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

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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 NaNO₃) 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.

The research will integrate studies of ion-exchange thermodynamics on the FES, with high resolution surface microscopies and spectroscopy to probe the structure of FES in Hanford sediments and to describe how the chemical environment of sorbed Cs changes when HLW supernatants promote silica dissolution and aluminum precipitation. Newly available atomic-force microscopies and high-resolution electron-beam microscopies afford previously unavailable opportunities to visualize and characterize FES. Our overall goal is to provide knowledge that will improve transport calculations of Cs in the tank-farm environment. Specifically, the research will:

- Identify how the macroscopic sorption behavior of Cs on the micaceous fraction of the Hanford sediments changes after contact with simulants of HLW tank supernatants over a range of relevant chemical ([OH], [Na], [Al], [K, NH₄]) and temperature conditions (23°-80°C).
- Reconcile observed changes in sorption chemistry with microscopic and molecular changes in adsorption-site distribution, chemistry, mineralogy, and morphology/structure of the micaceous sorbent fraction.
- Integrate mass-action-solution-exchange measurements with changes in the structure/site distribution of the micaceous-sorbent fraction to yield a multi-component/site-exchange model relevant to high ionic strength and hydroxide concentrations for prediction of environmental Cs sorption.

Problem Statement

Environmental Management Concerns

- Single Shell Tanks (SST's) containing high level wastes have leaked supernate containing large amounts of radioactive ¹³⁷Cs (10⁶ Ci) and other co-contaminants into the Hanford vadose zone.

- In select locations ^{137}Cs has exhibited “expedited” migration (up to 50 meters when predicted migration distances are < 10 m) saturated zone. The reasons for “expedited” migration are unclear.
- Deep ^{137}Cs migration has been observed beneath the SX tank farm at Hanford with REDOX wastes as the carrier, causing significant regulatory and stakeholder concern.

Scientific Context

- Micaceous 2:1 layer silicates are the primary environmental sorbents of Cs. Cs^+ is strongly sorbed by specific structural sites on these solids that exhibit nanometer scale dimensions with unique steric and geometric attributes.
- Micaceous 2:1 layer silicates exist as a small mass fraction of Hanford vadose zone sediments. These are known to impart significant Cs^+ sorptivity to Hanford subsurface sediments.

Science Issues

- REDOX wastes were self-concentrating by boiling, and contain molar plus concentrations of Na^+ , NO_3^- , OH^- , and $\text{Al}(\text{OH})_4^-$. The sorption behavior of Cs^+ from this complex waste matrix is not known.
- The chemical composition and temperature of the REDOX wastes is “harsh” and will induce dissolution and precipitation reactions upon contact with Hanford vadose zone sediments, possibly changing mineral surface structure and the selectivity of the micaceous fraction for Cs^+ . The extent, kinetics, and impacts of these reactions on contaminant fixation and migration are unknown.
- There exists no literature information upon which to base scientifically credible estimates of Cs^+ adsorptive-retardation beneath SST’s that have leaked high pH-high ionic strength waste waters.

Research Progress

Research since the last time of reporting (May, 1998) has continued to investigate, 1.) the Cs retention characteristics of a mica containing composite sediment from the Hanford formation, and 2.) the mineral association of ^{137}Cs in 35-year old contaminated sediment from beneath a leaked single-shell tank at Hanford (SX-109). Highlights from this work will be presented in the text that follows. Studies to determine the influence of high base on highly selective sorption/exchange of Cs to the micaceous fraction of the Hanford sediments were initiated at the beginning of the fiscal year as planned in the proposal. The results of these experiments are preliminary and are not reported here.

- 1.) *Thermodynamics of Cs Exchange.* Adsorption isotherms of Cs were measured over a wide sorbate range on homo-ionic Hanford sediments (Na^+ , K^+ , Ca^{2+}) in salt solutions of different concentration. The objective of these measurements was to relationships to predict the

magnitude of Cs⁺ adsorption to Hanford sediment. Salt concentrations ranged between 10⁻² – 10^{.69} mole/L to bracket those observed in natural and HLW impacted environments. The results were analyzed in terms of a conditional thermodynamic equilibrium constant (K_v) for the generalized exchange reaction:



where $K_v = [\text{A}^{u+}]^v [\text{N}_{\text{CsX}}]^u / [\text{Cs}^+]^u [\text{N}_{\text{AXu}}]^v$ and N is mole fraction of the exchanger phase components (AX_u, CsX). The mole fractions are defined as follows:

$$\text{N}_{\text{CsX}} = [\text{CsX}] / ([\text{CsX}] + [\text{AX}_{u}]) \text{ and } \text{N}_{\text{AXu}} = [\text{AX}_{u}] / ([\text{CsX}] + [\text{AX}_{u}])$$

