

# Radiation Effects in Nuclear Waste Materials

Pacific Northwest National Laboratory

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## Progress Report

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## **Research Objective**

The objective of this multidisciplinary, multi-institutional research effort is to develop a fundamental understanding at the atomic, microscopic, and macroscopic levels of radiation effects in glass and ceramics. This research will provide the underpinning science and models for evaluation and performance assessments of glass and ceramic waste forms for the immobilization and disposal of high-level tank waste, plutonium residues and scrap, and excess weapons plutonium. Studies will focus on the effects of ionization and elastic collision interactions on defect production, defect interactions, diffusion, solid-state phase transformations, and gas accumulation using actinide-containing materials, gamma irradiation, ion-beam irradiation, and electron-beam irradiation to simulate the effects of  $\alpha$ -decay and  $\beta$ -decay on nuclear waste glasses and ceramics. This program will exploit a variety of structural, optical, and spectroscopic probes to characterize the nature and behavior of the defects, defect aggregates, and phase transformations. Computer simulation techniques will be used to determine defect production, calculate defect stability, defect energies, damage processes within an  $\alpha$ -recoil cascade, and defect/gas diffusion and interactions. A number of irradiation facilities and capabilities will be used, including user facilities at several national laboratories, to study the effects of irradiation under different conditions.

## **Research Statement**

A significant challenge facing the environmental management and restoration activities at DOE facilities is the stabilization and immobilization of high-level tank waste, high-level sludge in the fuel storage basins, and Pu residues/scrap. In addition, the immobilization and disposal of surplus weapons-grade Pu is becoming a growing technological and political issue that is historically and politically tied to environmental management and restoration activities. These high-level wastes will be converted to glass or glass-ceramic waste forms for permanent disposal in a geologic repository. A key challenge is to develop predictive strategies and models, based on sound scientific understanding, to fully assess long-term performance. Self-radiation effects from  $\alpha$ -decay and  $\beta$ -decay can significantly impact long-term performance. Waste forms for the disposal of Pu residues/scrap, surplus weapons-grade Pu, and other high-actinide waste streams may differ significantly in composition from the waste forms for high-level tank wastes and will experience significantly higher radiation doses and He production. The current baseline data and scientific understanding of radiation effects in glass, glass-ceramics, and crystalline phases are critically lacking. Without a fundamental understanding of radiation effects at the molecular, microscopic, and macroscopic levels, meaningful predictions of performance are not possible. This lack of understanding of the radiation-damage processes that occur also makes it impossible to extrapolate the limited existing data bases to larger doses, lower dose rates, different temperature regimes, or different compositions.

## Research Progress

Work to date under this project has resulted in two manuscripts that have been submitted to journals for publication. These manuscripts are: W.J. Weber, R.C. Ewing, and A. Meldrum, "The Kinetics of Alpha-Decay-Induced Amorphization in Zircon and Apatite Containing Weapon-Grade Plutonium or Other Actinides," submitted to Journal of Nuclear Materials; and N.J. Hess, W.J. Weber, and S.D. Conradson, "Initial Results from Zr, U, and Pu XAS on Self-Radiation Effects in Glass and Ceramics," submitted to Journal of Materials Research. Other highlights of research progress are discussed below.

### Theory, Simulations, and Modeling

#### Molecular Dynamics Simulation of Exciton Propagation in Network Materials

A semiempirical exciton propagation model that is applicable to covalently bonded networked systems has been developed. The model has been integrated into a molecular dynamics semiempirical methodology utilized at Pacific Northwest National Laboratory (PNNL). The exciton propagation algorithm is being tested on a model crystalline Si system that presents the simplest case and can be compared to other theoretical, simulation, and experimental results. The approach is a modification of the tight-binding checkerboard method of Hall and Whaley.<sup>1</sup>

Initial tests have included propagating an exciton in a perfect lattice and in a distorted lattice consisting of eight atoms in a periodic diamond lattice. The exciton transfer probabilities are determined from the off-diagonal elements of the one electron Hamiltonian. The hole transfer probabilities are determined from the off-diagonal elements corresponding to the  $3sp^3$  hybrid orbital overlaps between neighboring atoms. The electron transfer probabilities are determined from the off-diagonal elements for two distinct cases: 1) the electron transfers along the conduction band via the overlap between the  $4s$  orbital of one Si atom and the  $3sp^3$  hybrid orbital of the neighboring atom; and 2) the transfer occurs via the overlap of the  $4s$  orbitals between neighboring atoms. Based on these tests, the former case is the preferred electron transfer mechanism in a perfect lattice, while the latter case is the preferred electron transfer mechanism for a distorted lattice. Current results indicate that the transfer of the excited electron utilizes both transfer pathways.

