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EFFECTS OF ALPHA DECAY DAMAGE ON THE STRUCTURE AND LEACHING RATES OF A GLASS-BONDED CERAMIC HIGH LEVEL WASTE FORM

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Argonne National Laboratory has developed a glass-bonded sodalite ceramic waste form to immobilize fission products and plutonium that accumulate during the electrometallurgical conditioning of spent nuclear fuel. To investigate the effects of alpha decay damage on the structure and leaching characteristics of the ceramic material, ^{238}Pu has been incorporated into the ceramic waste form. The ^{238}Pu, with its higher specific activity, significantly increases the rate of alpha damage to the waste form. Long term studies have begun with periodic examination of the ^{238}Pu loaded ceramic material. A number of characterization techniques are used to study the alpha decay damage on the structure of the waste form. In addition, PCT type leachate studies will be performed to determine the effect of alpha decay damage on the durability of the ceramic waste form. Preliminary results from this study are presented.

INTRODUCTION

High level nuclear waste (HLW) that contains sufficient quantities of actinides undergoes various degrees of alpha radiation damage to the matrix material. This damage results from dissipation of energy from both the alpha particle and the recoil nucleus that emitted the alpha particle. The alpha particle, with an approximate energy of 5 MeV and a typical range of 20 μm, imparts its energy to the surrounding matrix by both electronic excitation and direct elastic collision. The recoiled nucleus, with energies of approximately 85 keV and ranges of only tens of nanometers, disrupts the greatest number of neighboring atoms primarily by elastic collisions. For the alpha decay of ^{239}Pu in a crystalline matrix, the ejected alpha particle may dislocate hundreds of matrix atoms by the end of its track. The recoiled ^{235}U nucleus may displace over 1000 local atoms, depending on the materials atomic density. Over the expected lifetime of a geological repository, HLW forms containing large amounts of actinides would accumulate significant structural damage that may adversely influence the materials performance. To investigate the α radiation effects on potential waste form materials, accelerated α damage studies are conducted by incorporating a high activity radionuclide such as ^{238}Pu (274 times the activity of ^{239}Pu) or ^{244}Cm into the material of interest [1,2]. Another method is to irradiate the material with heavy ions or He ions [3]. One may also study geological specimens that contain actinides [4]. Alpha-decay studies of crystalline materials or glass materials containing actinide host crystalline phases revel that the crystalline material may become amorphous due to accumulation of dislocated matrix atoms [5,6]. Amorphization of crystalline phases leads to lattice 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 [7]. 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. For the most current review on effects of α-decay damage, see reference 8.

Argonne National Laboratory has developed a durable ceramic waste form (CWF) to immobilize alkali, alkaline earth, rare earth and halide fission products and transuranics that accumulate during the electrometallurgical processing of spent nuclear fuel. Accelerated α-decay studies have been initiated to study the effects of alpha decay on the ceramic waste form.

The electrometallurgical spent fuel treatment process was developed to condition specific types of Department of Energy (DOE) spent nuclear fuel that are not suitable for direct disposal in a geological repository. The electrometallurgical process uses an electrorefiner containing a eutectic molten salt to desolve the fuel. Currently, Argonne National Laboratory is processing spent EBR-II sodium bonded metallic fuel at Argonne's facility in Idaho [9]. The electrometallurgical process produces, in addition to the CWF, a pure uranium product, and a metallic waste form containing the cladding material and metallic fission products that are non-reactive in the electrorefiner (Tc, Ru, Rh, Nb, Pd, Ag, Zr and Te). The active fission products and transuranics that accumulate during fuel conditioning are removed from the eutectic salt by mixing the salt with a zeolite material. The CWF is produced by mixing salt-occluded zeolite with a glass binder and processing the mixture at high temperatures and pressures using a hot isostatic press (HIP). During the HIPing process the zeolite is converted, in-situ, to the mineral phase sodalite to form a compacted, glass encapsulated CWF [10]. The resulting ceramic is durable and has a leach resistance far superior to Savannah River Environmental Assessment (EA) borosilicate glass and comparable to Savannah River High Level Waste glass for matrix elements [11]. This paper describes the production of the ^{238}Pu loaded CWF, the characterization methods and preliminary results for both ^{238}Pu and ^{239}Pu CWF materials.

