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Abstract

A sodalite/glass ceramic waste form has been developed to immobilize highly radioactive nuclear wastes in chloride form, as part of an electrochemical cleanup process. Simulated waste forms have been fabricated which contain plutonium and are representative of the salt from the electrometallurgical process to recover uranium from spent nuclear fuel. X-ray absorption fine structure spectroscopy (XAFS) and x-ray absorption near-edge spectroscopy (XANES) studies were performed to determine the location, oxidation state and form of the plutonium within these waste forms. Plutonium, in the non-fission-element case, was found to segregate as plutonium(IV) oxide with a crystallite size of at least 20 nm. With fission elements present, the crystallite size was about 2 nm. No plutonium was observed within the sodalite or glass in the waste form.

INTRODUCTION

Sodalite/glass composite waste forms are being developed at Argonne National Laboratory for disposal of radioactive fission elements in salt form from the electrometallurgical treatment of spent EBR-II nuclear reactor fuel[1,2]. The salt waste from the electrometallurgical process consists primarily of an LiCl/KCl eutectic salt loaded with various other fission-product chloride salts. In addition, this salt contains up to 2 mol % actinide chlorides, namely, uranium, plutonium and neptunium chlorides. The salt from the treatment process is sorbed by zeolite 4A, which has an aluminosilicate cage structure of nominal composition $Na_{12}(AlSiO_4)_{12}$ and is known for its ability to contain or "occlude" other species within the cage structure. The zeolite 4A, with its occluded fission-element salts, is mixed with glass and heated to high temperatures and pressures to convert the zeolite to a more thermodynamically stable sodalite form and consolidate the waste form. Primary considerations in this process are (1) questions of reactivity of the various salts with the zeolite structure as raised by thermodynamic calculations and (2) the fate of the fission elements in the resulting waste form. The objective of this work was to determine the fate of plutonium in this waste form via XAFS and XANES synchrotron techniques.[3,4] Other techniques such as tunneling electron microscopy (TEM) can show crystal structure in great detail but do not have the ability to see the plutonium within the sodalite cage structure. The XAFS technique provides a unique means of determining the local environment of the plutonium where other techniques are effectively blind and is capable of doing so *in situ*.

EXPERIMENTAL

Sample Preparation

The plutonium stock salt (36 wt% plutonium by assay) was produced by reacting plutonium metal in an LiCl/KCl eutectic salt (58 mol % LiCl, 42 mol % KCl) with a slightly substoichiometric amount of cadmium chloride. The mixture was heated to approximately 500 °C, then raised to 650 °C, sufficient to drive the reaction and distill off the resulting cadmium metal. For the case using plutonium chloride only, this stock salt was diluted with additional LiCl/KCl eutectic salt to produce a final salt that was 1.5 mol % plutonium. For the case involving the addition of simulated fission elements, the stock plutonium salt was diluted with a simulated fission-element salt (see Table 1 for composition) to produce a salt that was also 1.5 mol % plutonium. The stock plutonium salt and simulated fission-product salt were manufactured in an argon atmosphere glovebox with oxygen levels typically at 0.2-0.4 ppm, and water levels around 1 ppb.

Table 1. Simulated fission element salt composition prior to plutonium chloride addition.

Species	LiCl-KCl	NaCl	KBr	RbCl	SrCl3	YCl3	KI	CsCl
wt%	69.7958	14.9454	0.0231	0.3305	1.0121	0.7007	0.1542	2.5066
Species	BaCl2	LaCl3	CeCl3	PrCl3	NdCl3	SmCl3	EuCl3	
wt%	1.1982	1.2217	2.3303	1.1502	3.8969	0.6872	0.0470	

The simulated fission product salt was transported to the glovebox containing the plutonium stock salt in a hermetically sealed leak-checked vessel. The zeolite 4A powder was dried, assayed for water content (0.56 wt% by pyrolytic water weight loss) and transferred in a hermetically sealed, leak-checked vessel.

