Plutonium in Crystalline Ceramics and Glasses

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This article is a short qualitative summary of a chapter in the forthcoming book Advances in Plutonium Chemistry: 1967–2000, edited by Darleane Hoffman for the Amarillo National Research Center. The authors' intent here is to give an overview of the history and science of plutonium in ceramics and glasses, and they refer readers to the chapter for more technical details.

Introduction

The investigation of plutonium in glasses (amorphous ceramics lacking long-range order), in crystalline ceramics, and in composite materials composed of multiple crystalline or glass and crystalline phases, relies on multidisciplinary studies of physics, chemistry, and materials science. It involves the study of the plutonium atoms in materials with only short-range periodicity, as in glasses, to materials with long-range periodicity, as in crystals. The materials studied over the past 30 years include simple binary crystals, used to investigate the electronic structure of plutonium, to complex glasses and ceramics selected not only for the safety and durability that they provide for the immobilization of nuclear waste and plutonium, but also for the high flexibility they offer in composition. The lack of long-range order at the atomic level in glasses permits the inclusion of a broad range of waste elements, but it renders more difficult the interpretation of data from many commonly used experimental techniques. Regardless of the challenge, much of the research conducted in this field over the past few decades has been motivated by the use of plutonium as a surrogate for all nuclear-waste actinides or on its own in immobilization studies, in order to develop a durable glass or ceramic matrix that can resist leaching and mobilization of the plutonium on a geologic time scale.

The need for stability over a very long period, relative to the half-life of ²⁵⁹Pu or other long-lived actinides in high-level waste (HLW) is the essential driver of many compositional studies involving structural refinement, such as determining plutonium site valences and coordination, measuring the stability of the matrix under the effect of irradiation, and assessing its alterability under conditions expected in a geologic repository for waste disposal.

This article will present a review of the glass and ceramic systems in which plutonium can be dissolved and the flexibility of these materials in retaining various grades of plutonium, which often cannot be purified without great expense and difficulty. Since glass-matrix and ceramic materials often differ in their composition and technique of preparation, they are presented in separate and parallel sections, as is done in the book chapter being summarized.

The current international effort associated with the immobilization of excess weapons plutonium and plutonium residues within the nuclear-weapons complexes has resulted in pilot-scale and industrial facilities for plutonium immobilization located around the world. These facilities are currently processing or are in the testing phase for the processing of significant quantities of plutonium that may be incorporated into glasses or ceramics. The pouring of one such test glass at Savannah River is pictured in Figure 1.

Historical Aspects

Ceramic materials have been considered as viable waste forms for the disposal of commercial high-level nuclear-waste solutions in solid form since the 1970s, leading to many published studies on plutonium in glass and ceramics¹⁻⁵ and review publications that include valuable information on plutonium glasses.6 The plutonium remaining in the radioactive HLW resulting from defense-waste reprocessing and commercial HLW worldwide is minimal and leads to concentrations in the waste form of below 0.05 wt%. But in many cases, higher concentrations were studied at the laboratory scale as surrogates for all actinides and to investigate the effects of high radiation on the matrices. In 1994, 14 of the 20 countries participating in the international experience on radioactive-waste management⁷ selected glass as a waste form for geologic disposal. These glassy waste forms have been produced on a large scale for over three decades in Europe (the Marcoule and La Hague facilities in France, the Pamela facilities in Belgium and Germany), China, India, Japan, Russia, and in the United States (the Defense Waste Processing Facility and the West Valley Demonstration Project), leading to the processing of thousands of metric tons of HLW glass. Ceramic forms have also been fabricated for over a decade on a commercial scale. The Synroc Demonstration Plant, constructed at Lucas Heights, Australia, was commissioned in 1987 and utilizes hotpressing to consolidate Synroc, a dense, multiphase titanate-based waste form, from simulated reprocessed liquid HLW using the Purex* process.

With the end of the Cold War, new programs involving the management and disposition of weapons-grade plutonium have emerged. Specifically, as a result of the Strategic Arms Reduction Treaties and agreements made by presidents of the United States and Russia (START I, 1991, and START II, 1993), tens of thousands of nuclear weapons are being retired in both countries. These disarmament activities are expected to produce a surplus of more than 50 metric tons, pure and impure, of weapons-grade plutonium in each country, along with hundreds of tons of highly enriched uranium (HEU). According to the National Academy of Sciences, this resulting plutonium inventory represents " ... a clear and present danger to national and international security."

