Accelerated Alpha Radiation Damage in a Ceramic Waste Form, Interim Results

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ACCELERATED ALPHA RADIATION DAMAGE IN A CERAMIC WASTE FORM, INTERIM RESULTS

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ABSTRACT

Interim results are presented on the alpha-decay damage study of a ^{238}Pu-loaded ceramic waste form (CWF). The waste form was developed to immobilize fission products and transuranic species accumulated from the electrometallurgical treatment of spent nuclear fuel. To evaluate the effects of α-decay damage on the waste form, the ^{238}Pu-loaded material was analyzed by 1) x-ray diffraction (XRD), 2) microstructure characterization by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) with energy and wavelength dispersive spectroscopy (EDS/WDS) and electron diffraction, 3) bulk density measurements and 4) waste form durability, performed by the product consistency test (PCT). While the predominate phase of plutonium in the CWF, PuO$_2$, shows the expected unit cell expansion due to α-decay damage, currently no significant change has occurred to the macro- or microstructure of the material. The major phase of the waste form is sodalite and contains very little Pu, although the exact amount is unknown. Interestingly, measurement of the sodalite phase unit cell is also showing very slight expansion; again, presumably form α-decay damage.

INTRODUCTION

The ceramic waste form (CWF) used for this study was developed to immobilize fission products and actinide materials that accumulate during the electrometallurgical treatment of spent nuclear fuel at Argonne National Laboratory in Idaho in support of the ANL/DOE Spent Fuel Demonstration Project [1]. Fission products and transuranic actinides concentrate in a molten, LiCl-KCl eutectic salt during electrometallurgical treatment of spent fuel. The contaminated eutectic salt is removed from the electrorefiner and processed into the CWF for final disposal in a geological repository. The waste form produced during fuel conditioning will contain roughly 0.2 weight percent Pu, primarily of ^{239}Pu isotopic composition. Of regulatory interest to the repository is the waste form behavior [2]. To investigate potential, long-term behavior of alpha-decay damage on the actual CWF, but in a much shorter period, tests were initiated using a CWF containing surrogate fission products and ^{238}Pu as opposed to ^{239}Pu. The use of ^{238}Pu, with its high specific activity of 6.3 x 10^{13} decays/min g and half-life of 88 years, allows significant α-decay dose in a matter of years as opposed to thousands of years in the case of ^{239}Pu. Thus the term accelerated alpha damage. The data presented concludes the first year of a four-year study. The current accumulated alpha decay dose is approximately 5 x 10^{17} α-decays/gram of material. The total accumulated dose at the end of the four-year study will be approximately 2 x 10^{18} α-decays/gram of material.

Many literature reviews have been compiled on radiation damage to materials [3] In particular, α-decay studies of crystalline materials or glass materials containing actinide host phases reveal that the crystalline material may become amorphous due to accumulation of dislocated matrix atoms [4, 5]. Amorphization of crystalline phases leads to volume increases that may in turn lead to microcracking. Swelling and cracking of the material usually have detrimental effects on the performance of the waste form [6]. After prolonged exposure, He or

other gas bubbles may develop. However, some crystalline materials, such as PuO_2, UO_2 and ZrO_2 for example, show little damage to the crystalline structure after prolonged radiation exposure[3]. This study wishes to address these issues relating to the CWF.

EXPERIMENTAL

A detailed description of the processing of the CWF is found elsewhere [7]. The process first involves occluding the salt in dry (< 0.5 wt% moisture) zeolite 4A. The zeolite is then mixed with a glass binder and consolidated at a temperature of 1100 K and a pressure of 34 MPa. During this processing, the zeolite converts to sodalite. The composition of the pre-processed mixture is shown in Table 1. The fission product surrogate salt contains KBr, KI and the chlorides of Na, Rb, Sr, Y, Cs, Ba, La, Ce, Pr, Nd, Sm and Pu. In this study, the CWF was loaded to approximately 2.5 wt% ^{238}Pu. This Pu loading is roughly 3 to 20 times the actual Pu (elemental) loading of the CWF produced during the fuel treatment process. As indicated in Table 2, Pu in the eutectic salt is in the chloride form. After contacting with the zeolite, the Pu converts to the oxide. This reaction is presumably due to the reaction with oxygen from residual water in the zeolite.

