

Determination of Transmutation Effects in Crystalline Waste Forms

Project 555382



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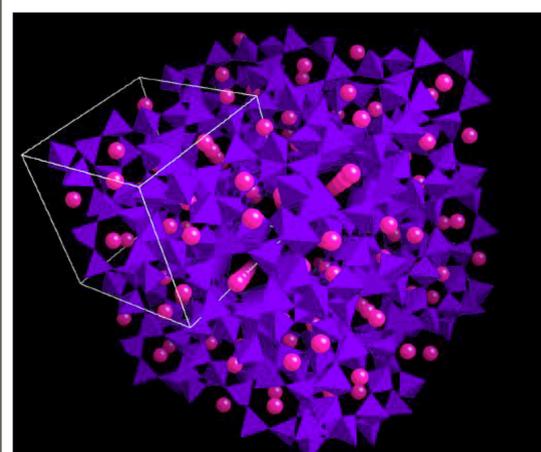


Abstract

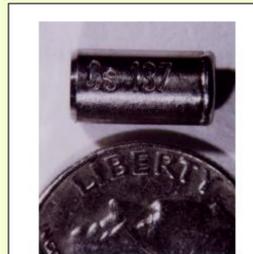
The overall goal of this project was to study key scientific issues related to the long-term stability and performance of crystalline waste forms under consideration for containment and disposal of nuclear waste. Our research efforts were focused on development of techniques to study the effects of transmutation of ^{137}Cs to ^{137}Ba in highly-radioactive crystalline pollicite ($\text{CsAlSi}_2\text{O}_6$). Small, sealed, stainless steel capsules containing pollicite had been in storage for over 20 years. The decay of ^{137}Cs to ^{137}Ba has placed the pollicite structure under significant strain because of the limited solubility of ^{137}Ba in pollicite. These studies will help evaluate the long-term stability and performance of the many crystalline waste forms being considered for the disposal and stabilization of radioactive waste.

We studied both surrogate samples and actual, ^{137}Cs pollicite radioactive samples (~20 years old). Analytical techniques that pushed the envelope of existing capabilities were used. The effects of transmutation on pollicite 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.

This research was done as a collaboration between Argonne National Laboratory and Pacific Northwest National Laboratory.



The crystal structure of cubic pollicite. The Cs ions are rendered as magenta spheres, while the (Si, Al) O_4 tetrahedra appear in blue. The unit cell is shown as a block outline of a cube in this perspective rendition.



Pollicite capsule, shown with dime for scale.

Table 1. Radioactive Pollicite Sample Characteristics and Identification.

Series (year)	Serial number	Original mCl activity	Present mCl activity	Original ^{137}Cs mass fraction (total pellet) ^a	Present ^{137}Cs mass fraction (total pellet) ^b	Original ^{137}Ba as fraction of total Cs^+	Present ^{137}Ba as fraction of total Cs^+
1979	AD91	111	78	0.0575	0.0139	0.415	0.155
1979	AE87	44	28	0.0136	0.0050	0.154	0.057
1979	AE53	42	27	0.0130	0.0048	0.147	0.054
1984	AE89	4.0	2.8	0.0012	0.00035	0.0140	0.004
1984	AE784	16	11.5	0.0051	0.0015	0.0573	0.017
1989	ACS10	6.0	4.8	0.0019	0.0004	0.0211	0.0044

^a As of year 1999.
^b Based upon 0.0844 g pollicite/pellet.
^c Based upon 0.0075 g total pellet.

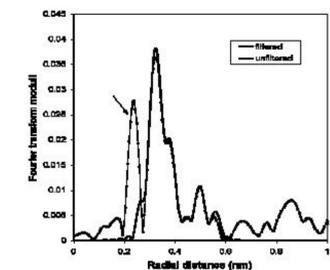
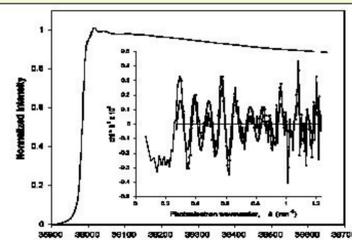
Background

Originally fabricated as radiation sources for tumor treatments, the samples originated from sealed, 300 micrometer-thick, stainless steel capsules that are approximately 3 mm long and 1 mm in diameter. Inside the capsules is a loosely consolidated pellet of pollicite, with a mass of approximately 80 mg. These samples of pollicite range in age from 10 years to 20 years old. The amount of ^{137}Cs in each capsule and the resulting in-growth of radiogenic ^{137}Ba are shown in Table 1.

