

STUDY OF ALPHA-DECAY DAMAGE IN A GLASS-BONDED, SODALITE CERAMIC WASTE

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ABSTRACT

A glass-bonded, sodalite ceramic waste form that contains fission products, uranium, and plutonium is intended for disposition in a geologic repository. Over the many years the waste is expected to be in the repository, there is a potential for waste form degradation due to alpha decay damage. To investigate the effects of alpha-decay damage in glass-bonded, sodalite ceramic waste forms, several waste forms were produced with a ^{238}Pu loading of 1.8 weight percent. This loading is roughly ten times greater than the plutonium loading for all isotopes in the waste form intended for the repository. Due to the higher specific activity of ^{238}Pu as well as a higher fraction of total plutonium, the same number of alpha decays per gram of material has been achieved after four years as a waste form of nominal composition after ten thousand years. This paper describes the results of different tests near the completion of a four-year study. Trends of these ^{238}Pu -doped waste forms include volume expansion of crystalline phases and possible increases in the release rates of several elements in the chemical durability tests. There have not yet been any indications of macroscopic swelling by density measurements, amorphization by x-ray diffraction, or microstructural changes by electron microscopy. Overall, the observed changes to the waste form due to alpha-decay are not of sufficient magnitude yet to cause concern over waste form degradation.

INTRODUCTION

A ceramic waste form (CWF) was developed to immobilize a salt containing fission products, uranium, and plutonium for disposition in a geologic repository. [1] The salt originates from electrometallurgical treatment of sodium-bonded nuclear fuel, described elsewhere.[2] During the extended time that the waste form resides in

the repository, damage due to alpha decay may change the fundamental properties of the waste form. Such changes could affect the chemical durability of the waste form, requiring additional testing to assure the waste form still performs acceptably. The purpose of this work is to ascertain whether the waste form will fundamentally change due to alpha-decay damage while disposed in the repository and, if it does, how the change affects the release of radionuclides.

The ceramic waste form produced for this study is primarily comprised of a sodalite phase and a glass phase. Typically, the sodalite regions are several microns across and are surrounded by glass. In addition, there are minor phases of plutonium oxide, nepheline, and halite. The plutonium oxide and halite tend to be present as small (2 μm or less) inclusions in the glass phase, somewhat displaced from the boundary of the sodalite region. The data acquired in this study suggest that most of the plutonium is present as plutonium oxide, with a very small fraction of Pu as a silicate or aluminosilicate.

To obtain alpha-decay damage on an accelerated scale, ceramic waste forms were produced so that they contained 1.8 weight percent ^{238}Pu . This differs from a nominal CWF that will contain about 0.2 weight percent plutonium, mostly of the ^{239}Pu isotope. Due to the high specific activity of ^{238}Pu , a dose of 1.4×10^{18} alpha decays/gram of material can be obtained after 4 years for a waste form containing 1.8 weight percent ^{238}Pu . In contrast, a waste form with 1.8 weight percent ^{239}Pu would accumulate the same dose after 1100 years. The damage is further accelerated by the higher loading of Pu. The 1.8 weight percent loading of ^{238}Pu is ten times the expected, nominal plutonium concentration in the ceramic waste form produced from the electro metallurgical process. Thus, it would require around 10,000 years for a waste form of nominal composition to acquire the dose that will be obtained in this study.

DESCRIPTION OF WORK

A 4-year study is nearing completion, with 3.5 years already past corresponding to a dose of 1.2×10^{18} alpha decays/gram of CWF material. During this study, samples containing Pu-238 have been tested periodically. The production of these samples is described in an earlier paper [3]. Several tests are being applied to ascertain damage that may be manifested in multiple ways. First, x-ray diffraction is used to monitor changes in the crystalline components of the waste form. Second, density is measured through water immersion tests to determine whether macroscopic swelling is occurring. Third, microstructure is monitored for changes using both scanning and transmission electron microscopy. Finally, chemical durability is being tested using the Product Consistency Test (PCT) [4], a leach test originally designed for high-level waste glass but applicable to ceramics.