Table 1. Weight percent of each component in the pre-processed mixture.

Component	LiCl/KCl Eutectic Salt	Fission Product - Surrogate Salt	Zeolite 4A	Glass binder	Elemental Pu
Weight %	4.1	1.7	64.7	25.0	2.5

The ^{238}Pu-loaded CWF is being analyzed on a periodic basis to evaluate α-decay damage to the waste form. The testing schedule is planned for a minimum of 4 years. The methods used to study the extent of α-decay damage on the CWF are separated into the following sections:
1) Waste form microstructure and elemental distribution is being investigated by scanning electron microscopy (SEM) in conjunction with energy and wavelength dispersive spectroscopy (EDS/WDS). Transmission electron microscopy (TEM), in conjunction with electron diffraction (ED) and EDS, is also being performed.
2) Powder x-ray diffraction (XRD) is used to monitor bulk phase composition and changes to major phase lattice parameters.
3) Density measurements on the CWF are being performed by an immersion method. Density measurements provide information on macroscopic swelling as a function of cumulative dose.
4) Durability of the ^{238}Pu-loaded CWF, with cumulated α-decay dose, is compared to the non-radioactive CWF reference material using the PCT-A leach method [8]. The leach test uses a crushed material with a −100 to +200 mesh size fraction, demineralized water for the leachant, and a surface area to volume ratio of 2000 m^{-1}. Elemental determination of the leachate is performed by inductively coupled plasma-mass spectrometry.

RESULTS

MICROSCOPY

The microstructure (Figures 1a and b) of the ^{238}Pu-loaded CWF is very similar to the reference (non-Pu loaded) CWF and consists of 5 to 20-micron diameter sodalite grains surrounded by the glass binder. Plutonium is found primarily as PuO_2 in the glass intergranular boundaries between sodalite grains. Figure 1a shows the microstructure shortly after the material was produced. Figure 1b shows the microstructure after one year of accumulated alpha damage. As can be seen, the two micrographs are indistinguishable with no visible indication of α-decay

effects. A second Pu containing phase has been identified by TEM as a tetragonal aluminosilicate material (Figure 2). This tetragonal phase has not been observed in the CWF containing 0.2 wt% Pu and its presence is possibly due to the greater Pu loading used in this study. In addition, a strongly faceted, needle-like structure containing Pu has been observed as shown in Figure 2.
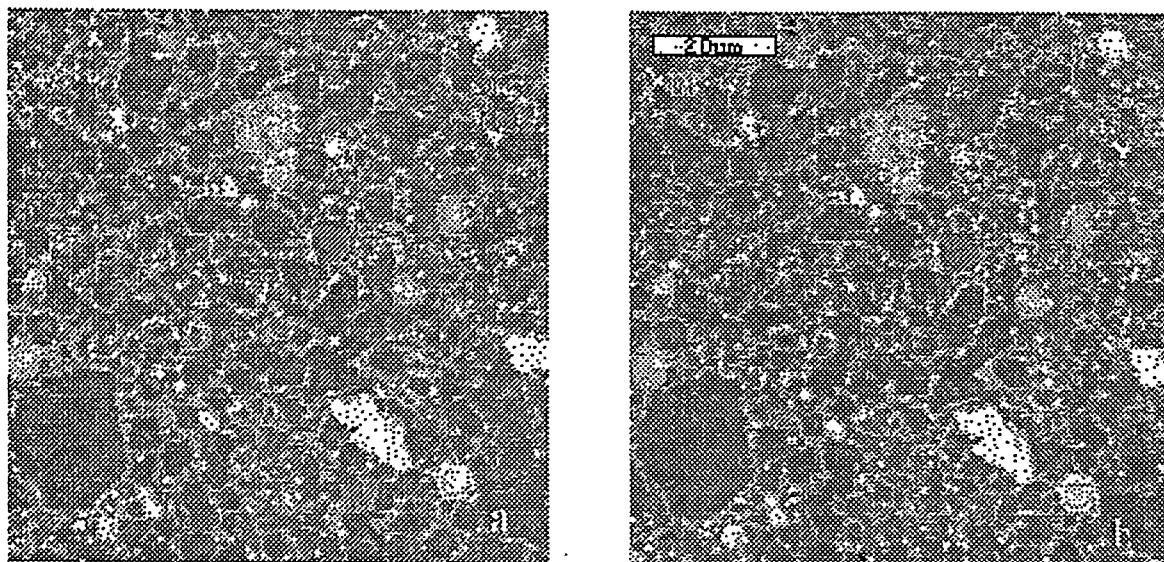

