Waste produced during the production and purification of weapons-grade nuclear material is stored in underground tanks at the Hanford site in Washington state. Since their burial, many of the storage tanks have leaked caustic nuclear waste contaminated with radioactive Cs-137, Sr-90, and I-129 into the surrounding soils. The effects on the natural soils of these particular radionuclides in a highly caustic solution are largely unknown, as are the transport properties. Recent work has shown that zeolite-type aluminosilicate phases form in clay mineral systems weathered under near-field exposure to Hanford-type nuclear waste. The transport and sequestration of Cs-137, Sr-90, and I-129 in the sediments is partially controlled by the cation adsorption-exchange properties of the parent clay minerals and these zeolitic neophases. This project seeks to isolate the effects of these new phases on contaminant adsorption by identifying the contaminant binding structures, assisting in the identification of neoformed phases, probing the kinetics of phase formation and contaminant uptake, and investigating the mobility of these specific radionuclides in silicon-induced precipitates from synthetic tank waste representative of that at the Hanford site. In work at Penn State University, these objectives are being accomplished through the use of solid-state nuclear magnetic resonance (NMR) spectroscopy.

In our most recent work, samples from 20:1 and 10:1 parent solution silicon to aluminum (Si/Al) ratio homogeneous nucleation trials (supplied by collaborator J. Chorover and group) have been characterized with multinuclear solid-state NMR. Single-pulse Al-27, Na-23, and Si-29 spectra have been acquired at an external magnetic field strength of 7.05 T for samples exposed to 10^-5 M and 10^-3 M concentrations of Cs, Sr, and I individually and as a mixture in the parent solution. The aluminum spectra for both Si/Al ratios show a single peak in the 58-63 ppm range tailing toward negative chemical shift values. It was not possible to adequately fit this peak to a quadrupolar powder pattern or a single Gaussian or Lorentzian lineshape for any sample, supporting a wide aluminum chemical shift distribution as the source of the observed tailing. The sodium spectra for the 20:1 Si/Al samples also display a single broad peak with a tail, while the spectra of the 10:1 Si/Al samples appear to have features which may be indicative of multiple sodium sites. It is difficult to confirm the presence of multiple sites or determine the number of sodium sites from these data, as the intensity of some features is similar to that of the spectral noise. The silicon spectra for both Si/Al ratios contain multiple resonances between -85 and -103 ppm separated by roughly four ppm. The resolution is better for the 20:1 Si/Al samples, whose spectra can be fit well with five Gaussian/Lorentzian lineshapes. The five visible peaks in the silicon spectrum and the single featureless aluminum peak are consistent with the NMR literature of zeolitic materials. These five different chemical shifts result from silicate tetrahedra with varying numbers of nearest neighbor aluminate tetrahedra. Based on the results of spectral curve fitting, we have calculated uniform silicon to aluminum ratios for the solid 20:1 samples of 1.48 +/- 0.03. The spectral resolution of the 10:1 Si/Al ratio samples is such that the certainty of any particular fit is low. In addition to providing structural information, the silicon spectra show variation in intensity and minor variation in peak position as a function of the concentration of contaminant ion present in the parent solution. This allows us to postulate that the concentration of contaminant ion plays a role in the kinetics of homogeneous precipitate formation.