To address the problem of how best to manage the surplus plutonium from disarmament activities, the United States has adopted a two-part strategy. The almost 20 metric tons of impure plutonium in the form of scrap, residues, and so on, will

^{*}Purex stands for plutonium-uranium extraction; a diagram can be found at http:// www.ieer.org/ensec/no-2/purex.html.



Figure 1. Laboratory pouring of Pu-borosilicate glass at Savannah River. (Courtesy of D. Karraker.)

be immobilized into a crystalline ceramic matrix, and the more than 30 metric tons of relatively pure plutonium will either be made into a mixed-oxide (MOX) fuel for nuclear reactors or immobilized into crystalline ceramic forms. While both glassy and crystalline ceramic matrices have been studied for the immobilization of plutonium, the currently preferred immobilization medium in the United States is a titanate-based ceramic under development.⁹ At this time, the preferred methodology for final disposition in a U.S. government repository is a "can-in-canister" process,¹⁰⁻¹³ where plutonium ceramic cans are placed in HLW glass canisters. Similarly, two Russian options are considered:¹⁴ either homogeneous glass or ceramic compositions with an internal radiation barrier using induction melting, or can-in-canister glass or ceramic compositions with an external radiation barrier using induction melting.

In January of 1994, the Committee on International Security and Arms Control of the National Academy of Sciences (NAS) published the results and recommendations⁸ of an extensive multiyear study evaluating disposition options for the management of excess plutonium resulting from nuclear-disarmament activities. They concluded that "the two most promising alternatives for achieving these aims (long-term plutonium disposition) are: fabrication and use as fuel, without reprocessing, in existing or modified nuclear reactors; or vitrification in combination with high-level radioactive waste." A third possibility, involving burial of plutonium in deep boreholes, was also mentioned for possible future consideration.

As a result of the NAS study, a concentrated effort began in the 1990s. This effort focused on the investigation and assessment of the recommendations made by the NAS and, more specifically, consideration of the various reactor options and the vitrification immobilization recommendation. The effort on immobilization was later expanded to include initial screening of over 70 potential solidification matrices in addition to glass. Ceramic forms, both glassy and crystalline, emerged as the leading solidification matrices, and no "showstoppers" indicating the matrix to be too leachable or sensitive to radiation damage were identified for either the glassy or crystalline forms. An independent review team further concluded that "the two forms and their processes are similar in many ways," and both glassy and crystalline forms were able to satisfy existing criteria.¹⁵ Some of the noncrystalline ceramic systems were similar to the borosilicate glass compositions currently in worldwide use for immobilizing high-level radioactive wastes. The glass systems considered are borosilicates, soda-alumino phosphates, lanthanide silicates, and alkali-tin silicates (Table I). Various crystalline assemblages in crystalline ceramics were also tailored so that they could incorporate plutonium effectively. Some of the ceramic phases of interest have been zircon and zirconolite, pyrochlore, perovskite and titanite, monazite, and apatite (Table II). In either glass or ceramic, plutonium is uniformly distributed and an integral part of the material's structure. Both glassy and crystalline ceramic systems are able to achieve the desired results of immobilization of plutonium into highly durable waste-form products that would make reclaiming and reuse of the plutonium for military purposes difficult. Of these systems, the crystalline ceramic forms were determined to have more advantages in processing and product performance.9 In the following sections, the important features of these vitreous and crystalline materials, along with relevant considerations, observations, and results, are described.

Table I:Summary of Various Formulations of Glasses Containing Plutonium (wt%).																	
Reference: Glass ID:	[16]	[17] France SON58	[17] UK 189/209	[17] Germany VG98/3	[17] Belgium 78/7	[3]	[4]	[18]	[19]	[20]	[21]	[22]	[23, 24]	[23, 24]	[25]	[26, 27]	[28]
AI_2O_3		0.1	0–5	1	5			6.0	4.8	3.8	9–9.5	19	2.2	2.6	4		18.6
B_2O_3	19–20	19	11–22	10		11	9	7.0	7.6	7.8	4–5	10.4	8.9	12.7	13		
BaO									0.2	0.2	4					3.6	0.16
CaO				2		6	4	2.0	1.2	1.2							0.02
Fe ₂ O ₃		0.6	2.7	1	16			10.0	12.5	11.7					4.7	18.1	0.08
Gd_2O_3										0–2		7.6	3.8	3	11		
K₂O									3.5	3.6			7.7	4	1.5		0.24
La_2O_3											9–23	11					0.14
Li₂O			4			4		4.9	4.4	4.3			3.9	3.4	4		
MgO			6	0.4				0.7	1.4	1.3							
Na ₂ O	9–10	9.4	8	22		21	11–13	9.1	8.6	7.6			9.2	9.0	5	12.0	23.4
Nd_2O_3												11.4					0.43
P_2O_5					48										2	66.3	55.00
PbO											11–13						
SiO ₂	45-47	44	41–51	42		58	67–75	50.6	49.6	49	26–35	25.8	45.4	42.8	42		
Sm_2O_3											6–18						0.06
SnO													2.2	1.8			
TiO ₂				3.5			5		0.6				2.1	2.2			
ZnO							7 ª						3.1				
ZrO ₂								0.7		0.9	0.1-0.2	1.2	4.9	5			0.47
Others	19–23	23	9.7	16	28			3 [⊳]					0.9	0.5	1		1.4
PuO ₂	~3	~3	~3	~3	~3	~1	7	1.0	4–7℃	2–7°	6.9 and 15⁰	11.4 to	6	~8.5	10 and	22 ئ	~1
											15	10			20 as Fl	4	