Figure 1. a) Back scattered electron image of ^{238}Pu-loaded CWF shortly after the material was prepared. This image is considered representative of the overall sample. Brightest regions are PuO_2, darkest regions are sodalite, medium dark regions are glass, and medium light regions are high Pu aluminosilicate. b) Same sample region after approximately one year (5×10^{17} α-decay/g) dose accumulation.

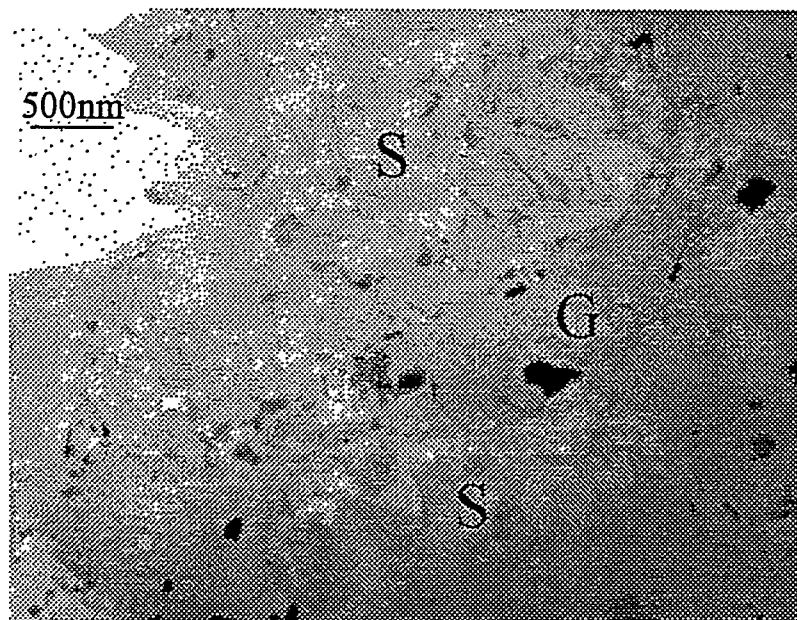Figure 2. Low-magnification bright field image showing typical microstructure of ^{238}Pu-loaded CWF. The two main phases are labeled S: sodalite phase and G: glass phase. Plutonium containing phases are seen as the dark objects. These include PuO_2 fluoride structures, tetragonal Pu aluminosilicates and the strongly faceted, needle-like, Pu-containing material observed in the upper right of the micrograph.

X-RAY DIFFRACTION

The waste form is comprised of four crystalline components as indicated by x-ray diffraction. The weight percent of the four crystalline phases is shown in Table 3 and compares well with the reference (non-Pu loaded) CWF. The amorphous content of the sample was measured to be 22 percent, which corresponds to the target quantity of added glass binder of 25 weight percent within experimental uncertainty. The plutonium containing aluminosilicate and high Pu containing sodalite phases observed by TEM are not observed by XRD, probably due to the low relative amounts of the phases present in the waste form. Regardless the majority of the Pu is in the oxide form.

