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Determination of Transmutation Effects in Crystalline Waste Forms

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Executive Summary

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 the radioactive decay of ^{137}Cs to ^{137}Ba in crystalline pollucite ($\text{CsAlSi}_2\text{O}_6$). Cesium-137 is a fission product of uranium and is a major contaminant at U.S. Department of Energy production facilities. Pollucite is an aluminosilicate (ceramic) waste form being considered for long-term storage of ^{137}Cs .

If the structure of the pollucite is damaged by radioactive decay, it may be less effective at containing the ^{137}Cs . Most work on radiation effects in waste forms has focused on structural damage from alpha radiation. However, beta radiation results in transmutation, which changes both the valence and the ionic radius of the element. The purpose of this project was to determine whether the chemical differences between cesium and barium reduce the structural integrity of the pollucite waste form. The techniques developed in these studies may also be useful for evaluating radiation damage in other crystalline waste forms.

The work focused on evaluation of several ^{137}Cs sources originally fabricated for tumor treatment. These sources were small, sealed, stainless steel capsules containing pollucite in which varying amounts of the usual nonradioactive ^{133}Cs had been replaced by radioactive ^{137}Cs . The capsules ranged from 10 to 20 years old. It was expected that the decay of ^{137}Cs to ^{137}Ba would place the pollucite structure under significant strain, because previous studies showed that this structure can accommodate only about 10% Ba (by weight) of Ba, compared to 40% (by weight) of Cs. For comparison, we also studied nonradioactive pollucite and various other materials containing Cs and Ba.

To investigate the effects of transmutation on pollucite, we used three complementary analytical techniques: X-ray synchrotron studies (EXAFS/XANES), solid-state nuclear magnetic resonance (NMR), and transmission electron microscopy (TEM). The synchrotron and NMR approaches are highly developmental analytical approaches that push the envelope of existing capabilities.

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

Synchrotron methods (XANES/EXAFS) were used to examine the Cs and Ba L-edge (at ~5-6 keV) and K-edge (~35-38 keV) x-ray absorption edges. These studies were done at the Advanced Photon Source at Argonne and at the Stanford Synchrotron Research Laboratory (SSRL) in Stanford, California. Subtle, yet significant, differences were noted between the K-edge spectra of the radioactive and nonradioactive 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 show that the radioactive pollucite sample retains the expected tetragonal structure.

One of the oldest, most radioactive samples was chosen for TEM examination because it contained the most radiogenic barium—nearly 16% of the total cesium has decayed to barium—and was expected to show the largest effect.[†] The samples were examined at Argonne using a JEOL 2000 FX Mark II TEM operated at 200 keV accelerating energy. Bright field transmission images revealed a homogeneous, crystalline matrix, with no evidence of distinct barium phases or ex-solution phenomena resulting from the transmutation of ¹³⁷Cs to ¹³⁷Ba. Electron diffraction patterns were obtained from several portions of the sample. Excellent agreement between the observed diffraction spacings and literature values for pollucite indicates that no substantial damage was done to the crystal structure, despite substantial transmutation.

Solid-state NMR studies of nonradioactive pollucite containing milligram levels of Cs, Al, and Si were conducted at Argonne. The use of NMR to analyze solids is a recent extension of traditional solution-state NMR. 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 ²⁷Al at room temperature. These results indicate that this method may be able to distinguish the influence of Ba on Al, and thus on the tetragonal structure of pollucite, for example. Other results provided the first spectroscopic evidence that the pollucite framework differs for normal and Ba-containing pollucite. The NMR work was the most developmental of the three techniques used. We did not progress to NMR study of radioactive samples, but our success with nonradioactive samples will likely lead to applications beyond the

[†] Not all of the cesium in the samples is radioactive ¹³⁷Cs. Thus, some Cs will remain after transmutation to barium is complete.

pollucite samples studied. In particular, the success with aluminum is significant given the importance of Al in many waste forms under consideration.

Conclusions

We used several advanced techniques to assess structural effects caused by the beta-decay transmutation of ^{137}Cs to ^{137}Ba in radioactive pollucite that had aged for nearly one half-life of the ^{137}Cs . This transmutation might affect the stability of the aluminosilicate pollucite crystal because of chemical differences between Cs^+ and Ba^{2+} . Although the amount of barium exceeded the amount the structure was expected to tolerate, our observations indicate that the pollucite structure remained remarkably unaffected by the transmutation. This suggests the presence of a metastable, yet robust, state. Although our observations are limited, these are, to our knowledge, the only available data in which transmutation effects have been isolated from other radiation damage phenomena. The virtual null result for transmutation effects on the pollucite is encouraging from a regulatory and modeling point of view. However, this behavior may not be characteristic of aged waste forms in general.

1 Research Objectives

1.1 Purpose of Project

The overall goal of this Environmental Management Science Program project was to develop research tools to investigate the effect of transmutation, that is, the radioactive decay of a radioisotope to an isotope of another element, on the stability of a crystalline matrix. This process is an important issue in the assessment of the long-term stability, and hence performance, of a waste form. Most work on radiation effects in waste forms has focused on alpha radiation, which produces more displacements than beta radiation. However, beta radiation results in transmutation, which changes both the valence and the ionic radius of the element undergoing decay. These changes in coordination chemistry may destabilize the waste form and hence permit higher releases of the radionuclide contaminants to the accessible environment.

Little is known about the mobility of Cs in pollucite. Only a few studies [1-3] have examined leaching following transmutation or irradiation of pollucite or closely related aluminosilicates. These studies seem to have contradictory results. The results may indicate that prior to radiation-induced amorphization, the accumulated defects may lead to higher leachability of Cs [3], whereas once amorphization occurs, the Cs becomes trapped in the collapsed structure [2]. A more thorough analysis of the effect of accumulated defects from both transmutation and ionization processes on the pollucite structure is needed to assess the impact on Cs mobility.