The K_v is often termed a selectivity coefficient that is a measure the binding affinity of the sorbate (Cs) relative to the index or saturating cation (e.g., A^{u+}_(aq)) that was either Na⁺, K⁺, or Ca²⁺ in this case.

The Cs⁺ - Na⁺, Cs⁺ - K⁺, and Cs⁺ - Ca²⁺ exchange data each conformed to a single K_v relationship in the different salt solutions {Figure 1., where E(CsX) is the equivalent fraction of Cs on the exchanger [= adsorbed Cs concentration/cation exchange capacity]}. Cs⁺ was sorbed in great preference to the other cations, with K_v ranging from 10 to 10¹⁰. Consistent with ionic radius and hydration enthalpy, K⁺ was the most effective competitor for Cs. The dependence of K_v on E(CsX) indicates the presence of approximately three different types of exchange sites in the sediment with different adsorption/exchange energies. A high affinity site is present at low concentration, e.g., log E = 10⁻⁴. The high affinity site exists in the sediment at a total concentration of 10⁻⁸ mol/g, which is 1% of the operational frayed edge site pool defined by silver-thiourea exchange (data not shown). The high affinity site is

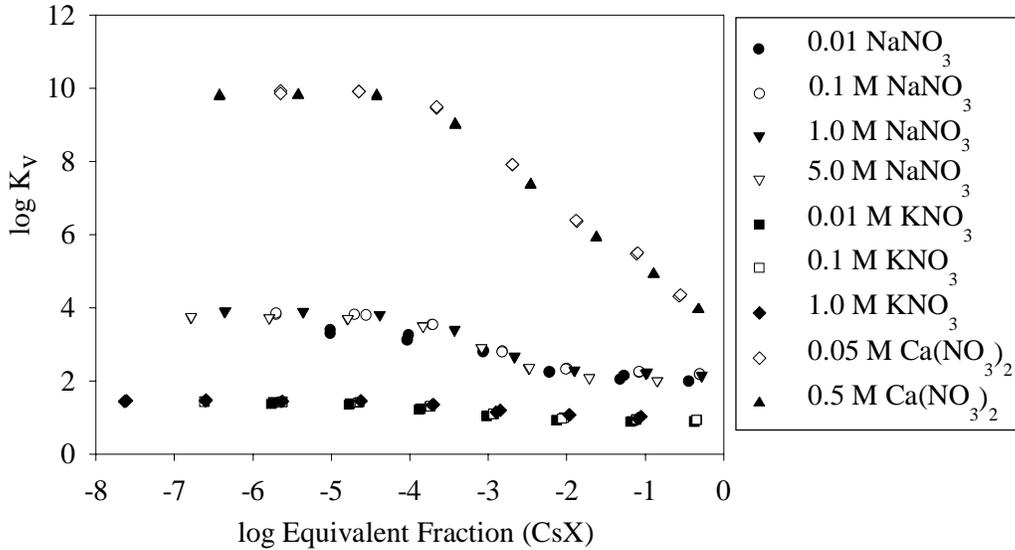


Figure 1. Dependence of the conditional thermodynamic equilibrium constant on surface saturation (CsX) and electrolyte concentration.

