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by

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ABSTRACT

This paper will describe the preparation and progress of the effort at Argonne National Laboratory-West to produce ceramic waste forms loaded with $^{238}$Pu. The purpose of this study is to determine the extent of damage, if any, that alpha decay events will play over time to the ceramic waste form under development at Argonne. The ceramic waste form is glass-bonded sodalite. The sodalite is utilized to encapsulate the fission products and transuranics which are present in a chloride salt matrix which results from a spent fuel conditioning process. $^{238}$Pu possesses approximately 250 times the specific activity of $^{239}$Pu and thus allows for a much shorter time frame to address the issue. In preparation for production of $^{238}$Pu loaded waste forms $^{239}$Pu loaded samples were produced. Data is presented for samples produced with typical reactor grade plutonium. X-ray diffraction, scanning electron micrographs and durability test results will be presented. The ramifications for the production of the $^{238}$Pu loaded samples will be discussed.

INTRODUCTION

The treatment of spent fuel from the Experimental Breeder Reactor II (EBR-II) is taking place using electrometallurgical technology [1]. This technology involves the use of a molten salt electorefiner that separates the active fission products, i.e., Cs, Sr, Ba, Rb, and the transuranics, i.e., Pu, Np, Am, Cm, from the uranium and noble metal fission products when processing spent metallic alloy fuel. The active fission products and the transuranics remain in the salt which is a eutectic mixture of KCl and LiCl. Contacting the salt at elevated temperatures with zeolite 4A enables the capture and encapsulation of the salt with the fission products into the aluminosilicate framework of the zeolite [2].

The resulting zeolite is then mixed with a small amount of glass binder (25 wt%) and subjected to high pressure and temperature in a specially designed steel can [3]. This processing takes place in a Hot Isostatic Press (HIP). The typical processing conditions involve temperatures in the 873-1173 K (600-900 °C) range and pressures of 15-25 kPSI. The zeolite undergoes a phase transformation to sodalite. The production of samples for this study was accomplished using a simpler device, a Hot Uniaxial Press (HUP). The processing temperatures and pressures are very similar to those utilized in the HIP. Comparison of the products produced using the two devices indicates that they are very similar in phase composition and microstructure.

The purpose of this study is to document the effect of alpha decay events in a ceramic waste form. This is being accomplished using $^{238}$Pu to simulate 1000 years of alpha decay events in a four year study. A quantity of several dozen samples will be produced. The samples will be monitored periodically using a variety of techniques to assess the type and extent of damage that occurs. These techniques will include the following: X-ray diffraction, scanning electron microscopy, transmission electron microscopy, durability testing, differential thermal analysis and thermo mechanical analysis. This paper contains results from some of these methods and techniques.

The characterization and testing of several samples of ceramic waste form loaded with approximately 3 wt% $^{239}$Pu as preparatory step for the actual accelerated alpha damage study is presented here. The conclusions drawn from this examination will impact the $^{238}$Pu study soon to be started and the understanding of the actual high level waste form to be produced in the near future.
EXPERIMENTAL

I. Sample Production

Hot Uniaxial Press (HUP)

Eutectic salt (LiCl-KCl) containing approximately 25 wt.% PuCl₃ was produced by combining eutectic salt, metallic Pu, and FeCl₂ in an alumina crucible. The crucible contents were heated to 773 K (500 °C) and mixed at 25 RPM for 24 hours. After cooling, an ingot of material was removed from the crucible and ground to a fine powder in an electric mill. A laboratory magnet was utilized to remove metallic iron from the remaining salt. A greater than 90% efficiency of iron removal was achieved with magnetic separation.

The salt was contacted with zeolite 4A resulting in the capture and encapsulation of the salt into the aluminosilicate framework of the zeolite, as previously mentioned. Salt/zeolite contacting was completed in 24 hour increments at 773 K (500 °C), with mixing from 25 to 100 RPM. Salt/zeolite contacting was terminated when free salt was determined to be less than 0.05 wt.%. A total of 13.6 wt.% salt was added to the zeolite. Salt-contacted zeolite was then combined with 25 wt.% glass binder. The salt-loaded zeolite with glass binder comprises the composition of the ceramic waste form.

