Fixation Mechanisms and Desorption Rates of Sorbed Cs in High-Level Waste Contaminated Subsurface Sediments: Implications to Future Behavior and In-Ground Stability

(Project Number: 73758)

Principal Investigator

John M. Zachara
Pacific Northwest National Laboratory
P.O. Box 999, MSIN K8-96
Richland, WA 99352
(509) 376-3254 (phone)
(509) 376-3650 (fax)
john.zachara@pnl.gov

Co-Investigators

James P. McKinley
Pacific Northwest National Laboratory
P.O. Box 999, MSIN K3-61
Richland, WA 99352
(509) 375-6861 (phone)
(509) 375-6954 (fax)
james.mckinley@pnl.gov

Calvin C. Ainsworth
Pacific Northwest National Laboratory
P.O. Box 999, MSIN K3-61
Richland, WA 99352
(509) 375-2670 (phone)
(509) 375-6954 (fax)
calvin.ainsworth@pnl.gov

R. Jeff Serne
Pacific Northwest National Laboratory
P.O. Box 999, MSIN K6-81
Richland, WA 99352
(509) 376-8429 (phone)
(509) 376-5368 (fax)
jeff.serne@pnl.gov

Research Objective

The high-yield fission product ^{137}Cs is a major contaminant of the vadose zone at Hanford and other DOE sites. Over 100 kCi of ^{137}Cs was discharged to the vadose zone in the S-SX tank farm at Hanford through the leakage of high-level waste from tanks SX-108 and SX-109. Although ^{137}Cs is strongly sorbed by subsurface sediments, certain waste characteristics, such as high Na^+, can expedite its migration and reduce its retardation to low values.

This project is focused on defining the in-ground geochemistry of sorbed ^{137}Cs released from high-level waste tanks, so that better future projections can be made of Cs mobility in the vadose zone. The project will study Cs-contaminated subsurface sediments from various Hanford tank farms to 1) determine the mineralogic and surface site residence of sorbed Cs in contaminated sediments varying in current Cs content and original waste composition, 2) establish geochemical factors and processes controlling Cs desorbability and desorption kinetics from contaminated sediment and Cs-enriched sediment particles, and 3) define and parameterize a kinetic model for Cs desorption that incorporates multi-site behavior and heterogeneous intra-particle Cs distribution.

Research Progress and Implications

This project is in its first year since its renewal. A series of eight samples, ranging in ^{137}Cs concentration (from 10^5 to 10^8 pCi/g), was obtained from the Hanford River Protection Program by the placement of a slant borehole beneath leaked tank SX-108 in the S-SX tank farm. This core was the first ever collected at Hanford from the zone immediately beneath a leaked single-shell tank. Two of the samples that contained 10^8 pCi/g-^{137}Cs were the hottest geologic materials ever brought to the ground surface at the Hanford Site.

Samples of the eight sediments were dispersed on slides and contacted with a phosphor-imaging slide to identify mineral grains containing ^{137}Cs. The mounted grains were then manipulated and isolated into mineral fractions containing medium-high, low, and non-detectable ^{137}Cs concentrations. Grains in each of these fractions were then identified by a combination of methods, including X-ray diffraction and electron microprobe. The mineral particles containing high levels of ^{137}Cs were invariably micas. Those particles containing small levels of radioactivity were characteristically quartz grains that showed surface precipitates of zeolites that resulted from waste-sediment geochemical interaction (Figure 1). Particles without radioactivity included feldspars and clean quartz grains. These results allowed us to confirm that primary sorbents for ^{137}Cs in the waste-impacted sediments were micas (biotite and muscovite). Many persons had speculated that harsh chemical characteristics of the tank waste [for example, high OH^- and $Al(OH)_4^-$] would induce the formation of secondary minerals (zeolites and aluminosilicates) that might further sequester ^{137}Cs. We saw no evidence that such phenomenon was widespread.

