PNNL-14232

Pacific Northwest
National Laboratory
Operated by Battelle for the
U.S. Department of Energy

Effects of Self Irradiation from ^{238}Pu on Candidate Ceramics for Plutonium Immobilization

D. M. Strachan
R. D. Scheele
A. E. Kozelisky
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Prepared for the U.S. Department of Energy
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PNNL-XXXXX

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Pacific Northwest National Laboratory
Richland, Washington

Summary

In this report, we summarize the information gathered at the Pacific Northwest National Laboratory (PNNL) on the effects of radiation damage to candidate titanate ceramics for the immobilization of weapons-ready plutonium. We cover the information gathered since the last report (Strachan *et al.* 2002) on the pyrochlore and pyrochlore-rich baseline specimens that had been resintered in April and May 2002.

Radiation damage to these ceramic materials is being investigated to provide data that were missed when we overestimated the amount of time it would take for radiation damage to render these materials amorphous. During the course of the decay of ^{239}Pu to ^{235}U in the repository or, in the case of these studies, the decay of ^{238}Pu to ^{234}U, the damage to the crystalline structure is expected to cause macroscopic swelling and eventual amorphization of the ceramic (loss of crystallinity). Although we are also determining the effect of radiation damage on the dissolution rate of the ceramic in water, the results from those studies will be reported in a separate report.

When we prepared the original radiation-damage specimens, the information in the literature led us to believe that we would not see significant damage until three or more years had passed. In our initial studies, we observed, however, that the pyrochlore mineral (ideally $CaUTi_2O_7$) in these specimens changed very rapidly and, by the time the first measurements were made (3 to 6 months), the crystallinity had degraded significantly (Strachan *et al.* 2000). Furthermore, some of the elemental dissolution rates for the ^{238}Pu-bearing ceramic were approximately 1000 times higher than the elemental dissolution rates for the companion ceramics made with ^{239}Pu. We were unsure whether the higher dissolution rate for the ^{238}Pu-bearing ceramic was due to more rapid radiation damage to the ceramic or if radiolysis of water caused the faster dissolution rate.

To obtain data missed because of the faster-than-expected radiation damage, we resintered selected pyrochlore and pyrochlore-rich baseline specimens at the original sintering temperature (1350°C) to re-establish the original crystalline phase assemblages. These resintered specimens allowed us to recover the swelling and crystal structural data that were missed during the first 6 to 12 months of radiation damage and to help identify the causes for increased dissolution rates for the more active ^{238}Pu-specimens.

The x-ray diffraction (XRD) analyses show that the changes in the lattice parameters for pyrochlore are essentially linear with time and dose [$4.8(1) \cdot 10^{-5}$ nm/d].[a] Although there should be no Pu in the rutile phase, there is a small but real change in the lattice parameters with increasing time. In large part, this change is probably due to the alpha irradiation from the surrounding pyrochlore.

For the pyrochlore-baseline material, similar to the pure phase pyrochlore, the XRD analyses show that the pyrochlore phase expands linearly with time and dose [$4.68(2) \cdot 10^{-5}$ nm/d]. The change in cell volume of the brannerite is much different than the changes for the pyrochlore and zirconolite phases. The a_0 and b_0 lattice parameters increase initially for the first 100 days after which the a_0 parameter decreases while

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[a] The value shown in ( ) is the uncertainty in the last place.

the b_0 parameter continues to increase. At this same time, brannerite begins to go amorphous. The angle in the zirconolite generally decreased, but not in a continuous manner.

In this testing, the “true” density (the density exclusive of the surface-connected porosity) of the ^{238}Pu-pyrochlore stored at 25°C (room temperature) decreased 6% while the ^{238}Pu-pyrochlore specimens stored at 250°C decreased 2%. The “true” density of the ^{238}Pu-pyrochlore-rich baseline stored at 25°C decreased 12% while the ^{238}Pu-pyrochlore-rich baseline ceramic stored at 250°C dropped 2%. Since the mass of the specimens is not changing, these decreases in “true” density of the pyrochlore and pyrochlore-rich ceramics indicate that the apparent volume of the specimens is increasing with radiation damage and that the damage is partially healed when the specimens are stored at 250°C. The “true” densities of the pyrochlore-rich baseline ceramic decrease more rapidly than the pyrochlore ceramic.

The results from the dimensional measurements also indicate that the ceramics expanded as they were exposed to internal α-irradiation over 250 days. The diameters of the individual ^{238}Pu-pyrochlore specimens stored at 25°C increased about 0.1 mm for the nominal 10-mm-diameter specimens or about 1% while the diameters of those stored at 250°C increased about 0.3%. In contrast to the “true” densities, the volume expansions of the specimens based on the expansion of the crystal unit cell and the bulk dimensions agreed within experimental error.

Our results from the physical-properties measurements suggest that the titanate waste form for the immobilization of weapons-ready Pu should perform well in the repository. During the first 100 years of storage, the ceramic should swell approximately 3%. There should be no microcracking, and the ceramic should remain intact.

Acronyms

DOE	U.S. Department of Energy
MIT	Massachusetts Institute of Technology
NNSA	National Nuclear Security Administration
PIP	Plutonium Immobilization Project
PNNL	Pacific Northwest National Laboratory
QA	quality assurance
SEM	scanning electron microscope
XRD	x-ray diffraction

Acknowledgements

The authors wish to thank Dr. William Weber (Pacific Northwest National Laboratory), Dr. Lynn Hobbs (Massachusetts Institute of Technology), and Dr. Gita Golcar for many helpful discussions on the effects of radiation damage. Dr. Todd Schaef is acknowledged for his many hours of maintaining the X-ray diffractometer. Mr. William Danker and Mr. Andre Cygelman at the U.S. Department of Energy/National Nuclear Security Administration have been very supportive of these studies over the past 5 years. Pacific Northwest National Laboratory is operated for the U.S. Department of Energy by Battelle under Contract DE-AC06-76RL01830.

Contents

Figures

1.0 Introduction

In this report, we summarize the information gathered at the Pacific Northwest National Laboratory (PNNL) on the effects of radiation damage to candidate titanate ceramics for the immobilization of weapons-ready plutonium. We cover the information gathered since the last report (Strachan *et al.* 2002) on the specimens that had been resintered in April and May 2002. Radiation damage to these ceramic materials is being investigated to provide data that were missed when we overestimated the amount of time it would take for radiation damage to render these materials amorphous. During the course of the decay of ^{239}Pu to ^{235}U in the repository or, in the case of these studies, the decay of ^{238}Pu to ^{234}U, the damage to the crystalline structure is expected to cause macroscopic swelling and eventual amorphization of the ceramic. Although we are also determining the effect of radiation damage on the dissolution rate of the ceramic in water, the results from those studies will be reported in a separate document.

When we prepared the original radiation-damage specimens, the information in the literature led us to believe that we would see significant damage after three or more years had passed. We observed, however, that the pyrochlore mineral (ideally $CaUTi_2O_7$) in these specimens changed very rapidly and, by the time the first measurements were made, the crystallinity had degraded significantly (Strachan *et al.* 2000). Furthermore, some of the elemental dissolution rates for the ^{238}Pu-bearing ceramic were approximately 1000 times higher than the elemental dissolution rates for the companion ceramics made with ^{239}Pu.

To obtain data missed because of the faster-than-expected radiation damage, we resintered selected ^{238}Pu-bearing pyrochlore and pyrochlore-rich baseline specimens at the original sintering temperature (1350°C) to re-establish the original crystalline phase assemblages. These resintered specimens allowed us to recover the swelling and crystal structural data that were missed during the first 6 to 12 months of radiation damage and to help identify the causes for increased dissolution rates for the more active ^{238}Pu-specimens.

In this report, we refer the reader to our earlier reports for the specifics on storage, testing, and characterization (Strachan *et al.* 2001a; Strachan *et al.* 2001b; Strachan *et al.* 2002). In this report, we present and discuss the results from the size, density, and crystallographic measurements.

1.1 Quality Assurance Program

The information summarized in this and earlier reports was gathered by the PNNL Plutonium Immobilization Project (PIP). Scientific investigations were performed in accordance with technical implementing documents and the Plutonium Immobilization Project Quality Assurance (QA) Program Description, ETD-019, latest revision. The PIP staff members were trained and qualified to perform these scientific investigations and analytical methods described in the following sections. Quality Assurance oversight was provided by PNNL QA personnel (surveillances) as well as the client QA organization (annual audits). The PIP QA program was evaluated by the client and determined to be compliant with the *Quality Assurance Requirements and Description*, DOE Office of Civilian Radioactive Waste Management (DOE/RW-0333P).

2.0 X-Ray Diffraction Results

The discussion below pertains to the results from the x-ray diffraction (XRD) studies that have been performed on the resintered specimens. There are two sections, one dealing with the diffraction patterns as a whole and one dealing with the effects of radiation damage on the lattice parameters. There are fewer data from the analysis of the lattice parameters than we have diffraction patterns due to a December 2002 failure of the computer used for analyzing the patterns.

2.1 Diffraction Patterns

The diffraction patterns for the resintered ^{238}Pu-bearing specimens have been obtained from the same specimen and the same specimen surface starting as early as 2 days after the specimen was resintered. In August 2002, the x-ray tube in the diffractometer had to be replaced. When this was done, the intensity of the x-ray beam increased. Using the patterns from the alumina (Al_2O_3) Standard Reference Material (SRM 1976) from the National Institute of Standards and Industry, we were able to document the change in intensity because a pattern from this SRM is obtained at the start or end of the day on which specimens are analyzed. The intensity increased by a factor of 3 with the new tube relative to the old tube at the end of its life. The intensities of the diffraction peaks have been corrected in the following figures.

2.1.1 Pyrochlore Specimens

Because of differences in the phase assemblage between the ^{238}Pu-pyrochlore specimens originally stored at 250°C and those stored at room temperature and 125°C, we monitored the changes in two resintered pyrochlore specimens stored at room temperature with XRD. One of these specimens had originally been stored at 25°C[a] (8P19-6) for 930 days and the other at 250°C (8P20-6) for 1070 days previous to being resintered. After resintering, these specimens were stored at the same temperatures as before resintering.

