ENVIRONMENTAL AND WASTE MANAGEMENT: ADVANCEMENTS THROUGH THE ENVIRONMENTAL MANAGEMENT SCIENCE PROGRAM

Organized by

T. Zachry

Symposia Papers Presented Before the Division of Environmental Chemistry
American Chemical Society
Anaheim, CA March 28 – April 1, 2004

ENVIRONMENTAL WEATHERING OF ALUMINOSILICATE CLAY MINERALS: SOLID-STATE NMR STUDIES OF TRANSFORMATIONS LEADING TO RADIONUCLIDE SEQUESTRATION

Karl T. Mueller[1], Garry Crosson[1], Jon Chorover[2] and Sunkyung Choi[2]
[1]Department of Chemistry, Penn State University,
152 Davey Laboratory, University Park, PA 16802
[2]Department of Soil, Water and Environmental Science,
University of Arizona, Tucson, AZ 85721-0038
ktm2@psu.edu

Mobilities of radionuclides (such as ^{137}Cs and ^{90}Sr) are governed by their interactions with natural soil particles in the saturated and unsaturated zones at Department of Energy sites (*e.g.* Hanford Site, Savannah River Site). High surface area aluminosilicate clay minerals are a component of the natural soils beneath the leaking waste tanks at these sites and serve as possible radionuclide sorbents. However, due to the characteristics of the contaminant medium (high pH, high Al and high ionic strength), clay minerals are susceptible to transformations during exposure to tank waste leachates. To gain a better understanding of fundamental processes taking place in the vadose and saturated soil environments in these polluted areas, we are currently studying the transformation of clays under specific chemical conditions that mimic the composition of the contaminant solutions[1].

In these studies, specimen clay samples are reacted for varying time periods (up to one year) with simulated tank waste leachate (STWL) solutions containing fixed concentrations of (non-radioactive) Cs and Sr (at levels of 10^{-3}, 10^{-4} and 10^{-5} M). Mineral dissolution and transformation are followed with solution analysis, x-ray diffraction, solid-state nuclear magnetic resonance (NMR) and a number of other analytic methods. We report here results from ^{27}Al magic-angle spinning (MAS) NMR at variable magnetic field strengths (up to 18.8 T), ^{29}Si MAS NMR and ^{1}H/^{29}Si cross-

polarization MAS (CPMAS) NMR and evaluate these results along with those of other parallel analytic studies. A number of neophases are identified through these analyses and representative ^{27}Al MAS NMR results at a moderate magnetic field strength (7.0 T) are shown in Figure 1. The use of solid-state NMR at multiple fields (Figure 2) allows for superior resolution of resonances from different species and in this way solid-state NMR results are used to quantify the reaction kinetics.

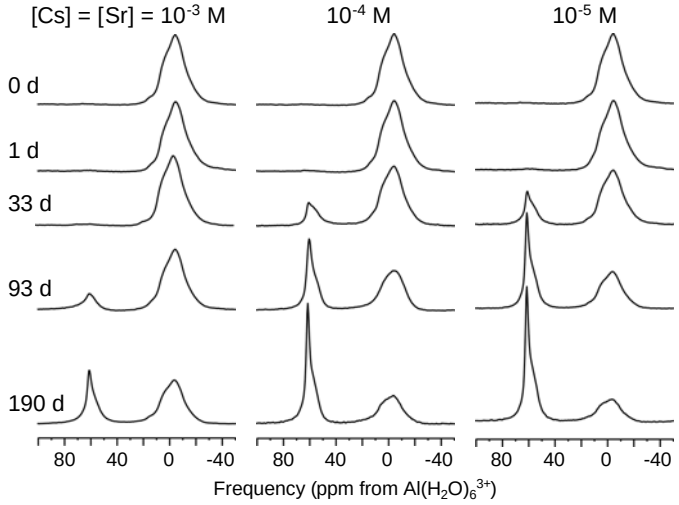

Figure 1. ^{27}Al MAS NMR spectra of weathered kaolinite as a function of exposure and initial Cs and Sr concentrations in the simulated tank waste leachate.

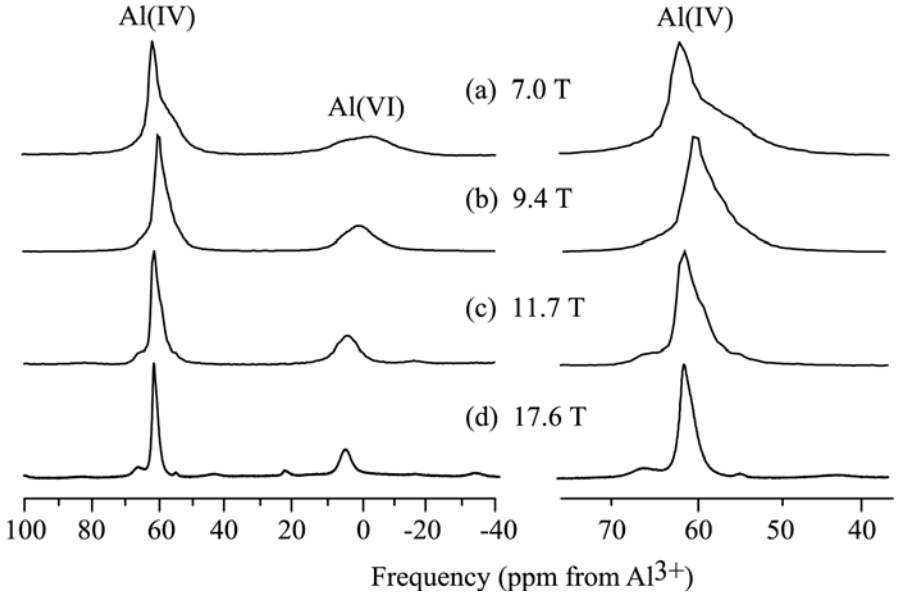

Figure 2. Variable magnetic field NMR studies of weathered kaolinite exhibit increased resolution at the highest fields.

As neophases are formed, Cs and Sr sequstration varies and one additional question of interest is the location of the Cs and Sr species within the original clays or neophases. Results of initial double resonance experiments incorporating Cs (and possibly Sr) nuclides will be reported.

ACKNOWLEDGEMENTS
The Department of Energy EMSP program currently supports this work *via* grant DE – FGO7-99ER15012. A portion of the research described here was performed in the Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory.

REFERENCES

1. J. Chorover, S. Choi, M. K. Amistadi, K. G. Karthikeyan, G. Crosson, and K. T. Mueller, *Env. Sci. Technol*. **27,** 2200-2208 (2003).