Powder x-ray diffraction was performed with a Scintag X1 diffractometer that uses Cu-K α radiation. Approximately 2 wt% of LaB $_6$ (NIST standard reference material 660) was mixed with the CWF, which was ground to a powder, as an internal standard for instrument alignment purposes. The same CWF and LaB $_6$ specimen was used for all XRD analyses. Refinement of the XRD pattern was performed with General Structure Analysis System (GSAS) software [5] and quantitative phase analysis of the CWF was performed using the SIROQUANT software package [6].

Density was periodically measured by a water immersion technique. The density is determined by first weighing the sample then determining the buoyancy weight of the sample in water. To ascertain the uncertainty in the density measurement and to check calibration, a CWF containing no Pu and an aluminum standard were tested along with the sample. Each measurement was performed with the same monolithic sample.

Electron microscopy was performed using a Zeiss DSM 960A scanning electron microscope (SEM) equipped with secondary and backscatter electron detectors and a JEOL 2010 transmission electron microscope (TEM). Both microscopes have detectors for energy x-ray spectroscopy capability and the SEM also has a wavelength-dispersive x-ray detector. Only one sample was mounted for repeated SEM analyses. For TEM analyses, a new sample from the original batch of samples is used for each time period studied since the more delicate samples could only be analyzed once.

The Product Consistency Test-B (PCT-B) is a 7-day static immersion test that modifies the standard PCT-A procedure. All the material, which has been used or will be used for testing, was ground and sieved to a specified size range. For testing, the samples were washed in ethanol to remove fines. Samples were also washed in water, which is analyzed, to collect material that readily dissolves. Then the cleaned material and leachant (ASTM type I water) were added in specified quantities to a stainless steel test vessel. The ratio of sample surface area to volume of leachant was 2000 m^{-1} . Next, the sealed vessels were placed in an oven at 90°C for 7 days. Upon test completion, the leachate was filtered and collected. Two volume percent nitric acid was then added to the vessels and returned to the oven at 90°C overnight to remove any sorbed material from the vessel. Finally, the water wash solutions, leachates, and acid strip solution were analyzed for elemental release. Methods included alpha spectroscopy, inductively coupled plasma-mass and atomic emission spectrometry (ICP-MS and ICP-AES), and ion specific electrode for chloride.

RESULTS AND DISCUSSION

Based on x-ray diffraction data, the volumes of sodalite and PuO $_2$ unit cells have increased with dose. The percent change in volume is plotted for each of these phases in Fig. 1. The accumulation of defects in the PuO $_2$ lattice causes the large, initial increase of volume for plutonium oxide, as described elsewhere [7]. After this large increase, the unit cell of PuO $_2$ continues to expand more gradually, at a rate proportional to the in-growth of UO $_2$. For sodalite, some unit cell expansion is also occurring, most notably after a dose of 9.5×10^{17} alpha decays per gram. This increase may be the result of exceeding a threshold limit of accumulated defects. These defects are largely caused by recoil nucleus in the PuO $_2$ phase since that is where almost all the plutonium is found. In the sodalite phase, defects probably result from alpha radiation since no plutonium has been detected in sodalite and the distance of the recoil nucleus in decay is too small to affect sodalite. Based only on the increases in volume for the sodalite and PuO $_2$ unit cells, the volume increase of the CWF on a macroscopic scale would be approximately 0.23 percent. The largest contributor of this expansion is sodalite, which comprises the largest portion of the waste form.

No macroscopic swelling, which would be indicated by decreasing density, has been observed. Table I lists the values for density recorded at different doses. On average, the density of the waste form is $2.424 \pm 0.006 \text{ g/cm}^3$. To detect a reduction in density at a 2σ confidence level, the density would have to be less than