^a Formulated by substitution from Na₂O and SiO₂.

bas U₃O₈

^c The authors give "as-batched compositions,"but optical observation indicates that the solubility of plutonium is exceeded—the glass includes crystals.

Tablell: Potential Plutonium or Actinide-Bearing Phases.

Structure Type	Composition
Oxides	
fluorite	ThO ₂ ; UO ₂ ; PuO ₂
pyrochlore	$A_2B_2X_6Y;RE_2Ti_2O_7;Gd_2Ti_2O_7$
zirconolite	CaZrTi ₂ O ₇
perovskite	CaTiO ₃
zirconia, ceria	ZrO ₂ ; CeO ₂
Silicates	
zircon	ZrSiO ₄
apatite	$Ca_{4-x}RE_{6+x}(SiO_4)_6O_{1+0.5x}$
titanite	CaTi(SiO ₄)O
Phosphates	
monazite	CePO ₄ , LaPO ₄
apatite	$Ca_{10-y}RE_y(SiO_4)_y(PO_4)_{6-y}F_2$
sodium	NaZr ₂ (PO ₄) ₃
zirconium	
phosphate	
(NZP)	
thorium	$Th_4(PO_4)_4P_2O_7$
phosphate	
diphosphate	

Plutonium in Ceramics andComposites

There have been two principal motivating factors over the past three decades for the interest in studies of plutonium in ceramics and composites. The first is related to developing fundamental scientific knowledge of radiation damage or the electronic and nuclear properties of plutonium in a wide range of solids. Such knowledge can be obtained by studying self-radiation effects from α decay^{29–35} or by using electron paramagnetic resonance (EPR)³⁶⁻³⁹ and optical spectroscopy techniques.40 The second factor is driven by the proposed use and stability of crystalline host phases for the immobilization of actinides from nuclear waste generated by the reprocessing of spent commercial nuclear fuels or from the production of nuclear-weapons materials.41-43

Recently, issues related to the disposition of excess weapons plutonium and plutonium residues from weapons production have prompted renewed interest into plutonium incorporation into crystal structures, solubility limits, and the effects of

radiation.43,44 In the specific case of excess weapons plutonium in the United States, the disposition of the plutonium may be done through incorporation into MOX nuclear fuel or into nonfertile (i.e., inertmatrix) fuel for burning in reactors, or by incorporation into ceramics for eventual disposal in a geologic repository.45,46 Similarly, the increasing worldwide inventory of plutonium generated by commercial nuclear-power production has initiated interest into the potential use of inert-matrix fuel to burn plutonium and other actinides, such as americium, without producing additional fissile material.47-

Much of the basic research regarding plutonium in ceramics has been focused on using ²³⁸Pu to study self-radiation effects due to α -decay events and both ²³⁹Pu and ²⁴²Pu in EPR studies. The short halflife of ²³⁸Pu, 87.7 years, ⁵³ allows sufficient α -decay events (radiation effects) to occur in reasonable laboratory time frames (several years), compared with 239Pu, which has a half-life of approximately 24,000 years.⁵³ Basic studies of radiation effects using short-lived actinides such as ²³⁸Pu have

several unique advantages. If the actinide is uniformly distributed, self-radiation from α decay produces bulk property changes, something that is usually obtainable only by neutron irradiation. Furthermore, the self-irradiation effects are produced by charged particles (α particles and recoil nuclei) of well-defined energies, rather than from the spectrum of recoil energies that is produced under neutron irradiation. Such well-defined energies make it easier to interpret and model observed behavior. One of the objectives of studies using short-lived actinides is to make comparisons to natural mineral analogues in order (1) to develop an understanding of α -decay damage over geologic time periods, (2) to develop scientifically based predictive models for geologic age dating, and (3) to assess the performance of nuclear waste forms.