In this three-year research program, we used cutting-edge experimental approaches to investigate this little-understood issue. The work was a collaboration between Argonne National Laboratory (ANL) and Pacific Northwest National Laboratory (PNNL). We focused on the effects of transmutation on pollucite ($\text{CsAlSi}_2\text{O}_6$), a cesium aluminosilicate that has been proposed for the long-term immobilization of radioactive cesium. In this ceramic waste form, the ^{137}Cs decays to ^{137}Ba , causing barium to build up in the pollucite samples over time. We selected pollucite for this study for the following reasons:

- We had access to several well-characterized samples of ^{137}Cs -containing pollucite that had been stored under ambient conditions for up to 20 years.
- Cesium has a high activity ($t_{1/2} = 30.13$ years), leading to the buildup of significant levels of Ba in these samples.
- Cesium continues to be an important constituent of the waste management effort within the DOE complex.

Pollucite, also known as Cs-leucite, has a cubic symmetry (space group $Ia\bar{3}d$) at temperatures above $\sim 100^\circ\text{C}$. The crystal structure comprises a network of vertex-sharing $(\text{Al},\text{Si})\text{O}_4$ tetrahedra. The Cs is contained in wide channels that exist parallel to the $\langle 111 \rangle$ directions. These channels do not intersect but are connected via $\langle 110 \rangle$ side channels. At temperatures below 100°C , pollucite undergoes a reversible displacive phase transition to a tetragonal phase, which has spacegroup $I4_1/a$. The c/a ratio of the tetragonal phase is only 1.0051, and so it was not recognized as a distinct phase until recently [4]. The crystal structure of cubic pollucite is illustrated in Figure 1.

Figure 1. The crystal structure of cubic pollucite. The Cs ions are rendered as magenta spheres, while the $(\text{Al}, \text{Si})\text{O}_4$ tetrahedra appear in blue. The unit cell is shown as a block outline of a cube in this perspective rendition near the $[111]$ crystallographic direction. The tetragonal phase would be almost indistinguishable to the eye from this representation.

1.2 Overview of the Research Approach

Regarding the problem of establishing the effects of transmutation on pollucite, our hypothesis was that

- Transmutation will lead to changes in the bonding and structural characteristics of the Ba and Cs in the pollucite samples, and
- These changes can be detected by techniques that probe the structural characteristics at the atomic level.

We approached this problem from three experimental directions:

1. X-ray absorption near edge (XANES) and extended x-ray absorption spectroscopy (EXAFS) were used to look at the atomic environment of both the barium and cesium in the radioactive pollucite samples. The EXAFS and XANES studies were carried out at the Advanced Photon Source (APS) at Argonne National Laboratory and at the Stanford Synchrotron Research Laboratory (SSRL) at Stanford University.
2. Toroid-cavity solid-state nuclear magnetic resonance (NMR) was used to look at the near-neighbor environment of the aluminum and silicon in the pollucite samples. This work was performed at ANL.
3. Transmission electron microscope studies (TEM) were performed to look for new and unusual phases that may have formed as a result of transmutation. This work was performed at ANL.

1.3 Cesium in Nuclear Waste Management

At the Hanford site in Richland, Washington, reprocessing of spent nuclear fuel rods resulted in the generation of enormous quantities of high-level liquid waste. As produced, the liquid waste contained too much radioactive decay heat to be stored as solid waste in steel tanks; therefore the principal heat-generating isotopes, ^{137}Cs and ^{90}Sr , were separated from the liquid waste by ion exchange and solvent extraction processes, respectively. Eventually, the Cs was converted to solid CsCl that was then doubly encapsulated and stored underwater in large, monitored ponds. Similarly the Sr was converted to SrF_2 and stored. However, because of the ~30 year half-life of these isotopes and the volatility and corrosion problems associated with halides such as these, long-term waste forms are currently being sought.

Potential waste forms for Cs storage include silicate glass, glass-ceramics, cesium-loaded zeolites, and pollucite. Of these candidates,

pollucite, a cesium aluminosilicate, offers the following advantages. Its structure can accommodate more than 40 wt% Cs into its structure. As a result, it will produce a highly dense waste form, comparable in density to glass and much denser than the glass-ceramic or zeolite alternatives. In addition, the measured and calculated solubility of pollucite and the leachability of Cs in the pollucite structure are all about three orders of magnitude less than those measured for the candidate silicate glass [5]. These advantages could be affected depending on how pollucite responds to transmutation, however. Although the pollucite structure can accommodate more than 40 wt% Cs, previous data indicated that it can accommodate only about 10 wt% Ba. [6]

1.4 Sealed Pollucite Samples

The x-ray and TEM analyses were performed on ^{137}Cs -containing pollucite in capsules that were originally fabricated as radiation sources for tumor treatments. The samples are sealed, stainless steel capsules that are 300 micrometers thick and approximately 3 mm long and 1 mm in diameter. Inside each capsule is a loosely consolidated pellet of pollucite, with a mass of approximately 80 mg (Figure 2). These samples of pollucite range in age from 10 to 20 years (Table 1). The amount of ^{137}Cs in each capsule and the resulting decay in-growth of ^{137}Ba also appear in Table 1.

Figure 2. Pollucite capsule, shown with dime for scale.

Table 1. Radioactive Pollucite Sample Identification and Characteristics (as of 1999).

