Environmental Management Science Program

Project ID Number 55382

Determination of Transmutation Effects in Crystalline Waste Forms

Denis M. Strachan
Pacific Northwest National Laboratory
MS K6-24
P.O. Box 999
Richland, Washington 99352
Phone: 509-376-0677
E-mail: Denis.Strachan@pnl.gov

Nancy J. Hess
Pacific Northwest National Laboratory
MS K6-24
P.O. Box 999
Richland, Washington 99352
Phone: 509-376-9898
E-mail: nancy.hess@pnl.gov

Jeffery A. Fortner
Argonne National Laboratory
9700 S. Cass Avenue
Argonne, Illinois 60439
Phone: 630-252-1951
E-mail: fortner@cmt.anl.gov

Edgar C. Buck
Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439
E-mail: buck@cmt.anl.gov

June 1, 1998

Determination of Transmutation Effects in Crystalline Waste Forms

Denis M. Strachan, Pacific Northwest National Laboratory

Nancy J. Hess, Pacific Northwest National Laboratory

Jeffery A. Fortner, Argonne National Laboratory

Edgar C. Buck, Argonne National Laboratory

Research Objective

To determine the effect of transmutation of ^{137}Cs to ^{137}Ba on crystalline waste forms by examining old samples of pollucite ($\text{CsAlSi}_2\text{O}_6$) in stainless steel capsules.

Research Progress and Implications

In this report, we summarize the research that has taken place during the second year of the 3-year project. This project is being carried out at Pacific Northwest National Laboratory and Argonne National Laboratory.

The original intent in this project was to use high-energy EXAFS to obtain information on the chemical state of the ^{137}Ba in pollucite without opening the stainless steel capsules. Using this approach, we hoped to avoid changing the chemical state of the ^{137}Ba . To evaluate the extent to which high-energy EXAFS data can be interpreted, we analyzed a number of Cs and Ba standards in addition to Ba-doped pollucite samples. The standards included a variety of structures from simple oxides and halides to titanates and silicates. While the EXAFS signal from the simple oxides and halides were low in amplitude the analysis of the EXAFS and the Fourier transforms resulted in reasonable data. We obtained extremely weak EXAFS signals from the more complex silicates and titanates with distant first neighbor atoms. In addition, the amplitudes of the Cs K-edge EXAFS are

Figure 1. Cesium (a) and Barium (b) K-edge EXAFS.

about half as intense as the corresponding Ba K-edge EXAFS (Figure 1). Several factors may have contributed to the apparent differences between the Cs and Ba K-edge data, such as core-hole lifetime broadening, weak photoelectron backscatters, and low charge density of the large low-valence cations. Also, long interatomic distances appear as low frequency oscillations in the XAS and these features could have been inadvertently removed when we tried to extract the EXAFS. Artifacts that have no possible structural origin often dominated the Fourier transforms from these compounds. A number of signal processing techniques were employed in an attempt to minimize these artifacts but they generally resulted in severe distortions of the weak EXAFS signal.

Regardless of the specific origin, these factors reduce the extent to which the Cs K-edge EXAFS data can be interpreted. We conclude that Cs and Ba K-edge EXAFS can be used successfully for materials where the structure is relatively simple and the material is well ordered. However, in materials with low atomic number backscatterers and low symmetry such as pollucite, it is not possible to determine the effects of ^{137}Cs beta decay and transmutation on the pollucite structure. However, one can reasonably hope to identify the presence of metallic Ba clusters or BaO, if either are the result of transmutation.

To overcome the shortcomings with the high-energy EXAFS, we have explored the use of nuclear magnetic resonance (NMR) spectroscopy to examine the local structure of the cesium in some laboratory-prepared pollucite. Small quantities, typical of what we expect to recover from the sealed capsules, proved to be sufficient material to obtain spectra with both magic-angle spinning and static NMR techniques (Figure 2). The chemical shift is expected to be sensitive to local structure and to disorder. We expect to prepare a sample from the ^{137}Cs pollucite when we open a capsule.

Figure 2. Nuclear Magnetic Resonance Spectra From Cs-Containing Materials Sample (Above) Along With Reference Materials. The Spinning Frequency Of Magic Angle NMR Is Indicated In Parentheses.

Planned Activities

We have prepared documentation for a safety review of a procedure for opening a capsule of pollucite containing up to 80 mCi of ^{137}Cs . We anticipate opening the first capsule of radioactive pollucite in July 1998. The material will be loaded into sample cells for EXAFS, NMR, and Analytical Electron Microscopy.