The density distribution of both the electron and the hole for a fixed lattice configuration has been calculated. In the perfect lattice, the exciton density distributes itself in groups of two unit cells and fluctuates between groups of atoms. In the distorted lattice, the exciton density is localized at the defect. The energetics of these two states indicate that trapping of the exciton at a distorted (defect) site is preferred. Thus, the exciton force contribution to the ions should yield to distortion from a perfect lattice state.

These initial studies have utilized a small periodic system to test, debug, and optimize the methodology. Due to constraints of *ab initio* and tight-binding methods on computer memory, other theoretical and simulation activities have focused on small molecular clusters or nanoparticles systems (~200 atoms) with surfaces. The current approach for exciton propagation uses a deterministic set of equations with matrices that require memory of the order of  $N^2$ ; consequently, computations are currently constrained to small systems. To expand this approach to significantly larger systems (i.e., >1000 atoms), a Monte Carlo approach to simulate the exciton propagation in the network will be implemented. Application of this methodology to amorphous silica and other glasses will begin this summer.

### **Defect Energies in Crystalline Ceramics**

Activities under this task are focused on using computational methodologies to determine fundamental defect energies in complex ceramics relevant to nuclear waste applications. Such defect energies are often difficult to determine experimentally, particularly for multi-cation ceramics. Two fundamental energy parameters important to radiation effects are the threshold displacement energies for the various cations and anions and the migration energies of radiation-induced defects (e.g., interstitials and vacancies). Both energy minimization methods and molecular dynamic simulations can be used in determining these energies. Initial work under this project has utilized energy minimization methodology, as described below. Computational-intensive molecular dynamic (MD) simulations, which are currently being developed and applied to SiC under a BES-sponsored project at PNNL, will be applied to ceramics relevant to nuclear waste applications later this summer. The initial MD simulations will focus on zircon ( $ZrSiO_4$ ) using new interatomic potentials developed by R.W. Grimes at Imperial College, UK. (The MD simulations will also be used to study primary displacement processes in energetic displacement cascades.)

Displacement energies,  $E_d$ , and defect migration energies,  $E_m$ , are fundamental parameters controlling defect production, defect migration, and the kinetics of microstructure growth and phase transformations. These energies are not easily determined experimentally for many ceramic materials; however, advances in computational methodologies and their application to ceramics materials provide a means to determine these energies for a number of ceramic materials of interest. Although computationally intensive MD methods can be used to determine these energy parameters, energy minimization methods, such as utilized in the GULP code (General Lattice Utility Program, by J.D. Gale, Imperial College, London, UK), can be used to determine  $E_d$  and  $E_m$  for a number of ceramics. Calculations of  $E_d$  and  $E_m$  for several ceramics have been performed using GULP and compared to experimental values where available.

GULP uses a Mott-Littleton approximation to simulate isolated defects in extended solids. Two of its many options are particularly useful in the present work. For determining  $E_d$ , the ion “translate” option permits the movement of a selected ion to a point along a prescribed vector, after which the lattice is relaxed to determine if the ion returns to its original position, or assumes a new equilibrium position, such as an interstitial site. For determining defect migration energies, GULP contains a useful “transition” state option.

The validity of using GULP for these computations was established by calculating  $E_d$  and  $E_m$  in several ceramic materials where these energies are reasonably well known. The computational results show excellent agreement with accepted experimental values. For example, the calculated  $E_d(\text{Al})$  and  $E_d(\text{O})$  in  $\text{Al}_2\text{O}_3$  were 19.4 and 56.1 eV, respectively, in good agreement with accepted experimental values (20 and 50 eV, respectively). The cation migration energy for MgO was calculated to be 2.4 eV, also in good agreement with accepted values (2.0-2.3 eV). Additional results for oxide ceramics with good supporting data bases (i.e.,  $\text{Al}_2\text{O}_3$ , MgO, ZnO) have been obtained and support validation of the methodology. Calculations have been initiated on ceramics relevant to nuclear waste, such as zircon, which have limited data bases. In the case of zircon, preliminary calculations indicate a displacement energy of 23 eV for oxygen.