Series (year)	Serial number	Original activity, mCi	Present ^a activity, mCi	Mass fraction of total pellet, g ^b		Fraction of total original Cs, g ^c	
				Original ¹³⁷ Cs	Present ^a ¹³⁷ Ba	Original ¹³⁷ Cs	Present ^a ¹³⁷ Ba
1979	AD92	121	78	0.0375	0.0139	0.425	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	AE889	4.0	2.8	0.0012	0.00035	0.0140	0.004
1984	AE784	16	11.5	0.0051	0.0015	0.0572	0.017
1989	AG510	6.0	4.8	0.0019	0.0004	0.0211	0.0044

^a As of 1999.

^b Based on 0.0844 g pollucite/pellet.

^c Based on 0.0075 g total Cs/pellet.

2 Methods and Results

2.1 Experimental Approach: X-ray, NMR, and TEM Studies

In this effort to understand the effects of radiation damage on pollucite materials, we used three methods: synchrotron x-rays, NMR, and TEM. All three involved new or advanced experimental techniques, equipment, or applications. The best possible measurement of the effect of radiation damage would be a direct comparison of the Cs and the Ba environments within the pollucite. In principle, synchrotron x-ray methods are well suited to answer this question. However, for reasons discussed below, this direct comparison was not forthcoming from the x-ray studies. Instead, several indirect x-ray methods were combined to investigate the question.

The NMR approach involved developing a miniaturized NMR instrument and adapting mathematical techniques to this smaller scale. This instrument detects not only distance within a crystal structure, as in x-ray studies, but also symmetry. The TEM studies were intended to determine whether any unexpected or unusual phases have formed in the radioactive pollucite.

The x-ray studies were conducted at the SSRL in Stanford, California, and at the APS at Argonne National Laboratory. The studies at the APS made use of new instrumentation that became available at the facilities of the Materials Research Collaborative Access Team (MRCAT). The suite of spectroscopic tools used to characterize the radiation effects on a range of length scales included x-ray diffraction (XRD with Rietveld analysis)

[7], real-space analysis of the diffraction pattern or pair distribution function (PDF) analysis [8], x-ray absorption near edge structure (XANES) [9], and extended x-ray absorption fine structure spectroscopy (EXAFS) [10]. The combination of these techniques provides structural information at the atomic to next-nearest-neighbor length scale (EXAFS), from the nearest neighbor to the ~1.0 nm length scale (PDF), and at the bulk length scale (XRD-Rietveld analysis). In addition, analysis of the XANES profile may provide insights regarding the electronic environment of the Cs ion.

The x-ray absorption studies focused on the L-edge (~5-6 keV) and K-edge (~35-38 keV) absorptions of Cs and Ba. Initial absorption experiments were performed on intact pollucite capsules. Later samples included radioactive pollucite removed from the capsules, synthesized nonradioactive (surrogate) pollucite containing Cs and Ba, and reference materials (chiefly CsCl and BaO).

The ideal method for directly comparing the Cs and Ba environments within the pollucite would be EXAFS. However, in tests of radioactive pollucite to date, we have been able to measure an absorption edge signal from the Cs only. The relatively small amount of radioactive Cs in the original material means that an equivalently small amount of Ba is present now in the matrix of the pollucite. This small fraction has remained essentially undetectable at two synchrotrons (APS and SSRL). Without similar data from the Ba within the pollucite, it is difficult to draw any direct conclusions about the possibility of radiation-induced changes in the ceramic structure.

However, lacking a direct method, we pursued two less direct indicators. The first of these is XRD. If long-range structural changes have occurred as a result of the Cs radioactive decay, these will be apparent in a diffraction scan. The interpretation could be somewhat ambiguous, though, especially if the changes are not large scale. The second indirect method is to look for differences between the nonradioactive samples and the radioactive samples with Cs-edge EXAFS. If there is significant damage to the ceramic matrix, some changes may be visible in the EXAFS data.

2.2 X-ray Studies

2.2.1 Exploratory Studies: Encapsulated Pollucite

Because EXAFS offered the most promising avenue to direct comparison of Cs and Ba, several experiments were undertaken to determine the possibility of measuring the EXAFS of Cs and Ba *in situ*, through the stainless steel capsule. This approach would eliminate any

possibility of contamination caused by opening the capsule and exposing the sample to the atmosphere. It would also allow identification of possible metallic Ba colloids prior to exposure to air that would lead to oxidation and potential destruction of the colloids. In addition, leaving the radioactive sample within its original welded vessel significantly reduces the safety hazard of working with these samples.

At SSRL, initial EXAFS experiments were conducted on encapsulated, nonradioactive pollucite samples containing the stable isotope ^{133}Cs . These samples were fabricated by the manufacturer of the radioactive pollucite sources. (The experiments were done using a wiggler endstation [beamline 4-2] at SSRL). The results demonstrated that acquisition of Cs K-edge EXAFS from the encapsulated pollucite samples would require cooling the sources to at least 77 K. In addition, although EXAFS spectra could be obtained from the ^{133}Cs pollucite in the stainless steel capsules, the signal-to-noise ratio was quite low and insufficient for detailed EXAFS analysis.

Similar tests were later done at the APS. On an unoptimized insertion device beamline (Sector 2-ID), it was possible to find the K absorption edge of Cs from pollucite inside a stainless steel capsule, but the data quality was poor. The route to improvement was obvious but not within the scope or schedule of this project. With a specially designed experiment and plenty of time, it would be possible to obtain data of reasonable quality on Cs in this configuration. However, it was determined that using the same technique to measure the Ba EXAFS was not practical unless the sample had a very high Ba loading.

These initial results suggested that to obtain high-quality EXAFS spectra, it would be necessary to thin the steel encapsulation or to remove the pollucite sample from the encapsulation. These options were considered viable and pursued. K-edge and L-edge spectra were obtained for both Cs and Ba from radioactive pollucite removed from capsules. It is those data that are reported here.

