

**Project ID:** 55382

**Project Title:** Determination of Transmutation Effects in Crystalline Waste Forms

**Date:** March 1, 2000

**Researchers:** Argonne National Laboratory, Chemical Technology Division, 9700 S. Cass Avenue, Argonne, IL 60439

Donald T. Reed	(630) 252-7964	reedd@cmt.anl.gov
Jeff Fortner	(630) 252-7732	fortner@cmt.anl.gov
Rex Gerald	(630) 252-4214	gerald@cmt.anl.gov
Jeremy Kropf	(630) 252-9398	kropf@cmt.anl.gov

Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99352

Nancy Hess	(509) 376-9808	nancy.hess@pnl.gov
------------	----------------	--------------------

### ***Research Objectives***

The overall goal of this project was to study key scientific issues related to the long-term stability and performance of crystalline waste forms under consideration for containment and disposal of nuclear waste. Our research efforts were focused on the effects of transmutation of  $^{137}\text{Cs}$  to  $^{137}\text{Ba}$  in crystalline pollucite ( $\text{CsAlSi}_2\text{O}_6$ ). This transmutation issue is important to all crystalline nuclear waste forms, including spent fuel.

In the research completed, we studied both surrogate samples and actual,  $^{137}\text{Cs}$  pollucite radioactive samples (~ 20 years old). Analytical techniques that pushed the envelope of existing capabilities were used, leading to limited, but significant, progress.

This research was done at Argonne National Laboratory in collaboration with Pacific Northwest National Laboratory.

### ***Research Progress and Implications***

The effects of transmutation on pollucite were investigated by three complementary methods: solid state nuclear magnetic resonance (NMR), X-ray synchrotron studies (EXAFS/XANES), and transmission electron microscopy (TEM). The NMR and synchrotron approaches are highly developmental analytical approaches that extend current capabilities.

Six sealed capsules of radioactive pollucite, see Figure 1, were utilized at Argonne in this study. These varied in age, total activity, and barium content - so they represented various stages of transmutation. Our initial goal was to analyze these samples *in situ* to avoid the effects of exposure to oxygen and water on the sample. We have since taken three of these radioactive sources apart to extend the range of applicable analytical approaches.



Figure 1.  $^{137}\text{Cs}$  pollucite capsule, shown with a dime for scale.

### **Synchrotron-Based Techniques**

Synchrotron methods (XANES/EXAFS) provide the best chance of meaningful *in situ* analysis of radioactive pollucite samples within unopened stainless steel capsules. Analyses of the Cs K-edge, at Stanford Synchrotron

Research Laboratory (SSRL) and the Advanced Photon Source (APS), were largely unsuccessful due to limitations in signal intensity and poor signal quality.

The Cs and Ba L-edge absorption (at ~5-6 keV) and K-edge (~35-38 keV) absorption were analyzed at both SSRL and the APS. This was done for the radioactive samples and a series of nonradioactive surrogates to establish structural trends. Significant differences were noted between the K-edge spectra of the radioactive and non-radioactive samples (see Figure 2). These data, although preliminary, show that synchrotron-based methods hold significant potential and promise as a tool to investigate structural/performance issues for complex waste forms.

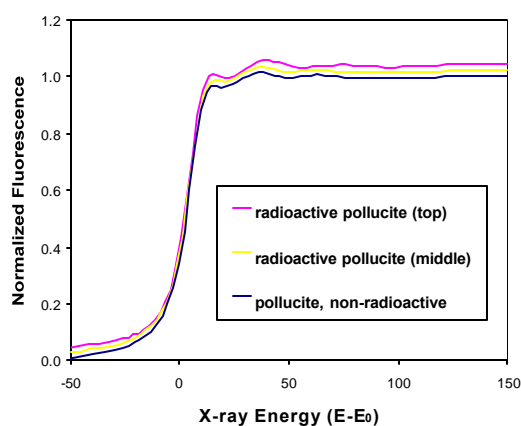


Figure 2. K-edge XANES at the Cs edge for radioactive and non-radioactive pollucite. These data show small but significant differences in the Cs-Al and Cs-O distances that point to differences in the structure due to transmutation.

### Solid-State NMR

Solid-state NMR studies of milligram levels of Cs, Al, and Si were conducted to establish structural changes in pollucite due to transmutation. The NMR work performed was by far the most developmental of the three techniques used, yet our success in this approach will likely lead to applications beyond the pollucite samples studied. Solid-state NMR can provide nearest-neighbor information

relevant to radionuclides within the crystalline waste form.

The most promising NMR results were obtained for  $^{27}\text{Al}$  at room temperature (see Figure 3). Spectra recorded with longer pulses showed the narrow central transition peak and a second broader peak at a higher field. This broad resonance may be the central transition for Al nuclei at sites near Ba substitutions, where the electronic environment around Al is distorted from the normal tetrahedral environment in aluminosilicates (T-sites). These results are significant given the importance of Al in many waste forms under consideration.

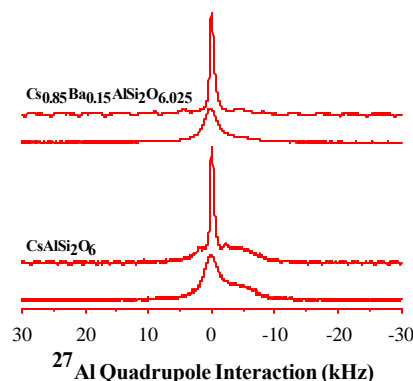


Figure 3. Solid-state NMR spectra of  $^{27}\text{Al}$  in pollucite for both magic angle spinning (top of the two curves for each sample) and static toroid cavity NMR (bottom). The similarity in the spectra show that static toroid cavity NMR can be used to obtain nearest-neighbor structural information on milligram level samples.

### *Planned Activities*

This three year research project was completed in September 1999, so no future activities are planned. A renewal proposal to extend the capabilities developed to other waste form issues was submitted.