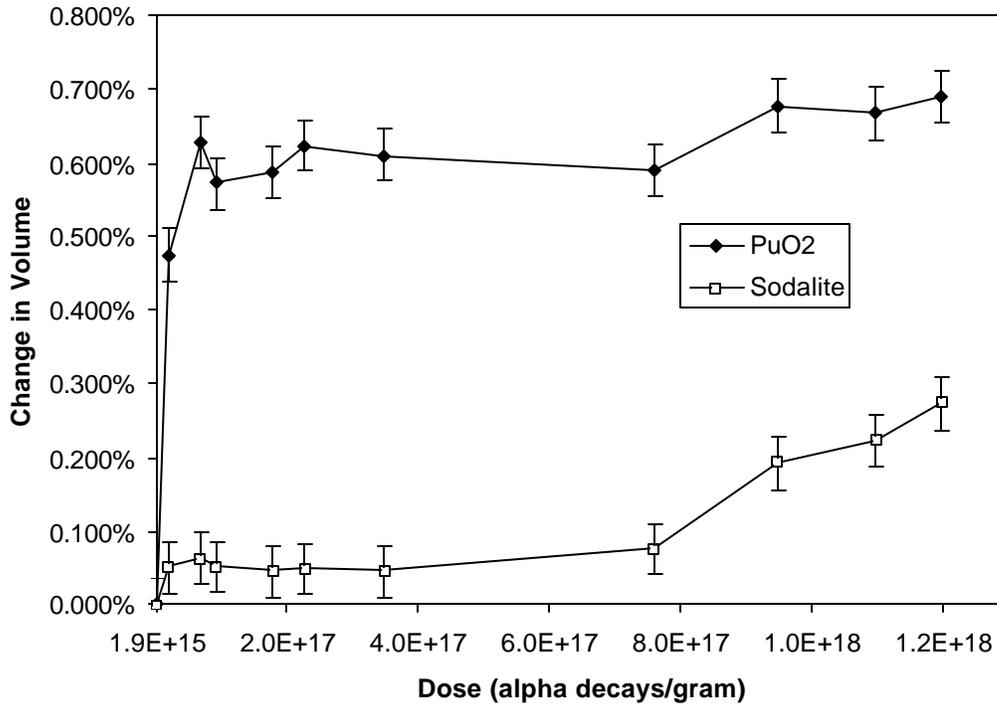


Figure 1. Expansion of the PuO₂ and Sodalite Unit Cells.

2.412 g/cm³. This decrease would correspond to volume increase of 0.5 percent. If all of the expansion of the sodalite and plutonium oxide translated to expansion of the ceramic waste form, then this increase in volume would be on the same order as the error at one sigma. Thus, swelling cannot yet be detected, especially when considering that some of this expansion may be accommodated by the porosity inherent in the waste form.

A Product Consistency Test (PCT) has been performed on the ²³⁸Pu-loaded waste forms aged for 0.2 and 2 years. Though only two tests have been carried out, they still provide information that may be helpful to evaluate waste form performance in view of the other tests. The data acquired thus far is given in Table II. The release of Al did not change significantly, which may indicate that dissolution of the overall matrix of the waste form is not increasing. While the release of Al remained about the same, the normalized releases of other constituents such as Cl, B, Pu, Nd and Cs may be increasing. Between the two tests, better analytical methods were developed to increase both the accuracy and precision of the measurements. Thus, no conclusions can yet be drawn on whether these elements are increasing until the completion of the next PCT. Regardless, the release of Pu (the element of most concern) is still not very large compared to the releases of other waste forms. The final dataset will be acquired at the conclusion of the 4 years and will hopefully elucidate whether the releases of these elements are indeed increasing.

Table I. Density as a Function of Number of Decays Accumulated. Measurements for CWF without Pu and an aluminum standard are also shown as a check and reference standard. Units of density are g/cm³.

Dose (α-decay/gram)	²³⁸ Pu CWF Density	Non-Pu CWF Density	Al Std. Density
4.9E16	2.424		2.690
1.2E17	2.417		2.700
2.3E17	2.419		2.694
3.7E17	2.420		2.692
4.5E17	2.425	2.342	2.693
7.5E17	2.425	2.339	2.699
8.6E17	2.426	2.346	2.697
9.3E17	2.420	2.346	2.694
1.0E18	2.434	2.334	2.699
1.1E18	2.426	2.340	2.696
1.2E18	2.434	2.341	2.701
Avg ± 1σ (%RSD)	2.424 ± 0.006 (0.23%)	2.342 ± 0.004 (0.19%)	2.696 ± 0.004 (0.13%)

If the release of Cl, B, Pu, Nd and Cs are indeed increasing, the higher release would be consistent with where most of the energy released during alpha decay is deposited. Most of the plutonium and rare earths reside as oxide inclusions within the glass displaced from the sodalite regions. Cesium is also found primarily in the glass phase. Because of the general distribution of plutonium, the two phases that will have the most energy

deposited during alpha decay will be the plutonium oxide and the glass. The majority of the damage is then greatly localized since the recoil nucleus after an alpha decay imparts most of the energy released and only travels a short distance of tens of nanometers. Higher numbers of dislocations in the PuO₂ and glass may lower the durability of those areas so that more B is released from glass and more Pu from the dissolution of the oxide. A higher release of Cl may indicate that alpha particles are gradually reducing the durability of the sodalite but may also indicate that more halite is being released as more glass is dissolving. Regardless, the release of Pu after 7.4×10¹⁷ alpha-decays/g of material is still quite low.

