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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 1.7 years of a 3-year project.

Sediments from the Hanford formation were reacted with a series of simulated Hanford Waste Tank Solutions. These solutions comprised of (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 $NaAlO_2$, and (5) 2.8 m NaOH, 3.7 m $NaNO_3$, 0.13 m $NaAlO_2$, and 50 mg/L $CsNO_3$. Reactions were carried out at 25 and 50°C. Colloidal particles (<2µm)

were collected from these batch reactors after 1, 10, 25, and 50 days. The supernatant solution was 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.

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 three major layered aluminosilicates, namely chlorite, kaolinite and illite. Upon reaction with the alkaline aluminate solutions, the characteristic peak of chlorite became broader with time as it appeared to shift to a smaller c-axis spacing. Where the untreated sample gave a relatively narrow peak at 1.4 nm, the treated samples broadened to span from 1.2 to 1.4 nm. This preliminary result suggests that the interlayer hydroxide in the chlorite was degraded by the alkaline solution. A new type of mineral, identified as the feldspathoid cancrinite, was found to be formed. 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 tritration 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.

Sorption studies of Cs on reacted sediments and colloids formed show different sorption affinities for different minerals and colloids formed 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. Reaction of pure minerals with simulated tank solutions showed that montmorillonite and kaolinite increased sorption affinity after reactions, but illite showed decreased Cs sorption after reactions.

Several different column experiments have been conducted under saturated and unsaturated conditions. *In situ* colloid mobilization from Hanford sediments in combination with Cs transport is being studied in a long-term column study where a Hanford tank leak is simulated. Enhanced Cs transport was observed during a leaking scenario (high ionic strength). A large fraction of colloidal material was mobilized during subsequent dilution of the inflow solution, carrying with it a fraction of the presumably irreversibly sorbed Cs. Cesium transport after dilution of the waste solution (low ionic strength) was extremely limited. Systematic tests with solutions of different ionic strength are currently conducted to investigate Cs and colloid transport in different sediment matrices. Cesium as well as colloid transport are 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 will be compared with the results of the batch sorption experiments. The

unsaturated column system has been completed, and is currently being tested. Different porous plates were tested for their ability to allow colloids to pass through. A sintered glass frit was found to be the best material.

Preliminary experiments have been performed to test the possibility to visualize colloids during flow in porous media using MRI. Colloids synthesized from reacting Hanford sediments were tagged with the paramagnetic ion Cu to render them visual in H-NMR. Extensive sorption tests with Cu were performed to obtain optimal Cu loading on the colloid surfaces. These tests included adsorption with different Cu solution concentrations, desorption with Ba, and kinetic ad- and desorption studies. Selected Cu-loaded colloids were tested for T-1 relaxation times in NMR. Cu-tagged colloids lowered the T-1 relaxation times, and it might be possible to determine a calibration curve of colloid concentrations vs T-1 relaxation. Different porous matrices were tested for their magnetic contamination in MRI. Glass beads, silica sand, and Hanford sediments showed a large line-width, making MRI problematic. Even removal of exchangeable iron and sesquioxides made only small improvements. We will increase Cu loading on the colloids to enhance MRI signals.

Planned Activities:
We will finalize the characterization of the colloids obtained from the different treatments described above. This includes completion of XRD, NMR, FT-IR, SEM, and TEM measurements. Cesium sorption studies will be continued, and in particular, we will determine ion exchange and selectivity coefficients as function of temperature. In addition, we have obtained new Hanford sediments, which differ somewhat from the original sediments we have used so far. We will react the new sediments with one selected simulated tank waste solution, and compare the extracted colloids with the ones obtained from the old sediments. 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. MRI visualization of colloid transport will be attempted using the NMR facility at EMSL.

Time Line:

Synthesis of colloidal material:	June, 2001 to February, 2002.
Steady-state transport studies:	June, 2001 to February, 2002.
Characterization of colloidal material:	June, 2001 to February, 2002.
Sorption/exchange isotherms for Cs:	June, 2001 to April, 2002.
Spectroscopy of Cs-colloid complexes:	June, 2001 to May, 2002.
Transient transport studies:	June 2001 to August, 2002.
Writing of final reports:	March, 2002 to September, 2002.

Information Access:
A WEB site has been established for reporting and dissemination of research results. The WEB site can accessed through the home page of Markus Flury at http://akasha.wsu.edu. Technical manuscripts summarizing the results obtained so far are in preparation.