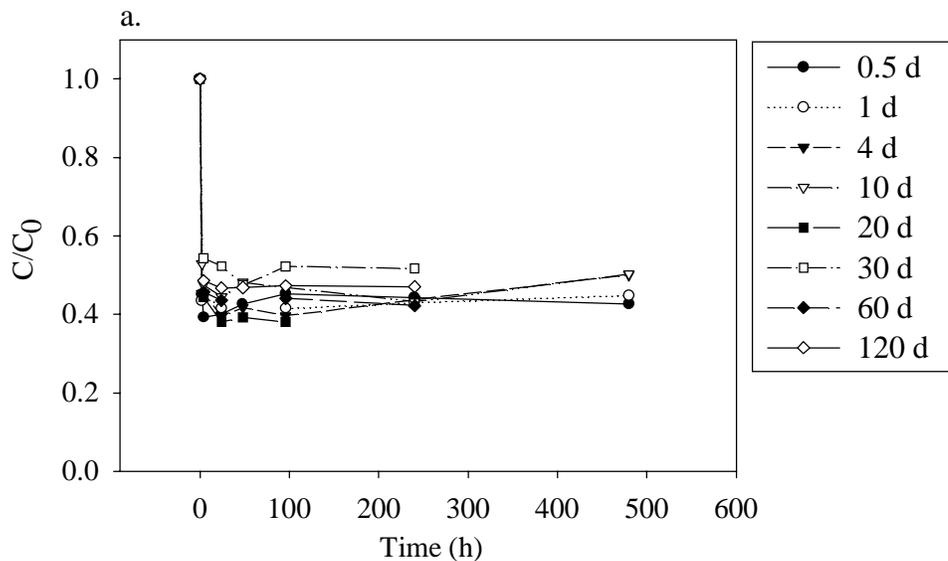
slightly lower in concentration than is $^{137}\text{Cs}^+$ in HLW (e.g., 10^{-7} mol/g). The exchange coefficient functions in Figure 1 can be used to model Cs^+ adsorption by ion exchange in Hanford sediments.

2.) *Desorption and Fixation of Cs.* Cesium is known to diffuse within the interlammellar space in specimen illites, leading to its partial or complete fixation. Fixation is highly significant in the Hanford sediments. If fixation occurs, ^{137}Cs may be held in place by the geomeia for sufficient periods to allow full decay to daughter products. Fixation, therefore represents a natural attenuation process that may prevent Cs migration to groundwater and that should be quantified as a basis for the “leave-it-in-place” remediation scenario.

Several experiments have been performed to evaluate Cs^+ fixation and one is shown here. In that experiment, $^{137}\text{Cs}^+$ (at 10^{-4} mol/L representative of HLW supernatant) was adsorbed to Hanford sediment in two different salt solutions (0.005 and 5 mol/L) and these were allowed to age for periods ranging from 0.5 to 120 day. After the aging period, the salt solutions with residual unadsorbed Cs^+ were removed and replaced with K^+ containing electrolyte. The K^+ was present at a concentration (10^{-2} mol/L) that was 100 times the total Cs^+ concentration. Cesium concentrations in the aqueous phase were then followed for extensive time periods to assess the extent to which K^+ induced Cs^+ desorption from the sediment (Figure 2a,b).

Cesium that is not desorbable by 100 times molar excess of K^+ is effectively fixed. The Y-axis in Figure 2 defines the normalized concentration, C/C_0 , where C is the concentration at any time (t), and C_0 is the initial soil bound concentration after the adsorption/aging period. Importantly, the initial adsorbed concentration in 5 mol/L salt (3.7×10^{-7} mol/g) was 38 times lower than that in 0.005 mol/L salt (1.4×10^{-5} mol/L) as a result of the mass action effect of Na^+ .

The desorption behavior of Cs^+ was similar in the two different salt solutions. That is, a significant fraction of the adsorbed Cs was immediately released upon K^+ addition. After this initial desorption episode that was presumed to be an ion-exchange displacement, little additional Cs^+ was released by the sediment. There was slight tendency for the shorter-aged samples to release more Cs^+ , but a distinct correlation with aging time was not observed. In spite of the noted similarity, there was, a major difference in the fractional extent of Cs^+ desorption in the two salt solutions (Figure 2a,b). In 5 mol/L Na^+ , approximately 55 % of the adsorbed Cs^+ was desorbable, while 85 %, on average, was released in 0.005 mol/L Na . However, because significantly more Cs^+ was adsorbed in 0.005 mol/L Na^+ , a larger Cs^+ concentration was actually fixed at low salt than at high salt, e.g., 2.10×10^{-6} mol/g as compared to 1.66×10^{-7} mol/g. These results support two important conclusions: 1.) Cs^+ fixation occurs on only a subset of the high affinity exchange sites and 2.) Na^+ competes with Cs^+ for access to fixation sites. This latter conclusion was unexpected given the significant differences in ionic radius and hydration energy of Na^+ and Cs^+ . The fixation process is presumed to involve highly selective exchange followed by the dehydration and interlamellar migration of the Cs^+ ion.