A graph of the XRD scans from 8P19-5 is shown in Figure 2.1. From this series, one can see qualitatively the change in lattice parameters that take place in the pyrochlore unit cell as the diffraction peaks shift to lower diffraction angles. The intensity of the peaks decreases by about a factor of 6 over the span of 256 days, and the peaks become broader. These changes occur as the damage to the long-range crystallinity of the solid is destroyed from the alpha particles that are emitted from the decaying ^{238}Pu and the subsequent recoil of the decaying atom. It is the recoiling ^{234}U that causes the most damage; approximately 1000 bonds are destroyed by each recoiling atom (Weber *et al.* 1998). There is a small amount of rutile (TiO_2) or hafnium-rutile [$(Hf, Ti)O_2$] present in this specimen as evidenced by the diffraction peaks at about 27.5° and 36° 2θ, which remain essentially unaffected by the radiation (Ebbinghaus *et al.* 1999). Any damage that occurs to this phase is probably from the alpha particles that come from the surrounding pyrochlore phase. There is a single diffraction peak at approximately 32° 2θ that is consistent with a zirconolite. However, it occurs only in the first diffraction pattern. If it were a true phase in this specimen, the diffraction peak would gradually decrease with time and dose, not disappear after 3 days.

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[a] In this document, "room temperature" and "25°C" are used interchangeably.

During the initial damage of the pyrochlore that had been stored at 250°C, we noted an extra diffraction peak that suggested the presence of a zirconolite (Strachan *et al.* 2002). After sintering these specimens, we noted that the diffraction pattern had changed significantly to one that suggested the presence of pyrochlore and up to two zirconolites, each with different lattice parameters, in particular a larger c_0 dimension (see Section 2.1.1). Although the pattern for 8P20-6 was identical to that of 8P19-5 when the specimens were made in 1999, the resintered material appears quite different (Figure 2.2). We suggest that this is a result of radiation damage at 250°C at which temperature some diffusion is possible with a concomitant phase separation. Locally, the constituents are consistent with a different phase assemblage than the pure pyrochlore in the original specimen. Resintering at 1350°C for 2 h provided enough energy for the new phases to form consistent with the local chemistry, but insufficient for enough diffusion to take place to make the original pyrochlore phase. As with 8P19-5, the diffraction peaks in the XRD pattern for 8P20-6 shift to lower angles and become broader and less intense, decreasing by about a factor of 4 over 246 days of exposure.

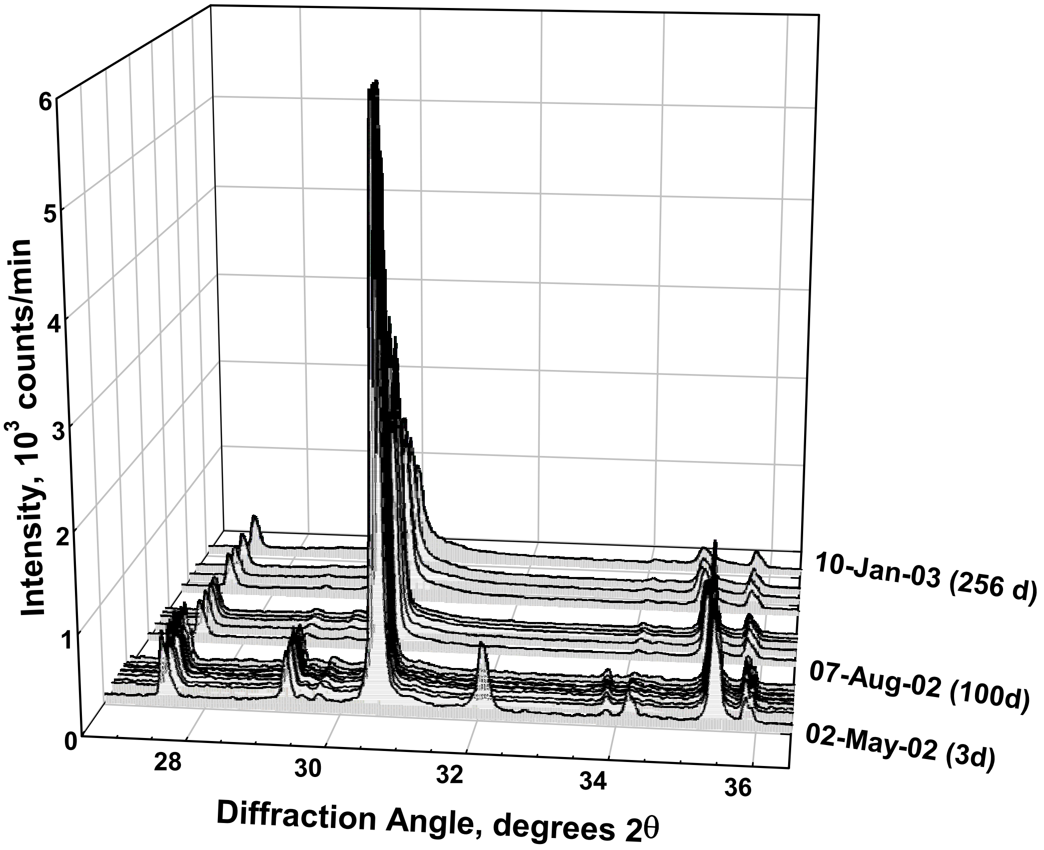

Figure 2.1. A Series of XRD Patterns from ^{238}Pu-Bearing Pyrochlore Showing the Progress of Radiation Damage in Specimen 8P19-5 Stored at 25°C

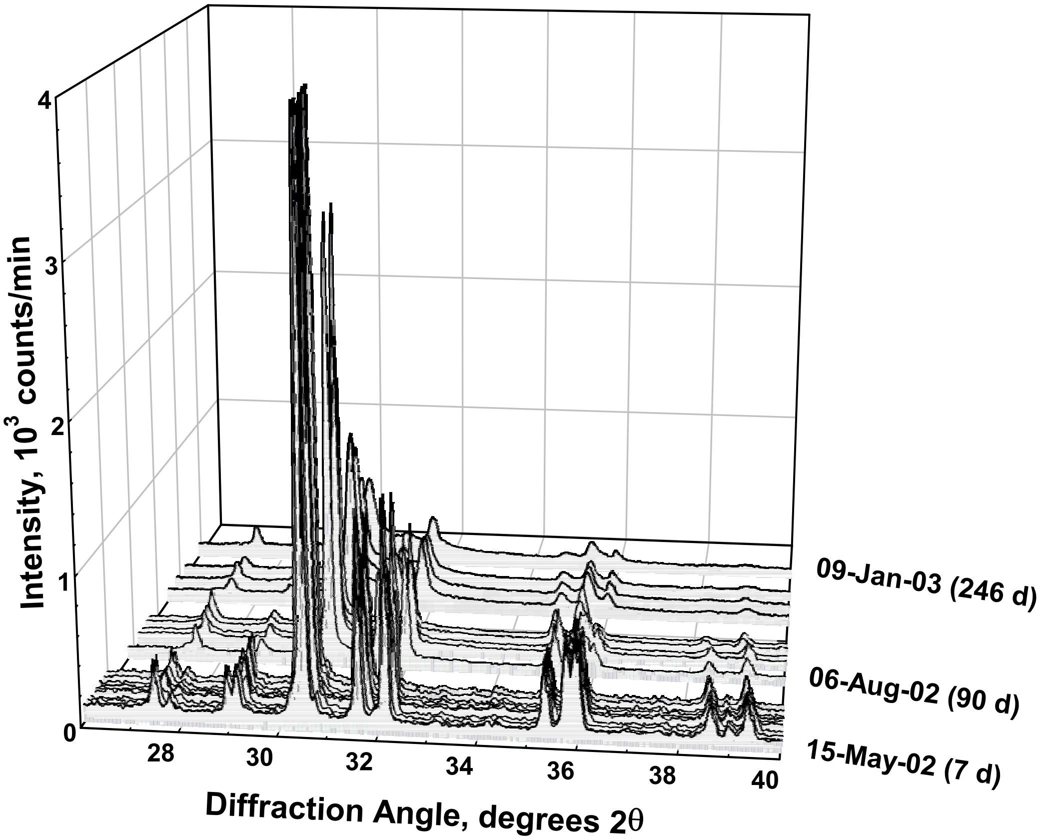

Figure 2.2. A Graph Showing the Progress of Radiation Damage in ^{238}Pu-Bearing Pyrochlore in Specimen 8P20-6 that Had Been Stored at 250°C and Currently Stored at 250°C

2.2 Pyrochlore-Baseline Specimens

The pyrochlore-baseline specimens consisted of four phases: rutile or Hf-rutile, pyrochlore, brannerite, and zirconolite. The two specimens held aside for x-ray diffraction analyses are 8PB1B-14 (25°C) and 8PB1B-3 (250°C). Before resintering, these specimens had been subjected to radiation damage at 125°C and room temperature, respectively, for 1070 days. As can be seen in Figure 2.3, brannerite (peaks at 26.7°, 29.2°, and 32.8°; there is also a peak lying under or near the main pyrochlore and zirconolite peaks at about 32.5° two theta) appears to be quite susceptible to radiation damage and is essentially rendered amorphous in 100 days. Essentially, the same rate of degradation occurs in brannerite at 250°C (Figure 2.4). The difference between the 8PB1B-14 and 8PB1B-3 is the lower rate at which the zirconolite is rendered amorphous in the 250°C-stored specimen (8PB1B-3) for which the main peaks decrease in intensity by a factor of 3 compared with a factor of 5 in the 25°C-stored specimen.

