MASTER**DISCLAIMER**

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

CONF-8110113--2

A REVIEW OF RADIATION EFFECTS IN SOLID-NUCLEAR-WASTE FORMS

W. J. Weber

September 1981

To be presented at the
Third Argonne Workshop on
Basic Problems in Nuclear
Waste Management. Argonne
National Laboratory,
October 1-2, 1981

Prepared for the
U.S. Department of Energy
Under Contract DE-AC06-76RLO 1830

• Pacific Northwest Laboratory
Richland, Washington 99352

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MGW

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

MATERIALS CHARACTERIZATION CENTER

RADIATION EFFECTS*

*Section 6 of PNL-3802,
A State-of-the Art Review
of Materials Properties of
Nuclear Waste Forms

Pacific Northwest Laboratory
Richland, Washington 99352

6.0 RADIATION EFFECTS

Radiation effects on the stability of high-level nuclear waste (HLW) forms are an important consideration in the development of technology to immobilize high-level radioactive waste because such effects may significantly affect the containment of the radioactive waste. Since the required containment times are long (10^3 to 10^6 years), an understanding of the long-term cumulative effects of radiation damage on the waste forms is essential. Radiation damage of nuclear waste forms can result in changes in volume, leach rate, stored energy, structure/microstructure, and mechanical properties. Any one or combination of these changes might significantly affect the long-term stability of the nuclear waste forms. This report defines the general radiation damage problem in nuclear waste forms, describes the simulation techniques currently available for accelerated testing of nuclear waste forms, and reviews the available data on radiation effects in both glass and ceramic (primarily crystalline) waste forms.

6.1 BACKGROUND ON RADIATION EFFECTS

This section discusses the sources of radiation effects in high-level nuclear wastes and the various state-of-the-art simulation techniques currently available for accelerated testing of the different waste forms.

6.1.1 Sources of Radiation Effects in Nuclear Waste Forms

The chief sources of radiation in the high-level nuclear waste forms are beta decay of the fission products (primarily cesium and strontium) and alpha decay of the actinide elements (uranium, neptunium, plutonium, americium, and curium). Spontaneous fission of some of the actinide isotopes and alpha-neutron reactions are sources of fission fragments and neutrons, but these radiation sources can generally be ignored because of their low production rates. Projected numbers of beta, alpha, and neutron events per metric ton of heavy metal for a commercial high-level waste are shown in Figure 6.1 for storage times up to 10^6 years (Roberts, Turcotte, and Weber 1981). In

FIGURE 6.1. Cumulative Doses for a Commercial High-Level Waste (Roberts, Turcotte, and Weber 1981)

general, beta decay of the fission products predominates during the first 500 years with high radioactivities and high waste-form heat generation, while alpha decay predominates at longer times with a much lower heat generation rate.

Radiation damage in the waste forms is primarily produced by 1) the displacement of waste-form constituent atoms from their normal sites by elastic collisions of the nuclear projectiles with the atoms, 2) ionization effects, and 3) the transmutation of radioactive parent nuclei into different elements. These effects are discussed in the following two sections as related to the radiation sources (i.e., beta decay and alpha decay).

6.1.1.1 Effects of Beta Decay

Beta decay produces high-energy beta particles and gamma radiation that interact with the entire waste form solid primarily by ionizing processes and produce very few direct atomic displacements. From collision theory, beta particles are estimated to produce on the order of one displacement per decay event, and gamma radiation is relatively unimportant in displacement production (Roberts, Turcotte, and Weber 1981; Jenks and Bopp 1973). Displacements can also be produced in ionic solids by ionization, the principal interaction mode of beta particles and gamma radiation with solids. The electronic excitations caused by ionization can be localized (as separated or associated electron-hole pairs) and persist for sufficiently long times that the lattice becomes unstable and produces permanent ion displacements, a process often referred to as radiolysis (Hobbs 1976). In this manner, substantial displacement damage can be produced by ionizing radiation in those ionic solids where this mechanism is efficient (halides, hydrides, and azides). However, numerous ionic solids (mostly oxides) do not exhibit this effect, and it has not been established experimentally that this mechanism does occur in any of the waste forms currently under consideration.