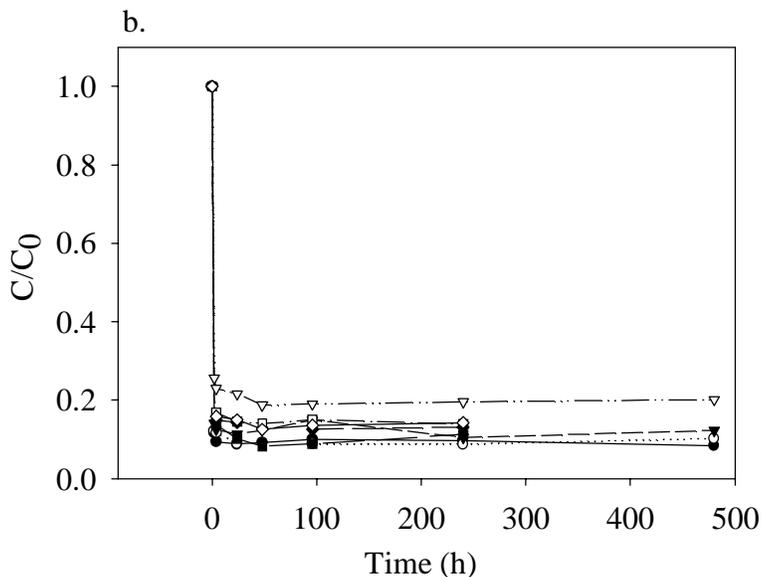


Figure 2. Desorption of Cs^+ from Hanford sediment by 10^{-2} mol/L K^+ after aging from 0.5 to 120 d. a.) Cs^+ contact and aging in 5.0 mol/L NaCl; and b.) Cs^+ contact and aging in 0.005 mol/L NaCl. Initial Cs^+ contact solution was 10^{-4} mol/L Cs^+ . C/C_0 is the normalized adsorbed concentration, e.g., the adsorbed concentration at time t (c) divided by the initial adsorbed concentration at the start of desorption.

3.) *Cs Distribution in Hanford Micas.* The differential abilities of micaceous minerals in Hanford sediments to immobilize Cs, and the variable binding of Cs to disparate reactive sites on mica plates, are under investigation using wet-chemical experimentation and compositional imaging. Flakes of three micaceous minerals (biotite, muscovite, and vermiculite) were identified in Hanford sediments using a binocular microscope and carefully hand-picked and segregated for experimentation. Each mica separate was reacted with Cs, by suspension in solution concentrations of 10^{-2} to 10^{-4} M Cs, for periods of one and three months. The reacted micas were washed and air dried, then mounted as whole flakes or sectioned to expose external and internal surfaces. Micas were hypothesized to preferentially sorb Cs at relatively high energy frayed-edge sites, and to strongly bind Cs by displacement of K at internal sites accessed by diffusion along crystallographic cleavage planes.

The distribution of Cs was investigated using the electron (EMP) and X-ray (XMP) microprobes. In biotite, Cs was preferentially sorbed at the edges of broken platelets (Fig. 3a). This result supported the hypothesis that Cs is more strongly bound at edge sites, but did not address the (frayed or unfrayed) nature of those sites. Examination of sectioned biotite (Fig. 3b) also supported the hypothesis that internal sites can sequester Cs from solution.

Data from these studies are near the detection limit for the EMP method (note the granularity in the Cs image below). We are utilizing the X-ray microprobe technique (at the ANL synchrotron light source; e.g., Fig. 3b) to produce data with a higher compositional resolution to more fully evaluate our hypotheses; preliminary data from this method are at relatively low optical resolution, but show promise for detection of Cs with 100 times the sensitivity of EMP methods.