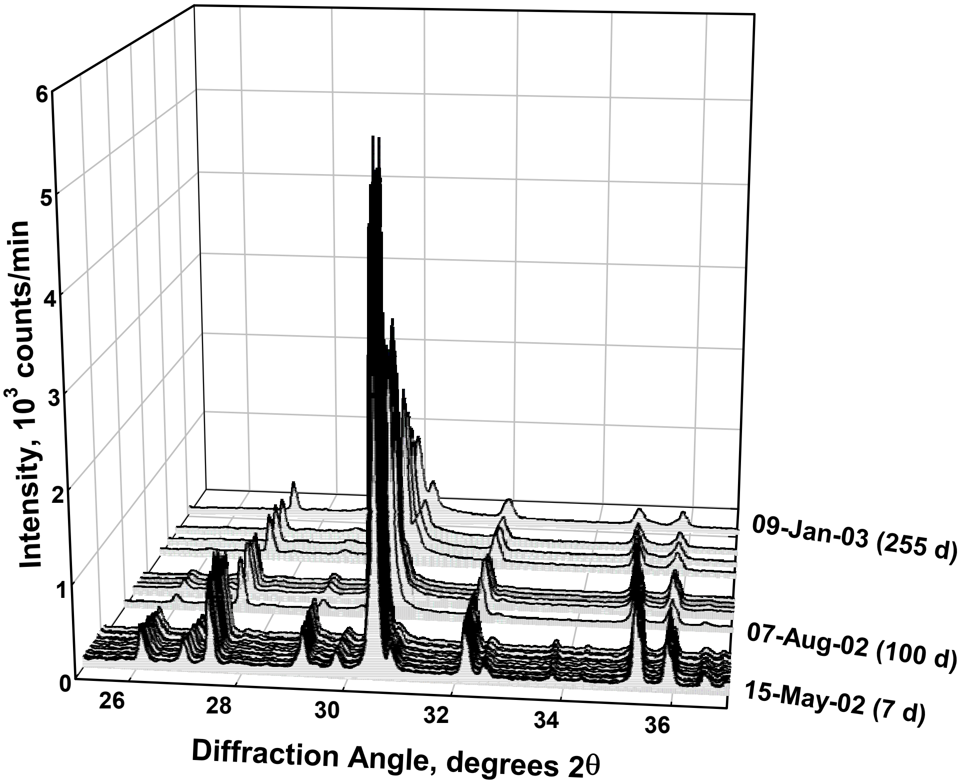

Figure 2.3. A Graph Showing the Progress of Radiation Damage in ^{238}Pu-Bearing Pyrochlore-Baseline Specimen 8PB1B-14 that Had Been Stored at 25°C

2.3 Unit Cell Parameters

Over the first 140 days before the computer crash, we were able to obtain refinements of the unit cell parameters from the XRD patterns discussed briefly in Section 2.1. Here, we discuss the changes in the unit cell parameters with increasing time and the corresponding alpha dose. One problem with calculating a dose as a function of time is that we do not have a quantitative measure of the amount of Pu in each phase where there is more than one phase. Other than rutile, each of the titanate phases contain ^{238}Pu and, therefore, becomes damaged as the ^{238}Pu decays. Nevertheless, we have shown the number of alpha decays per gram of ceramic specimen as one of the axes in the following graphs.

We determined the lattice parameters for the various phases with a Rietveld refinement of the powder pattern (RIQAS, MDI, Livermore, CA). Each of the data points in the following graphs have error bars that come from the errors associated with the Rietveld fit. Although one of the outputs from the program is the phase composition, we do not report it here because the correct atomic content of each phase is

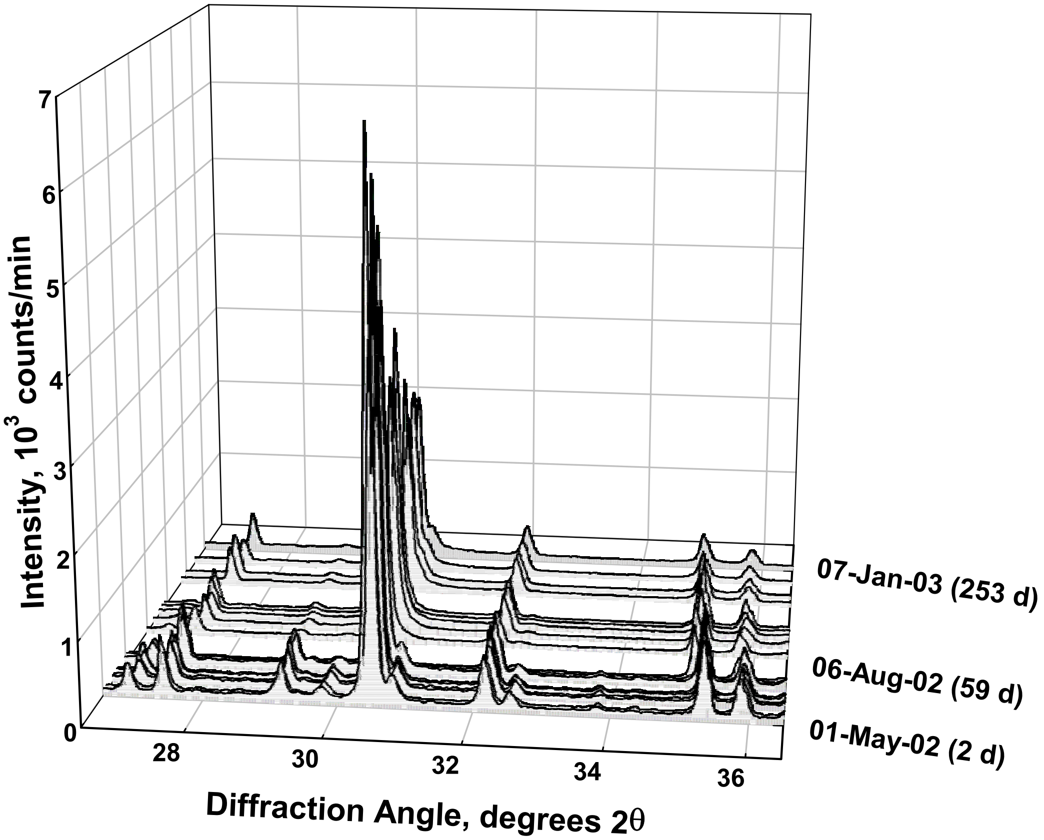

Figure 2.4. A Graph Showing the Progress of Radiation Damage in ^{238}Pu-Bearing Pyrochlore-Baseline Specimen 8PB1B-3 that Had Been Stored at 250°C

unknown, and the distribution of the atoms on the different sites within the structure is equally unknown. The unit cell dimensions are accurate at early time and become less accurate as the radiation damage shifts, diminishes, and broadens the peaks.

2.3.1 Lattice Parameters for the Phases in the Pyrochlore Ceramic Specimens

The specimen 8P19-5 (stored at room temperature) is composed of two phases, pyrochlore and rutile. The changes in the lattice parameters of these two phases are shown in Figure 2.5 and Figure 2.6. The changes in the lattice parameters for pyrochlore are essentially linear with time and dose [$4.8(1)\cdot10^{-5}$ nm/d],[a] which is what we reported in our last report (Strachan *et al.* 2002). As noted in our earlier discussion, the change in overall dimensions and density is not linear over the same time. Although Pu is not soluble in the rutile phase (Ebbinghaus *et al.* 1999), there is a small but real change in the rutile lattice parameters with increasing time. This change is likely a result of the alpha dose to rutile from the alphas emitted from the surrounding pyrochlore phase. Examination in a scanning electron microscope (SEM) is needed to confirm this result.

For the pyrochlore-based material that had previously been stored at 250°C (specimen 8P20-6), zirconolite had grown into the phase assemblage, and it had survived the resintering at

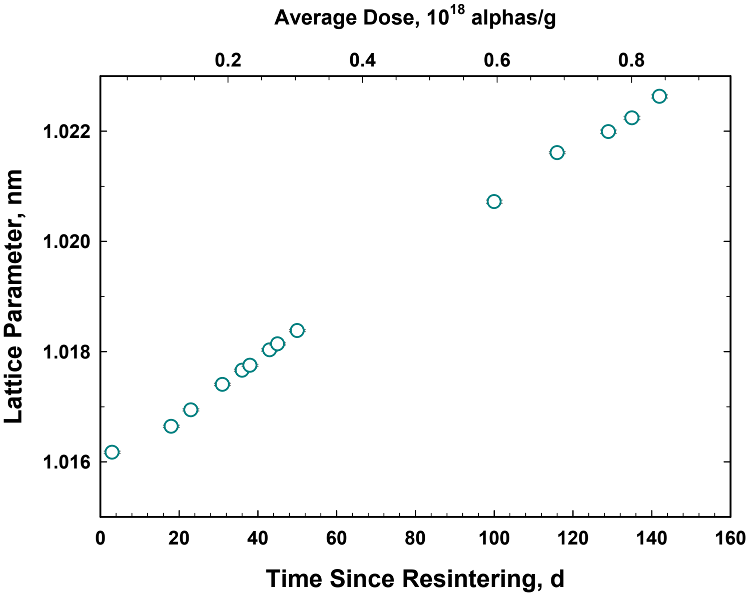

Figure 2.5. The Change in the Pyrochlore Lattice Parameter in Specimen 8P19-5 with Time and Radiation Damage (alpha decays /g). Although the error bars are shown, they are smaller than the size of the symbol.