### **Damage Cascades from $\alpha$ -decay**

Displacement damage in zircon ( $\text{ZrSiO}_4$ ) caused by  $\alpha$ -decay of substitutional actinides on the Zr sites is being studied at the atomic scale using the binary collision approximation computer code MARLOWE. With MARLOWE, the collisional phase of the displacement cascade is modeled, following collisions of individual atoms in the zircon crystal structure until they no longer have enough energy to permanently displace another atom. From this method, information is obtained on cascade morphology and energy deposition as a function of material and irradiation conditions, such as the projectile mass and energy and the displaced atom type, as well as producing cascades at much higher energies and greater numbers than possible with MD.

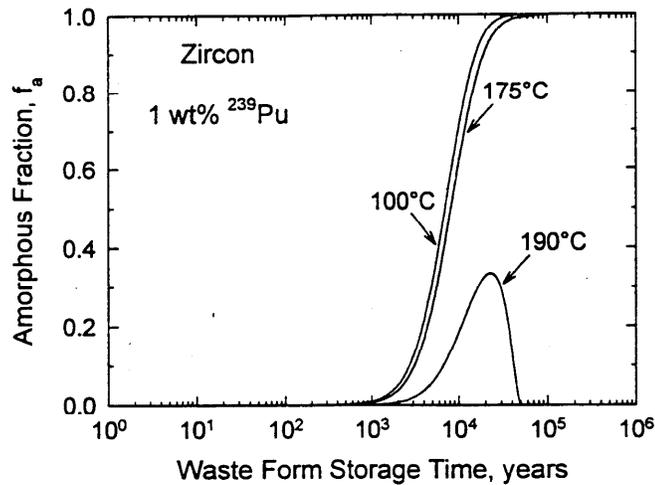
The decay of  $^{238}\text{Pu}$ , which results in a 5.5 MeV  $\alpha$ -particle and a 94 keV recoiling  $^{234}\text{U}$  nucleus, is being used as a test case because of the availability of experimental data. The  $\alpha$ -particle has an extremely long path (relative to the “cascade” concept) and loses most of its energy to electronic excitation rather than displacement damage. The average recoiling  $^{234}\text{U}$  creates a cascade about 25 nm in diameter, initially displacing about 650 atoms (120 Zr, 60 Si and 470 O). The fractions of the initially displaced atoms that remain after the cascade energy dissipates and after subsequent local annealing occurs by diffusion will be determined from further modeling using MD and stochastic annealing simulations. Cascade morphology was studied as a function of Zr recoil energy, revealing that the threshold energy for subcascade formation (more than one distinct damage region per cascade) is about 4 keV, which is consistent with lower-Z metals such as aluminum (2 keV). Because of its high atomic mass,  $^{234}\text{U}$  recoils produce cascades that are significantly more compact than those from Zr recoils. Thermal spike

effects on defect survivability may be significantly different for  $t^{34}\text{U}$  recoils as compared to those of lighter ions, although the effect of recoil mass may not be as large in zircon as those observed in metals because of the light elements involved.

### **Models of $\alpha$ -decay-induced Amorphization**

Zircon and apatite form as actinide host phases in several high-level waste forms and have been proposed as host phases for the disposition of Pu residues, excess weapons-grade Pu, and other high-actinide waste streams (e.g., highly separated commercial nuclear waste in France). Additionally, closely related structure types appear as actinide-bearing phases among the corrosion products of spent nuclear fuel and high-level waste glasses. Self-radiation damage from  $\alpha$ -decay of the incorporated Pu or other actinides can affect the durability and performance of these actinide-bearing phases. For both zircon and apatite, these effects can be modeled as functions of storage time and repository temperature and validated by comparison with data from natural occurrences. Natural zircons and apatites, with ages up to 4 billion years, provide abundant evidence for their long-term durability because of their widespread use in geochronology and fission-track dating. Detailed studies of natural zircons and apatites,  $^{238}\text{Pu}$ -containing zircon, a  $^{244}\text{Cm}$ -containing silicate apatite, and ion-irradiated zircon, natural apatite, and synthetic silicate apatites provide a unique basis for the analysis of  $\alpha$ -decay effects over broad time scales. Models for  $\alpha$ -decay effects in zircon and apatite have been developed that show  $\alpha$ -decay of Pu and other actinides will lead to a crystalline-to-amorphous transformation in zircon, but not in apatite, under conditions typical of a repository, such as the Yucca Mountain site. (Details of these models are provided in a manuscript that was submitted for publication.)