Samples of four ^{137}Cs-containing sediments from the SX-108 borehole that varied in distance from the tank, pH, and ^{137}Cs concentration were placed in Na^+, Rb^+, K^+, and NH_4^+ electrolytes of
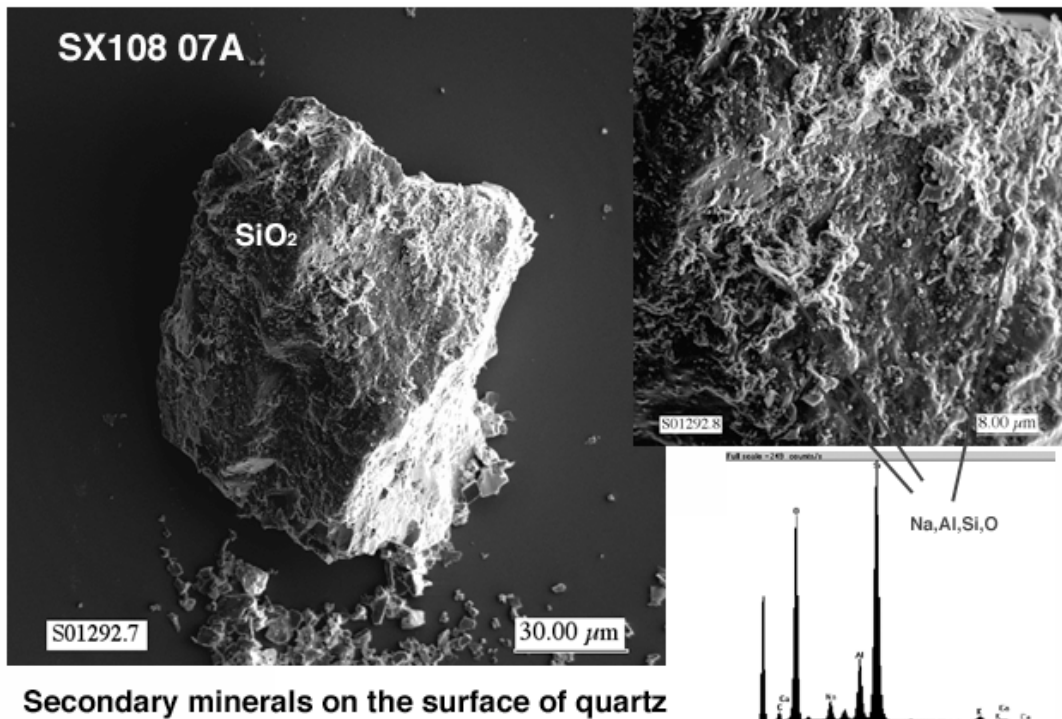
Figure 1. Secondary Zeolite on the Surface of a Quartz Grain from SX-108 Sample 07. The zeolite precipitate retains a small amount of ^{137}Cs.

different compositions to study the rate and extent of ^{137}Cs desorption. These sediments have been contaminated for more than 20 years. Example results of these studies using K^+ electrolyte are shown in Figure 2. Cs^+ desorption occurs rapidly (within 10 d) when the contaminated sediment is contacted with electrolyte. Additional ^{137}Cs is released when the ionic strength is increased by a factor of 20, indicating an ion exchange process. Generally, it was found that from 25-40% of the adsorbed ^{137}Cs was readily desorbed in electrolyte. Desorption studies performed with an acidic, Fe(III)/Al(III) complexing media showed enhanced release of ^{137}Cs. These studies implied that secondary surface precipitates of Al and Fe oxides, resulting from waste sediment reaction, inhibit Cs exchangeability with the aqueous phase.

