
Immobilization of Radionuclides in the Hanford Vadose Zone by Incorporation in Solid Phases

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Executive Summary

The production and extraction of Pu, U and other strategic elements from irradiated uranium fuels has been a major component of the DOE mission since the early 1940's. At the Hanford site, the fluids resulting from extraction of spent fuel rods from 9 nuclear reactors were stored in 177 underground tanks during the period of 1944 to 1990, in areas known as "tank farms". The chemical extraction processes employed at the Hanford site ultimately produced hyperalkaline, high level waste (HLW) fluids that were stored in underground tanks. Many of these contained large concentrations of NaNO_3 (often $> 1 \text{ mol L}^{-1}$) and hydroxyl ions, with pH values > 10 common and some in excess of 14, large concentrations of dissolved Al (which presumably stayed in solution as aluminate ions and possibly aluminate polymers) quantities of unrecovered U and Pu, numerous fission daughter products, organic ligands (from the extraction and purification processes), and a number of other inorganic ions.

Sixty-seven of the single shelled tanks are known or thought to have leaked, allowing from 1,920,000 to 3,456,000 L of waste fluids to migrate into the underlying vadose zone. The actual composition of these leachates is not fully known but the existing data, indicate that many of these fluids were highly alkaline (pH values > 13), and that many contained large concentrations of dissolved NaNO_3 and $\text{Al}(\text{OH}_4)^-$ as well as substantial quantities of ^{137}Cs , ^{60}Co , ^{90}Sr , ^{99}Tc , $^{234,238}\text{U}$, and other radioactive elements. Upon reaction with the underlying soil and sedimentary matrix this situation will potentially result in the formation of a number of complex precipitates that could incorporate radioactive contaminant species from the tanks. Reaction of the tank fluids with the soil matrix will cause some dissolution of the soil minerals, releasing Si into solution, and decreasing pH. These solution conditions promote the formation of Al- and Si-hydroxide gels, hydrotalcites, Al-(hydr)oxides zeolites and other secondary phases. All of these potential phases have high surface reactivities, and should serve as strong sorbents and/or coprecipitates for contaminant ions present in the leachate (Cs, Co, Sr, Tc, U, etc.). Additionally, partial dissolution of the ambient soil minerals and precipitation of these secondary solids could result in significant alteration to the porosity and flow paths of the surrounding porous media. When coupled together, these chemical and physical transformations should result in dramatic changes in the fate and transport of the contaminant ions associated with tank fluids. Clearly, more information is needed before an understanding of the complex geochemical environment in the vadose zone beneath the Hanford tanks is attained.

In this three-year collaborative project, we are studying the incorporation of representative contaminant species (Cs, Co, Sr, Tc, and U) in carefully controlled model systems to gain a more fundamental understanding of sorption, neoformation, precipitation, and exchange processes that might immobilize these contaminants in solid matrices impacted by alkaline tank fluids. This activity will provide mechanistic information on many of the geochemical processes occurring beneath the HLW tanks. Additionally we will directly measure the solid-phase speciation of a number of contaminants from sediment samples obtained from directly beneath suspected, leaking HLW tanks.

This data will be critical in the ongoing efforts to predict radionuclide transport and stability in subsurface zones at Hanford that have been impacted by tank waste. It will also be critical in assessing the potential for remobilization of any subsurface contamination by accidental spills that may occur during current and future remediation activities at Hanford, such as the possible sluicing and of solids within the HLW tanks.

Research Objectives

We are investigating (1) the effect of aging on the stability of sorption complexes (of Cs, Co, Sr, Tc, and U ions) on Al-oxide and Al-oxyhydroxide surfaces formed from neutralization and homogeneous nucleation of alkaline aluminate solutions; (2) the sorption/coprecipitation of these elements in solids formed from reaction of alkaline aluminate solutions with simple systems of representative minerals and mineral coatings found in the soils and sediments underlying the Hanford Tank Farm (e.g., quartz, feldspars, biotite, muscovite, chlorite, clay mineral, augite, hornblende, ilmenite, magnetite, hematite, Fe(III)-oxyhydroxides, and Mn(IV)-(hydr)oxides); and (3) the sorption/coprecipitation of these elements in solids formed from reaction of alkaline aluminate solutions with soil and sediment samples obtained from the Hanford site. These latter experiments will be conducted in batch as well as flow through systems(4). To couple these laboratory studies to precipitation processes occurring in the Hanford vadose zone beneath the Tank Farm, we will characterize the particle coatings and precipitate phases in contaminated core samples from this zone. These investigations will utilize X-ray Absorption Fine Structure (XAFS) spectroscopy, vibrational spectroscopy, NMR spectroscopy, electron and X-ray microprobe analyses, transmission electron microscopy, X-ray photoelectron spectroscopy, and other characterization studies of the speciation and spatial distribution of these ions in several model systems chosen to simulate the natural systems as well as contaminated sediments from the sites.

Research Progress and Implications

This project formally began in the fall of 1999. Since that time we have: 1) developed detailed experimental protocol, 2) identified and obtained specimen mineral samples as well as uncontaminated sediment samples from the Hanford site, 3) initiated batch sorption experiments with Co, Sr, and Cs, in HLW tank simulant solutions, 4) initiated long-term aging studies, and 5) begun initial XAFS studies of these systems.