2.2.2. Exploratory Studies: Standards and Nonradioactive Pollucite

In addition to initial analyses of the encapsulated samples, EXAFS spectra were collected at SSRL on several Cs and Ba standards and on Ba-substituted pollucite synthesized from oxides. Through these experiments, we evaluated the information content of the K- and L_{III} -edges of Cs and Ba. The standards examined included a variety of structures ranging from simple halides and oxides to more complex silicates and aluminotitanates, e.g., CsCl , CsNO_3 , CsAlTiO_4 , BaO , BaCl_2 , BaAl_2O_4 , and BaSiO_3 . In the Ba-substituted pollucite samples, the Ba concentration varied from 0.05 to 0.20 mole fraction Ba.

These initial experiments were very instructive for two reasons. First, for the Cs standards, the amplitude of the Cs K-edge EXAFS had low intensity, as a result of the low charge density associated with monovalent ions having large ionic radii. The K-edge EXAFS of bromium displays similar behavior [11]. In contrast, for the Ba materials, the amplitude of the K-edge EXAFS was noticeably more intense.

Second, low-*r* (low radial distance) features were observed in the Fourier transforms of both the Cs and Ba K- and L_{II} -edge EXAFS that could not possibly arise from simple backscattering off of nearest neighbor atoms. Initially, these features were attributed to experimental artifacts, such as beam instability and crystal glitches. Because of the diminished EXAFS intensity, efforts to remove these features increased the likelihood that the remaining EXAFS signal would become distorted. We currently believe that these low-*r* features arise from either multiple-electron excitation processes or atomic x-ray absorption, as discussed below.

2.2.3 X-ray Diffraction Results

The radioactive capsule selected for detailed XRD evaluation at SSRL (AE 889, see Table 1) had a calculated absorbed dose of 6.3×10^7 gray (Gy), or approximately 10^{18} beta decays/g. Note that the dose calculation is based only on the dose from the beta particles, because the self-absorption of gamma radiation is limited. In 1984, the amount of ^{137}Cs substituted in the pollucite was 0.035 mole fraction, with the remainder being ^{133}Cs . Given a half-life of 30.04 years, the amount of Ba incorporated in the structure at the time of the measurements (1999) was 0.012 mole fraction. Samples were prepared at ANL for x-ray diffraction analysis by the PNNL team at SSRL.

Rietveld analysis of the XRD pattern of this pollucite sample indicates a 0.5 to 1% volume expansion of the tetrahedral structure as measured at 50 K and minor displacement of the Cs cation toward the face of one of the 6-membered rings. The real-space pair distribution function (PDF) obtained from Fourier transformation of the diffraction pattern indicates significant correlated movement of the (Si,Al)-O pairs and large static disorder between Cs-O pairs, as discussed below. Analysis of the Cs K-edge XANES revealed substantial contributions from the Cs atomic absorption. This likely results both from the exceedingly long Cs-O bond distances in the pollucite structure, which diminish the fine structure EXAFS oscillations, and from the destructive interference of the backscattered photoelectron from static disorder between Cs-O pairs.

The sample was found by XRD to be tetragonal with space group $P4_1/c$ and lattice parameters $a = b = 1.364390(33)$ nm and $c = 1.38145(6)$ nm. These lattice parameters are approximately 1.0 and 0.4% larger, respectively, than the lattice parameters determined by Palmer et al. as

interpolated to 50 K [4]. Typically, a larger-than-expected lattice parameter can be explained by the substitution of cations with larger ionic radius into the lattice or by structural disorder. Substitution-induced lattice expansion is unlikely for this pollucite sample, since x-ray fluorescence analysis did not reveal elemental impurities. However, structural disorder may be a factor. While the fractional coordinates are nearly identical to those observed by Palmer et al. [4], the thermal parameters are significantly larger, suggesting greater disorder in our sample. Large thermal parameters have been observed in other pollucite samples [4,12, 13]. Structural disorder leading to lattice expansion could be due to synthesis conditions, transmutation effects [14], or radiation-induced defects, such as vacancies, interstitials, and trapped electronic excitations that also lead to structural distortions.

The interpretation of these results was clarified by examining the calculated and experimental pair distribution functions, $G(r)$, which are shown in Figure 3a. The contribution of each atomic pair to the total atomic distribution function was identified by using the results of the Rietveld refinement of the diffraction data as input parameters to the program PDFFIT [15]. From this simulation, we discovered that decreasing the Debye-Waller factors from the values obtained in the Rietveld refinement gave a better agreement with the PDF experimental data. On the basis of this observation, we conclude that the large thermal factors obtained in the Rietveld refinement were due to static, long-range disorder. The partial contributions from the different atom pairs were calculated and are shown in Figure 3b. This step allows each gaussian of the partial reduced pair distribution function fit to be assigned to an atomic pair.

Figure 3. Comparison of the experimental PDF with modeled PDF. (a) Experimental PDF (circles), modeled PDF using Gaussians (thick solid line), and the difference curve (thin solid line). Positions and sigmas of the Gaussians are noted above peaks. (b) The calculated partial reduced pair distribution function. The contributions from each pair are labeled above peaks. Pairs involving Cs are shown with thick dashed lines. Note that these pairs dominate the PDF at radial distances greater than 0.3 nm.

2.2.4 X-ray Absorption Results (XANES and EXAFS)

Work by PNNL at SSRL

The PNNL team analyzed several aspects of the Cs K-edge spectra of nonradioactive pollucite and Cs standards. The background-subtracted, normalized absorption spectra of pollucite obtained at the SSRL is shown in Figure 4a. As a result of the long core-hole lifetime at this energy, the Cs K-edge absorption edge spans approximately 30 eV, and the XANES profile is relatively featureless. Also apparent in the inset of Figure 4a is the low amplitude of the EXAFS oscillations.