Synchrotron-Based Techniques

Synchrotron methods (XANES/EXAFS) were used to examine the Cs and Ba L-edge (at ~5-6 keV) and K-edge (~35-38 keV) edges at both SSRL and the APS. Subtle, yet significant differences were noted between the K-edge spectra of the radioactive and non-radioactive samples. Powder x-ray diffraction (XRD) was also carried out at the SSRL.

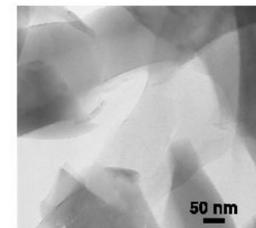
The interatomic distances determined by XRD and EXAFS are in agreement and reflect the tetragonal character of the radioactive pollicite sample. The singular disagreement is the Cs-Cs distance determination along the [011] direction separating the 8-membered rings. The analysis of the XRD indicates that this distance is 0.485 nm while the EXAFS data indicates a substantially longer 0.518 nm distance. The XRD determination will reflect the Cs-Cs separation that is averaged over a large number of unit cells whereas the EXAFS determination will reflect only the local Cs-Cs separation. Perhaps the radiation-induced defects have increased the average Cs-Cs separation as seen by EXAFS but not in a correlated manner that would be detected by long-range, diffraction-based spectroscopy such as XRD.



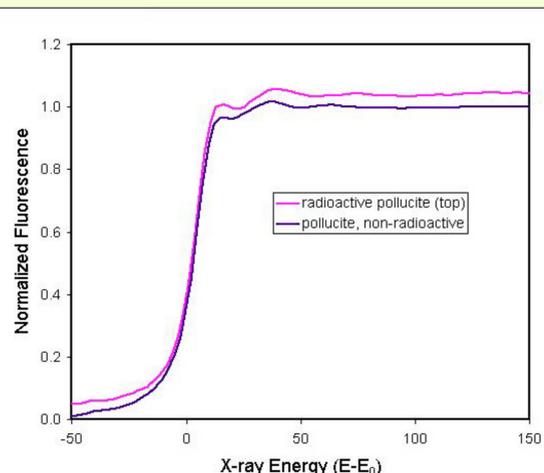
Above: Normalized x-ray absorption spectra and EXAFS (inset) before (thin line) and after filtering (thick line). Below: Fourier transform moduli of the unfiltered (thin line) and filtered (thick line) EXAFS. Atomic EXAFS or multielectron processes produce the low R feature, indicated with an arrow, that is removed by filtering.

Transmission Electron Microscopy (TEM)

The AD92 sample was chosen for TEM examination because it contained the most radiogenic barium- nearly 16% of the total cesium (Table 1), and was expected to show the largest effect. The samples were examined using a JEOL 2000 FX Mark II TEM operated at 200 keV accelerating energy. The sample temperature was maintained at approximately 100 K with the liquid nitrogen coolant in order to minimize electron beam damage, which is often rapid in a framework aluminosilicate sample. Bright field transmission images revealed a homogeneous, crystalline matrix, with no evidence of distinct barium phases or ex-solution phenomena resulting from the ^{137}Cs to ^{137}Ba transmutation. Electron diffraction patterns were obtained from several portions of the sample; the combined data appear in Table 2. Excellent agreement between the observed diffraction spacings and literature values for pollicite indicates that no substantial damage was done to the crystal structure, despite the transmutation of nearly 16% of the cesium to barium over the elapsed 20 years. A systematic contraction of the observed lattice spacings by about 2% is indicated in the final column of Table 2, which may originate from the cryogenic temperature of the experiment. Concurrent high-resolution x-ray diffraction work by the PNNL team using the Stanford Synchrotron Source Laboratory (SSRL) demonstrated that the pollicite had undergone a subtle transformation to a tetragonal phase at room temperature. This cubic to tetragonal transition normally occurs at lower temperature (~0 °C), and likely arises from residual strain present as the pollicite lattice accommodates the excess barium.