The multi-site model of Cs adsorption that we developed in our FY97 EMSP project provided excellent predictions of desorption extent after estimates were made of the exchangeable fraction. Our multi-site equilibrium model was linked with a diffusion model to simulate the time variant kinetics ^{137}Cs release from the contaminated sediments in different electrolytes. The model showed that desorption of the exchangeable ^{137}Cs pool can be quite rapid, if high electrolyte concentrations exist.
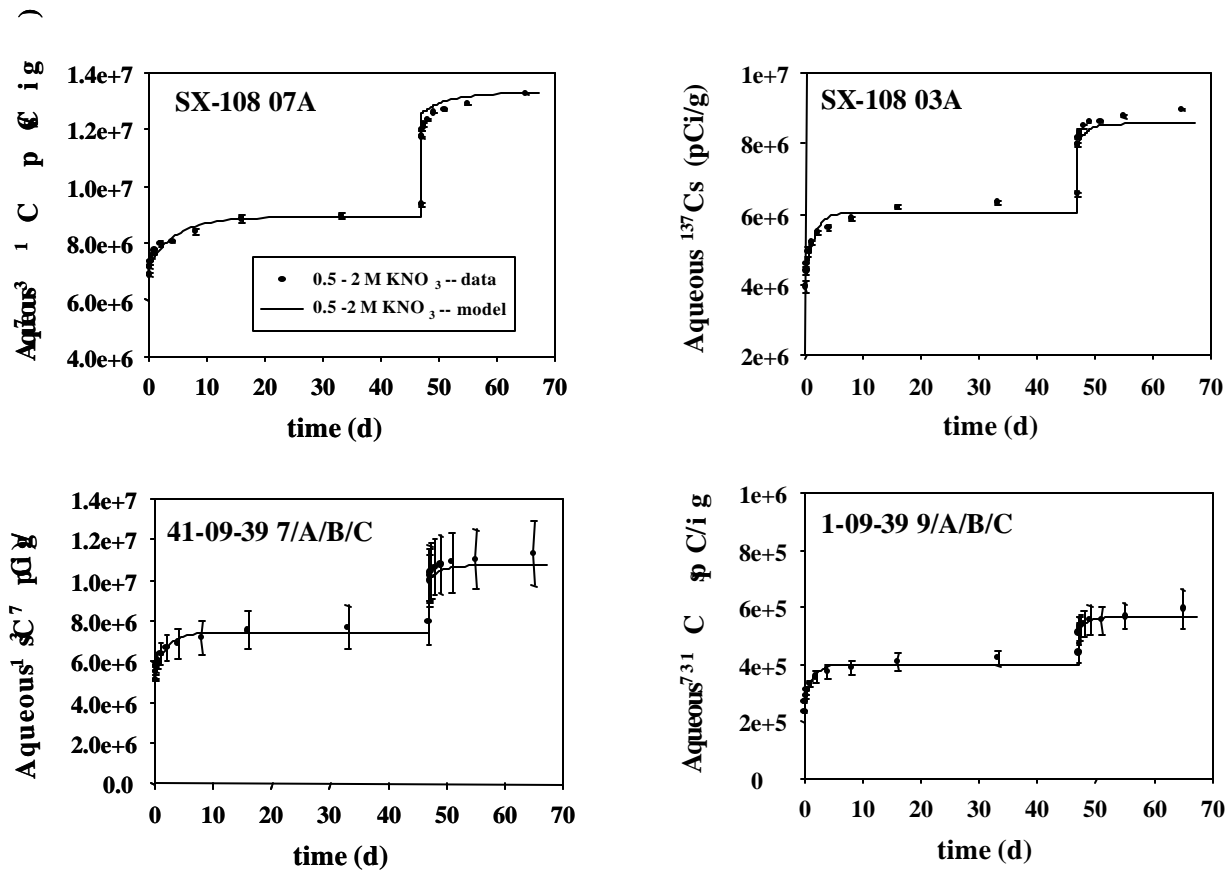
Figure 2. Aqueous Exchange Data and Results of Three-Site Model Simulations for KNO$_3$ or RbNO$_3$ Exchange at 0.1 M (0 to 47 days) and 2.0 M (47 to 64 days) with ^{137}Cs-Contaminated Sediments

Three important implications of our project work are known to date:

- Approximately 25-40% of the in-ground, sorbed pool of ^{137}Cs is exchangeable in the S-SX tank farm and could be transported to groundwater if high electrolyte concentrations existed.

- Mobilization and further transport of ^{137}Cs is not expected, however, unless tank waste retrieval operations (for example, sluicing) release significant volumes of water with high Na concentrations (>1.0 mol/L).

- Models developed by this project and its predecessor can be used to estimate the future transport behavior of ^{137}Cs in Hanford tank farms and to evaluate the effects of different leak-loss scenarios on ^{137}Cs mobilization and transport.

Planned Activities

We intend to study other ^{137}Cs-contaminated materials from different Hanford tank farms over the next two years. These studies will allow us to develop a comprehensive understanding of the waste composition, geochemical, and mineral structural factors controlling the long-term

behavior of ^{137}Cs in Hanford sediments. This information will be integrated into our kinetic desorption model that will be used to forecast future mobilization and transport of ^{137}Cs in response to various environmental management and waste retrieval scenarios.

Information Access

Zachara JM, SC Smith, C Liu, JP McKinley, RJ Serne, and PL Gassman. 2001. "Sorption of Cs+ to micaceous subsurface sediments from the Hanford Site, USA." *Geochimica et Cosmochimica Acta* (In press).

McKinley JP, RJ Serne, JM Zachara, CJ Zeissler, and RM Lindstrom. 2001. "The distribution and retention of ^{137}Cs in sediments at the Hanford Site, Washington." *Environmental Science and Technology* (In press).