The effects of ionization from beta-gamma interaction with the waste form solids include covalent bond rupture, valence changes, H_2O and OH^- decomposition (an important consideration for waste forms with a high water content), and decomposition of unstable molecular ions. Additionally, a radiation-induced change in the leach rate can result from radiolysis of the atmosphere and ground water in the presence of the intense ionizing radiation field (beta-gamma) associated with beta decay. Radiolysis of air or nitrogen in the presence of water can result in the formation of nitric acid (Jones 1959). Water radiolysis may result in the formation of various reactive-free radical and ionic species as well as hydrogen peroxide (Burns and Moore 1976; Draganic and Draganic 1971).

Another potential source of radiation-induced changes is the transmutation of the fission products. The two main sources of transmutations are the intermediate-lived fission products, ^{137}Cs (30.2 years half-life) and ^{90}Sr (28.1 years half-life), which undergo the following decay schemes:

Transmutations can involve valence changes and major changes in atomic radii. Glass waste forms are more likely to tolerate these changes because they already have 10 to 25 elements present, including substantial concentrations of barium and zirconium. The crystalline phases in ceramic waste forms have ordered structures and are less likely to accommodate these kinds of changes.

6.1.1.2 Effects of Alpha Decay

Alpha decay results in the formation of two particles: a high-energy alpha particle (~4–6 MeV) and a recoil nucleus (~0.1 MeV). Nearly all the energy of the recoil nucleus is lost through elastic collisions with the waste form constituent atoms, producing several thousand atomic displacements. The alpha particle, on the other hand, dissipates most of its energy by ionization but still undergoes enough elastic collisions to produce several hundred atomic displacements. It is generally assumed that the primary source for radiation damage in nuclear waste solids is from displacement damage. Since alpha decay produces several orders of magnitude more displacements than any other radiation source as illustrated in Figure 6.2, most of the studies on radiation effects in waste solids have emphasized alpha decay effects.

The ionization dose from the alpha particles is significant and may exceed the ionization dose from beta-gamma radiation as illustrated in Figure 6.3 for commercial high-level waste. Consequently, all the ionization effects discussed in the previous section also apply for alpha particles. These effects (ionization-induced displacements, covalent bond rupture, valence changes, and water and air radiolysis) may also be significant as related to displacement damage; however, experimental evidence at this time tends to suggest that displacement damage dominates.

In complex ceramic waste forms, where the crystal size is small (0.1 to 10 μm), the alpha particles, which have a range of ~20 μm , effectively bombard

FIGURE 6.2. Cumulative Atomic Displacements in Commercial High-Level-Waste Solid (Roberts, Turcotte, and Weber 1981)

FIGURE 6.3. Sources of Ionizing Radiation Doses in Solidified Commercial High-Level Wastes from LWR Fuel Reprocessing. Burnup 33,000 MWd/MTHM; 5-Year cooling prior to reprocessing and solidification; 170 kg solidified waste/MTHM.

the entire solid, including the nonactinide-containing phases; the damage from the recoil nuclei, however, because of their short range ($\sim 0.01 \mu\text{m}$), is confined to the phase in which the actinides are chemically incorporated. Consequently, alpha decay actually results in two related but different damage mechanisms: alpha-recoil damage (i.e., damage resulting from the synergistic effect of both alpha particle and recoil nucleus) in the actinide host phases and alpha particle damage in the nonactinide-containing phases.

Transmutation effects from the alpha decay of the actinides are generally ignored because the relatively few events produce only modest compositional changes over very long times.

6.1.2 Simulation Techniques

The effects of radiation on nuclear waste solids are produced by the decay of radioactive waste species contained within the waste form. The radiation damage accumulates over the decay time of these radioactive species and thus occurs over a period of hundreds to a million or more years. Laboratory experiments to test the radiation stability of proposed nuclear waste forms must, therefore, be accelerated simulation experiments. This section reviews the simulation techniques now being used to obtain data on the radiation stability of nuclear waste solids.