The final salts for each case were milled in a laboratory blade mill at 12,000 rpm three times at intervals of one minute, the salt powder decaked between intervals. The milled salt was then added to sufficient zeolite 4A to produce a blended mixture loaded to 3.8 chlorides per zeolite unit cell (typically 12 wt% of the total zeolite/salt mass). This loading was slightly below the theoretical maximum loading[3] of 4 chlorides per unit cell attainable by sodalite. The mixture was placed in an alumina crucible at 500 °C and mechanically stirred, the mixture decaked at 1.5 hour intervals. The blended zeolite/salt mixture was examined via x-ray diffraction (XRD) techniques and found to display a clean zeolite 4A pattern with small traces of LiCl and PuO_2 visible as well.

The zeolite/salt mixture was mixed with glass powder in a 3:1 ratio to make a 4 g sample for pressing. The 4 g powder sample was placed within a 1" I. D. graphite die and pressed using a uniaxial press to a cold starting pressure of 2500 psi. The press, inserted in the floor-mounted glovebox furnace well, was then heated at a rate of 1.4 °C/min. The pressure was increased on the die at a rate such that the pressure reached its limiting value of 8400 psi when the press temperature reached 650 °C. At this point, no further pressure was added. It was, in fact, allowed to freely decrease as the temperature climbed to the final value of 750 °C, chosen as the optimum point between speed of conversion to sodalite versus possible conversion to other more thermodynamically favorable products seen at higher temperatures. This protocol prevented the sample from becoming fluid enough to squeeze out between the die and piston walls. The sample was held at 750 °C for three hours and the furnace was then turned off to cool overnight. The press was removed from the furnace well and the sample extracted from the graphite die. XRD character-

ization of the resultant ceramic composite indicated a complete conversion to sodalite, with PuO_2 a small component.

Small bulk pieces of this material were then mounted using a styrene epoxy and covered with Kapton for containment and transported to the Materials Research Collaborative Access Team (MRCAT) insertion device beamline (Sector 10) at the Advanced Photon Source for XAFS/XANES analysis.   In the simulated fission salt case, half of the bulk ceramic pieces were kept in an anhydrous state, the remainder were allowed to absorb water from the atmosphere (~50% relative humidity) for 96 hours prior to sample mounting to observe any environmental water absorption effects upon the plutonium. The eutectic salt cases were kept in an anhydrous state.

XAFS/XANES Standards

Representative plutonium-containing standards were used in the course of this investigation. Each standard was prepared[4] to cover a particular plutonium oxidation state. The following standards were used: $Pu(III)F_3$, $Pu(IV)O_2$, $NaPu(V)O_2CO_3$ and $Ba_3Pu(VI)O_6$. The standards are all fine powders dispersed on Kapton tape and encapsulated in a styrene matrix. Since the actinide L edges are all at fairly high energy (>15 keV), the encapsulation matrix is essentially transparent.
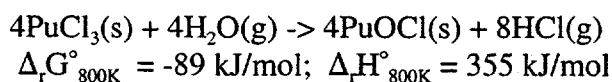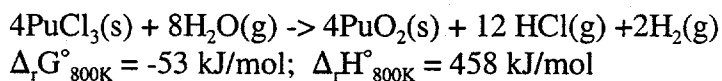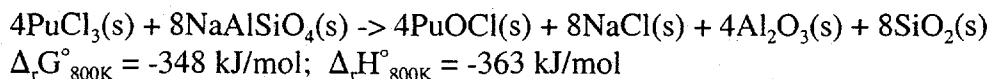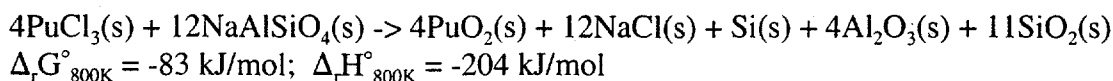
Synchrotron Characteristics

The APS synchrotron ring operates at 7 GeV, 50-100 mA. The undulator A magnet used at the MRCAT beamline was tapered and scanned. The monochromator is a cryogenic double Si(111) crystal in pseudo channel-cut mode, with a thin web first crystal. At the energies used in this experiment, the beam position is essentially fixed. Harmonic rejection was accomplished using an Rh coated mirror. Four detectors were used with the following characteristics: I_0 filled with 15% Ar/85% N_2, I_t filled with 15% Ar/85% N_2, I_f filled with argon gas and I_{ref} filled with nitrogen. The energy resolution of the system was ~4 eV at 18 keV with the resolution being estimated from a measurement of the rocking curve width and vertical slit size. The beam size was 1 mm H x 0.7 mm V.