For electron microscopy, the important points are not what is observed but what is not observed. As seen in Fig. 2, the overall microstructure does not change. Using transmission electron microscopy, a search for microcracking and debonding was conducted but none were observed. Such features could have resulted from defects caused by alpha particles and recoil nuclei, as evidenced by expansion of sodalite and PuO₂. Specimens did contain bubbles and voids in both sodalite and glass areas as shown in Fig. 3. The bubbles and voids appear to be primarily produced during processing since these voids occur in waste forms that do not contain Pu. There is no indication at this time that the observed bubbles are due to the accumulation of radiolytic gas products (H₂O, H₂, O₂, Cl₂, etc) or He from alpha decay. Still the formation of bubbles and amorphization of the sodalite phase may

cause microcracking or debonding. To investigate this possibility, an electron beam was focused on an area within the sodalite phase, amorphizing the material and creating bubbles, but still no microcracking or debonding was observed. Further details on TEM analyses are reported elsewhere [8].

Table II. Normalized Elemental Release (NR) in g/m² for a 7-day PCT is given below for samples after 0.2 years (4.0×10¹⁶ a decays/g) and 2 years (7.4×10¹⁷ a decays/g). The values shown for the Pu-doped samples are the averages from triplicate tests including wash solutions, leachates, and acid strips. The measurement uncertainty is at one standard deviation.

Elements		NR after 0.2 yrs	NR after 2 yrs
Major elements	Si	Not measured	0.038 ± 0.004
	Al	0.035 ± 0.004	0.034 ± 0.003
Salt	Na	Not measured	0.23 ± 0.01
	Cl	0.38 ± 0.04	0.74 ± 0.07
	Li	0.44 ± 0.04	0.48 ± 0.03
	I	Not measured	0.21 ± 0.05
Potential glass	K	0.09 ± 0.07	0.13 ± 0.02
	B	0.23 ± 0.02	0.35 ± 0.04
Actinides	Pu	0.0007 ± 0.0002	0.0020 ± 0.0002
Rare earths	Nd	0.0012 ± 0.0001	0.0048 ± 0.0005
Other	Cs	0.15 ± 0.02	0.35 ± 0.04