6.1.2.1 Actinide Doping Techniques

The long-term effects of alpha decay in nuclear waste forms can be effectively simulated in the laboratory by incorporating a short-lived actinide isotope, such as ^{238}Pu (87.7 years half-life) or ^{244}Cm (18.1 years half-life), in either a simulated waste form or the proposed actinide host phase (or phases) and allowing it to damage by self-radiation. This technique accurately reflects the long-term damage from alpha decay in the proposed waste forms. The technique is the basis for the test procedure drafted by the International Standards Organization (ISO) as a Standard Method for Testing the Irradiation Stability of Solidified Radioactive Waste (ISO/DIS 6962). The Materials Characterization Center (MCC) in the United States has also proposed a standard test procedure (MCC-6) based on actinide doping for accelerated testing of alpha decay effects.

6.1.2.2 Neutron Irradiations

Neutron irradiations take three different approaches, all involving in-reactor irradiations, to induce radiation damage in nuclear waste forms. One approach is to irradiate the test specimens of the proposed waste forms in a fast-neutron flux of a research reactor (Roberts, Jenks, and Bopp 1976; Reeve et al. 1980, 1981). The fast neutrons undergo elastic collisions with atoms in the waste solid, producing energetic primary knock-on atoms that undergo further elastic collisions as they slow down, resulting in numerous displacements. It is argued that the resultant displacement damage correlates with the damage from alpha decay, particularly the displacement damage from the recoil nuclei; however, such correlations are never easily made or easily interpreted. The method is simple and produces only moderately radioactive samples; however, it does have two disadvantages that must be considered:

- As no alpha particles are produced in this approach, there is no simulation of effects of helium atom deposition in the structure or any synergistic effect of the alpha particle damage with the recoil nucleus damage.
- In multiphase waste forms, all phases will experience the same fast neutron dose; whereas, in reality, some phases will contain no actinides and, therefore, will not experience recoil nuclei damage. These nonactinide-containing phases will be subject only to beta-gamma radiation and to alpha particles, which originate in the actinide-containing phases.

Another neutron irradiation technique (Antonini, Lanza, and Manara 1979) involves doping the waste form with ^{235}U (oxide) and irradiating test specimens in the neutron flux (thermal or fast) of a reactor. Such irradiation causes the ^{235}U to fission, producing high-energy fission fragments, which cause displacements. This method provides a less accurate simulation of alpha decay damage than does fast neutron irradiation, and correlation of the damage to alpha decay damage is difficult, if not impossible, as recently pointed out by Weber (J. Nucl. Mater., in preparation). This technique also results in highly active specimens that must be stored for some time to allow sufficient radioactive decay before examination.

The third technique (Malow and Andresen 1979) involves utilizing the high ^{10}B (n, α) cross section for slow neutrons. Boron-containing or boron-doped waste forms are irradiated in the slow-neutron flux of a reactor, producing alpha particles ($E_{\text{max}} = 1.78$ MeV). High rates of helium formation are possible, and borosilicate glasses require no actual boron doping. A major disadvantage is that the damage produced is not completely equivalent to alpha-recoil damage.

6.1.2.3 Charged-Particle Irradiations

Charged-particle irradiations with electrons, protons, alpha particles, or heavy ions (Ni, Pb) offer a technique for simulating radiation damage in very short times without the difficulties associated with handling radioactive materials. The results, however, are difficult to interpret because the effects are concentrated in a narrow surface layer and in a small area, making post-irradiation analysis more difficult. The assumptions behind these methods are as follows:

- All the energetic particles, including high-energy electrons ($E > 0.5$ MeV), produce displacement damage that probably can be correlated with the displacement damage from alpha decay.
- Heavy-ion irradiation should simulate the damage from recoil nuclei.
- Alpha bombardment, particularly with alphas emitted by an actinide source, provides a realistic simulation of irradiation effects due to alpha particles in the nonactinide-containing phases.
- High-energy electron irradiations (>0.5 MeV) can simulate high-energy beta damage. Low-energy electron irradiations (<0.5 MeV) cause only ionizing damage, which can simulate beta-gamma ionization effects.