Applied research on plutonium in crystalline ceramics has included studies of self-radiation effects in ²³⁸Pu-doped Synroc and its constituent phases.54,55 Self-radiation effects have also been studied in a ²³⁸Pudoped celsian glass ceramic,⁵⁶ which was another multiphase waste proposed early on. The reported radiation-induced swelling in these materials is shown in Figure 2. Other applied research has focused on the use of ²³⁹Pu in single-phase ceramics proposed for the immobilization of waste actinides and excess weapons Pu. One such ceramic proposed for plutonium immobilization is zircon (ZrŜiO₄),⁴² where Pu⁴⁺ can be readily accommodated by substitution on the Zr⁴⁺ site,⁵⁸ as illustrated in Figure 3a. Under a reducing atmosphere, where Pu³⁺ is the preferred valence state, the most stable configuration for Pu³⁺ accommodation is as a defect cluster consisting of two Pu³⁺ substitutions on nearneighbor Zr4+ sites and a neighboring charge-compensating oxygen vacancy, V₀. as illustrated in Figure 3b.



Figure 2. Macroscopic swelling in ²³⁸Pu-doped Synroc⁵⁴ and ²³⁸Pu-doped glass ceramic.⁵⁷



Figure 3. Stable configurations for incorporations of plutonium in zircon ($ZrSiO_4$): (a) Pu^{4+} substituted on a Zr^{4+} site, and (b) Pu^{3+} as a defect cluster consisting of two Pu^{3+} substitutions on near-neighbor Zr^{4+} sites and a neighboring charge-compensating oxygen vacancy. (Courtesy of R.E. Williford, Pacific Northwest National Laboratory.)

As in the case for zircon, plutonium and other actinides can be accommodated on the Zr site in stabilized ZrO_2 , which is a candidate material to use as an inert matrix for plutonium burnup in a reactor or accelerator-based neutron source.^{47–49,52} Some of the first tests of ZrO_2 -PuO₂ as a nuclear-fuel material, however, were performed in the early 1960s at the Hanford Site in Washington state.⁵⁹

Plutonium in Glasses

Over the past 40 years, an enormous amount of work has been conducted worldwide at national laboratories, in academia, and by industry on developing vitrification technologies for the immobilization of a variety of potentially hazardous materials. At a 1996 international workshop,⁶⁰ the status of industrial experience was presented by Belgium, China, France, Japan, Russia, the United Kingdom, and the United States. Building on this experience, existing vitrification technologies, procedures, equipment and facilities, and solidification matrices were examined for possible use in vitrifying uranium, plutonium, and a variety of other actinides (including curium, americium, and neptunium).61-67

Because glasses have a random network structure (three-dimensional [SiO₄] tetrahedron for silicate and chain structure for phosphate where only three corners of a [PO₄] are cross-linked), they can incorporate a wide range of chemical elements.^{68,69} For HLW glasses, borosilicate compositions that include 30–40 different elements (and in fact, significant variations in the amounts of these components) are used routinely. Such compositions produce a highly durable glass product. Most elements play one of three basic roles in glass structures: network formers, network modifiers, and intermediates. As presented in the hypothetical borosilicate glass structure in Figure 4, the network is primarily formed of the chains of borate and silicate polyhedrons. Lithium, sodium, and calcium are typical glass modifiers that will create nonbridging oxygens in the network and also provide the charge balance in the vicinity of the plutonium-oxygen polyhedrons. Because glasses that contain significant amounts of uranium and rare-earth elements have been prepared for at least a century (so-called Anna yellow, containing uranium, and various colors of Löffler rareearth glasses from the Bohemian glass plant, 1900s–1930s), glass-matrix network structures could be expected to incorporate actinides, including impure as well as pure plutonium. The dissolution of actinides, and also of many minor components, has been demonstrated in both americium/ curium and plutonium vitrification.^{70,71}