Table 3. Crystalline phase composition of ceramic waste form in weight percent. LaB_6 was added to the sample as an internal standard for refinement purposes.

Crystalline Phase	Sodalite $Na_4(AlSiO_4)_3Cl$	PuO_2	Nepheline $NaAlSiO_4$	Halite $NaCl$	LaB_6 NIST SRM 660
Crystalline Weight Percent found in Waste Form	84	3	7	3	3

X-ray diffraction patterns were acquired from the [238]Pu-loaded sample on days 2, 21, 72, 97, 146, 240 and 365 from the time the pellet was produced. For structural refinement, the LaB_6 standard was used to determine instrumental constants. The LaB_6 standard is not expected to sustain damage from radiation so the lattice parameter should not change with time. The average LaB_6 lattice parameter value of 0.415695 ± 0.000006 nm and matches very well with the NIST certified value. This excellent agreement of the measured lattice parameter of the LaB_6 standard to the NIST certified value adds confidence to the measured lattice parameters of PuO_2 and sodalite found in the sample. After pattern refinement, the lattice parameters of PuO_2 and sodalite were compared to previous determinations. Unit cell expansion of the PuO_2 phase is clearly shown in Figure 3 and has reached saturation with, to date, an overall expansion of 0.6%. The self-irradiation saturation level for PuO_2 appears to occur after approximately 100 days. This expansion is less than the 1% volume expansion that has been reported elsewhere [3] but may be due to initial crystal imperfections. The unit-cell expansion of PuO_2 follows a profile observed by other investigators [9]. The authors of ref. [9] have postulated that the maximum results from a supersaturation of defects in the lattice followed by a lattice dilation due to defect migration to sink regions. After the decrease in lattice parameter, the expansion will increase gradually with the in-growth of [234]UO_2 in the solid solution at a rate of $\Delta a = +0.00045$ Å/year [10]. In the case of the sodalite phase, a unit-cell expansion with time response similar to PuO_2 is possibly observed (also shown in Figure 3). This expansion of approximately 0.1% is questioned, however, considering the small quantity of Pu in that phase, as determined by microscopy, and the greater uncertainty in the sodalite lattice parameter measurement.

Density Measurements

The density of a [238]Pu-loaded CWF sample has remained unchanged during the testing period to date. The density of the [238]Pu-loaded CWF, as determined by immersion in water, is 2.42 ± 0.01 g/cm^3. This density compares to an average density of 2.35 ± 0.02 g/cm^3 for non-Pu CWF HIP material. The higher density of the [238]Pu-loaded CWF is attributed to the high Pu loading in the sample. Increase in density of the sample provides the most direct evidence of