The production of samples for this study was accomplished using a hot uniaxial press (HUP). The HUP is essentially a pin and die assembly located within a furnace. The locally manufactured device utilized a graphite die with a 0.5 in (1.3 cm) bore. The die and pin were coated with boron nitride powder to allow retrieval of samples. An average sample was produced by loading 1-2 grams of material into the die, resulting in a pellet approximately 0.25-0.50 inches (0.65-1.3 cm) thick. A heating rate of 5 K/min. was used to increase the temperature of the samples to 1023 K (750 °C). At temperature, the pressure applied to the sample was maintained at 3.4E4 kPa (5060 psig) for 1-3 hours. The pressure was removed and the samples were allowed to cool naturally, achieving ambient temperatures in approximately six hours.

II. Characterization and Testing

A) X-ray Diffractometer (XRD)

The X-ray diffractometer used is a Scintag X1 Powder X-Ray diffractometer (Scintag Inc., CA) with a theta-theta goniometer. Cu K-alpha X-Ray tube with normal focus and top loading powder sample holder. A environmental chamber which allows for remote loading and containment was used in conjunction with a glovebox for analyzing the plutonium loaded waste form.

B) Scanning Electron Microscopy (SEM) with Energy Dispersive Spectroscopy (EDS)

The SEM work was performed with a Zeiss DSM 960A digital scanning electron microscope. The energy dispersive detector was provided by Oxford Instruments.

C) Durability Testing

The samples were subjected to a crushed leaching test. This was conducted in manner consistent with ASTM C1285-94, the Product Consistency Test (PCT) [4]. The test was conducted for 7 days at 363 K (90 °C) using a surface area to volume of leachant ratio of 2000 m⁻¹. The test material was the -100 to +200 mesh size fraction. The normalized release rate of plutonium was measured using alpha counting. The leach solutions were filtered and the solid material removed from the vessels prior to performing an acid strip of vessels using 1 M HF/6 M HNO₃ to remove any plutonium that had remained attached to the vessel walls. The pH and the chloride release were also measured. Additional elemental analyses are pending.

RESULTS

I. X-Ray Diffraction (XRD)

Figure 1 displays a series of three XRD patterns. Fig. 1A is the pattern of the initial salt used for contacting with the zeolite 4A. The Pu content is 26 wt%, as the element. The Pu compound identified is K₂PuCl₄. This is the common compound of Pu found in KCl/LiCl salt. The pattern shows no major contributions from PuO₂.

Fig. 1B is the salt contacted zeolite 4A. The salt at this point is fully captured within the zeolite cage. This statement is corroborated by the determination of the "free salt" present in this material. The free salt was less than 0.05 wt%. The free salt is determined by washing a known quantity of salt contacted zeolite with water and performing a chloride analysis on the solution. The presence of PuO₂ is very apparent at this point. No remaining K₂PuCl₄ pattern is observed and the PuO₂ pattern is clearly evident. The conversion of the plutonium to the oxide takes place in the salt contacting step. This is most likely a result of the reaction of the K₂PuCl₄ with the small amount of residual water present in the zeolite. The zeolite had been dried to a water
content of less than 0.3 wt% prior to being introduced into the glovebox, however, experience has shown that this material can extract moisture from the glovebox atmosphere.

Figure 1C is the pattern of the sample produced in the HUP. The presence of several phases is clearly shown with the most certain being: sodalite (major), plutonium oxide (major), sodium chloride (minor) and zeolite A (very minor). The very minor zeolite A pattern was shown to be an artifact of an incomplete conversion. This was remedied by increasing the HUP hold time from 1 hour to 2 hours in subsequent samples and this phase has since diminished in presence below detection limits.

