

Project 86814

We have completed the studies on reactions of minerals with caustic Hanford tank waste solutions. Systematic studies on the effects of different anions, cations, and the radionuclide Cs-137 were completed and technical manuscripts on these experiments were submitted for publication. The concentration of NaOH and the type of anion played the dominant roles in determining minerals formed. Increasing NaOH concentration and temperature enhanced the formation of feldspathoids; when NaOH concentration was high (e.g., 16 M), stable cancrinite and sodalite formed rapidly. Cancrinite formed in the presence of nitrate or sulfate; sodalite formed in the presence of chloride, carbonate or without added anions. Low concentration of Cs (< 100 mM) did not affect the formation of lepispheric cancrinite and sodalite, whereas only highly crystalline cancrinite formed when Cs concentration was >250mM. The presence of K did not alter but slowed down the formation of cancrinite and sodalite. The presence of divalent cations led to the formation of intermediate or stable silicates, aluminates, hydroxides or even aluminosilicates. We investigated the incorporation of Cs and the stability of the incorporated Cs in feldspathoids, zeolites, and allophane that may form in the sediments under conditions mimicking Hanford tank leaks. The incorporated Cs was quantified by atomic absorption spectroscopy after digestion in 1 M HCl. Cancrinite, sodalite, LTA zeolite, the 3-D cross-shaped zeolite, and allophane were capable to preferentially incorporate Cs when they form in the alkaline simulants. The internal sites of feldspathoids and zeolites were accessible by ion exchange reactions. Incorporated Cs in sodalite and cancrinite cannot be easily replaced by other cations. This is likely due to the result of the small aperture size of the beta-cage in sodalite the the epsilon-cage in cancrinite. The hydration energy and the size of cations are important in determining if the ions can be replaced by other cations. Large undisturbed sediments cores were sampled in the ERDF pit between the 200E and 200W tank farms at Hanford in 2003. These cores have been characterized and bottom plates and a sprinkler head for water application for unsaturated flow experiments have been constructed. Several membrane types and porous plates have been tested for potential use as suction devices at the bottom. Stainless steel membranes in combination with nylon meshes were the most suitable materials and the bottom plates have been designed to accommodate these membranes. The cores are being instrumented with tensiometers and TDR sensors, and unsaturated flow experiments are currently being conducted. We experimentally determined colloid stability of natural colloids extracted from vadose zone sediments. Colloid stability was assessed with three different methods: the batch turbidity method, column mobilization experiments, and dynamic light scattering. Critical coagulation concentrations (CCC) were determined for pure Na and pure Ca electrolyte solutions, as well for mimicked Hanford vadose zone pore waters with varying sodium adsorption ratio (SAR). Critical coagulation concentrations obtained from the batch turbidity method were sensitive to initial colloid mass concentrations, settling time, and CCC criteria. The CCC values determined from dynamic light scattering were lower than those determined from the batch turbidity method. The CCC was strongly affected by the SAR and the absolute electrolyte concentrations. For conditions at the Hanford site, our results suggest that colloids likely will form stable suspensions in the vadose zone pore water. Colloid transport experiments were conducted under steady-state water flow conditions with effective water saturations ranging from 0.56 to 1.0. Under saturated conditions, no colloids were removed from the liquid phase during transport, while under unsaturated conditions colloids were removed from the mobile water region. Colloid removal increased with decreasing system saturation. Under constant chemical conditions, colloids captured within the column could quantitatively be recovered in the column outflow by re-saturating the column after each unsaturated-flow breakthrough. Through microscopic observations in a glass micromodel containing suspended air bubbles, we found that colloids did not adhere to the liquid-gas interface. Using the extended DLVO theory, free energies of Lifshitz-van der Waals, electrostatic and Lewis acid/base interactions between colloids, sediments and the liquid-gas interface were calculated based on their independently determined surface thermodynamic properties. Experimental results and surface thermodynamic calculations support the hypothesis that colloids were retained near the liquid-gas-solid interface. The reactive transport model FLOTTRAN was used to simulate cesium transport of the column experiments. Discrepancies observed between the experiments and the numerical model indicated that kinetic limitations may be present in the ion exchange reactions and that the local equilibrium assumption adopted by FLOTTRAN may not be valid. FLOTTRAN currently does not simulate kinetic ion exchange reactions. New code was written to enable FLOTTRAN to model kinetic ion exchange reactions. A major restructuring of the code was required since the global implicit scheme utilized by FLOTTRAN only solved the aqueous species transport equations in a