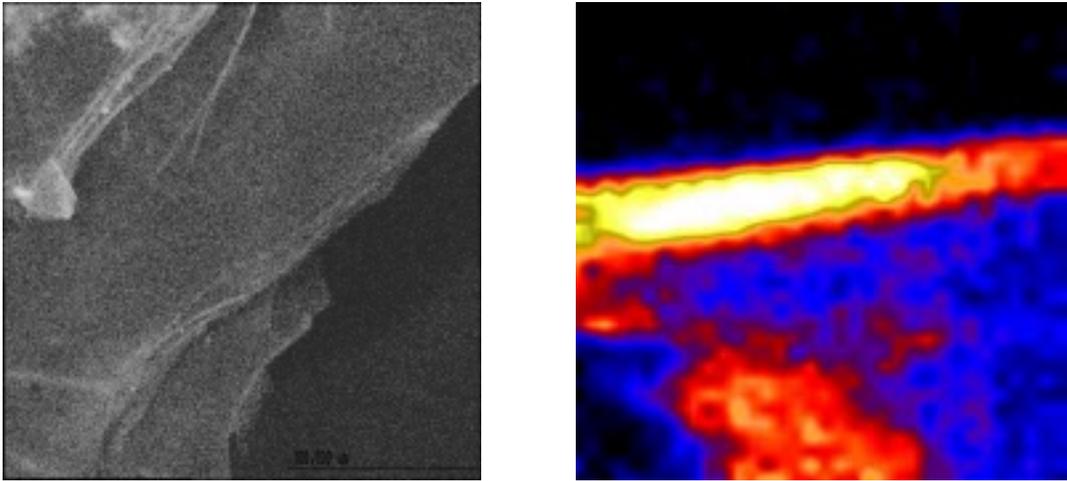


Figure 3. Adsorbed Cs⁺ distribution maps for Hanford Site biotite exposed to a solution of 10⁻² M Cs for 3 months. The left image is by EMP analysis of a plan-view specimen (200 micrometers across) and the right is by X-ray microprobe of a thin section (100 micrometers across). White intensity is proportional to Cs⁺ concentration. Cs⁺ is preferentially bound at platelet edges in plan-view (left image) and within internal, structural channels (right image).

Investigations of different micaceous minerals suggest that muscovite and vermiculite do not sorb Cs as strongly as biotite. Data to date are preliminary, and these results have not been confirmed.

4.) *Identification of Cs-sequestering Minerals in Contaminated Hanford Sediments.*

Contaminated sediments from Hanford core 41-09-39 collected beneath Hanford Site storage tank SX-109 were examined to determine the relative abilities of different *in situ* minerals to bind and sequester Cs from leaked wastes. It is unlikely, given the physicochemical differences among these minerals, that Cs would be found to be evenly distributed across the different mineral species.

Sediment samples from several (closely spaced) depths beneath a leaked tank were assayed for Cs contamination using bulk chemical techniques. These sediments were then wet-sieved and size-segregated for further study.

We wished to optically identify mineral components of each size fraction and instrumentally determine the chemical association of Cs with dissimilar grains. Mineral grains from each size fraction were dispersed in a binding agent on glass slides. Optical examination showed some mineralogic differences between size fractions, but in general the sediments consisted of primary silicate mineral grains, including abundant feldspars and micaceous minerals, along with secondary or detrital Fe oxides and clay minerals. After optical examination and preliminary mineral identification, mineral grain mounts were placed in a phosphorescence detector and incubated overnight. The detector stores gamma radiation chemically on a phosphor screen, allowing the detection and comparative quantitation of radiation from materials having relatively low activity. Exposure and digitization of phosphorescent images yielded radiation maps (autoradiographs) of dispersed particles, showing the relative abundance of Cs on mineral grains.

The comparison of mineral dispersions with radiation intensity maps allowed the identification of individual mineral grains having either “Cs positive” or “Cs negative” characteristics. New preparations were made from these mounts, in which twenty positive and twenty negative grains remounted in physically separate clusters. The “positive” and “negative” properties of the segregated grains were confirmed by repeating the radiation imaging step. This step allowed the direct determination of mineral phase identity for individual particles.

Mineral identities, primarily for “positive” grains but also for a minority of “negative” grains, were established using transmission electron microscopy (TEM) methods. Compositional information (collected using energy-dispersive X-ray spectroscopy) was collected in the microscope and combined with electron diffraction patterns captured on film. The combined data were used to search the JCPDS X-ray powder diffraction library for mineral identification (X-ray diffraction patterns are synthesized from electron diffraction data). Preliminary results indicated that Cs was not significantly bound to Fe oxides and non-phyllosilicates in these sediments. Cs was preferentially bound by smectites and micas. These results have not been confirmed, and require additional experimentation to complete.

