

Project Title: Mineralogic Residence and Desorption Rates of Sorbed ^{90}Sr in Contaminated Sub-surface Sediments: Implications to Future Behavior and In-Ground Stability

Project Number: 1022407

Principal Investigator: Peter C. Lichtner (LANL)

1 Research Objective

^{90}Sr desorption process will be quantified in coarse-textured Hanford sediments contaminated by different waste types and a reaction-based reactive transport model developed to forecast ^{90}Sr concentration dynamics in Hanford's 100-N plume. Previous research has addressed ^{137}Cs desorption from HLW-contaminated sediment providing results critical for HLW tank farm closure decisions. This renewal focuses on ^{90}Sr with the objective of providing fundamental knowledge to predict future in-ground behavior as required for sound remedial decisions. Preliminary observations that suggest that 10-y sorbed ^{90}Sr in coarse-textured sediment resides in the interiors of basaltic lithic fragments. This intraparticle retention defines a new conceptual model for ^{90}Sr retardation that is tentatively attributed to internal domains of phyllosilicates formed from the weathering of basaltic glass. Research will characterize the spatial locations, composition, and reactivity of these intra-grain phyllosilicate domains using spectroscopic, microscopic, and wet chemical methods. Intra-grain porosity, diffusivity, and tortuosity will be estimated using emersion experiments coupled with particle imaging (using electron, X-ray, and NMR techniques). Desorption rates and extent will be measured from contaminated Hanford sediments of different waste impact in electrolytes that promote isotopic exchange, ion exchange, and/or dissolution. Desorption results will be interpreted with a geochemical-physical model that incorporates aqueous speciation, mass transfer, and other important factors. Batch and column experiments will be performed with sediments from Hanford's 100-N plume to quantify factors controlling long-term release rates and river stage effects. Newfound understanding and geochemical parameters will be incorporated into the FLO-TRAN reactive transport code for simulation of 100-N plume dynamics.

2 Research Progress and Implications

Work to date during the third year of a three year project involved continued modeling of Sr-sorption experiments conducted at PNL and developing a multi-scale model for Sr-transport in Hanford sediments.

An example showing the fit to the measured Sr sorption isotherm and the effects of the complex SrNTA^- is shown in Figure 1 in which two isotherms are shown at different NTA concentrations of 0.015 M and 0.0015 M. The sorbed concentration decreased in proportion to the amount of NTA added at low Sr concentrations, but had no effect at higher Sr concentrations above approximately 0.01 M. Considerable difficulties were encountered in collecting experimental data in measuring sorbed Sr concentrations on Hanford sediments because of the interaction with minerals in the sediments as sorbed species were leached from the sample.

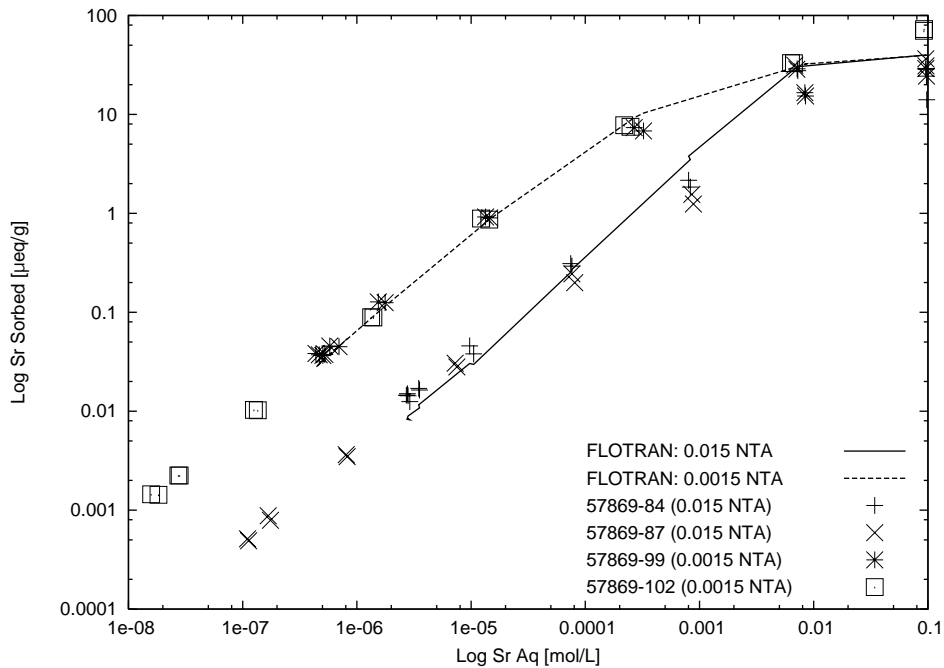


Figure 1: The effect of NTA on Sr sorption.