RESULTS AND DISCUSSION

Thermodynamics

Of primary concern in this experiment is the fate of the plutonium. Thermodynamic calculations using $HSC^{5,6}$ indicate probable reaction paths at process temperature and, therefore, the likely species to be found in the experiment:

$4PuCl_3(s) + 8H_2O(g) \rightarrow 4PuO_2(s) + 12\ HCl(g) + 2H_2(g)$
$\Delta_r G°_{800K} = -53\ kJ/mol;\ \Delta_r H°_{800K} = 458\ kJ/mol$

$4PuCl_3(s) + 4H_2O(g) \rightarrow 4PuOCl(s) + 8HCl(g)$
$\Delta_r G°_{800K} = -89\ kJ/mol;\ \Delta_r H°_{800K} = 355\ kJ/mol$

$$4PuCl_3(s) + 12NaAlSiO_4(s) \rightarrow 4PuO_2(s) + 12NaCl(s) + Si(s) + 4Al_2O_3(s) + 11SiO_2(s)$$
$$\Delta_rG°_{800K} = -83 \text{ kJ/mol}; \quad \Delta_rH°_{800K} = -204 \text{ kJ/mol}$$

$$4PuCl_3(s) + 8NaAlSiO_4(s) \rightarrow 4PuOCl(s) + 8NaCl(s) + 4Al_2O_3(s) + 8SiO_2(s)$$
$$\Delta_rG°_{800K} = -348 \text{ kJ/mol}; \quad \Delta_rH°_{800K} = -363 \text{ kJ/mol}$$

These calculations are necessarily approximate because nepheline was used as a stand-in for zeolite 4A. In both cases, either the oxide or the oxychloride is predicted to be a likely reaction product, whether the pathway is from reaction with water present in the system or destructive attack of the zeolitic structure. XRD results do not display zeolite decomposition products, which may belie the accuracy of using nepheline as a zeolite substitute or indicate that kinetics play a prime role in this system.

XANES Results

XANES data is acquired to determine the plutonium oxidation state. Data were acquired for the $PuCl_3$/LiCl/KCl and found to be a good match to the Pu^{+4} oxidation state.[4] (See Figure 1.)
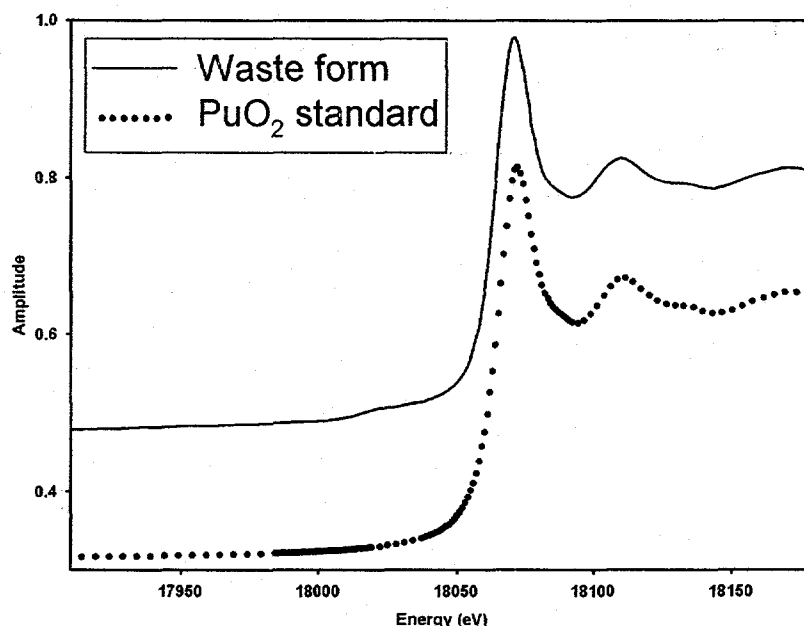
**Figure 1** XANES data for plutonium L_{III} edge in case using the plutonium bearing LiCl/KCl salt compared to Pu(IV) standard.