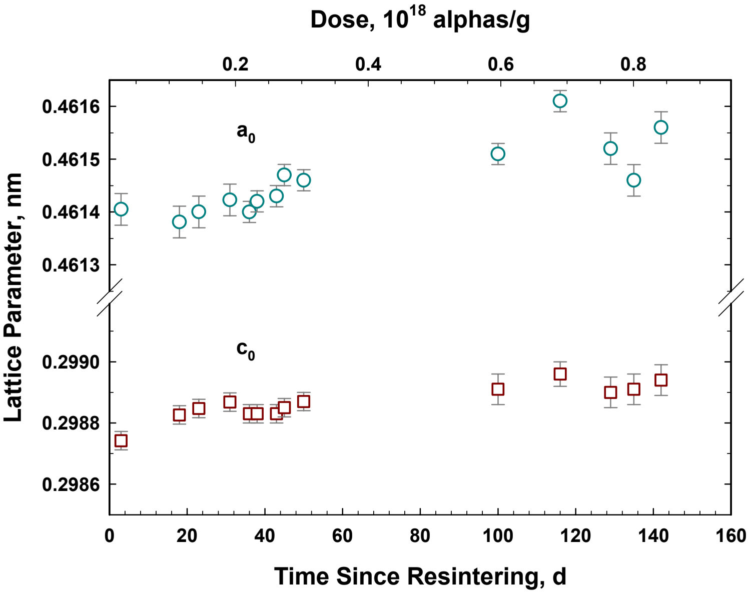

Figure 2.6. The Change in Lattice Parameters in the Rutile in Specimen 8P19-5 with Increasing Time and Radiation Damage (alpha decays/g)

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[a] The value shown in ( ) is the uncertainty in the last place.

1350°C. This is likely the result of diffusion processes that occurred during radiation damage over 1070 days at 250°C. Diffusion left the local structure and composition inconsistent with rapid reformation of pyrochlore. In fact, there was some evidence of zirconolite in the original ceramic (Strachan *et al.* 2001b). When this specimen was resintered, there was sufficient energy to form phases consistent with the local structure and chemistry, but insufficient to re-establish the pyrochlore phase that is consistent with the overall composition. A careful SEM analysis is needed to resolve this question. The changes in the pyrochlore phase were similar to those that took place in the pyrochlore stored at room temperature. The results for the pyrochlore in specimen 8P20-6 are shown in Figure 2.7. The change in the lattice parameter is linear with time and dose [$6.5(1)\cdot10^{-5}$ nm/d], which is higher than rate of change in the pyrochlore stored at room temperature. We still do not have a good explanation for the higher rate of increase in the lattice parameters for 8P20-6 as compared with 8P19-5. One would have predicted the rate of change to be less for the specimen stored at the higher temperature because at the higher temperature, there should be some annealing of the damage. It is possible that this pyrochlore contains more Pu than the pyrochlore in the room temperature-stored ceramic because of the phase separation that may have taken place during the previous storage at 250°C.

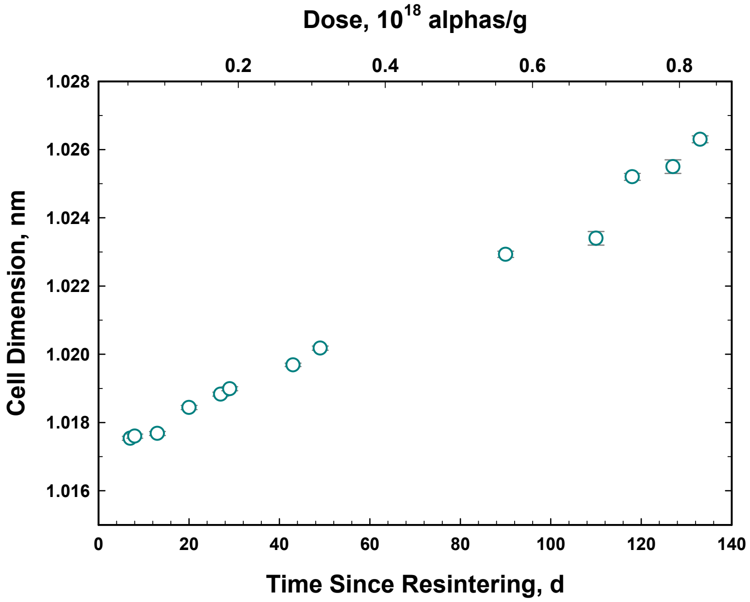

Figure 2.7. The Change in the Lattice Parameter for Pyrochlore in Specimen 8P20-6 with Increasing Time and Dose

The data for the zirconolites in specimen 8P20-6 are shown in the next two figures. In Figure 2.8, the variation of the lattice parameters for one of the zirconolites is shown. For this zirconolite, the initial c_0 cell parameter is 1.15 nm. The other zirconolite is shown in Figure 2.9 and has an initial c_0 value of 1.13 nm.

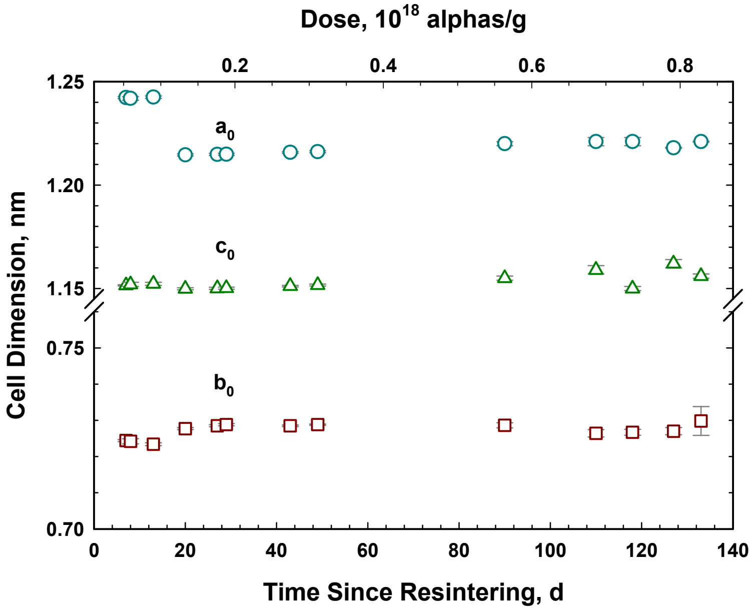

Figure 2.8. The Variation in the Lattice Parameters for the First Zirconolite Phase in Specimen 8P20-6 with Increasing Time and Dose (alpha decays/g)

After approximately 140 d ($8.3\cdot10^{17}$ alphas/g), the c_0 has expanded to 1.15 nm.

2.3.2 Lattice Parameters for the Phases in the Pyrochlore Baseline Ceramic Specimen

For the pyrochlore-baseline material, specimens 8PB1B-14 (25°C) and 8PB1B-3 (250°C), similar results have been obtained; that is, the pyrochlore phase expands linearly with time and dose [$4.68(2)\cdot10^{-5}$ nm/d] (Figure 2.10), which is the same as seen in specimen 8P19-5. There are three phases identified in the XRD pattern. The three phases are pyrochlore, brannerite [ideally UTi_2O_6], and zirconolite.

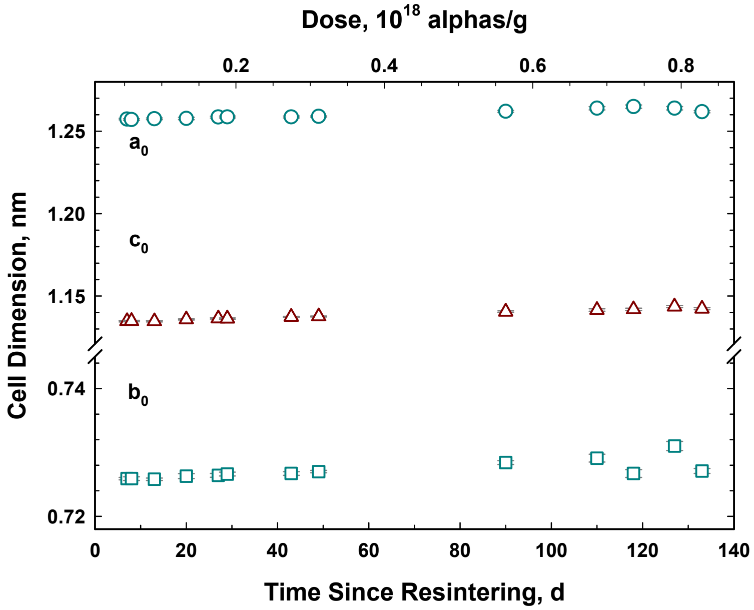

Figure 2.9. The Change in Lattice Parameters for the Second Zirconolite in Specimen 8P20-6 with Increasing Time and Dose

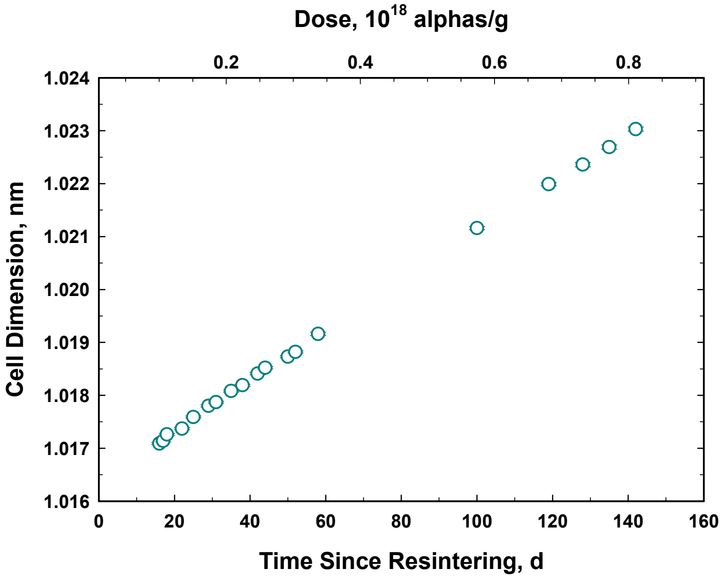

Figure 2.10. The Variation in the Lattice Parameter for Pyrochlore in Specimen 8PB1B-14 with Increasing Time and Dose (alpha decays/g)

The change in cell volume of the brannerite is much different from the changes for the other phases. The change in the lattice parameters is shown in Figure 2.11, and the change in the cell angle in Figure 2.12. The a_0 and b_0 lattice parameters increase initially for the first 100 days after which the a_0 parameter decreases while the b_0 parameter continues to increase. At this same time, brannerite begins to go amorphous (Figure 2.3). The c_0 parameter continuously decreases with time. The cell angle decreases slowly, and then at 100 days, the decrease becomes rapid. Since the brannerite phase appears to be susceptible to radiation damage, the change in lattice parameters and the peak width and height make it difficult to determine lattice parameters. This can be seen in the increase in the error associated with each of the data points. While the lattice parameters for the zirconolite in the pyrochlore-rich baseline material increased with increasing time, only the a_0 lattice parameter in this material expanded; b_0 decreased and c_0

decreased slowly (Figure 2.13). The angle in the zirconolite generally decreased, but not in a continuous manner (Figure 2.14).