Based on glass structures as well as bonding energies, an empirical correlation has been made between Pu-based glasses and other radioactive-waste glass systems.72,73 The correlation is summarized in Figure 5, which focuses on the small fraction of the ternary diagram (glass formers, modifiers, intermediates) where the glasses used in the nuclear industry are found. The compositional ternary diagram illustrates the relationship between plutonium glasses that have been proposed as waste forms in the United States and various HLW glasses from around the world. Superimposed on the figure is a transuranic (TRU) wasteglass composition. A commonality exists between the many different radioactive waste-glass systems (including actinide glasses), based on radioactive waste-glass compositions and the structural role components play in a glass. The glass formers



Figure 4. Hypothetical borosilicate glass structure; primarily formed of chains of borate and silicate polyhedrons. Lithium, sodium, and calcium glass modifiers create nonbridging oxygens in the network and provide charge balance in the vicinity of the plutonium-oxygen polyhedrons. (Courtesy of D. McKeown.)

occupy 60–85 wt% of the structure as well as up to 25 wt% intermediates, and 15–40 wt% are modifiers.

The ability to include significant amounts of plutonium in glass systems was demonstrated more than 20 years ago. For example, 7 wt% PuO₂ was dissolved into a HLW borosilicate glass composition,19 and the solubility of PuO₂ in the German GP98 glass was determined to be 4.4 wt%.74 More recently, even higher plutonium loadings have been demonstrated on a laboratory scale for selected systems²⁶ (see Table I). Others have succeeded in dissolving over 11 wt% PuO₂ in lanthanide silicate glasses using several PuO₂ source materials, but the maximum loadings have not yet been determined.²² Feng et al.²⁵ investigated the possibility of including plutonium at a much higher concentration (at least 25 wt% PuO₂) when melted under reducing conditions. Hence, plutonium can be included in many glass systems. The optimum amount may not be determined solely by solubility considerations, but by criticality constraints and by the effect, if any, of Pu content on durability.

There have been a variety of glass systems studied for the immobilization of actinides, including plutonium. Among these systems are borosilicate compositions, lanthanide silicates, and iron phosphate systems.²⁶ The latter two glass systems were expected to have a high degree of compatibility with actinide oxides and have been found to produce actinide glass products that can be more durable than the HLW glass compositions currently in production. In fact, a lanthanide silicate is currently used in the Savannah River Am/Cm vitrification75 and a sodium alumino phosphate has been selected as a waste form in Russia.14

Several factors influence the valence and coordination of actinides in glasses: the stability of a particular valence state, the oxidation–reduction potential of the melt, the size of the actinide ion relative to the site it occupies, and the coordination afforded by the crystal lattice in the glass. In common with other "hard" polyvalent ions, there is no preferred directional bonding of plutonium. The 5*f* orbitals are sufficiently shielded from the ionic environ-

ment that they do not exert a directional effect. The actinides, as with other "hard" polyvalent ions like Al and Zr, attract a shield of negative ions to achieve a charge balance that makes plutonium a potential glass network intermediate, as illustrated in Figure 4.

The valence of actinides in glasses has been determined by optical-absorption spectroscopy, extended x-ray absorption fine structure (EXAFS) spectroscopy, and x-ray absorption near edge structure (XANES) spectroscopy. In addition, the valence state of actinides can be reliably determined through examining their bonding properties using x-ray photoemission spectroscopy. All of these methods identified the normal valence state of plutonium in a borosilicate glass matrix as Pu(IV) and generally at a high coordination number of 6-8. In the melts prepared under flowing oxygen, no valence higher than Pu(IV) could be obtained, but in a reducing atmosphere of flowing CO/CO_2 or excess graphite, plutonium could be reduced to Pu(III).

As with ceramics, the α decay of plutonium can lead to some changes in structure and a potential degradation of properties in glass systems. Self-radiation effects have been studied in a wide range of relevant glass compositions containing ²³⁸Pu.⁷⁶ Because of the already random structure of these glasses, the effects of self-radiation are generally small at the ambient temperatures expected over the decay time for plutonium. This is illustrated in Figure 6, where the maximum volume expansions or compactions from self-radiation damage are only of the order of 1%. Under conditions of elevated temperatures, such as in the presence of fission products, data on radiation effects are limited. In this situation, the combined effects of radiation damage and the high mobility of defects and ions in the glasses could lead to even less degradation because of annealing processes; however, increased degradation due to phase separation may also occur.

Long-Term Disposition

Chemical durability and resistance to self-radiation damage are the most important technical performance properties of a radioactive waste form. Leaching provides a physical measure of how well the glass or ceramic structure can incorporate radionuclides and retain them in its matrix if exposed to water in a repository setting. Resistance to self-radiation damage determines how rapidly the structure and properties of either a ceramic or glass will degrade due to the effects of ionization and elastic nuclear collisions from the α particles and recoil nuclei released by



Figure 5. Compositional ternary diagram displaying high-level waste (HLW), transuranic (TRU), and Pu glasses; the coordinates given at the apex of the striped triangle give the position in the (glass former, glass modifier, intermediate) larger ternary diagram. (After References 72 and 73.)