The first two assumptions are difficult to completely justify because correlation of damage produced by different particles is never straightforward, and irradiation damage from a single particle type may be quite different from the real case, where the synergistic effects of all the radiation species are included. The last two assumptions are more easily justified for the specific cases indicated; post-irradiation analysis, however, is still limited because of the small volume irradiated.

6.1.2.4 Gamma Irradiations

The effects of gamma radiation on the properties of nuclear waste forms or on leach rate (due to radiolysis of the atmosphere and ground water surrounding the waste form) are most effectively and accurately simulated by performing irradiation testing in a gamma-radiation facility that incorporates a ^{60}Co source. Dose rates on the order of 2.5×10^6 R/hr are easily obtainable, and in some facilities dose rates of $\sim 10^7$ R/hr are achievable with some heat generation.

6.1.2.5 Transmutation Simulation

Techniques for simulating transmutation effects in nuclear waste forms are limited. At present, only one experimental procedure has been utilized to study transmutation effects. In this technique (Chick et al. 1980; Weber, Wald, and Gray 1980), nuclear waste forms and selected single-phase materials are neutron-irradiated to convert a large fraction ($\sim 12\%$ in that study) of the natural ^{133}Cs to ^{134}Cs , which then transmutes to ^{134}Ba with a 2.06-year half-life. Immediately after irradiation, the materials are annealed to remove the neutron damage, and changes in waste form properties are then monitored as a function of the transmutation ingrowth.

6.1.3 Radiation Damage in Natural Minerals

Another approach to help understand the complex effects of radiation damage in nuclear waste forms, particularly crystalline waste forms and their proposed actinide host phases, is by evaluating radiation damage in natural minerals. Radiation damage in natural minerals results from the alpha decay of the uranium and thorium nuclides incorporated within the crystal structure. The damage in the minerals manifests itself in several ways, such as the formation of fission tracks, pleochroic halos, and metamict minerals (Ewing, 1981).

Most of the interest in this area has centered on the metamict minerals, particularly those that are isostructural or structurally similar to proposed actinide host phases in crystalline waste forms. Metamict substances are those which were originally crystalline but have become amorphous. Although

the mechanism for loss of crystallinity in these minerals is not clearly understood, damage caused by the decay of the uranium and thorium nuclides is certainly critical in metamictization. Comparison of metamict and nonmetamict polymorphs, such as thorite and huttonite (ThSiO_4), may provide a basis for understanding the susceptibility of different crystal structures to radiation damage (Ewing and Haaker 1980).

In recent years, several synthetic mineral types have been proposed as ideal hosts for actinides in nuclear waste ceramics, such as the supercalcine and SYNROC formulations, based on the apparent radiation and chemical stability of the closely related natural minerals over a wide range of geologic and geochemical environments. Many of these natural mineral analogues are only relatively stable with respect to radiation damage and often tend toward metamictization over long geologic time. The modification of the chemistry of the synthetic minerals in actual high-level waste ceramics may make some of these actinide host phases more susceptible to radiation damage.

In general, the natural mineral analogues of proposed actinide host phases in nuclear waste ceramics provide only qualitative information about the radiation stability of the proposed synthetic mineral phases. The available information on these natural analogues is often incomplete or inconsistent on such aspects as age, weathering, and change in leach rate as a result of metamictization. Clearly, the testing of radiation damage in simulated waste forms containing these proposed synthetic minerals is needed to conclusively demonstrate the structural and chemical stability of these phases to radiation damage.

6.2 RADIATION DAMAGE IN GLASS WASTE FORMS

Glass is a highly developed solid form for the storage of high-level nuclear wastes (Mendel 1978). As a result, most of the studies of radiation damage, both in the United States and abroad, have concentrated on proposed glass waste forms. The experimental results to date on the effects of radiation damage on volume, leach rate, stored energy, structure/microstructure, and mechanical properties of glass waste forms are reviewed below. Much

of the data represents radiation damage effects produced by alpha decay in actinide doped waste forms, since it is generally assumed that this mechanism is the primary source for radiation damage in nuclear waste forms (Section 6.1.1.2).