In specimen 8PB1B-3, the pyrochlore cell parameter increased at a rate of $3.40(6) \cdot 10^{-5}$ nm/d (Figure 2.15). The b_0 parameter in the brannerite phase of this specimen did not increase and is not shown in Figure 2.16; the a_0 parameter increased to about 100 days and then decreased while the c_0 parameter decreased and then increased, followed by a rapid decrease (Figure 2.16). Since the brannerite phase was rapidly becoming amorphous, the decrease at the end of the plot is uncertain and should not be over interpreted. The cell angle decreased uniformly with time until 100 days, after which it decreased rapidly (Figure 2.17). This behavior is probably the result of having fewer diffraction peaks on which to refine the lattice parameters, and those remaining diffraction peaks were broadening. In the zirconolite phase, the only cell parameter that changed significantly is the a_0 parameter (Figure 2.18), while the c_0 parameter did not change and is not shown. The cell angle remained nearly constant for the first 40 days of irradiation and then decreased to another constant value between 40 days and a little over 100 days (Figure 2.19).

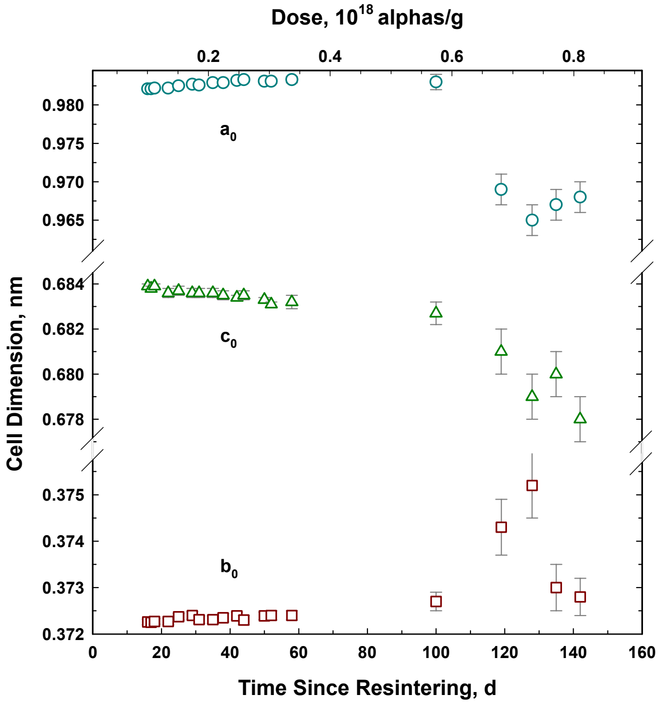

Figure 2.11. The Change in the Lattice Parameters for the Brannerite Phase in Specimen 8PB1B-14 with Increasing Time and Dose (alpha decays/g)

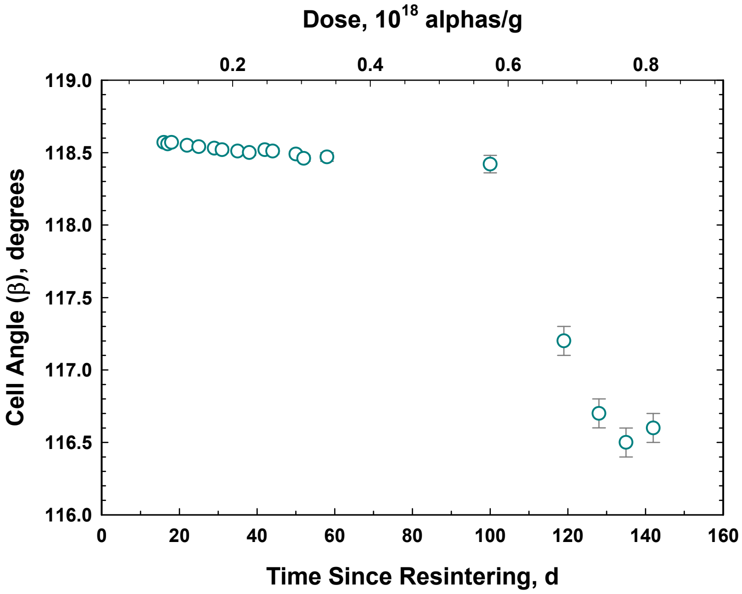

Figure 2.12. The Change in Cell Angle for the Brannerite Phase in Specimen 8PB1B-14 with Increasing Time and Dose

2.4 Unit Cell Volumes

In an effort to compare the XRD results with the results from the density measurements, we calculated the cell volumes that correspond to the cell dimensions given in Figure 2.5 through Figure 2.19, with the exception of the pyrochlore cells. Since the pyrochlore cell is cubic, the one dimension shown in the figures would yield a volume with the same slope. The result of these calculations for the phases other than pyrochlore is shown in Figure 2.20. As shown, the volumes of all the cell volumes increase with increasing time and dose. The volumes calculated for the brannerite phase in two specimens increase to a maximum and then rapidly decrease; in the case of specimen 8PB1B-3, the maximum is quite pronounced. The reason is likely the result of trying to refine the lattice parameters with a decreasing number of diffraction peaks that are becoming broader with the accumulation of radiation-induced damage.

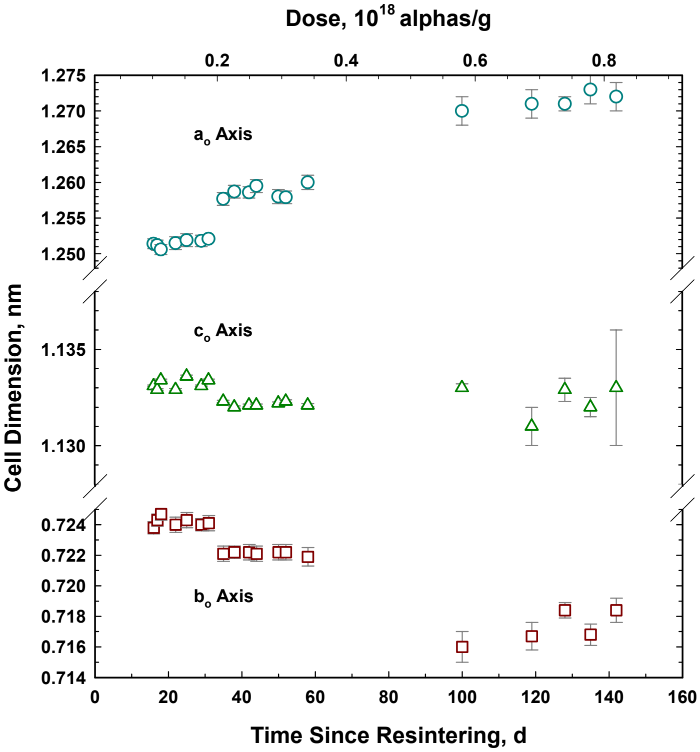

Figure 2.13. The Change in the Zirconolite Lattice Parameters in Specimen 8PB1B-14 with Increasing Time and Dose (alpha decays/g)

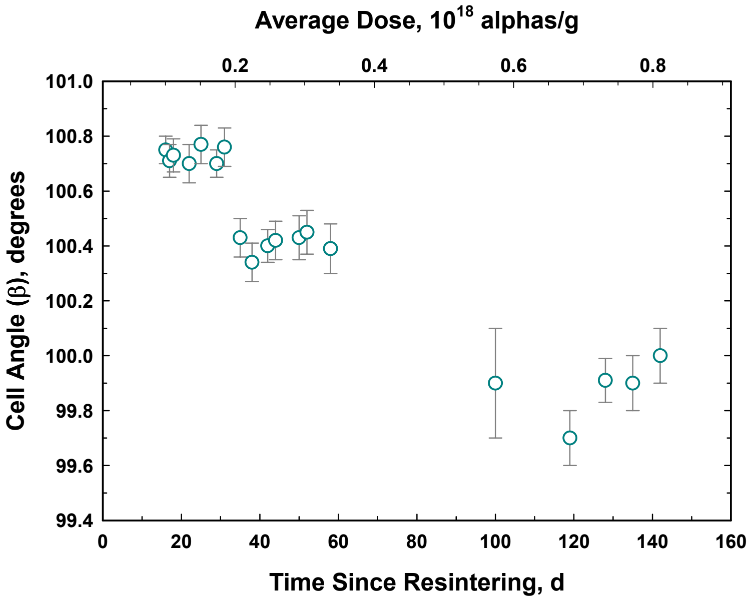

Figure 2.14. The Change in the Cell Angle for the Zirconolite Phase in Specimen 8PB1B-14 with Increasing Time and Dose

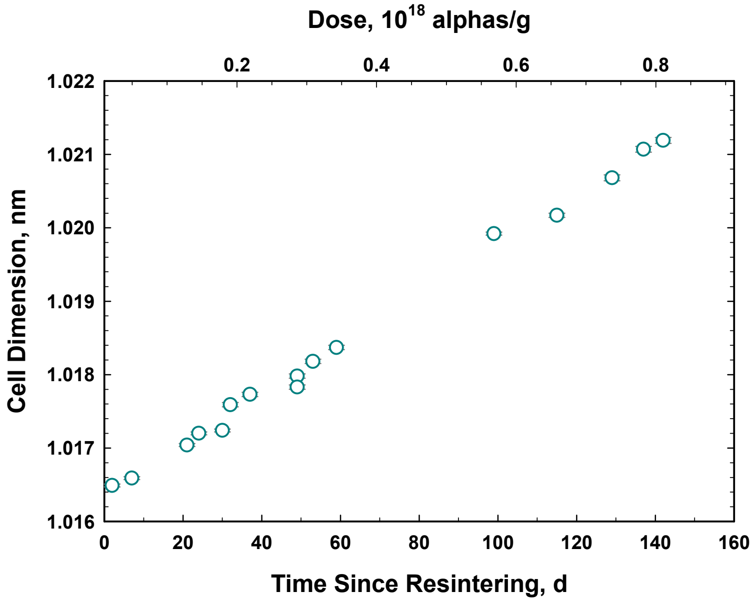

Figure 2.15. The Change in Lattice Parameter for the Pyrochlore Phase in Specimen 8PB1B-3 with Increasing Time and Dose