To model reactive transport of Sr in Hanford sediments taking into account multiple scales involved in inter- and intra-grain mass transfer, a prototype multi-scale continuum model was developed. The model is based on a generalized multiple interacting continuum (GMINC) formulation for a multicomponent system. The sub-grid scale or secondary continuum is represented as a one-dimensional subdomain that is coupled to the primary continuum at a selected set of nodes that need not include the entire primary continuum domain. The sub-grid problem is treated as a source/sink term in the primary continuum transport equations. A block-tridiagonal solution algorithm is used to solve the sub-grid scale problem. By sandwiching the primary continuum solve between the forward and backward solves of the block tridiagonal system of equations for the sub-grid domain, it is possible to rigorously decouple the two sets of equations. This approach provides a much more versatile and efficient solution method compared to a brute force approach that attempts to solve both sets of equations for primary and secondary continua simultaneously. It allows, for example, a distribution of subdomain sizes to be include in the simulation. This is illustrated in Figure 2 (left) for a single component system showing the breakthrough concentration for different grain sizes and a particle distribution representation of the Hanford sediment.

One difficulty encountered, however, was the lack of stability of the block tri-diagonal solver developed in the late 70's by Hindmarsh. It was found that for large times the solution to a single component tracer became unstable as shown in Figure 2 (right). A single component tri-diagonal solver did not have this problem. It is noted in the block tri-diagonal solver manual (Hindmarsh, Solution of Block-Tridiagonal Systems of Linear Algebraic Equations, UCID-30150, 1977) that:

The computation of the LU decomposition of each D_k involves partial pivoting, mean-

ing that rows are interchanged in a manner designed to control the growth of roundoff error. . . . However, these pivoting operations are done only within each block of rows of T separately. For this reason, it is conceivable that the overall algorithm may suffer from numerical instability (i.e. harmful growth of roundoff errors), if T is particularly unsuitable.

It is further noted that this instability may occur even for well-posed problems. Future work will investigate this situation more closely too see if a more stable algorithm can be developed. More details may be found in Lichtner (2006).

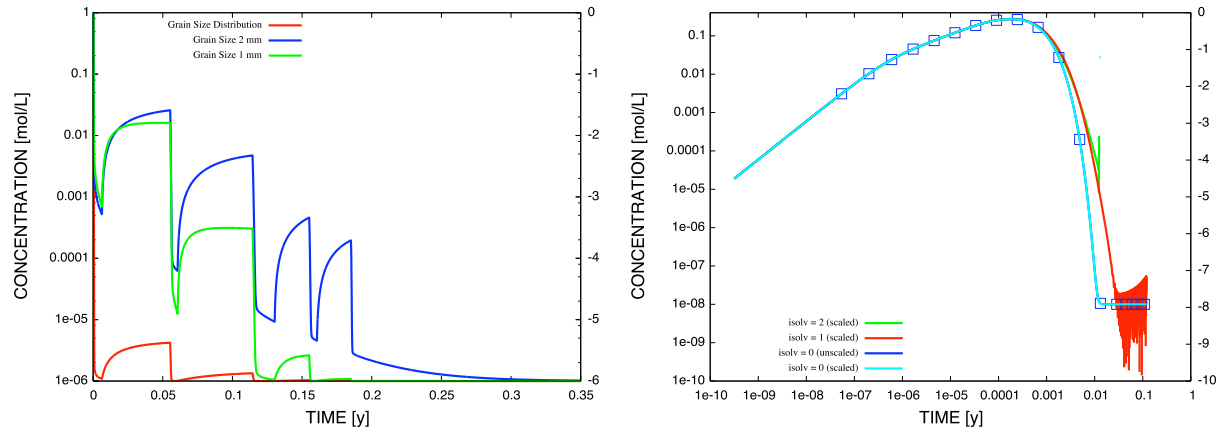


Figure 2: Left: Breakthrough curves for different particle distributions. Right: Breakthrough curve for a single component multiple interacting continuum simulation showing the instability arising from use of a block tri-diagonal solver (red curve).

3 Information Access

Lichtner, P.C. (2006) Multi-Scale Reactive Transport Equations and their Numerical Solution, Los Alamos National Laboratory report LA-UR-06-7888.