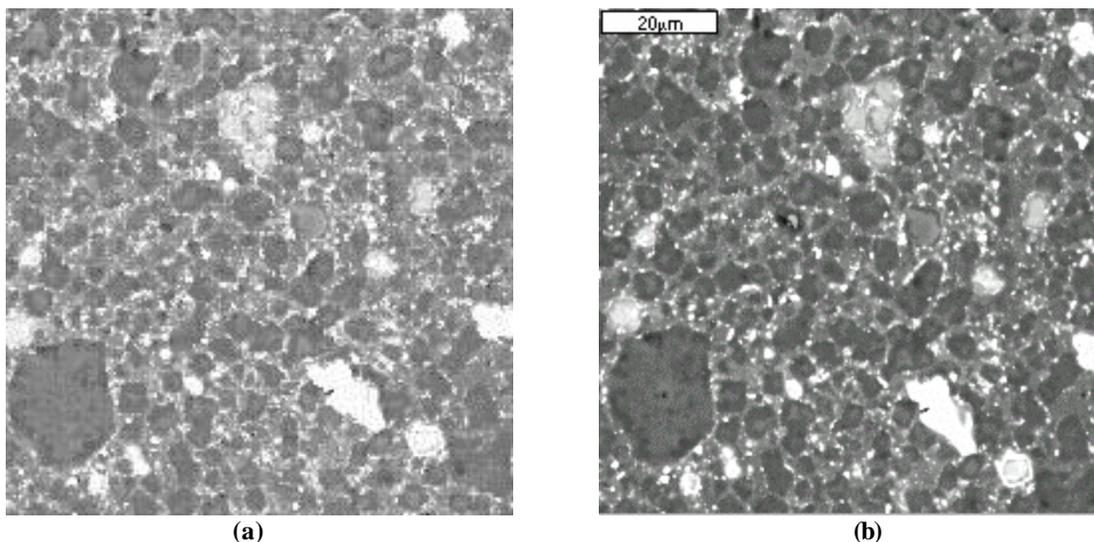


Figure 2. Backscattered Electron Images of Selected Region after (a) 0 Years and (b) 3 Years Obtained with a Scanning Electron Microscope. The size bar is 20 μm. No changes within the waste form have been observed. Typically, the darkest areas are sodalite, the gray areas are glass, and the brightest inclusions are PuO₂.

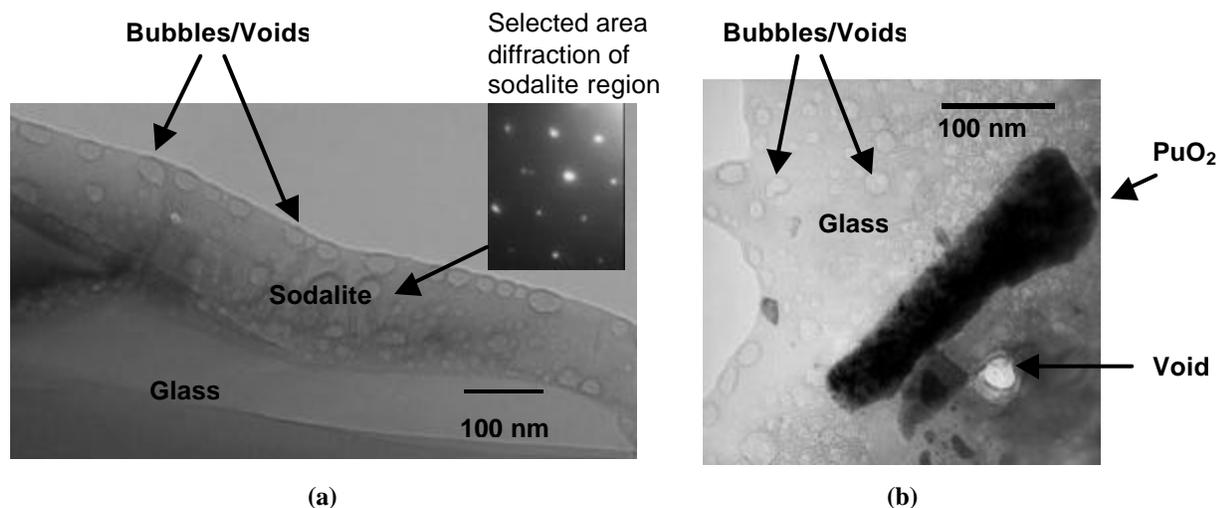


Figure 3. Transmission Electron Microscopy Images Showing Bubbles/Voids in (a) Sodalite and (b) Glass Regions. Despite the presence of the bubbles/voids that can have multiple sources, no debonding and microcracking is observed.

SUMMARY AND CONCLUSIONS

As the four-year study nears completion, potential trends have been identified for Pu-doped waste forms aged for up to 3.5 years. There are indications of certain crystalline phases increasing in volume but no indications of macroscopic swelling. The volume increase of the PuO₂ and sodalite crystalline phases due to defect accumulation from alpha decay is so small (less than 0.3%) that it is not yet possible to measure this change by density determination. Furthermore, microscopy investigation has found no indication of microcrack formation or phase debonding due to changes in phase volume, and there has been no indication of bubble formation from the accumulation of radiolytic gas or He, nor is there expected to be any. This is because the voids, which were produced during processing and which exist in both the glass and sodalite regions, should act as sinks for the accumulation of gas products produced during alpha decay. Any volume change might also be accommodated by this small amount of porosity inherent in the material. From the PCT results, increases in release for several elements are also observed, but additional data is required before concluding whether these increases will continue to increase at higher doses. Despite these increases, the release of Pu is still very low. Therefore, the chemical durability for the ceramic waste form is still acceptable for an alpha-decay dose obtained for tests nearing completion and will soon concur with a dose in a nominal waste form over ten thousand years. Samples

will continue to be tested past the four years if funding is available.

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