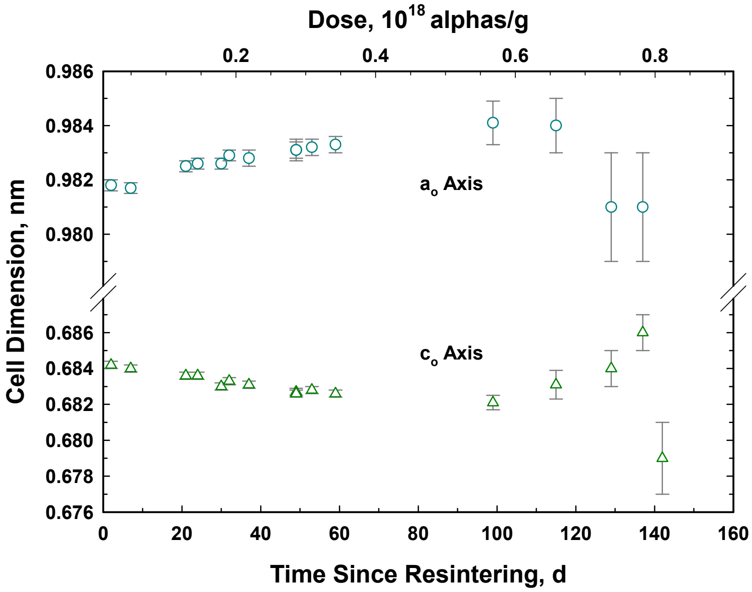

Figure 2.16. The Change in Cell Parameters in the Brannerite Phase in Specimen 8PB1b-3 with Increasing Time and Dose

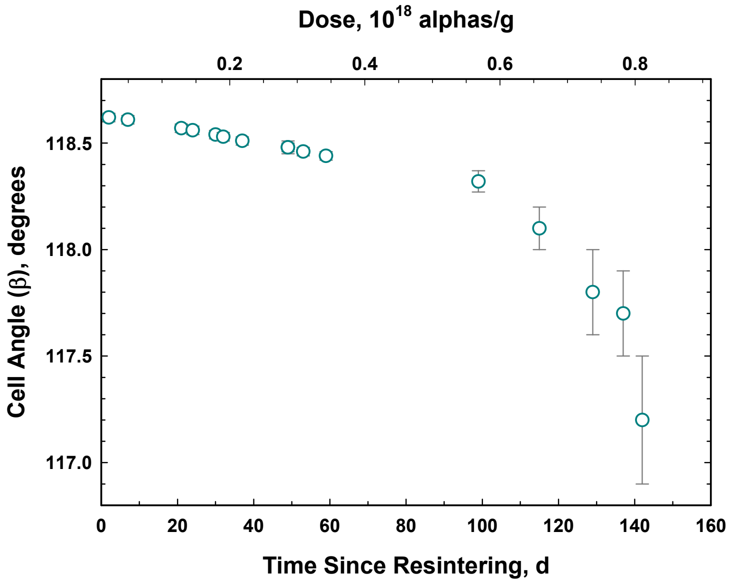

Figure 2.17. The Change in Cell Angle for the Brannerite Phase in Specimen 8PB1B-3 with Increasing Time and Dose

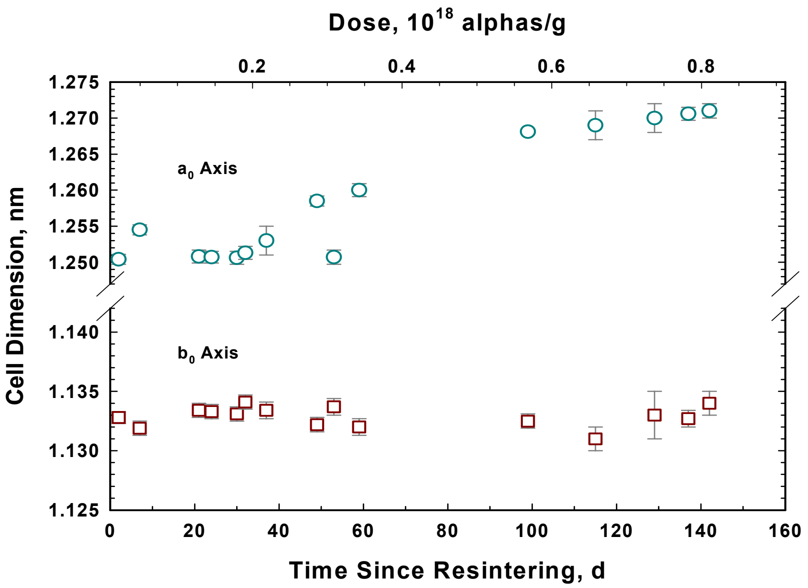

Figure 2.18. The Change in the Lattice Parameters for the Zirconolite Phase in Specimen 8PB1B-3 with Increaing Time and Dose

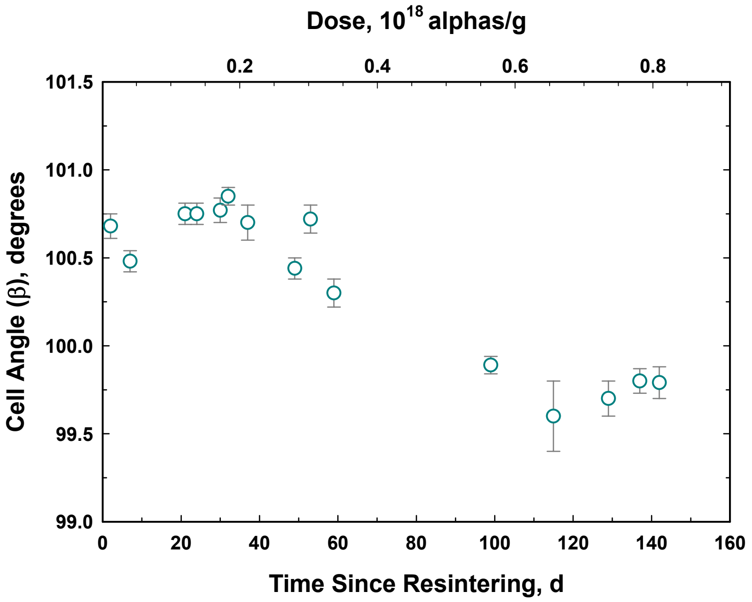

Figure 2.19. The Change in the Cell Angle for the Zirconolite Phase in Specimen 8PB1B-3 with Increasing Time and Dose

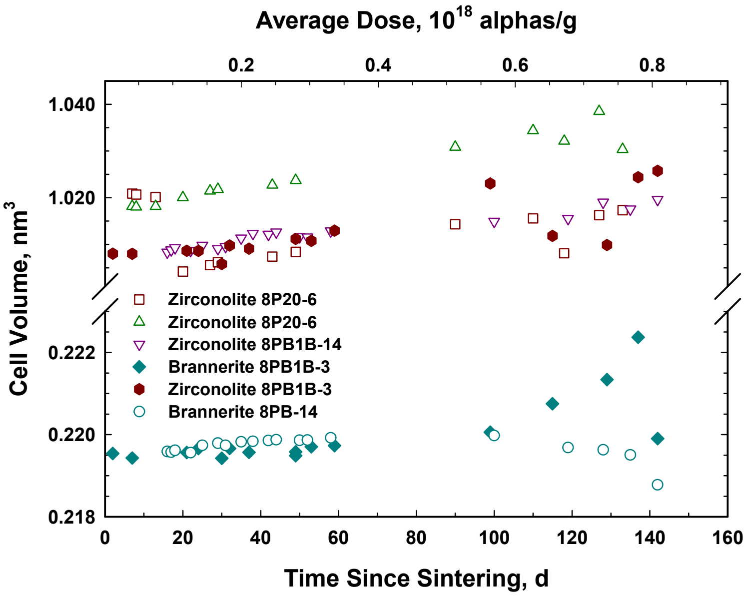

Figure 2.20. The Changes in Calculated Cell Volumes for the Brannerite and Zirconolite Phases Found in the Resintered Specimens

3.0 Density and Dimensions

Specimen density and dimensions provide information on the macroscopic effects of α-radiation on the ceramic. As with the expansion of the unit cells, we expect macroscopic swelling. This is important for the disposal of the ceramic material because it will be contained in a canister. Space for this swelling is needed to avoid premature failure of the containment system. Because the ceramic materials are multiphase and porous and not all the phases swell the same, the overall dimensions can change at a rate different from the change seen for the unit cells of the constituent phases.

We measured the "true" densities of the ^{238}Pu-ceramics tested over time. The "true" density is measured with a helium gas pycnometer that allows us to measure the density of a specimen exclusive of the open porosity. Previously, we determined that the specimens we are studying have densities that are about 90% of theoretical (Strachan *et al.* 2000). Shaw (1998) showed that when the measured density exceeds 90% of theoretical, essentially all of the pores are closed with respect to the surface. We are unable at this time to say if the closed porosity has remained closed, although the continuous nature of the data and the fact that the density does not increase would suggest it has remained closed (see below).

3.1 Effect of Internal α–Radiation on "True" Density

As illustrated Figure 3.1 for ^{238}Pu-pyrochlore and in Figure 3.2 for ^{238}Pu-pyrochlore-rich baseline, the "true" densities of these ceramics decrease with time and increasing internal α-radiation dose. Relative to the rate at room temperature (25°C), the rate at which damage accumulates in the specimen is substantially diminished in the specimen stored at 250°C.