XAFS Results

XAFS data are acquired to determine the local environment of a particular element. Figure 2 displays the χ-space data for a number of representative datasets. It shows that all of the unknown cases match the plutonium(IV) oxide standard within experimental error. Given that the XRD work on the samples before XAFS analysis indicated the presence of PuO_2, this was not a complete surprise. However, further work with the Fourier transform (FT) of the χ-space data, combined with a line width analysis of the XRD patterns, indicated PuO_2 crystallite sizes that were incompatible

with placement in the sodalite cages, given the known cage free diameter dimension[7] of 6.2 Å. Similarly, the Fourier transform of the χ-space data (see Figure 3) clearly indicate the essentially
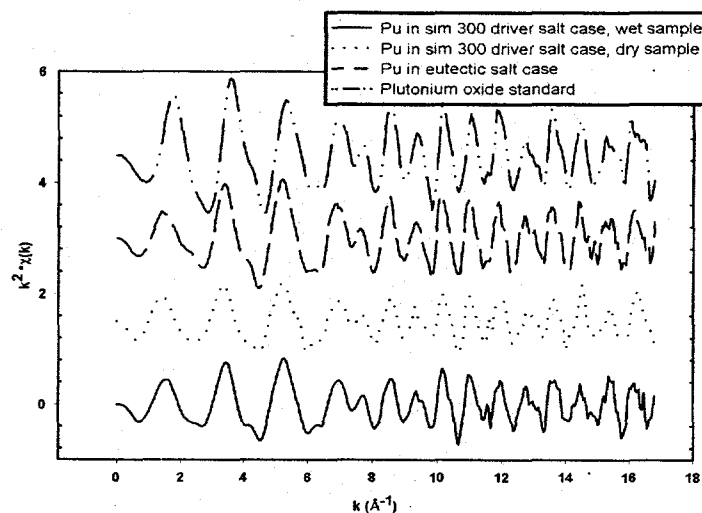
**Figure 2** Comparison of χ-space data for the various unknowns against the plutonium oxide standard.
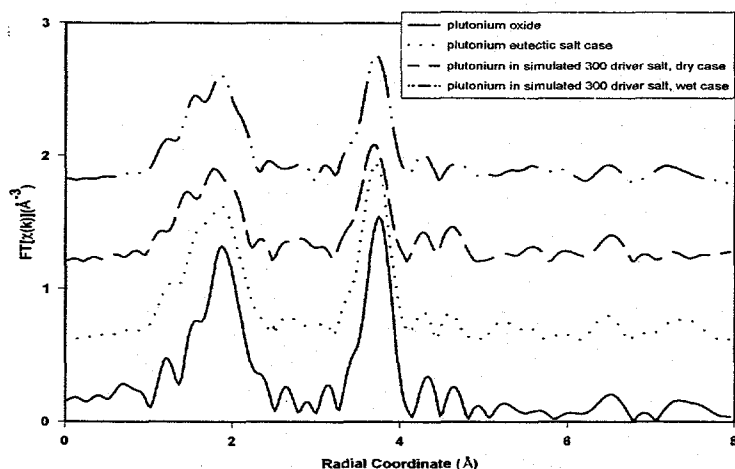
Figure 3 Comparison of radial shell data for the cases in figure 2 with the k-range = 3.3-15.5 Å, dk = 1 Å^{-1} and k^2 weighting.