PRODUCTION OF THE ^{238}Pu LOADED CERAMIC WASTE FORM

Formation of the ^{238}Pu loaded CWF used in the accelerated alpha damage study was performed using a hot uniaxial press (HUP) inside an argon-atmosphere glove box. To mimic conditions in the electrorefiner, 0.8 g of metallic ^{238}Pu were oxidized to the chloride form by adding the Pu to the eutectic salt and mixing at 773K in an alumina crucible. The eutectic salt composed of approximately 70:30 mole % LiCl:KCl was spiked with surrogate fission products to simulate the dissolution of 70 driver fuel assemblies. The fission product surrogate salt contains KBr, KI and the chlorides of Rb, Sr, Y, Cs, Ba, La, Ce, Pr, Nd, Sm and Eu. Iron chloride was also added to the Pu/salt mixture to act as an oxidant for the Pu. To ensure that the $FeCl_2$ oxidizing agent was entirely consumed a small amount of metallic ^{239}Pu was added to the salt and equilibrated at 773K for a short time to fully react with any residual iron chloride. After Pu conversion to $PuCl_3$ and thorough mixing with the salt, reduced Fe was magnetically removed from the salt. The final Pu loading in the salt was approximately 25 wt%. The next step in the process was to hot mix, at 773K, the Pu loaded salt with dried zeolite 4A (UOP, Houston TX). Finally, a commercial glass binder (Bayer, Baltimore, MD) was mixed with the zeolite and the mixture processed in the hot uniaxial press at a temperature of 1023K and pressure of 34 Mpa during which the zeolite converts to sodalite. The weight percent of each component in the pre-processed mixture is listed in Table I. The final HUP pellet has a diameter of 1.3 cm with the height, approximately 1cm, being dependent on the quantity of zeolite/glass added.

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

Component	LiCl/KCl Eutectic Salt	Fission Product Surrogate Salt	Zeolite 4A	Glass binder	Elemental ^{238}Pu
Weight %	6.1	1.7	64.7	25.0	2.5

CHARACTERIZATION OF THE ^{238}Pu LOADED CERAMIC WASTE FORM

Several analytical methods will be used to study the extent of α-decay damage on the CWF. These include:

1) Powder x-ray diffraction (XRD) which is used to monitor bulk phase composition and

changes to major phase lattice parameters. The XRD analysis involved powdering the ^{238}Pu-loaded HUP pellet and sieving through a 125 μm screen. A LaB_6 (NIST SRM 660) internal standard was also added to the powder (2wt %) to aid in lattice parameter determination. The powder was applied to a zero background slide and placed into a containment chamber. The analysis was performed with Cu K_α radiation with a scan rate of 0.5°/minute.

2) Density measurements on the CWF are performed by the immersion method using water. Density measurements will provide information on macroscopic swelling as a function of cumulated dose.

3) Microstructure data will be provided by scanning electron microscopy (SEM) using a Zeiss DSM 960A instrument and energy dispersive spectroscopy (EDS) (Oxford Instruments, UK). Transmission electron microscopy (TEM) with electron diffraction and EDS will also be used for much greater resolution.

4) Chemical durability of the CWF, as a function of α-decay cumulative dose will be determined by a PCT-A leach test [12]. The tests are conducted using a powdered material with a –100 to +200 mesh size fraction, DI water for the leachant with a surface area to volume ratio of 2000 m^{-1}. To date, leachate from both non-Pu and ^{239}Pu HUP pellets have been analyzed. Elemental determination was by ICP-OES. Plutonium analysis was performed by alpha counting. The pH and chloride release was also measured.

5) Thermal methods will be applied to the CWF. These include differential thermal analysis (DTA) which measures stored energy due to α-damage and phase transformations. Thermal expansion of the CWF will be determined by thermomechanical analysis (TMA).