II. Scanning Electron Microscopy

Figures 2 and 3 show the precursor material, the salt loaded zeolite, and the final product, respectively. It is important to consider both of these in conjunction with the XRD results presented in the last section to arrive at the most correct conclusions. Figure 2 is unremarkable in and of itself. It displays a variety of salt occluded zeolite pieces and agglomerates all of the same approximate composition. The apparent contrast in the micrograph image is attributable to the material and manner in which it is prepared for examination. The concentration of plutonium at this stage, prior to glass mixing, is 3.6 wt% as the element. No identifiable plutonium phases were detected, although, EDS results, not shown, clearly indicate that plutonium is present, presumably as the oxide (see the XRD results above). The material is most likely dispersed as very finely divided particles, i.e., much smaller than 1 micron.

Figure 3 displays two different magnifications of the sample after processing in the HUP, 1000X and 5000X. The glass fraction is 25 wt% with the remaining material being that which is featured in Fig. 2. The lighter contrasted phase, which is identified in Fig. 3B, is plutonium oxide. The other similar appearing phases in Fig. 3A were also identified as plutonium oxide. The size of these phases varies from a few microns to as large as 20 or 30 microns along their largest dimension. No such phases were identified in the precursor material (Fig. 2). The other phases present in Fig. 3 are identified as either sodalite or glass.

The PuO$_2$ phase appears to be insoluble in either of the matrix phases, sodalite or glass. The glassy phase would be the more fluidic phase at the processing conditions utilized. The softening point of this glass is approximately 773 K (500 °C). The glass could have acted as the solvent that would have allowed the PuO$_2$ particles to migrate and agglomerate into larger phases. This is a reasonable explanation based on the SEM, EDS and XRD results.

III. Durability Test Results

A short term durability test, the PCT, was performed on the material produced from the HUP. This was performed using the conventional methods as described above, see the experimental section. The normalized release rates for Pu and chloride and the pH are presented in Table I below.

Table I. Results from the 7 day PCT test. The test was performed in triplicate.

<table>
<thead>
<tr>
<th>Quantity Measured</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pu NRR (g/m$^2$day)</td>
<td>0.0066</td>
</tr>
<tr>
<td>Cl NRR (g/m$^2$day)</td>
<td>0.26</td>
</tr>
<tr>
<td>pH</td>
<td>8.9</td>
</tr>
</tbody>
</table>

The normalized leach rates for Pu are quite low. The chemical form of the plutonium in the waste form has been shown to be PuO$_2$. This has been shown to be an extremely leach-resistant form either surrounded by borosilicate glass [5] or in a pure phase compound with zirconium oxide or zirconium oxide/samarium oxide [6].

CONCLUSIONS

The preparation of the $^{239}$Pu loaded samples will commence in late Spring or early Summer of this year. Preliminary results from the characterization and testing of these samples will be presented at this conference. The $^{239}$Pu loaded results presented here illustrate several important points, however. First, the appropriate conditions to make the samples were determined.

Second, the chemical form and the morphology that the plutonium will take in the waste form have been identified. This second point has ramifications to the extent and localization of the radiation damage that should be expected. In particular, the high resolution microscopy work that will be performed to observe the radiation damage will be conducted via transmission electron microscopy (TEM). Great care will need to be used in preparing the samples so that the appropriate regions of interest are examined and the correct conclusions reached. TEM has been shown to be the most sensitive instrument in the detection of radiation damage in glasses and ceramics [7, 8], however its strength is its resolution and not its field of view.
The preliminary plutonium normalized release rates presented here appear to be very encouraging for the further development of the ceramic waste form.

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REFERENCES


Figure 1. Powder XRD patterns for: A) KCl/LiCl salt loaded with 26 wt% plutonium, B) a salt contacted zeolite 4A and C) a HUP processed ceramic waste form sample. Please text for details.
Figure 2. A back scattered electron image of the salt contacted zeolite.
Figure 3. Back scattered electron images of the HUP processed ceramic waste form. The magnification is noted in each image.