volume expansion due to α-decay damage, yet as mentioned none has been observed at the dose level of 5×10^{17} α-decays/gram of material.
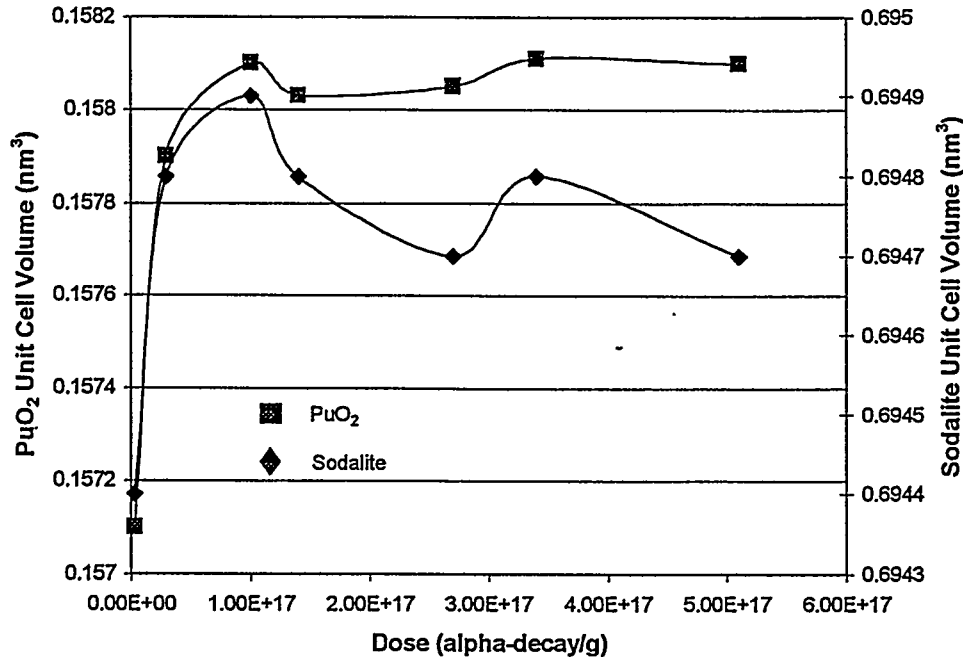

Figure 2. Unit cell volume change over time of PuO_2 (a) and (b) sodalite in CWF.

Durability Testing

Short-term, PCT-A durability tests performed on the ^{238}Pu-loaded CWF, and the results are shown in Table 4. The PCT is used to evaluate any changes in the dissolution behavior of the CWF with time as a result of α-decay damage. These results from the first PCT, determined shortly after the material was produced, indicate that the ^{238}Pu-loaded CWF degrades in a manner similar the reference (non-Pu loaded) CWF and other high level waste forms for the elements measured [11, 12]. The exception to this is the greater than expected release of Cs from the ^{238}Pu-loaded waste form, for which no current explanation exists. Two more PCT analyses will be performed on similar material that was produced at the same time as the material tested in Table 4 to determine degradation in durability after increased dose accumulation.

Table 4. Normalized elemental release in g/m^2 from a PCT (7-day) leachate solution of Pu-238 loaded CWF. The normalized release is the average value of triplicate tests. Also shown are the uncertainties associated with instrumental analysis.

Element	Normalized Release (g/m^2)	Relative Uncertainty $(\pm 1\sigma)$ (percent)	Element	Normalized Release (g/m^2)	Relative Uncertainty $(\pm 1\sigma)$ (percent)
Li	0.439	10	Al	0.035	10
K	0.090	80	Ce	0.001	30
Rb	0.165	10	Nd	0.001	20
Cs	0.148	10	Pu-238	0.001	25
Sr	0.016	40	Cl	0.376	10
Ba	0.009	25	Br	1.79	70
B	0.228	10			

CONCLUSIONS

The results of the first year of cumulated alpha-decay damage to the CWF indicate no microscopic or macroscopic alteration to the waste form as a whole. Only the PuO_2 phase has shown the expected unit cell volume increase resulting from lattice defects induced by alpha decay. The sodalite unit cell may also be expanding, but to much less extent than the PuO_2 phase. Because Pu is primarily concentrated to the intergranular glassy regions, the majority of decay damage is expected to occur locally in these regions. Due to the concentration of Pu in the radiation damage resistant PuO_2 fluorite structure, very little α-decay damage to the waste form as a whole is expected. The one exception to this may be the formation and accumulation of He bubbles resulting from alpha decay. Bubble formation would most likely accumulate in the intergranular regions as well and may be a source for swelling. The greatest magnification of such swelling may be in an increase of elemental release rates (decrease material durability) observed during leach testing. Interim results from bulk density measurements, which have remained constant, and waste form durability, which has performed similar to the reference CWF, indicate no adverse effects of alpha radiation damage to the waste form at an α-decay dose of 5×10^{17} decays/gram of material.

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