The experimental XANES profile in Figure 4a was compared to XANES simulations generated by self-consistent, relativistic, full multiple scattering ab initio methods [16]. Features in the EXAFS profile were examined by Fourier transform methods. The Cs K-edge XANES profile is broad and featureless, with multiple contributions that likely result from either atomic x-ray absorption processes or multiple-electron excitations, in addition to the dominant single-electron core-hole excitation. Further evidence for the additional contributions are found in the low-r region of the Fourier transform of the Cs K-edge EXAFS (Figure 4b), as discussed below.

XANES analysis. XANES simulations were performed using the ab initio, full multiple scattering code FEFF8 [16]. Spherically symmetric self-consistent scattering potentials were calculated in a cluster of 129 atoms centered around a Cs atom. The angular momentum projected density of states (L-DOS) was simultaneously calculated. The presence of the core hole produced by the x-ray absorption process generates changes in the local density of states around the absorber atom. However, to compare our L-DOS calculation with band structure calculations that do not consider x-ray absorption processes, the L-DOS was also calculated without the presence of the core hole. Figure 5 shows the calculated XANES and Figure 6 the calculated L-DOS without a core hole.

Although qualitative agreement between the calculated and experimental XANES is observed, there are differences in phase between features above the absorption edge. XANES calculations are very sensitive to the potential in the interstitial region that exists beyond the “muffin tin radius.” However, this calculation is especially challenging because of the long interatomic distance between the Cs atom and its oxygen neighbors. To obtain a better agreement with experiment, we have found it necessary to explore different core-valence radius and interstitial charge densities, which in turn affect the phase of the calculated XANES features. The results from L-DOS calculations are in qualitative agreement with calculations done by Anchell et al. [9] using Hartree-Fock theory. The ability to calculate both the L-DOS and the XANES makes possible to correlate features in the XANES and electronic properties of these systems. Thus, with additional work in this area, it may be possible to differentiate features that indicate atomic absorption processes from features that indicate multiple-electron excitation processes.

EXAFS analysis. A Fourier transform was taken over the EXAFS region ($0.265 < k < 1.25 \text{ nm}^{-1}$) of the inset spectrum in Figure 4a. The Fourier transform modulus (FTM) shown in Figure 4b reveals a large-amplitude peak centered at approximately 0.20 nm. Because there are no expected Cs neighbors in the structure at distances between 0.22 and 0.25 nm, we assume that this feature has no structural origin and that it must be due to insufficient background subtraction (for EXAFS analysis purposes).

Such features at low- r in the FTM are interesting in themselves, however, since they could contain information either about the chemical environment of the absorbing atom or about the absorbing atom itself. It has been shown that the atomic background is expected to contain features associated with the many-body relaxation of the atomic charge; these features could produce low- r peaks in the FTM [17]. An alternative explanation for low- r peaks involves photoelectron backscattering in the periphery of the absorbing atom [18]. This phenomenon, called “atomic” EXAFS (AXAFS), reflects the embedded nature of the absorbing atom in the potential of the crystal and could contain information about the chemical bond and interstitial charge distribution [19]. It has been claimed that this atomic effect is the cause of low- r features in the FTM of several systems [20-22]. Further investigation is under way to clarify the nature of the low- r peak in the FTM (Figure 4b). To remove this low-frequency contribution, the EXAFS were filtered by taking a back Fourier transform over the range from 0.22 to 0.60 nm. The filtered EXAFS was fit over the photoelectron wavevector range from 0.25 to 1.24 nm⁻¹ by using parameterized amplitude and phase-scattering waves calculated by *ab initio* multiple scattering theory [16]; the resulting FTM is also shown in Figure 4b. The best fit to the EXAFS is composed of five scattering paths.

Figure 4. (a) Normalized x-ray absorption spectrum and EXAFS (inset) before (line with ticks) and after filtering (plain line). (b) Fourier transform moduli of the filtered and unfiltered EXAFS. Atomic EXAFS or multielectron processes produce the low-r feature, indicated with an arrow; this feature is not fully removed in the spline but is removed by filtering.

Figure 5. Cs K-edge XANES profile calculated using FEFF8. As observed in the experimental EXAFS (Figure 4a), the Cs K-edge spans over 30 eV. Note that the zero of the energy scale is referenced to the absorption edge energy at 36005 eV.

Figure 6. Momentum projected density of states (L-DOS) calculated in the absence of a core hole using FEFF8. The highest peaks in the L-DOS spectrum occur at 8 and 21 eV, in good agreement with 7 and 23 eV calculated by Hartree-Fock methods [5]. The energy scale is set to zero at the Fermi energy.

Work by ANL at APS

At the APS, the ANL team examined the K- and L-edges of Cs and Ba in various standards, synthesized pollucite, and radioactive pollucite. The

greater intensity of the x-rays generated at the APS (a third-generation source) allows use of smaller samples and useful access to higher energy X-rays.

Figure 7 shows the spectra of several samples at the L_{II} absorption edge for Ba and Cs. Since Ba and Cs are neighbors in the periodic table, differences in their EXAFS signals are almost negligible for a similar environment. Cesium chloride was chosen as a reference material that would be easy to handle in mixed systems and to obtain a second calibration point for fitting the data. Barium oxide is a good standard for the oxygen neighbors in pollucite.