Based on these models, the critical temperatures above which amorphization cannot occur are  $15^\circ\text{C}$  and  $29^\circ\text{C}$  for silicate apatite containing 1 wt. % and 10 wt. %  $^{239}\text{Pu}$ , respectively, and are  $196^\circ\text{C}$  and  $218^\circ\text{C}$ , respectively, for zircon containing 1 wt.% and 10 wt. %  $^{239}\text{Pu}$ . These results suggest that apatite phases containing excess weapons Pu or other actinides will remain crystalline, due to high thermal recovery rates, under conditions expected for a near-surface repository, such as the Yucca Mountain site. In the case of zircon,  $\alpha$ -decay of Pu and other actinides will lead to amorphization at conditions expected in a near-surface repository; however, the initial elevated temperatures in a geologic repository may retard amorphization during early storage times. The predicted amorphization behavior for zircon containing 1 wt. %  $^{239}\text{Pu}$  is shown in Figure 1 as a function of time for several temperatures. These results show that the amorphization rate for zircon decreases rapidly above  $190^\circ\text{C}$ . At the higher temperatures, the amorphization rate is decreased even further due to both an increase in the recovery rate and a decrease in the actual  $\alpha$ -activity,  $A(t)$ , due to the longer time scales (approaching one half-life).



**Figure 1.** Predicted amorphization behavior in zircon.

The actual behavior for apatites and zircons containing actinides may differ slightly from that discussed above due to compositional variations and impurities, which have a significant effect on kinetic processes. These models will be refined as more experimental and computational data become available.

## Experimental Studies

### Pu-Containing Glasses and Ceramics

Density, XANES/EXAFS, diffuse x-ray scattering, and stored energy measurements have been performed on a suite of compositionally identical Pu-doped (1 wt.%) waste glasses prepared with different  $\alpha$ -activities by varying the  $^{239}\text{Pu}/^{238}\text{Pu}$  isotopic ratio. The resulting  $\alpha$ -activities in these glasses, which were prepared in July 1982, range from  $1.9 \times 10^7$  to  $4.2 \times 10^9$  Bq/g, and the accumulated dose ranges from  $8.7 \times 10^{15}$  to  $1.8 \times 10^{18}$   $\alpha$ -decays/g. Similar measurements have been carried out on a Pu-zircon (8.1 mole%  $^{238}\text{Pu}$  was substituted for Zr) prepared in August 1981; the  $\alpha$ -activity and accumulated dose in the zircon are  $5.6 \times 10^{10}$  Bq/g and  $2.6 \times 10^{19}$   $\alpha$ -decays/g, respectively. The macroscopic volume expansion of these glasses is shown in Figure 2 as a function of cumulative dose. The results suggest that for this range of  $\alpha$ -activities there is no significant effect of the  $\alpha$ -activity (i.e., dose rate) on the macroscopic density change in waste form glasses. Self-radiation from  $\alpha$ -decay in the Pu-zircon results in the simultaneous accumulation of point defects and amorphous domains that eventually lead to a completely amorphous state.<sup>2</sup> The macroscopic volume expansion of the zircon is much larger than in the glasses as a result of a radiation-induced crystalline-to-amorphous transformation, reaching a saturation value of almost 17%.<sup>2</sup>

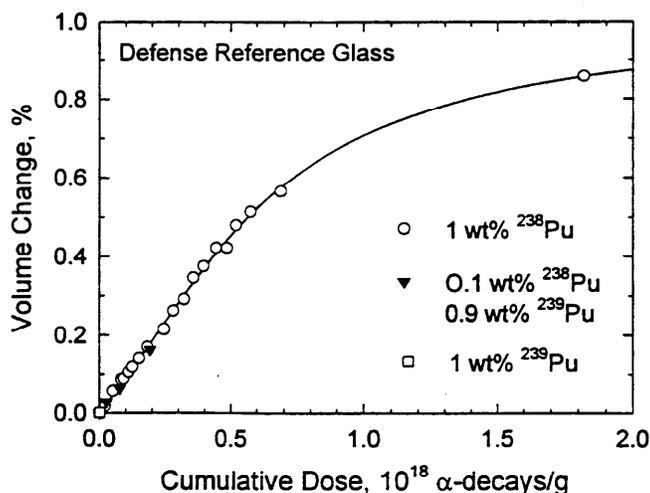


Figure 2. Macroscopic volume expansion as a function of cumulative dose.