TEM micrograph of radioactive pollicite from the AD92 capsule. The pollicite shattered during sample preparation, but each fragment has a homogeneous appearance. There is no evidence of phase separation or ex-solution precipitation.



K-edge XANES at the Cs edge for radioactive and non-radioactive pollicite. 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.

Table 2. Experimental electron diffraction data from radioactive ^{137}Cs -doped pollicite sample AD92 compared with two reference JCPDS-ICDD reference data. The final column is a ratio of the experimental data (taken at about 100 K) to the average of the corresponding reference values.

Experimental d-spacing (Å) sample AD 92	Normal Pollicite JCPDS-ICDD 25-194 (Å)	Synthetic Pollicite JCPDS-ICDD 29-407 (Å)	Ratio (experimental/reference) †
5.47	5.56 vf	5.28	0.980
3.54	3.56	4.83 vf	0.973
3.57	3.65 *	3.66 *	
3.30	3.41	3.41 *	0.965
2.86	3.23 vf	3.06 f	
2.82	3.06 vf	2.913 *	0.982
2.62	2.791 vf	2.684	0.977
	2.682	2.499	
	2.416	2.419 *	
	2.218	2.220	
	2.169	2.018	
	1.897	1.975 vf	
1.813	1.860 *	1.897 vvf	0.974
	1.736 *	1.862 *	
	1.709	1.737 *	
1.652	1.683	1.684 vf	0.982
	1.634	1.635	
	1.589	1.549	
	1.548	1.519	
	1.519		

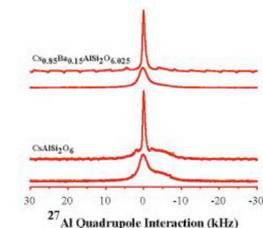
† As of year 1999.
 * Based upon 0.0844 g pollicite/pellet.
 † The TEM specimens were liquid nitrogen cooled to ~100 K, while the reference samples were measured at ambient temperature. This ratio of the electron diffraction to reference values may reflect thermal expansion effects.

Solid-State NMR

Solid-state NMR studies of milligram levels of Cs, Al, and Si were conducted to establish structural changes in pollicite due to transmutation. The NMR work performed was the most developmental of the three techniques used, yet our success in this approach will likely lead to applications beyond the pollicite samples studied. Solid-state NMR can provide nearest-neighbor information relevant to radionuclides within the crystalline waste form. Part of this effort was directed at the development of a miniature toroid cavity NMR detector suitable for handling a highly-radioactive specimen. The most promising NMR results were obtained for ^{27}Al at room temperature. 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.



Miniature toroid cavity solid-state NMR detector.



Solid-state NMR spectra of ^{27}Al in Ba-doped (non-radioactive) pollicite for both magic angle spinning (top) 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.

Conclusions

Pollicite that had aged for nearly one half-life of the ^{137}Cs had been stored under ambient conditions, and was examined by a variety of techniques to assess structural effects caused by the beta decay transmutation of ^{137}Cs to ^{137}Ba . This transmutation was expected to affect the stability of the pollicite crystal owing to the difference in ionic radius and charge between Cs^+ and Ba^{2+} . Although substantial barium had been generated in excess of the experimentally determined solubility from direct synthesis, our observations indicate that the pollicite structure remained remarkably unaffected by the transmutation. This suggests the presence of a metastable, yet robust, state.

Future Work

The virtual null result for transmutation effects on the pollicite is encouraging from a regulatory and modeling point of view, but is of quite limited scope vs. α -vs. β -aged waste forms generally. We wish to build upon experience gained from our pollicite study to include aging effects on spent nuclear fuels (SNF), fission product ceramic, and alteration products of SNF.

Acknowledgements

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