From Figure 3.1, we find that the "true" density of the ^{238}Pu-pyrochlore stored at 25°C decreased by 6%[(a)] while the ^{238}Pu-pyrochlore specimens stored at 250°C decreased by 2%. The smaller change in density at 250°C indicates that some annealing of the damage occurs at the higher temperature.

From Figure 3.2, we find that the "true" density of the ^{238}Pu-pyrochlore-rich baseline specimen stored at 25°C decreased by 12% while the ^{238}Pu-pyrochlore-rich baseline ceramic stored at 250°C decreased by 2%. As with the

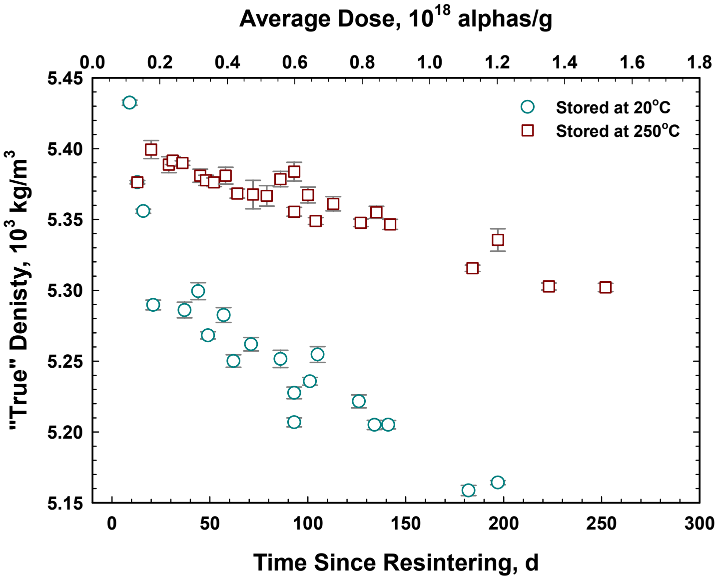

Figure 3.1. Effect of Internal α–Radiation on the "True" Density of ^{238}Pu-Pyrochlore Ceramic at 25°C and 250°C

(a) The error bars noted in these figures are the measurement error. The repeatability was not measured routinely. However, at the beginning of the project, the repeatability was measured at ~0.1%.

pyrochlore, the smaller change in density at 250°C indicates that much of the radiation-induced damage is healed as it occurs. We are unsure why there is a discontinuous change in the density in the 250°C specimens at 100 days, but it is likely caused by measurement error. There are changes in the unit cell dimensions that occur at this same time (see Section 2.3.1), but these occur much more gradually. One would expect a more continuous change in the "true" density rather than a discontinuous change seen in Figure 3.2.

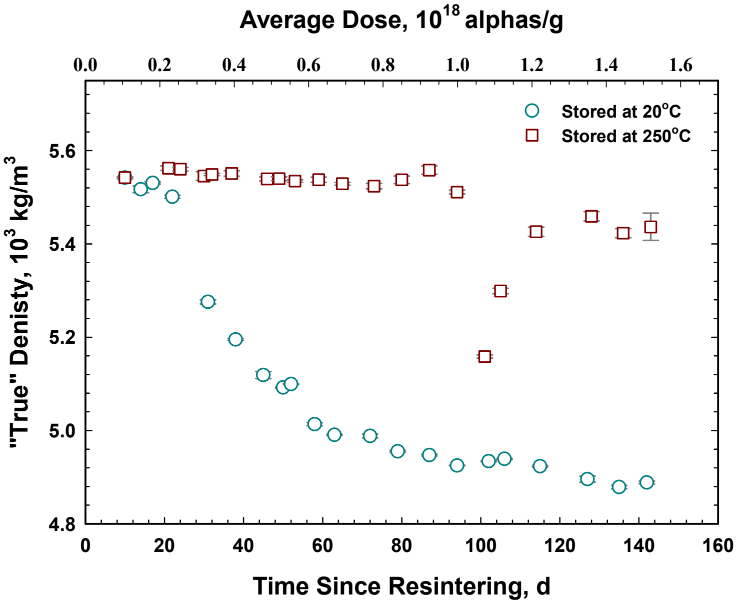

Figure 3.2. Effect of internal α-radiation on the "True" density of ^{238}Pu-pyrochlore-rich baseline ceramic at 25°C and 250°C

The significant differences between the 6% density change for pyrochlore and 12% for the pyrochlore-rich baseline both stored at room temperature suggest a large increase in closed porosity. Increases in the unit cell volumes are 2% to 3% (see Section 2.4). Since the He gas should penetrate all open porosity, only the closed porosity could affect the overall density as measured in the He gas pycnometer. Therefore, it is plausible that the radiation-induced swelling in the pyrochlore baseline ceramic caused some of the existing open porosity to close. This would indicate that the original open porosity after resintering was nearly closed, and a 2% increase in the size of the constituent grains in the ceramic was sufficient to close additional porosity. The difference between the measure geometric density and the "true" density for the pyrochlore-baseline ceramics is greater than that found for the pyrochlore ceramic (Table 4.1 in Strachan *et al.* 2000). Some consolidation occurred when the specimens were resintered, but the difference between the geometric ($4.5 \cdot 10^3$ kg/m^3) and the "true" ($5.5 \cdot 10^3$ kg/m^3) densities is much larger than the difference between the same densities in the pyrochlore ceramic specimens (Table 4.1 in Strachan *et al.* 2000). Thus, a significant fraction of the open porosity that existed in the pyrochlore-baseline ceramics could become closed as the constituent grains swelled. At the 250°C storage temperature, enough annealing of the radiation-induced swelling could have occurred to keep the porosity open. Further examination of these specimens in an SEM may reveal the reasons for large density change in the pyrochlore-baseline ceramic.

3.2 Effect of Internal α-Radiation on Specimen Dimensions

Consistent with the changes in the "true" densities, the dimensions of the resintered ^{238}Pu-bearing pyrochlore and ^{238}Pu-bearing pyrochlore-rich baseline ceramics increased with time or internal α-radiation exposure. The effects of temperature were again evident as the dimensions of the right circular cylindrical specimens increased more for those specimens stored at room temperature (25°C) than at 250°C. The effect of radiation on the dimensions will be illustrated by discussing the effects on the specimen diameter. We elected to report the changes in the diameter because the error in the height measurement was large. This will be evident in the following section, where we show pictures of representative specimens; it can also be seen in previous reports (Strachan *et al.* 2000 and Strachan *et al.* 2001b). In these pictures, it can be seen that the top and bottom surfaces of several specimens have features that affect the overall height measurement. Additionally, the rotating table on which the specimens rest during the dimension measurement has a 20- to 40-µm wobble that adds to the measurement uncertainty.

As seen in Figure 3.3, which provides the diameters of the individual ^{238}Pu-bearing pyrochlore specimens stored at 25°C, the specimen diameters increased about 0.1 mm for the nominal 10-mm-diameter specimens or about 1%. Inspection of Figure 3.3 shows that there were two different populations in the specimens tested. In addition to a small difference in the Pu content, the two specimens from batch 8P20 had been stored at 250°C before being resintered. The two from the 8P19 batch had been stored previously at room temperature. While the resintered diameters are different, the rate of change in the diameters is the same for the 8P19 and 8P20 specimens.

Comparing Figure 3.3 (25°C) and Figure 3.4 (250°C), we see that specimens stored at 250°C increase to a lesser extent than the specimens stored at room temperature. The 250°C specimens increased only 0.03 mm in diameter or 0.3%. As noted above, the 8P20 specimen has a smaller diameter after resintering than the 8P19, but they have the same rate of swelling.

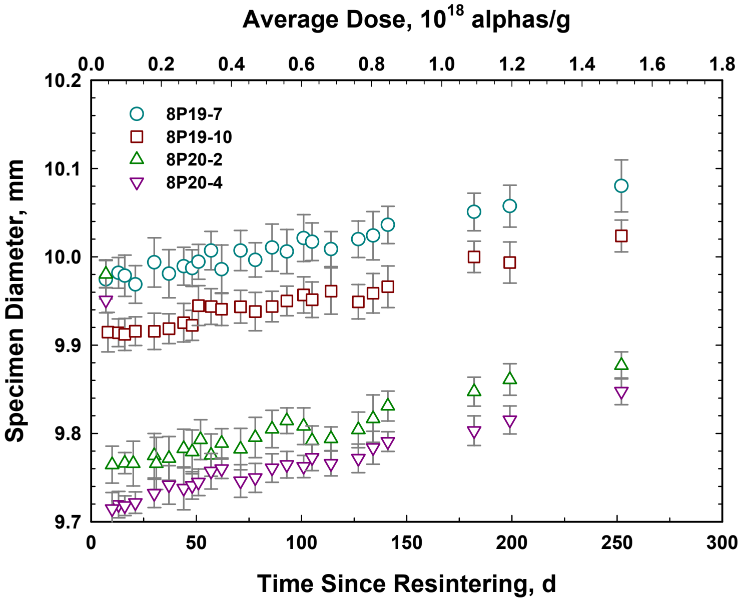

Figure 3.3. Effect of Internal α-Radiation on the Diameter of Individual Resintered ^{238}Pu-Pyrochlore Ceramic Specimens Stored at Room Temperature (25°C)

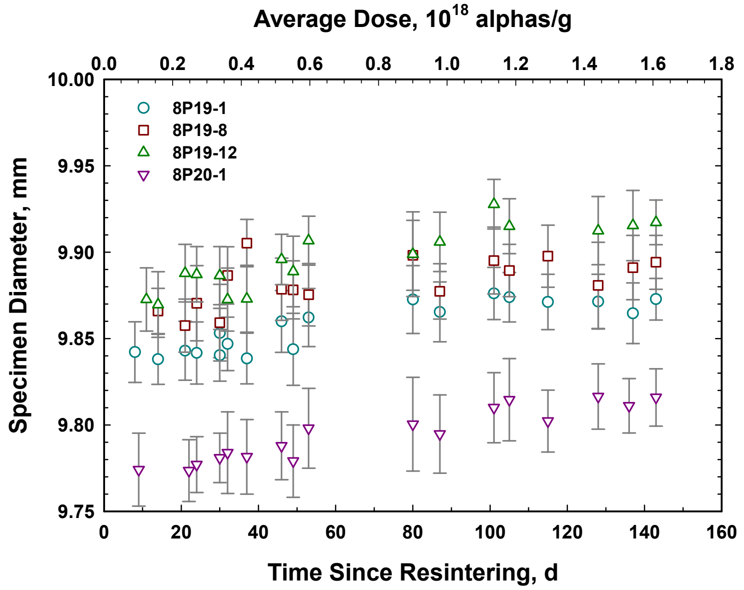

Figure 3.4. Effect of Internal α-Radiation on the Diameters of Individual Specimens of Resintered ^{238}Pu Pyrochlore Stored at 250°C

As shown in Figure 3.5, the diameters of the ^{238}Pu-pyrochlore-rich baseline ceramic specimens stored at 25°C increased about 0.06 mm or about 1%, which is about the same as the pyrochlore specimen. In comparison, the diameters of the ^{238}Pu-pyrochlore-rich specimens stored at 250°C, see Figure 3.6, increased nominally 0.03 mm or 0.3%, consistent with the previous observation regarding storage temperature.