Figure 6. Macroscopic volume changes in several ²³⁸Pu-doped simulated nuclear-waste glasses.^{57,77}

the decay of plutonium incorporated in the atomic structure.

For leach testing, many institutions worldwide have developed different protocols; it is often difficult to compare the diverse data presented in the literature. The most commonly used tests include those developed by the Material Characterization Center in the United States (MCC1), the soxhlet test used in Europe, the MCC3 test using powdered samples, and more recently the Product Consistency Test (PCT) developed at Savannah River. The temperature of testing is most frequently 90°C, but can range from room temperature to 200°C. The essential role played by the formulation of the glass is taken into account in expressing leaching "as normalized" by dividing the concentration measured in the leachate for any given component by its fraction in the glass. The normalized release of the component is therefore expressed as a concentration normalized to its content in the glass (g/l). For elements that are highly soluble and leach congruently, such as boron, lithium, and sodium, the normalized concentration truly reflects the glass durability. Other elements will display their "percolating" role, that is, the capability to slow the loss of the more mobile alkali elements and boron. The variation in size of the glass samples tested and the volume of leachant used are also corrected

by dividing the normalized concentration by the ratio of the surface area of glass exposed to the solution volume (S/V), in m^{-1}). In this case, the leaching is expressed in g/m^2 , as presented in Figure 7. Leaching periods of a few days at 90-100°C in deionized water have been used. It is clear that plutonium glasses and ceramics are more durable than most familiar commercial glass systems and that plutonium is better retained in the glass and ceramics than in the other components. This is primarily due to the fact that the plutonium diffusion coefficient in glass is extremely low $(10^{-18} \text{ cm}^2 \text{ s}^{-1})$. Second, the leaching of plutonium becomes less congruent with increasing temperature or decreasing leachate-renewal frequency. Better understanding of plutonium leaching behavior was attained by varying both the temperature (room temperature to 100°C) and the water-renewal rate (static, various renewal rate and soxhlet reflux).78

The degradation effects of self-radiation damage from Pu decay in most of the crystalline phases of interest and for many dif-



Figure 7. Normalized leaching of silicon, boron, and plutonium from various glasses.

ferent glasses are fairly well known. Largely because of multiple uses (and sponsors) for ceramics in high-radiation environments and the continual support of fundamental research, an atomic-level understanding of dynamic self-radiation damage processes in ceramics is emerging that provides predictive models of performance under all disposition scenarios, as illustrated in Figure 8 for crystalline phases, Gd₂Ti₂O₇ and ZrSiO₄, proposed for the immobilization of plutonium. Similar understanding and models could be developed for glasses. One of the more exciting outcomes from the fundamental research has been the recent discovery 79,80 of a chemically durable, radiation-resistant class of ceramics (gadolinium zirconate pyrochlores) that can readily accommodate plutonium and other actinides yet remain structurally unaffected by self-radiation damage for millennia, as illustrated in Figure 8. This discovery has been recognized by the U.S. Department of Energy as one of the top 101 discoveries within the Office of Science during the past 25 years.⁸¹ Application of this breakthrough technology could eliminate issues involving the degradation of ceramic waste forms due to selfradiation effects.

Conclusion

Two final examples will be cited to attest to how glasses and ceramics provide industrial solutions to the global problems of plutonium proliferation and environmental contamination. In the United States, plutonium will be disposed of in small



Figure 8. Relative radiation damage (i.e., radiation-induced amorphous fraction) as a function of cumulative α -decay events and equivalent storage times for Gd₂Ti₂O₇, ZrSiO₄, and Gd₂Zr₂O₇ containing 10 wt% ²³⁹Pu. The radiation resistance of Gd₂Zr₂O₇ was discovered by a team of researchers led by the University of Michigan and Pacific Northwest National Laboratory,^{73,80} which has been recognized by the U.S. Department of Energy as one of the top 101 discoveries during the past 25 years within the Office of Science.⁸¹

cans of a plutonium ceramic suspended in canisters of HLW glass produced at Savannah River. In Australia, the government has decided to use *in situ* vitrification (ISV) to stabilize the plutonium in the most contaminated pits of the Maralinga nuclear-weapons test range.⁸²

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