From the spectra of materials containing different mixtures of Cs and Ba, we determined that amounts on the order of 1% Ba (by mass) were detectable at the L-edges using the standard Stern-Heald configuration for fluorescence detection (filters and soler slits). For both the L- and the K-edges, the Ba fluorescence energy is higher than the Cs fluorescence energy, so in this experiment configuration, the Ba fluorescence signal will always ride on top of a large Cs fluorescence background signal. The ratio of Ba to Cs in this configuration would need to be greater than 1:10 in order to go beyond mere detection of the Ba atoms and perform EXAFS analysis.

A solid-state (Ge) detector will remove a large fraction of the Cs fluorescence background, allowing measurements to be made of primarily the Ba signal, even down to the 1% level. However, on a wiggler beamline at SSRL (a second-generation synchrotron source) the Ba L-edge signal was not detectable at all, even with the Cs fluorescence removed, implying that Ba was present at a lower level than expected. Results at the APS indicate that use of an insertion device beamline at a third-generation source (such as the APS) could significantly improve the sensitivity of the method to low-level impurities.

In August 1999, the Materials Research Collaborative Access Team (MRCAT) beamline became operational in the energy range necessary for K-edge work on these samples. Figure 8 shows the near-edge region (XANES) of three samples. Subtle yet systematic differences are observed, the origin of which remains unexplained.

Figure 7. XANES spectra at the L-edge for Cs and Ba reference samples. Cs and Ba edges are aligned at 0 for comparison.

Figure 8. XANES spectra at the Cs K-edge.

2.2.5 Summary of X-ray Results

The Cs and Ba L-edge absorption (at ~5-6 keV) and K-edge (~35-38 keV) absorption from *ex situ* samples (opened capsules) were analyzed at both SSRL and the APS. Subtle yet significant differences were noted between the Cs K-edge spectra of the radioactive and nonradioactive samples. The interatomic distances determined by XRD, PDF, and EXAFS analysis are summarized and compared to the tetragonal structure of Palmer et al. [4] in Table 2. In general, the agreement is excellent, and all techniques reflect the tetragonal character of the pollucite sample. The single 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 indicate a substantially longer distance of 0.518 nm. Both XRD and EXAFS techniques are more sensitive to Cs-Cs distance determinations because of the large number of electrons belonging to Cs relative to the other atoms in pollucite. While there is no obvious explanation for this disparity, 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.

In general, the aluminosilicate framework shows minor distortions that can be explained by small rotations along T-O-T (T $\equiv$ tetrahedrally coordinated Si or Al) bonds, leading to increased puckering of the 6- and 8-membered rings. In addition, the Cs atom is displaced along the $[1\bar{2}2]$ direction toward the center of one of the 6-membered rings. Thus, the beta radiation-induced effects lead to swelling of the lattice, as indicated by the slightly expanded lattice parameters for the tetragonal pollucite structure as well as puckering of the aluminosilicate channel encapsulating Cs.

In the final analysis, the necessary synchrotron x-ray facilities are only now nearing completion that would allow a direct *ex situ* characterization of the Ba within radioactive pollucite through EXAFS. With these facilities, it will still be necessary to remove the pollucite from the stainless steel capsule. Present facilities at the APS are able to detect 1% (by mass) of Ba, but when Cs is present, the ratio of Ba to total Cs must be greater than 1:10 before detailed analysis of the Ba environment (EXAFS) would be possible. However, in the long term, synchrotron methods (XANES/EXAFS) still provide the best chance of meaningful *in situ* analysis of radioactive pollucite samples within unopened stainless steel capsules, but such analyses are still developmental.

Table 2. Interatomic distances, in nanometers, as determined by XRD, PDF, and EXAFS analyses.

Interatomic distance	Ref. [4] at 298 K	XRD ^{a, b}	PDF ^a	EXAFS
T-O	0.164	0.165	0.17	Not observed
O-O	0.269	0.267	0.25	Not observed
T-T	0.313	0.315		Not observed
Cs-O	0.335	0.335 0.388	0.34	0.339 0.371
Cs-T	0.404	0.409	0.41	0.413
Cs-T	0.451	0.456		Not detected
Cs-Cs	0.482	0.485	0.49	0.518
Cs-Cs	0.578	0.576	0.57	0.576

^a Sample source: **capsule AE 889**

^b Reported number represents the average distance determined by analysis of XRD data.

2.3 Nuclear Magnetic Resonance Studies

We conducted solid-state NMR studies of nonradioactive pollucite containing milligram levels of Cs, Al, and Si to establish structural changes in pollucite 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 pollucite samples studied. Solid-state NMR can provide nearest neighbor information relevant to radionuclides within the crystalline waste form. As part of this effort, we developed a miniature toroid cavity NMR detector suitable for handling a highly radioactive specimen. A photo and a schematic representation of this device are shown in Figure 9. Only the principal elements of the detector are illustrated; for clarity, the ancillary tuning components and mounting supports are not shown. The central rod and outer cylinder are constructed of copper or other nonmagnetic electrical conductors.

The most promising NMR results were obtained for ²⁷Al in Ba-doped pollucite at room temperature with short, pulses (Figure 10). 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.

The general approach for NMR analysis of radioactive materials is dictated by the sample phase. Materials that are in solution are the most amenable to simple NMR analysis. The methods we are developing for solid-state NMR will also apply, in simplified form, to solution-state

analyses. Solid-state NMR is based on two main experimental methods: those that involve a static sample and container and those that involve rapid rotation (usually “magic angle spinning”) of the sample and its container. The latter method requires more elaborate and expensive equipment but usually provides more information. In addition, for our purposes, sample rotation involves substantial safety issues because of the possibility for dispersing a radioactive sample.