The testing schedule will be periodic and is planned for minimum of 4 years (1462 days) is summarized in Table II. Currently, 7 grams of ^{238}Pu loaded waste-form material have been prepared and half-dozen HUP pellets have been produced. The facilities were microstructure, thermal analysis and leach testing are to be performed will shortly accept the produced HUP pellets. XRD measurements have been performed on the first pellet. Other data presented here includes analyses of ^{239}Pu loaded HUP pellets.

Table II. Testing schedule and corresponding alpha decay dose rate for ^{238}Pu HUP pellets.

Testing Schedule (days)	Initial	273	365	548	731	913	1096	1279	1462
Dose (α decays/ gram)	1.4E15	3.8E17	5.1E17	7.6E17	1.0E18	1.3E18	1.5E18	1.8E18	2.0E18
Test	XRD Density SEM TEM PCT DTA TMA	XRD Density SEM	XRD Density SEM TEM	XRD Density SEM	XRD Density SEM TEM PCT DTA TMA	XRD Density SEM	XRD Density SEM	XRD Density SEM	XRD Density SEM TEM PCT DTA TMA

RESULTS AND DISCUSSION

As mention above, a hot uniaxial press was used to process the ^{238}Pu CWF instead of the hot isostatic press used in the electrometallurgical demonstration project. Previous comparisons of the HIP and HUP products by XRD, SEM, density, and leach testing confirmed that both products were similar with only a slight increase in porosity of the HUP product.

X-Ray Diffraction

XRD analysis was performed on the first ^{238}Pu loaded HUP pellet to confirm that the operation had produced the desired CWF. Figure 1 is an overlay plot showing the XRD patterns for the CWF, the salt-occluded zeolite, and the $PuCl_3$/eutectic salt mixture. The bottom pattern in Figure 1 matches patterns for K_2PuCl_5, and LiCl and KCl the eutectic salt components. The pattern illustrates that the metallic Pu has been oxidized to the chloride form with no indication of PuO_2, Pu metal or any forms of the Fe oxidant. The middle pattern of Figure 1 contains the zeolite A pattern shifted to low d spacing due to lattice contraction by the occluded salt, and PuO_2. The pattern shows no indication of the chloride species. Clearly, a portion of the $PuCl_3$ has converted to a distinct oxide phase during the hot mixing with the zeolite. It is assumed that Pu getters oxygen from residual moisture in the zeolite to form the more stable PuO_2 structure. Phases identified in the HUPed product (top pattern) includes sodalite, again shifted to low d spacing, PuO_2, and minor phases of nepheline ($NaAlSiO_4$) and halite (NaCl). As mentioned, HUPing of zeolite 4A at 1123K transforms the zeolite structure (S.G.: Fm3c) to sodalite, a stable feldspar material (S.G.: P43n) [13]. The measured lattice parameter for sodalite was 0.88581 nm giving a unit cell volume of 0.6951 nm^3. The lattice parameter for PuO_2 (S.G.: Fm3m) was 0.54047 nm and 0.1579 nm^3 for the unit cell volume. The non-crystalline content of the sample was measured to be 22 percent, which corresponds to the target quantity of glass binder added.

