

Research Objective: The primary goals of this project are to (1) quantify the kinetics and thermodynamics of dominant mineral dissolution and precipitation reactions considered to result in significant uptake of contaminants upon mixing of leaked tank fluids and Hanford soil and soil solutions; (2) quantify the kinetics of subsequent reactions that might enhance the mobility of the contaminants; and, (3) quantify the uptake of radionuclide contaminants in the secondary precipitates.

We propose to address three specific issues with respect to obtaining accurate rate laws and quantifying radionuclide uptake in systems representing waste fluids from tanks and other disposal sites at Hanford, Washington and minerals in Hanford sediments. The first two issues will build on the results we obtained in our previously funded EMSP project (70070). First, we will continue to quantify rates for selected sediment minerals as a function of recognized factors that control the kinetics of dissolution and precipitation in the unnatural system of waste solutions mixing with soils. These include the effect of high pH, high ionic strength (especially  $\text{NaNO}_3$  solutions), temperature, and saturation state. Dissolution of the sediment minerals primarily provides the source of dissolved Si necessary for precipitation of secondary phases.

Second, we will proceed in quantifying and characterizing the nucleation mechanisms for the secondary precipitates. Understanding nucleation mechanism, nucleation sites on soils minerals, and the role of reactive surface area in simultaneous dissolution and precipitation reactions are key unknown components in comprehending this contaminated vadose zone system. Previous work on the generation of colloids by reaction of Hanford sediments with tank simulants has indicated that homogeneous nucleation may be important at Hanford at least under the relatively high flow rate conditions of the column experiments. However, field evidence for substantial colloid transport is still lacking. Our previous work suggests that nucleation on mineral substrates may be just as important and that secondary phase overgrowths can passivate primary mineral surfaces and prevent their dissolution as well as cement sediment grains together. It is likely that secondary phases also remove contaminants from solution, by incorporation in the secondary phase structure or by formation of reduced metal solids. In a new addition to the project, we propose to investigate the effect of evaporation and wetting/drying cycles on the dissolution and precipitation processes involving secondary phases.

Third, the extent of simultaneous uptake or release of contaminants during primary phase dissolution, secondary phase precipitation, and subsequent secondary phase dissolution needs to be determined and correlated to the reaction kinetics. We intend to focus on understanding the extent of irreversibility of Cs and U uptake in secondary phases using a radiochemical counting approach coupled with characterization of powdered and single crystal mineral samples.

Our data will provide fundamental information useful for (1) comprehending the unsampled sub-tank sediments particularly with respect to as yet undetermined mass balances for the full distribution of released radionuclides, (2) estimating the conditions of formation and stability of colloidal and surface precipitates, and (3) predicting the future mobility of contaminants incorporated in precipitates via dissolution reactions.

Research Progress and Implications: This project just started in mid-April, 2003 and is a continuation of EMSP Project #70070. Results from Project #70070 can be found under that project's report.

Planned Activities: Our immediately planned activities include simulation of precipitation reactions of secondary silicate minerals incorporating U and Cs. These experiments will be conducted using batch and stirred-flow reactor kinetics experiments and single crystal or powdered mineral substrates. The initial substrates will be quartz or feldspar. Radionuclide uptake will be monitored using alpha- or gamma-spectrometry depending on the specific radionuclide investigated. A new graduate student has started to work on the project as of June. A post-doctoral researcher will begin to work on the project in July.

Information Access: No publications have yet resulted from the current project. Publications resulting thus far from the predecessor Project #70070 are given below.

- Bickmore B. R., Rosso K. M., Nagy K. L., Cygan R. T., and Tadanier C. J., 2003, Ab initio determination of edge surface structures for dioctahedral 2:1 phyllosilicates: implications for acid-base reactivity. *Clays and Clay Minerals*, in press.
- Bickmore B. R., Nagy K. L., Sandlin P. E., and Crater T. S., 2002, Quantifying surface areas of clays by atomic force microscopy, *American Mineralogist* 87, 780-783.
- Bickmore B. R., Nagy K. L., Young J. S., and Drexler J. W., 2001, Nitrate-cancrinite precipitation on quartz sand in simulated Hanford tank solutions, *Environmental Science & Technology*, 35, 4481-4486.
- Samson S. D. and Nagy K. L., 2002, Biotite dissolution in simulated Hanford tank waste, *Geochimica et Cosmochimica Acta* 66, A665-A665 (abstract, 2002 Goldschmidt Conference).