthesis process to test where cesium will be incorporated into the mineral phases. We will continue to use XRD, NMR, FT-IR, SEM, and TEM for mineral characterizations. We will continue the flow-through reaction experiments with simulated tank waste and Hanford sediments under steady-state flow conditions, and will expand the experimental conditions to include non-steady, i.e., infiltration-type, of experiments. Transport studies under saturated and unsaturated conditions will be continued. We will investigate colloid, Cs, and colloid-assisted Cs transport using breakthrough curves obtained from laboratory scale columns, using both steady-state and transient flow conditions. Besides the continued experimental work, a major effort will be devoted to data analysis and manuscript preparation.

Time Line:

Synthesis and characterization of colloidal material: June, 2002 to September, 2002.
Spectroscopy of Cs-colloid complexes: August, 2001 to September, 2002.
Steady-state transport studies with cesium-137: June, 2001 to November, 2002.
Transient transport studies with cesium-137: June 2001 to November, 2002.
Writing of technical manuscripts and final report: June, 2002 to December, 2002.

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. Two technical manuscripts describing the colloid mobilization experiment and the kaolinite transformations have been submitted to technical journals for review. Four more manuscripts describing cesium transport, colloid formation, colloid transport, and colloid-facilitated cesium transport are in preparation.