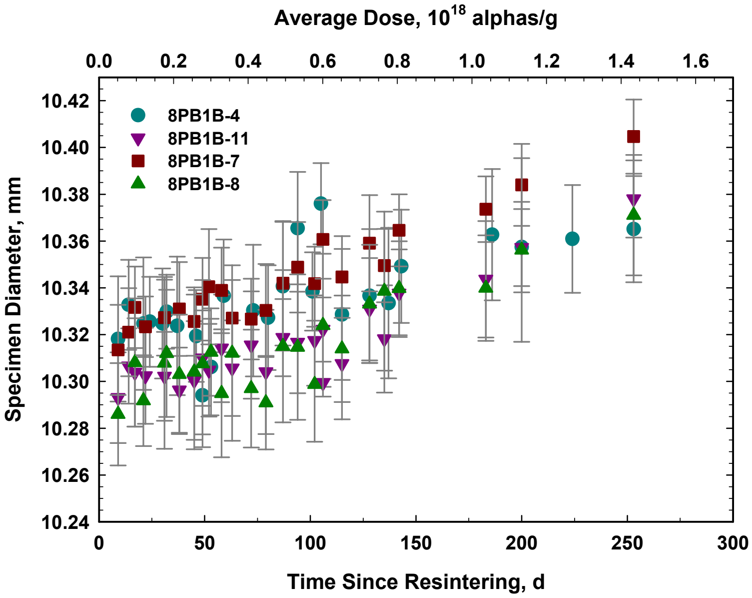

Figure 3.5. Effect of Internal α-Radiation on the Diameters of Individual Specimens of Resintered ^{238}Pu-Pyrochlore-Rich Baseline Stored at Room Temperature (25°C).

3.3 Physical Appearance

During the radiation-damage testing of the resintered specimens, we monitored the physical appearance of the specimens. In general, both the pyrochlore and the pyrochlore-rich specimens have changed little in appearance during this testing. Two extremes in the condition of the specimens are shown in Figure 3.7 and Figure 3.8. The condition of the specimen shown in Figure 3.8 is more typical of the general condition of most of the specimens. However, the case shown in Figure 3.7 is illustrative of some of the problems associated with measuring the dimensions of the specimens, especially the height. The height data tend to have a higher measurement error than the diameter measurement.

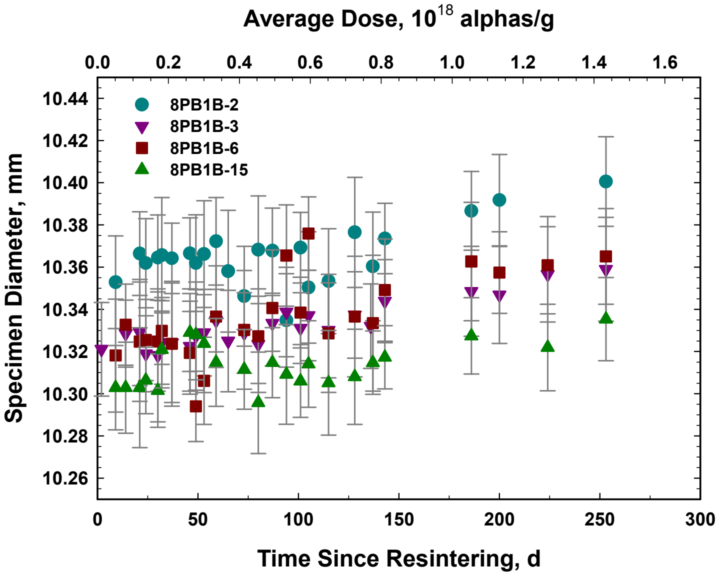

Figure 3.6. Effect of Internal α-Radiation on the Diameters of Individual Resintered ^{238}Pu-Pyrochlore-Rich Baseline Specimens Stored at 250°C

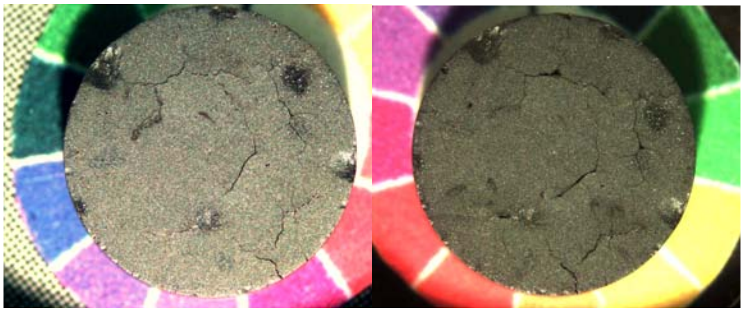

Figure 3.7. Physical Appearance of Specimen 8P19-12 After Resintering on 30-April-02 (left) and After 250 Days (07-January-03) of Radiation Damage (right) at 250°C

Figure 3.8. The Appearance of Specimen 8PB1B-3 After Resintering (01-May-02; left) and 250 days (07-January-03) of Radiation Damage (right) at 250°C

4.0 Discussion and Conclusions

Since resintering of selected ^{238}Pu-pyrochlore and –pyrochlore-rich baseline specimens in April and May 2001, the progress of radiation damage has been rapid. In some cases, most of the damage occurs in the first 40 days of alpha dose. Thus, it is not surprising that when we started to characterize the original specimens, most of the damage had already occurred. With these resintered specimens, we have been able to collect much of the data that were lost when we assumed that radiation damage effects would be manifest over much longer times. As with the original specimens, we are unable to accurately partition the total dose to the individual phases because we do not have information on the ^{238}Pu content of each phase. We hope to obtain this information this year.

The expansion of the crystalline unit cells correlates to the expansions of the specimen diameters. In both cases, the expansion is approximately 2 to 3 volume%. These data do not correlate well with the decrease in “true” density (volume expansion at constant mass). It is unclear why the decrease in the “true” density should be much higher. As the ^{238}Pu decays, alpha particles are released. These eventually become He that could cause the closed porosity to expand or bubbles to form in the solid. However, over the 250 days since the specimens have been resintered, approximately 10^{18} alpha decays have occurred or about $2 \cdot 10^{-6}$ moles of He. If all of the He accumulated in the specimens (approximately 400 mm^3), the total He gas would have caused no pressure increase assuming that the solid had about 10% porosity in which the He gas accumulated. Therefore, this is not a plausible explanation for the large decrease in “true” density.

Some of the open porosity could have become closed if the connections between the open pores were nearly closed after resintering. As the grains of the specimens swelled from radiation damage, the channels between the pores could become blocked to He migration. This would lead to an effective increase in the volume not accessible to the He gas in the pycnometer for the same mass of material—an effective decrease in the density. The change in open porosity would not add to the overall dimension change. Thus, in the He pycnometer, the change in measured density would be the sum of the dimensional swelling and the amount of closed porosity. We will have to analyze these specimens in an SEM to be able to understand what effects have caused the “true” density to decrease more than expected based on the volume expansion of both the bulk dimensions and the crystal unit cell.

For the pyrochlore in each of the specimens, the rate of increase in the unit cell parameter was about 10^{-5} nm/d. The bulk volume of the specimens also increases linearly. The increase is about 100 μm in 250 days or 0.4 μm/d. If all the unit cells for pyrochlore were perfectly stacked in the specimen and all of the increase in the individual cells gave rise to an increase in the specimen diameter, the rate of expansion would be about 0.5 μm/d. The unit cells, however, are not perfectly stacked, and there are more phases present than pyrochlore. So, an order of magnitude agreement suggests good agreement between the rate of diameter expansion and the rate of unit cell expansion.

Our results suggest, therefore, that a pyrochlore-dominated plutonium waste form might be expected to expand by about 3 volume% over a span of about 60 years in the repository. After 60 to 100 years, no change in waste form dimensions is expected. However, over the lifetime of the ^{239}Pu (10 half-lives or $2.4 \cdot 10^{5}$ years), approximately 0.4 mole of He gas is expected to be generated per kilogram of ceramic. It is beyond the scope of this study to determine the effect of He accumulation. At the low temperatures of the repository, He is expected to be trapped in the ceramic lattice or diffuse away. This accumulation does not result in a volume expansion. Therefore, no further degradation of the ceramic is expected after 10^5 years. The solid is not expected to develop extensive microcracks nor should the disposed form deteriorate into a powder. The specimens we have been characterizing have maintained physical integrity while being aggressively handled, especially when the specimens are repeatedly mounted on the XRD specimen holder. These data suggest that the assumptions made in the initial performance assessment at the geologic repository program (TRW 1997) for the physical state of the fully damaged ceramic were adequately conservative.

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