The issue of pollucite stability poses some interesting possibilities for solution NMR (e.g., Cs leaching), but the principal questions involve determination of structure in the solid state. Hence, static and/or magic angle spinning experiments will be the primary options. For most solids, static NMR experiments provide very little information about structure because there is too much information and it is distributed across a larger spectroscopic frequency range. Usually a broad and weak signal is observed, for which little analysis can be done. In some cases and for some nuclei, however, static NMR spectra of the solid state can provide useful information about structure and dynamics. Such is the case for ^{133}Cs in aluminosilicate materials.

Our preliminary experiments suggested that simple static NMR experiments might provide information about the Cs sites in pollucite. In fact, there was little difference between the NMR spectra recorded under static and spinning conditions. This was fortuitous for the pollucite investigation but is generally not the case for other nuclei, such as ^{29}Si , ^{27}Al , ^{17}O , etc. Spectra from such nuclei which would provide direct information about sites where transmutations occurred, must be obtained from spinning samples. We, therefore, have pursued static ^{133}Cs NMR experiments with pollucite because of the possibility of learning something about Cs and its surroundings without having to spin the sample. We are using the toroid cavity probe rather than a traditional solenoid probe because it offers several pragmatic advantages. The toroid cavity probe is itself a container that can be sealed and it is easier to load with a sample that must be handled in a glove box. Most importantly, it is three to five times more sensitive than the solenoid. Sensitivity is of essential importance because we are limited to 1-2 mg samples.

We also obtained spectra for ^{29}Si and ^{27}Al from rotating samples of pollucite. These experiments have shown that ^{29}Si NMR can reveal differences between Cs-pollucite and Ba-pollucite. The ^{29}Si NMR spectrum of a sample of Cs-pollucite (rotating at an angle of 54.74° with respect to the axis of the external magnetic field, and at a rate of 2000 Hz) shows two peaks that are separated by about 5 ppm. The ratio of signal intensities is 2:1, with the deshielded peak having the greater intensity. The synthesized Ba-pollucite (15% of Cs substituted by Ba) was spun at 3000 Hz. In contrast, the ^{29}Si NMR spectrum of the Ba-pollucite is a single broad peak with very weak features that is located at approximately the same chemical shift as the deshielded peak in Cs-pollucite. These

spectra represent the first spectroscopic evidence that the pollucite framework is different for the two types of pollucite. The transmutation of ^{137}Cs to ^{137}Ba is expected to cause defects in the pollucite aluminosilicate framework, and the silicon atoms are the next nearest atomic neighbors to that site. The aluminum atoms are also nearest neighbors. Therefore, ^{29}Si and ^{27}Al NMR may provide the most information about defect sites in radioactive pollucite. In principle, ^{17}O NMR should be even more sensitive to transmutation effects because of its direct proximity to the transmutation site; however, the low natural abundance of ^{17}O makes it a difficult nucleus to observe. The preliminary ^{133}Cs and ^{29}Si NMR experiments indicate that these nuclei may be able to characterize the lattice breakdown in pollucite.

Figure 9. Photo and schematic of miniature toroid cavity solid-state NMR detector.

Figure 10. Solid-state NMR spectra of ^{27}Al in Ba-doped (nonradioactive) pollucite for both magic angle spinning (top curves, each sample) and static toroid cavity NMR (bottom). The similarity in the spectra shows that static toroid cavity NMR is sufficient to obtain nearest neighbor structural information on milligram-level samples.

2.4 Transmission Electron Microscope Studies

The AD 92 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 radiation effects. Small fragments of the AD 92 pollucite were removed from the capsule in nitrogen-filled glove box. The pollucite fragments were embedded in an epoxy block and thin-sectioned using a Reichert ultramicrotome. The thin sections were floated onto a carbon-coated copper TEM grid, which was then mounted in a liquid-nitrogen-cooled TEM sample holder. The samples were allowed to desiccate in the TEM under vacuum over a weekend. The samples were examined using a JEOL 2000 FX Mark II TEM equipped with dual energy dispersive x-ray fluorescence spectroscopy (EDS) detectors and operated at 200 keV accelerating energy. The sample temperature was maintained at approximately 100 K with the liquid nitrogen coolant to minimize electron beam damage, which is often rapid in an aluminosilicate sample. Bright field transmission images revealed a homogeneous, crystalline matrix, with no evidence of distinct Ba phases or ex-solution phenomena resulting from the ^{137}Cs transmutation (Figure 11). Electron diffraction patterns were obtained

from several portions of the sample; the combined data appear in Table 3. Despite the liquid nitrogen cooling, the sample would amorphize rapidly in the beam, allowing only about 15 seconds of examination on a spot within the beam. Excellent agreement between the observed diffraction spacings and literature values for pollucite indicates that no substantial damage was done to the crystal structure of this sample, 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 3, which may be a result of the cryogenic temperature of the experiment.

Figure 11. TEM micrograph of radioactive pollucite from the AD 92 capsule. The pollucite was shattered during the ultramicrotome process, but each of the fragments has a homogeneous appearance. There is no evidence of phase separation or ex-solution precipitation.

Table 3. Experimental electron diffraction data from radioactive ^{137}Cs -doped pollucite sample AD 92 compared with JCPDS-ICDD reference data.

