

Project 86814

## Colloid-Facilitated Transport of Radionuclides Through the Vadose Zone

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**RESULTS TO DATE:** In the previous reporting period, we have clarified the qualitative mineral transformation pathways when Hanford sediments are reacted with caustic Hanford tank waste. The major finding was that cancrinite, sodalite, zeolite A and allophane form when Hanford tank waste leaks into subsurface sediments. Cancrinite and sodalite are the most stable phases. The morphology and crystallinity of the minerals formed vary with alkalinity, salinity, and the Si/Al ratio. Temperature affects the reaction rates, but not the reaction pathways. In this project period, we have further refined the reaction pathways by quantification of XRD patterns and determination of weight fractions of individual minerals. This allowed us to generalize the results as function of solution chemistry.

Based on our studies of Cs incorporation in feldspathoids, zeolites, and allophane we have determined Cs intraparticle diffusion coefficients in the minerals. The results of desorption kinetics experiments showed that Cs desorbed quickly from LTA zeolite and the Cs diffusion coefficient was close to that in solution; i.e., about  $10^{-9}$  m<sup>2</sup>/s. Solid-state NMR analysis supported the high mobility of Cs in LTA zeolite. Cesium desorption from cancrinite, sodalite, and allophane, however, was slow, suggesting that Cs was trapped in cages and channels of these minerals. Effective diffusion coefficients for Cs in cancrinite and sodalite were near  $10^{-14}$  m<sup>2</sup>/s.

The large undisturbed sediments cores, which were collected from the ERDF pit, are being irrigated at low flow rates representative for Hanford recharge, and are being monitored for colloid mobilization. Cores are continuously weighed and water content and water potentials are monitored.

We tested different porous materials for their suitability for in-situ colloid sampling in the vadose zone. Fiberglass wicks were found to be the most suitable material. Different colloids were used for the wick testing: feldspathoids, ferrihydrite, montmorillonite, kaolinite, and a mixture of mineral colloids extracted from Hanford sediments. Flow rate, pH, and colloid type affected colloid breakthrough. The mixture of mineral colloids extracted from the sediments moved almost conservatively through the wicks. These results suggest that for certain conditions and colloid types, fiberglass wicks can be acceptable tools for colloid sampling in the vadose zone. However, under many conditions studied here colloids were significantly retained inside the wicks.

We investigated in-situ colloid mobilization under transient flow conditions using columns repacked with Hanford sediments. Five series of unsaturated column experiments were performed with initial infiltration rates of 0.018, 0.036, 0.072, 0.144 and 0.288 cm/min. Colloids were eluted by the infiltrating water with the peak colloid concentrations in the outflow coinciding with the arrival of the infiltration front. The cumulative amount of colloids released was linearly proportional to the column water content established after steady-state flow rates were achieved. The colloid release rate coefficient increased nearly linearly with the increase of water content. We calculated forces exerted on colloids and found that electrostatic, Lifshitz-van der Waals interactions, and hydrodynamic forces were all less important than capillary forces in controlling colloid release. The reduction in capillary forces due to the increased water content during infiltration appeared to dominate in-situ colloid mobilization.

We investigated transport of Eu through Hanford sediments. Radioactive <sup>154</sup>Eu and <sup>155</sup>Eu are of interest at the Hanford site: both of them are fission products of <sup>235</sup>U. In addition, Eu can be used as an analogue for the geochemical behavior of trivalent actinides, such as Am(III) and Cm(III). We synthesized Eu

colloids. We conducted the following two sets of column transport experiments. For the first set of experiments, we flushed the column with europium hydroxycarbonate with different concentrations at a fixed flow rate of 0.018 cm/min. For the second set of experiments, we flushed the column with europium hydroxycarbonate at a fixed concentration but variable flow rates. Europium breakthrough peaks coincided with the colloid breakthroughs, indicating Eu transport was facilitated by colloids. High input Eu concentrations led to increased europium elution. The amount of europium on colloids decreased with elution time, indicating possible stripping of sorbed europium from carrying colloids.