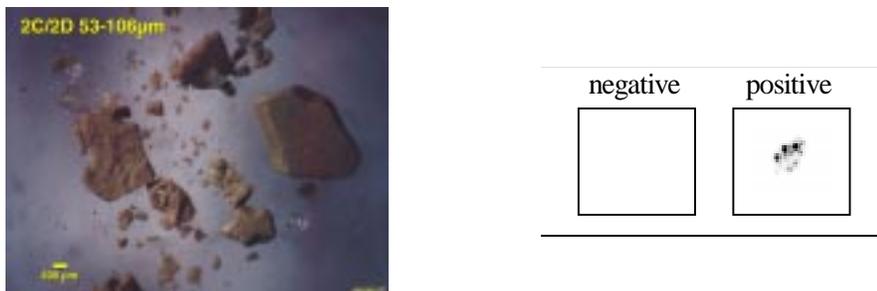


Figure 4. Optical image of segregated mineral grains (left), with final autoradiographic image (right) of segregated “positive” and “negative” particles. The darkness of autoradiographic spots indicates the radiation intensity; the clear area in the autoradiograph corresponds to grains that were “negative” for radiation. Clear, “negative” silicate grains are apparent in the optical image, as are “positive” phyllosilicate aggregates.

Implications to Site Restoration

Our proximity to Hanford has allowed us to share our results with site remediation contractors that are developing closure plans for the Hanford tank farms where massive subsurface ^{137}Cs contamination exists. This information exchange has occurred through Hanford's Groundwater-Vadose Zone Integration Project. We have shown that Cs migration depth is strongly controlled by Na^+ concentration over its entire concentration range to saturation with NaNO_3 . These observations and comparable ones with K^+ and Ca^{2+} electrolytes provide the basis for an improved mass-action model of Cs exchange-adsorption with Hanford sediments. Our desorption results from high sodium imply that a significant fraction of the sediment bound Cs becomes rapidly fixed and is not available for further migration. Further analysis of the desorption results and the performance of selected other experiments should allow firm guidance on whether in-ground Cs beneath the tanks can be left in place without environmental controls.

Planned Activities

The remainder of FY 99 activities will focus on the impacts of high base, variable temperature induced mineral dissolution on Cs^+ sorption in Hanford sediments and isolated mica fractions. We will identify whether the selectivity of the mica fraction for Cs^+ is changed by molar concentrations of hydroxide, and whether changes result from competitive ion effects (e.g., K^+ release by dissolution) or structural destabilization of the FES. The latter issue will be resolved by application of scanning probe microscopy and high-resolution transmission electron microscopy. In FY 00, similar studies will be performed using high-base waste stimulants containing $\text{Al}(\text{OH})_4^-$ at concentrations that mimic those in the SST's. At issue is whether $\text{Al}(\text{OH})_4^-$ precipitation that follows base neutralization will cause marked changes to Cs^+ sorption selectivity, kinetics, and reversibility. Important questions to be resolved include the nature of the precipitated Al-phase and whether it causes hydroxy pillaring and alteration of the structural environment of the FES. A combination of microscopy, solution phase thermodynamic measurements, and chemical modeling will be employed to interpret results and resolve hypotheses.

Publications and Presentations

Publications

Zachara, J.M., S.C. Smith, R.J. Serne, and P.L. Gassman. 1999. Highly selective Cs^+ adsorption by subsurface sediments from the Hanford site, U.S.A. *Clays and Clay Minerals* (Submitted).

McKinley, J.P., R.J. Serne, J.M. Zachara. 1999. Mineral phase association of Cs^+ in subsurface sediments contaminated with high-level nuclear waste. *Environmental Science and Technology* (Submitted)

McKinley, J.P., J.M. Zachara, and P.L. Gassman. 1999. Cs^+ distribution in natural micas: an electron and synchrotron X-ray microprobe study. *Clays and Clay Minerals* (In preparation).

Presentations

Zachara, J.M. New advances in the understanding of ^{137}Cs interactions with micas and implications to Cs geochemistry in the Hanford vadose zone. Keynote address given to the EMSP National Program Workshop, Chicago, Illinois. Aug. 1999.