Experimental d-spacing (Å), sample AD 92	Natural Pollucite JCPDS-ICDD 25-194 (Å) ^a	Synthetic Pollucite JCPDS-ICDD 29-407 (Å)	Ratio (experimental/reference) ^b
5.47	5.56 vf	5.58	0.980
	4.83 vf	4.84 vf	
3.54,	3.65 *	3.66 *	0.973
3.56,			
3.57			
3.30	3.42	3.42 *	0.965
	3.23 vf		
	3.06 vf	3.06 f	
2.86	2.913 *	2.914 *	0.982
2.82			
	2.791 vf		
2.62	2.682	2.684	0.977
	2.497 vf	2.499	
	2.416	2.419 *	
	2.218	2.220	
	2.162	2.018	
	1.897	1.975 vf	
		1.897 vvf	
1.813	1.860 *	1.862 *	0.974
	1.736 *	1.737 *	
	1.709	1.709	
1.652	1.683	1.684 vf	0.982
	1.634,	1.635,	
	1.589,	1.549,	
	1.548,	1.529	
	1.529		
1.429			

^a Major peaks in JCPDS-ICDD reference data (30% most intense) labeled by “*”. Very faint peaks indicated by “vf”; extremely faint peaks indicated by “vvf.”

^b The final column is a ratio of the experimental data to the average of the corresponding reference values. The TEM specimen was liquid-nitrogen-cooled to ~100 K, while the reference samples were measured at ambient temperature. This ratio may reflect thermal expansivity effects.

3 Relevance, Impact, and Technology Transfer

We used several advanced techniques to assess structural effects caused by the beta-decay transmutation of ^{137}Cs to ^{137}Ba in radioactive pollucite that had aged for nearly one half-life of the ^{137}Cs . This transmutation was expected to affect the stability of the aluminosilicate pollucite crystal because of chemical differences between Cs^+ and Ba^{2+} . Although the amount of barium exceeded the amount the structure was expected to be able to tolerate, our observations indicate that the pollucite structure remained remarkably unaffected by the transmutation. This suggests the presence of a metastable, yet robust, state. The virtual null result for transmutation effects on the pollucite is encouraging from a regulatory and modeling point of view. However, this behavior may not be characteristic of aged waste forms in general. Framework aluminosilicates are likely to play an important role as both low-level and high-level waste disposal media within the DOE/EM. Although our observations are limited, these are, to our knowledge, the only available data in which transmutation effects have been isolated from other radiation damage phenomena.

4 Project Productivity

The original goals of the project were met, with one caveat: we were unable to demonstrate satisfactory *in situ* EXAFS of the pollicite. The reasons were manifold, but they included technical and radiation safety issues. Productivity was otherwise impacted by transportation and facility issues concerning the handling of these highly radioactive samples. Neither ANL nor PNNL were able to provide dedicated facilities for this work within the budgetary constraints.

5 Personnel Supported

The following personnel were supported in part by the EMSP funding between October 1996 and September 1999. No person was supported full-time by this project. All personnel were full-time staff of their respective institutions, except as noted.

Argonne National Laboratory

1. Jeffrey A. Fortner (acting PI)
2. Denis M. Strachan (original PI, presently at PNNL)
3. Donald T. Reed
4. A. Jeremy Kropf
5. Scott B. Aase
6. Rex E. Gerald
7. Edgar. C. Buck
8. Luis Nuñez

Pacific Northwest National Laboratory

1. Nancy J. Hess
2. Maria-Elsa Reyes (graduate student)
3. F. Javier Espinosa Faller (post-doctoral student)

6 Transfer

6.1 Publications

Published in peer-reviewed journals and books

N.J. Hess, M.L. Balmer, S.D. Conradson, and B.C. Bunker (1997) "Ti XAS of a novel Cs-silicotitanate," *Journal of Solid State Chemistry*, vol. 129:206-213.

Published in unreviewed publications

J.A. Fortner, E.C. Buck, D.M. Strachan, and N.J. Hess, "Extended Electron Loss Fine Structure Analysis of Silicon-K Edges Using an Imaging Filter," *Microscopy & Microanalysis* **4** (Suppl 2: Proceedings) 706-707 (1998).

N.J. Hess, J.H. Sukamto, S.D. Rassat, R.T. Hallen, R.J. Orth, M.A. Lilga, and W.E. Lawrence (1997) "Characterization of electroactive Cs ion-exchange materials using XAS," *Materials Research Society Proceedings*, vol. 456:813-818.

Accepted/submitted for publication

N.J. Hess, F.J. Espinosa, S.D. Conradson, and W.J. Weber, "Beta Radiation Effects in ^{137}Cs -substituted Pollucite," *Journal of Nuclear Materials*, accepted.

6.2 Interactions

Researchers involved in this project participated in these meetings, workshops, conferences, and seminars.

- J. A. Fortner, EMSP Workshop, April 2000, Atlanta, Georgia. Presented poster of work to date.
- J. A. Fortner, EMSP workshop, July 1998, Chicago Illinois. Presented poster of work to date.
- J. A. Fortner, "Extended Electron Loss Fine Structure Analysis of Silicon-K Edges Using an Imaging Filter," *Microscopy & Microanalysis Conference*, Atlanta, GA, July 12-16, 1998.
- N.J. Hess "XAS Investigations of Cs Separation and Waste Storage," at *X-ray Spectroscopies of Environmental Interfaces: Theory and Experiment*, PNNL, Richland WA, Sept. 9-12, 1996.

6.3 Transitions

The information on cesium-to-barium transmutation effects (or lack thereof) was of interest to the Fuel Conditioning Program (FCP) at Argonne National Laboratory. The FCP has developed a glass-bonded ceramic waste form for disposal of fission products removed during fuel conditioning. This waste form will contain substantial ^{137}Cs in an aluminosilicate material, allowing direct inferences from the pollucite work presented herein. They will be issued a copy of this report.

6.4 Patents

None.

6.5 Future Work

Although aluminosilicate waste forms are likely to be of importance for cesium disposal, our observations may have limited application *vis-à-vis* aged waste forms generally. We wish to build upon experience gained from our pollucite study to include aging effects on spent nuclear fuels, fission product ceramics, and alteration products of spent nuclear fuels.

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