coupled manner. In order to simulate kinetic ion exchange, the sorbed species needed to be solved simultaneously with the aqueous component equations. In addition, a kinetic reaction subroutine was written to calculate the reaction term for kinetic ion exchange equations. This new version of FLOTRAN is currently being tested. Once verified, we will attempt to fit the colloid-facilitated Cs transport experiments using this new kinetic ion exchange capability. The component of the collaborative research effort with the University of Tennessee (John McCarthy) is directed at understanding the impacts of natural flow regimes on colloid transport. While experiments that impose steady-state flow conditions are critical for developing fundamental understanding of colloid-media interactions, flow in natural subsurface environments is dominated by transient flow involving temporary increases in water content and flow rate during rain events, followed by decreasing water content during drainage. Our experiments involve studies with model porous media (Accusand) and in Hanford sediments, and evaluating the transport of both model colloids (montmorillonite), as well as colloids derived from Hanford sediments. Because Hanford sedimentary deposits exist as sorted layers of coarse and fine sediments, the effect of such layering on the distribution of water flow through these layers and the subsequent impacts on preferential flow and colloid transport are also being evaluated. This study involves transport experiments in both two-dimensional media (containing a uniformly sized sand (Accusand) or Hanford sediments) and in large intact monoliths of Hanford sediments. The model system is a large "slab" of porous media (65 cm wide, 90 cm high, and 1 cm thick) with a trough for injecting a uniform line-source of infiltrating water at a controlled rate. The bottom of the slab is divided into ten ports so that effluent can be collected from individual preferential flow paths. Tension is applied to all the effluent ports to control the lower boundary condition. The line-source of water is initially distributed relatively uniformly across the top 2-4 cm of the porous media, but, even in uniformly sized Accusand, flow quickly resolved into a few narrow preferential flow paths that conduct the entire volume of water. These preferential flow paths exhibit a "memory effect" whereby subsequent inputs of water follow the same preferential flow paths as were initially established. The number and width of the flow paths is related to the irrigation rate. To evaluate what flow rates, colloid concentration and aqueous chemical conditions would be most informative, we are also conducting column experiments under transient saturation conditions that mimic transport within preferential flow paths in the slab. A series of vertical column transient-percolation experiments were conducted to examine the effects of irrigation rates (0.5%, 5%, and 10% of the saturated hydraulic conductivity [K_s]) and solution ionic strengths (2, 20, 100 mM NaNO₃, pH 7) on the transport of the montmorillonite colloids. The column is 2 cm in inner diameter and 65 cm in length. The initial water content of the packed Accusand was 10% in saturation. Our results indicate that there is an interactive effect on colloid transport between the irrigation rate and the solution ionic strength. High irrigation rate reduced the effect of ionic strength on colloid retention, although colloid migration could be reduced even at a high flow rate at very high ionic strength (100 mM). The effect of the irrigation rate on colloid transport is attributed to changes in both the water content and the pore water velocity. The input of water to the initially drained (10% saturation) column moved almost as plug-flow, increasing the water content as a steady front of higher water content as the water proceeded down the column. Initial breakthrough of water in the effluent was accompanied by the arrival of colloids at more than half the input concentration. As reported by previous studies, high water content facilitates colloid movement in porous media. Therefore, high irrigation rate apparently resulted in less retention of the colloid in the sand. The other factor influencing colloid transport was the pore water velocity, which was much faster during inputs of higher flow rates. For example, initial arrival of water at the bottom of the column took ~25 minutes at the 0.5% K_s flow rate, but only 4 minutes at the highest flow rate. At the higher pore water velocities, advection dominated and less dispersion was apparent in colloid breakthrough.