Project Identification Number: 27617

Project Title: Mineral Surface Processes Responsible for the Decreased Retardation (or Enhanced Mobilization) of ^{137}Cs from HLW Tank Discharges

DOE Report Number:

Publication Date: March 1, 2000

Lead Principal Investigator: John M. Zachara, Pacific Northwest National laboratory, P. O. Box 999, MISN K8-96, Richland, Washington 99352, (509) 376-3254 (phone), (509) 376-3650 (fax), john.zachara@pnl.gov.

Co-Principal Investigators: 1) R. Jeffrey Serne, Pacific Northwest National laboratory, P. O. Box 999, MISN K6-81, Richland, Washington 99352, (509) 376-8429 (phone), (509) 376-5368 (fax), rj.serne@pnl.gov 2) Paul D. Ellis, Pacific Northwest National laboratory, P. O. Box 999, MISN K8-98, Richland, Washington 99352, (509) 372-3888 (phone), (509) 376-2303 (fax), pd_ellis@pnl.gov, and 3) Paul M. Bertsch, University of Georgia, PO Drawer E/Bldg 737A, Aiken, South Carolina 29801, (803) 725-2472 (phone), (803) 725-3309 (fax), bertsch@srel.edu.

Number of Graduate Students Actively Involved in the Project:
None

Specific DOE problems that are being addressed by your project, and potential practical relevance to improved knowledge, techniques, processes or technology:
The project is investigating Cs geochemistry in Hanford sediments under chemical conditions relevant to high-level waste, single-shell tank leakage. Fundamental information developed by the research will be useful in assessing the long-term risk posed by massive in-ground concentrations of ^{137}Cs in the Hanford tanks farms, and in establishing scientifically credible closure plans. Project research results are now being used in improved reactive transport models to simulate Cs migration in the vadose zone beneath leaked single shell tanks in the S-SX tank farm at Hanford.

Research Objective:

Experimental research will determine how the sorption chemistry of Cs on Hanford vadose zone sediments changes after contact with solutions characteristic of high-level tank wastes (HLW). Our central hypothesis is that the high ionic-strength of tank wastes (i.e., > 5 mol/L $NaNO_3$) will suppress all surface-exchange reactions of Cs, except those to the highly selective frayed edge sites (FES) of the micaceous fraction. We further speculate that the concentrations, ion selectivity, and structural aspects of the FES will change after contact with the harsh chemical conditions of HLW and these changes will be manifest in the macroscopic sorption behavior of Cs. We believe that migration predictions of Cs can be improved substantially if such changes are understood and quantified.

Research Progress and Implications:

Key accomplishments are as follows:

- Cs sorption to Hanford sediment has been found to be a sensitive function of Na concentration up to saturation with $NaNO_{3(s)}$. High Na swamps all sorption sites except high-affinity ones on micas. Contrary to conventional wisdom, Na^+ and Cs^+ compete for high-affinity micaceous, FES sites. Cs migration is greatly expedited in $NaNO_3$ brines where K_d's can approach 0.
- The FES sites are associated primarily with biotite and vermiculitized biotite and not muscovite. Microbeam analyses (electron microprobe, synchrotron X-ray microprobe) of Cs-containing micas documentated Cs accumulation at specific areas on crystallite edges, and also in microscopic internal channels associated with weathering planes and physical fractures.
- A multiple-site, multi-component surface complexation model for Cs adsorption to Hanford sediments has been developed for Na^+, Ca^{2+}, and K^+ electrolytes. The model extends over the electrolyte concentration range found in dilute, concentrated, and self-boiling HLW tanks, and is suitable for linkage with a transport code.
- Cs sorption extent increases with both temperature and OH^- content of the aqueous phase. Higher base concentrations (e.g., > 1.0 mol/L) and temperature (e.g., 50^o C) promote oxidation and expansion of biotite crystallites, increases in CEC, and surface precipitation/armoring of the mica sorbents by Fe(III) oxides.
- Techniques for the isolation, identification, and counting of ^{137}Cs-containing mineral particles in contaminated sediment have been developed and refined by application to a single HLW-contaminated subsurface sediment collected from beneath leaked tank SX-109 at Hanford (10^5 pCi/g ^{137}Cs). The Cs-containing particles were primarily biotite, and the sorbed Cs was strongly resistant to desorption.

Planned Activities:

Our final experimental campaign is investigating the combined impact of high OH^- and $Al(OH)_4^-$ on Cs^+ adsorption by Hanford vadose zone sediments over a temperature range (35-95^o C) relevant to the subsurface discharge of self-boiling REDOX wastes. Experiments are tracking the concurrent dissolution of sorbing micaceous minerals and precipitation of Al oxides and the impact on Cs adsorption and fixation by the sediments. We are also working to finalize three other publications that have resulted from past research.

Information Access:

Zachara, J.M., S.C. Smith, J.P. McKinley, R.J. Serne, C. Liu, and P.L. Gassman. 2000. Sorption of Cs^+ to Micaceous Subsurface Sediments from the Hanford Site, Washington. *Clays and Clay Minerals* (submitted).

McKinley, J.P., R.J. Serne, J.M. Zachara, C.J. Zeissler, and R.M. Lindstrom. 2000
The Distribution and Retention of ^{137}Cs in Sediments Beneath Leaked Waste Tanks at the Hanford Site, Washington. *Environmental Science and Technology* (submitted).