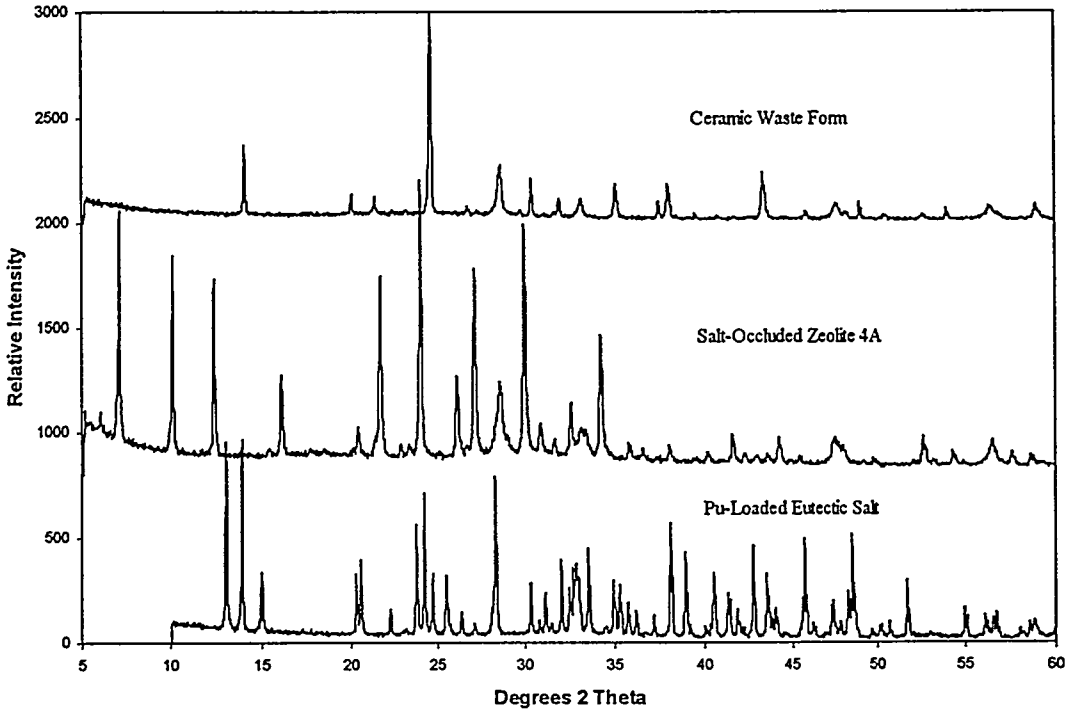

Figure 1. X-ray diffraction overlay plot of (bottom) the LiCl/KCl eutectic salt loaded with 30 wt% ^{238}Pu. The middle pattern shows the salt-occluded zeolite and PuO_2 that forms during the mixing with zeolite. The top pattern shows the sodalite CWF, PuO_2 and minor phases of nepheline and halite.

Density

The density of a ^{239}Pu loaded HUP pellet was determined by immersion in water. The density was determined to be 2.31 g/cm^3 which compares to an average density of 2.35 g/cm^3 for non-Pu CWF HIP material. Previous work with the leached (7-day PCT) powdered CWF determined that very little moisture uptake occurs. It is not expected, therefore, that the immersion test will influence the HUP pellet used for periodic testing.

Microstructure

The microstructure of a ^{239}Pu loaded HUP pellet is shown in Figure 2. In Fig 2a, the darker sodalite crystals are seen surrounded by the lighter colored glass binder. The bright contrast areas (magnified to 5000X in Fig. 2b) are identified as PuO_2 by EDS and are concentrated in the grain boundaries between sodalite crystals and the glass binder. The majority of the PuO_2 material appears to be insoluble in the glass binder or sodalite phases, although, EDS indicates a very minor presence of Pu in the sodalite. The glass, with a softening point of approximately 770K, could act as a solvent allowing the PuO_2 particles to migrate and agglomerate in the grain boundary regions.

