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

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Research Objective

Cesium (137) is a major component of high level weapons waste. At Hanford, single shell tanks (SST's) with high level wastes (HLW) have leaked supernate containing over 10^6 Ci of ^{137}Cs and other co-contaminants into the vadose zone. In select locations, ^{137}Cs has migrated further than expected from retardation experiments and performance assessment calculations. Deep ^{137}Cs migration has been observed beneath the SX tank farm at Hanford with REDOX wastes as the carrier causing regulatory and stakeholder concern. The causes for "expedited" migration are unclear.

This research is investigating how the sorption chemistry of Cs on Hanford vadose zone sediments changes after contact with solutions characteristic of HLW. Our central scientific hypothesis is that the high Na concentration of HLW will suppress surface-exchange reactions of Cs, except those to 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 HLW and that 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 has three objectives:

1.) Identify how the multi-component surface exchange behavior of Cs on Hanford sediments changes after contact with HLW simulants that span a range of relevant chemical (Na, OH, Al, K) and temperature conditions (23-80^0 C).
2.) Reconcile changes in sorption chemistry with microscopic and molecular changes in site distribution, chemistry, mineralogy, and surface structure of the micaceous fraction.
3.) Integrate mass-action-solution exchange measurements with changes in the structure/site distribution of the micaceous fraction to yield a multicomponent exchange model relevant to high ionic strength and hydroxide for prediction of environmental Cs sorption.

Research Progress and Implications

The project was initiated in September 1997. Since that date, research has investigated 1.) the mineralogic residence and speciation of ^{137}Cs in contaminated materials collected from beneath SST SX-109 at Hanford and 2.) the Cs ion exchange characteristics of a mica-containing composite sediment from the Hanford formation.

^{137}Cs Contaminated Materials - Three samples were obtained from the upper levels of Hanford borehole SX-41-09-39 in December 1997 that each contained in excess of 10^4 pCi/g ^{137}Cs. The coring was an EM supported activity that extended the borehole beneath SX-109 from 39.6 m to 5 m below groundwater (at 65 m) to define contaminant distribution in the vadose zone. Our objective in studying these materials was to confirm the hypothesized ^{137}Cs-mica association in sediments contacted by HLW.

- Contaminated sediments were size fractionated and counted. The highest activity was observed in the coarse sand fraction, but greater than 60% of total radioactivity was observed in the silt and clay. The adsorbed ^{137}Cs was not readily desorbed by Na.
- The mineralogy of the ^{137}Cs-containing size fractions was evaluated by X-ray diffraction (XRD), and mica comprised 15-20% of the materials on a mass basis. Three distinct mica types were observed: muscovite, biotite, and vermiculitized biotite.
- ^{137}Cs occupied less than 1% of the ion exchange capacity of the sediment, the remainder was comprised of Na^+ and K^+.
- Individual ^{137}Cs containing particles were isolated and are being characterized by single-particle XRD and TEM. Preliminary data indicates they are micaceous in composition.

Cs Sorption Chemistry on Hanford Vadose Zone Sediments - A bulk sediment (20 kg) sample representative of the 15-40 m depth interval at Hanford was established by compositing core subsamples from six RCRA wells placed around the uncontaminated periphery of the SX tank farm in the Hanford 200 West Area. Particle size distribution, mineralogy, chemical composition, cation exchange capacity with different index ions, and surface area have been measured on the composite sediment. Cs interaction experiments have been performed with the sediment as a precursor to ion exchange thermodynamic studies and contact experiments with HLW simulants. Key findings are as follows.

- Cs^+ sorbs rapidly to Hanford sediments by ion exchange. Cs^+ fixation by the micaceous component occurs slowly, but little Cs^+ desorption can be initiated by K^+ at 100-fold excess after contact periods of a month or more.
- Highly selective FES exist in the Hanford sediments and these represent < 0.1 % of the cation exchange capacity. The FES themselves exhibit great variation in their selectivity for Cs^+. Distribution coefficients on the FES range from $10\text{-}10^4$, and are strongly influenced by other cation concentrations.
- As hypothesized, high salt (Na^+) suppresses all Cs^+ sorption except that to FES. An increase in Na^+ concentration from 5 mol/L to $NaNO^3$ saturation (9 mol/L), however, induces further reductions to Cs sorption indicating that competitive ion exchange of Cs^+ and Na^+ occurs on the FES.

Implication - Our Cs^+ sorption measurements in saturated $NaNO_3$ are the first reported at such high Na^+ concentration. Sodium exhibits a mass action suppression on Cs^+ sorption from dilute concentration to saturation. Our preliminary measurements suggest that high Na^+, alone, may cause expedited Cs^+ migration below leaking tanks with salt cake (e.g., REDOX), although other effects resulting from high OH and $Al(OH)_4$ are also expected.

Planned Activities

Remaining FY 98 research will complete experiments and modeling for two manuscripts: one on the mineralogic residence and desorbability of ^{137}Cs in contaminated Hanford vadose zone sediments, and the other on Cs sorption thermodynamics and kinetics in the composite sediment. 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 determine 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 using p scanning probe microscopy, high resolution transmission electron microscopy, and X-ray absorption spectroscopy. FY 00 studies will focus on high-base waste simulants containing $Al(OH)_4^-$. At issue is whether $Al(OH)_4^-$ precipitation that follows base neutralization will change 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.