identical character of all of the specimens. Comparisons to the other plutonium standards gave clear mismatches, either when viewed from a radial shell viewpoint or from a frequency viewpoint in the χ-space data. Further comparison to the experimental data sets was accomplished using known crystallographic data input to FEFF8. Verification of the performance of the various programs (FEFF8[8,9], FEFFIT[10]) was double-checked by inputting the known PuO_2 crystallographic data and comparing it against the experimental data; it was found to have an excellent fit (see Figure 4). Fitting the FT data through the second shell (see Figure 5) gave excellent agreement.
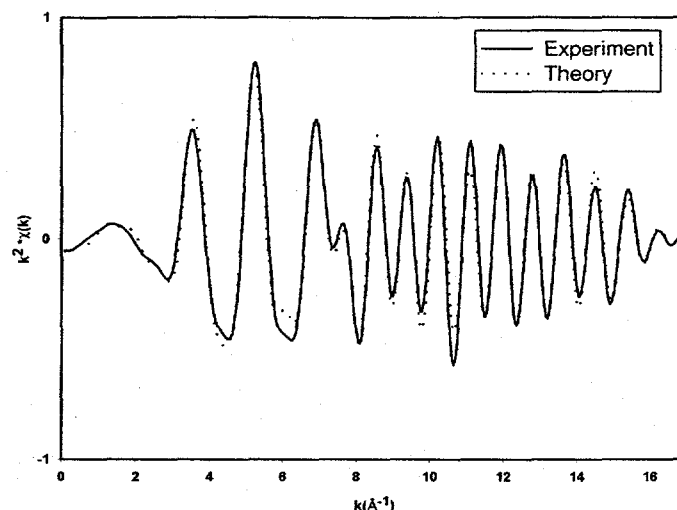
Figure 4 Comparison of fit to isolated 1st and 2nd shell data for the inverse transform isolated 1st and 2nd shells (3 shells used in fit) from the plutonium oxide standard.
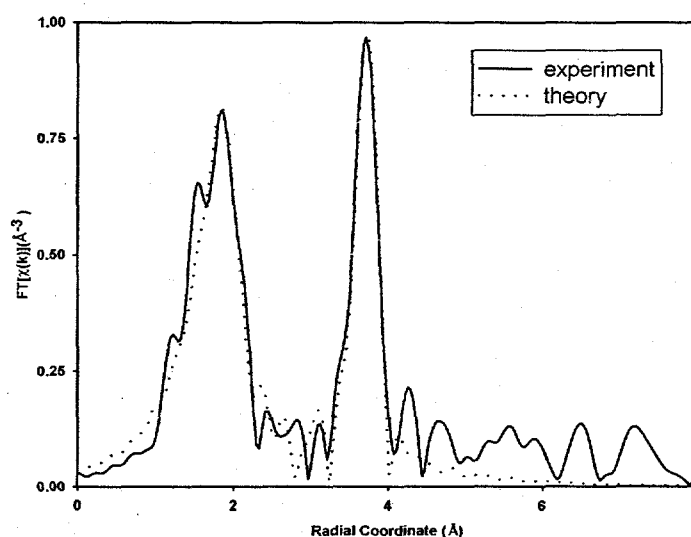
Figure 5 Comparison of fit to experimental Fourier transform data for the plutonium oxide standard using an r-range equal to 1.35-4.05 Å.

Other chemical species were considered using crystallographic data even with the essentially perfect match to the PuO_2 standard: PuO, Pu_2O_3, PuOCl, $PuCl_3$, K2PuCl5 and K_2PuCl_6. The first two species[11,12] yielded Pu-Pu distances that were completely discordant with the experimental data. PuOCl failed to yield a fit[11] that would reconcile the experimental radial shell amplitudes with the theoretical fit. The plutonium chloride[13] and potassium plutonium chloride[14-16] species also were a poor match to the experimental Pu-Pu distances.

Particulate Sizes

Comparison of the radial shell amplitude data of the simulated 300 driver salt cases, both wet and dry, against the PuO_2 standard indicated an average particle size compatible with a central plutonium surrounded, on average, by 7 plutonium nearest neighbors. A nominally filled 2nd shell consists of 12 plutonium atoms, which would give rise to 5.5 plutonium nearest-neighbors. This arrangement would give a particle size of about 13 Å, given the known Pu-Pu distance of 3.8 Å and the oxygen atoms which must surround the plutonium atoms to give charge balance. Given the previously discussed known sodalite cage free diameter of 6.2 Å, the plutonium oxide appears to be completely outside of the sodalite cage. Similar comparison of the plutonium-loaded eutectic-salt-only case yielded amplitudes that put the average crystallite size larger than that which could be determined by the XAFS technique. Comparing the PuO_2 lines determined crystallographically put the particulate size at 20 nm or possibly greater.

SUMMARY

XANES/XAFS techniques were used to determine the fate of plutonium within a sodalite/glass composite wasteform in two cases: where the plutonium was alone in an LiCl/KCl matrix and where simulated fission elements were added representative of the spent fuel electrometallurgical treatment process. The XANES data corresponded to the Pu^{+4} oxidation state data in Kropf et al.[4] The XAFS data clearly indicate the disposition of the plutonium as PuO_2 and with crystallite sizes that indicate the plutonium is outside of the sodalite cage structure. Comparing the hydrated and non-hydrated cases made with the plutonium-loaded simulated fission element salt show no changes in plutonium character.

ACKNOWLEDGEMENTS

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