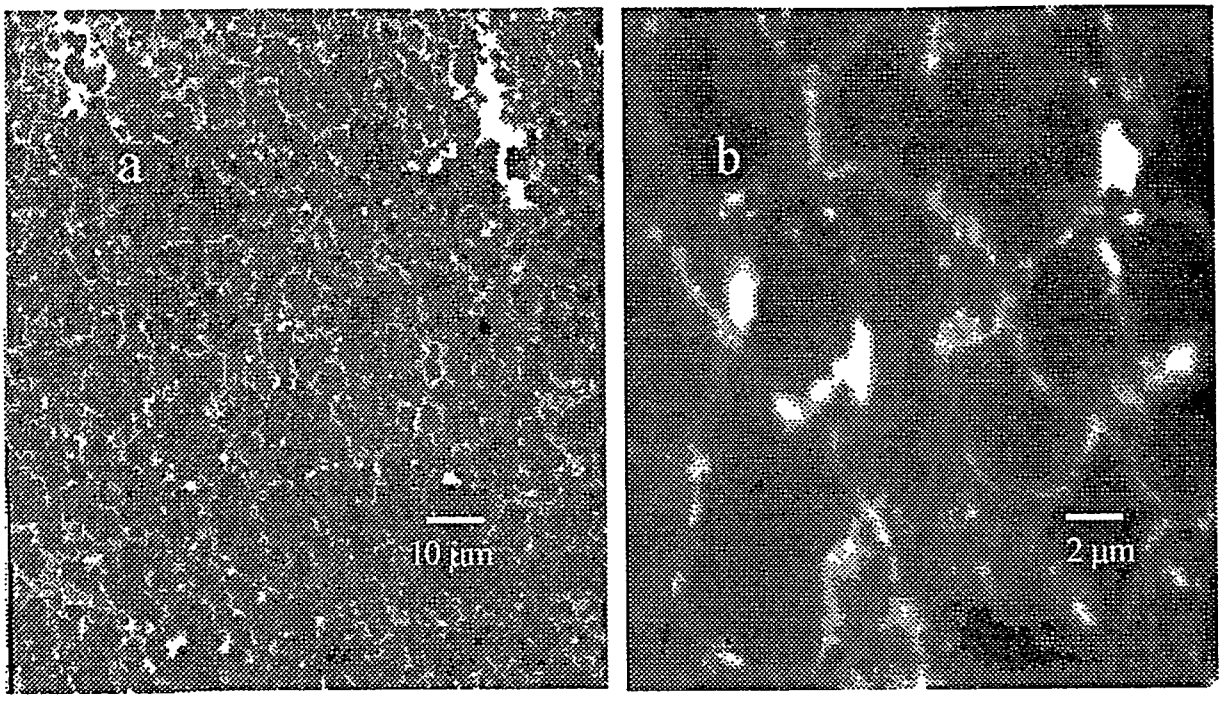

Figure 2. SEM backscatter image of the ^{239}Pu loaded CWF. Figure a) shows the larger zeolite crystals surrounded by the glass binder. The bright spots magnified in b) show the agglomerated PuO_2 regions in the glass grain boundaries between sodalite crystals.

Durability Testing

Short-term, PCT-A durability test performed on non-Pu loaded HUP products indicate that the CWF degrades in a manner similar the HIP CWF [14]. The normalized release rates (NRR) for the non-Pu loaded HUP pellets are shown in Table III and are quite low. A PCT-A test has also been performed on a ^{239}Pu loaded HUP pellet with a NRR of 0.007 g/m^2 day for Pu and 0.26 g/m^2 day for Cl. The NRR for the other elements featured in Table III are comparable for the ^{239}Pu-loaded sample.

Table III. Normalized elemental release rates (NRR) in g/m^2 day from a PCT (7-day) leachate solution of non-Pu loaded HUP pellets. Uncertainties associated with the triplicate measurements are 10% RSD or better. Less than values indicate normalized release rates below limit of quantification.

Li	Na	K	B	Al	Si	Cl	Cs
0.190	0.022	0.026	0.13	0.017	0.012	0.076	0.008

Rb	Sr	Y	Ba	La	Ce	Pr	Nd	Sm

0.032	<3E-4	<0.002	0.001	<0.008	<0.007	<0.040	<0.008	<0.050

CONCLUSION

Ceramic waste forms have been produced with ^{238}Pu loadings of approximately 2.5 wt%. Periodic testing will be performed on the CWF to measure the extent of α-decay damage on the material. The testing schedule will continue for a minimum of four years with a cumulative radiation dose of approximately 2.0×10^{18} α-decays/gram. Analyses include XRD, SEM, TEM density, chemical durability, and thermal measurements. XRD measurements have confirmed the presence of sodalite and PuO_2 in the ^{238}Pu-loaded CWF, and SEM analysis indicates PuO_2 concentrated in the grain boundaries between the sodalite crystals and glass binder. Leach testing of the ^{239}Pu-loaded CWF determined that the NRR for Pu was 0.007 g/m^2 day. Understanding the effects of α-decay damage on the performance of the CWF is of great importance in qualifying the waste form for acceptance into the Civilian Waste Management Repository program.

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