Initial results from the XANES measurements at the Pu and U  $L_m$ -edges indicate that Pu and U occur in more highly oxidized valence states in the Pu-doped glasses than in the Pu-containing zircon. XANES measurements at the Fe and Zr K-edges reveal that the Fe and Zr oxidation states are unaffected by accumulated dose. Analyses of the Zr K-edge and Pu and U  $L_m$ -edges in the EXAFS show that the trend of local structural modification as a result of self-radiation damage is highly element-specific. Analysis of the Zr K-edge in the EXAFS of the Pu-doped glass samples indicates that the first shell atoms, consisting of O atoms, are increasingly disordered with increasing accumulated  $\alpha$ -decay dose. However, the second and third shells, consisting of Si and O atoms, respectively, are much less affected. In contrast, analysis of the U  $L_m$ -edge EXAFS of the glass samples reveals a significant change in the first shell O atoms that is consistent with the reduction of U(VI) to U(IV) concomitant with the breakup of U(VI) oligomers that are present in the low-dose glass. Interestingly, analysis of the Pu  $L_m$ -edge EXAFS shows very little change in local structure with accumulated  $\alpha$ -decay dose, suggesting that the initial Pu environment in the glass is a stable configuration for this  $\alpha$ -activity level.

Because there is only one sample of zircon at a high dose (i.e., amorphized), it is not possible to draw conclusions about the systematic effects of self-radiation damage. The zircon cations reside in two distributions, one that is similar to a highly disordered zircon and a second that has Zr--Zr distances that are similar to baddeleyite, the monoclinic form of  $ZrO_2$ . However, in the fully amorphous state that was analyzed, the U daughter product is present as U(IV), and it resides in a site unlike that of the Pu parent, suggesting that it is not in thermal equilibrium with the host. The Pu is present as Pu(III) and resides in a site that is very similar to  $PuSiO_4$ , the plutonium analog of zircon. Whether these effects are the result of self-radiation or artifacts of synthesis conditions will be tested in upcoming experiments.

Stored energy measurements have recently been completed on these glasses. The protocols for the preparation of specimens for transmission electron microscopy have been developed, and specimens will be prepared once the protocols are approved.

### **Gamma-irradiation Studies**

Temperature-controlled capsules have been designed and constructed for irradiations studies using the PNNL gamma irradiation facility. Six different glass compositions have been prepared, cut into wafers, and polished. Samples of each composition have been loaded into four different temperature-controlled capsules for long-term gamma irradiation (3 months to 1 year). Each capsule will be held at a different temperature (50°C, 100°C, 150°C and 200°C). The glass samples are currently under irradiation in the PNNL gamma (Co-60) irradiation facility.

### **Electron and Ion Irradiation Studies**

Several reference glasses are being used in initial electron and ion irradiation studies at Argonne National Laboratory and at Los Alamos National Laboratory to determine the conditions under which beam-charging effects can be minimized. Approaches that are currently being investigated include: 1) using electron flood guns, 2) using carbon coatings, and 3) using metal (aluminum, silver, or gold) coatings. Several series of irradiations on glasses are planned for the summer 1997. In addition, several ceramic specimens have been prepared for irradiation at the HVEM-Tandem facility (Argonne National Laboratory); the first of these irradiation studies on ceramics is scheduled for June 1997.

### **Reference Samples**

Standard reference samples have been provided to Argonne National Laboratory and Los Alamos National Laboratory as part of informal collaborations. Single crystals of  $\text{UO}_2$  have been provided to Los Alamos National Laboratory and the University of New Mexico under similar informal collaborations. Samples of reference phosphate glasses have been received from the University of Missouri - Rolla for radiation effects testing as part of a collaboration with their EMSP project on glass.

## References

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2. Weber, W.J. ,1990, "Radiation-Induced Defects and Amorphization in Zircon." *J. Mater. Res.* **5**:2687-2697.