Europium can precipitate as its own colloidal phase or sorb to subsurface minerals. To identify the precipitated solid phases on surfaces of clay minerals and calcite that occur in Hanford sediments we investigated precipitation and adsorption of Eu in presence of EDTA and humic acids. After reacting with Eu solutions, the minerals were analyzed with X-ray diffraction, scanning electron microscopy, and X-ray energy dispersive spectroscopy. In pH range 3 to 5.5, nearly 50% of Eu was adsorbed by smectite and the adsorption did not show significant variation with pH, suggesting a strong interaction between Eu and the mineral. When  $\text{pH} > 6$ , Eu precipitated a short-range ordered  $\text{Eu}(\text{OH})_3$ ; the particle size was in the nanometer range. The presence of EDTA inhibited the precipitation of  $\text{Eu}(\text{OH})_3$ . The precipitation of Eu on calcite was affected by partial pressure of  $\text{CO}_2$ . When Eu solution was mixed with calcite in a closed system for three days, dissolution of calcite and new precipitates were observed. We believe that the new mineral is a solid solution of  $\text{CaCO}_3$  and  $\text{Eu}_2(\text{CO}_3)_3$ . On the contrary, when Eu solution was mixed with calcite in an open system, only calcite dissolution was observed. Under the natural pH condition (around 8) in the Hanford sediment, it is likely that Eu forms  $\text{Eu}(\text{OH})_3$  precipitates. The presence of ligand may inhibit the precipitation of  $\text{Eu}(\text{OH})_3$ , but it does not significantly reduce the adsorption of Eu on smectite.

At the University of Tennessee, we continued the studies on understanding the impacts of transient flow regimes and horizontal sediment layering on colloid transport. A transparent Hele-Shaw cell is employed in our 2-D experiments. To monitor the spatiotemporal variation of sand water content, we use a gamma-ray attenuation system. Preferential water flow occurred in the experimental sand (Accusand 20/30, 0.8 mm uniform diameter). However, the layering-structure changed the pattern of preferential flow-paths. All of the flow fingers were merged into the fine sand layer, and from which new fingers were generated in the underneath coarse sand, though the infiltrating water was concentrated into the reduced number of fingers. When preferential water flow arrived at the fine sand layer, which was inserted among coarse sand, water began to move horizontally within the layer. Once the water potential of the fine sand increased to a certain level, water was released into the below coarse sand. Obviously, water was transferred from the flow-fingers above to those below the fine layer via horizontal movement within the layer. Gamma-ray scanning of a 18-cm long area (across a flow-finger) of the insert layer indicated that the fine sand water contents were not uniform in horizontal direction, with a peak at the point where water entered the fine sand layer from the above coarse sand. With the water drained off the fine sand, difference of water contents along the horizontal layer was reduced. In addition, results obtained by scanning a narrow area around a vertical flow-finger clearly demonstrate a preferential water flow-path, with the inserted fine sand layer acting as a secondary water distributor.

Two sets of experiments were performed to demonstrate the effect of layering-structure on colloid transport in sands. One is transport of montmorillonite (Mt) in homogeneous coarse sand, and the other is in the same sand but with a 1.5-cm thick fine sand layer. Total concentrations of colloids (Mt plus in-situ silica colloid) were determined, whereas Mt concentration was analyzed with ICP based on Al measurement. The tests indicated that Al content in the in-situ silica colloids was very low, equivalent to 0.5-2 mg/L Mt. This is a negligible compared to the 250 mg/L injection concentration of Mt. The observed results reveal that both in-situ silica colloids from the sand and injected Mt particles exhibited preferential mobilization along the flow-fingers of water. The cumulative mass of the transported colloids varied among outlets. The inserted fine sand layer caused a reduction of the number of flow-fingers for colloid transport. Moreover, the detailed breakthrough curves verified that presence of fine sand layer in coarse sand lowered the Mt concentrations in the effluents, and the effect was enhanced as the texture of the insert layer became fine. This is attributable to the possible accumulation of Mt colloids in the fine sand layer. If this is true, fine sand layer would act as a secondary redistributor of water and colloids. We speculate that subsequent

flushes with water or other solutions will cause preferential transport of the colloids remobilized from the fine layer.

Our preliminary study demonstrates that there exists preferential transport of colloids in sand, and the transport is greatly impacted by presence of layering-structure. Flow-fingers can be merged if encountering a fine sand layer. However, new fingers with reduced number can be generated when water or colloids enter the below coarse sand from the fine layer. It is believed that subsequent redistribution of the water and colloids largely depends on the pattern and intensity of irrigation to the layered sands, and this further determines the radionuclide transport in Hanford sands. These preliminary results provide significant insights into understanding of colloid mobilization in Hanford sediments, which are rich in layering-structures, and suggest a necessity of systematic study on the issue of layering-structure effects.