There also exists a large volume of radiation effects data for earlier work on glass for other applications; this information is not included in this report. Primak (1977), however, has recently reviewed some of the data on radiation effects in simple glasses pertinent to the development of nuclear waste glasses. Reviews of extensive early work on radiation damage in glass are also available (Gilmour and Heenan 1965; Riley, Coppins and Duckworth 1958).

6.2.1. Volumetric Changes

The volume (or density) of high-level nuclear waste glasses can decrease, increase, or remain unchanged as a result of radiation damage. Volume changes can cause internal stresses in the waste glass, particularly in partially devitrified glass if differential volume expansions occur, and can also lead to possible strains in the metal canister. Almost all the data on radiation-induced volume changes in nuclear waste glasses have been obtained in actinide doping studies of alpha decay damage. There is also a very limited amount of data from neutron-induced fission damage and from electron irradiations.

6.2.1.1 Actinide Doping

Several waste glass compositions have been studied at the Pacific Northwest Laboratory (PNL) using the actinide-doping technique described in Section 6.1.2.1 (Mendel et al. 1976; Mendel et al. 1977; Ross et al. 1978; Ross and Mendel 1979; Weber et al. 1979). The compositions of these waste glasses are given in Table 6.1, along with the concentration of the actinide dopant ($^{244}\text{Cm}_2\text{O}_3$). One glass composition (PNL 77-260) was prepared in three initial forms: one vitreous and two partially devitrified (Weber et al. 1979). One of the partially devitrified glass forms (slow-cooled at 6°C/hr from 1050°C) contained large crystals (~ 25 to $100\text{ }\mu\text{m}$), and the other (700°C , 1 week) contained a fine dispersion of small crystals ($< 5\text{ }\mu\text{m}$). The change in density as a function of accumulated dose was measured. The density measurements were

TABLE 6.1. Composition of PNL Simulated High-Level Waste Glasses

COMPONENT	72-68-a	72-68b	76-68	76-260	E-G	P-G
Weight Percent of Component						
<u>Glass Components</u>						
SiO ₂	27.0	27.0	38.8	34.9	50.6	23.4
B ₂ O ₃	11.0	11.0	9.2	8.7	12.7	7.3
Li ₂ O	--	--	--	--	4.0	--
Na ₂ O	4.0	4.0	7.3	7.8	5.1	2.8
K ₂ O	8.0	4.0	--	1.9	--	2.8
TiO ₂	--	--	2.9	5.8	--	--
CaO	1.5	1.5	1.9	1.0	2.6	--
MgO	1.5	1.5	--	--	--	--
SrO	1.5	1.5	--	--	--	--
BaO	1.5	1.5	--	--	--	--
Al ₂ O ₃	--	--	--	1.9	--	--
ZnO	21.0	21.0	4.9	--	--	--
PbO	--	--	--	--	--	38.0
CuO	--	--	--	2.9	--	--
<u>Fission Products</u>						
Rb ₂ O	0.22	0.22	0.12	0.10	0.22	0.22
SrO	0.65	0.65	0.36	0.26	0.65	0.65
Y ₂ O ₃	0.02	0.02	0.20	0.15	0.02	0.02
ZrO ₂	3.04	3.04	1.70	1.33	3.04	3.04
MoO ₃	3.91	3.91	2.17	1.73	3.91	3.91
RuO ₂	1.82	1.82	1.02	0.76	1.82	1.82
Rh ₂ O ₃	0.30	0.30	0.17	0.14	0.30	0.30
PdO	0.91	0.91	0.51	0.44	0.91	0.91
Ag ₂ O	0.05	0.05	0.03	0.02	0.05	0.05
CdO	0.05	0.05	0.03	0.03	0.05	0.05
TeO ₂	0.45	0.45	0.25	0.19	0.45	0.45
Cs ₂ O	1.77	1.77	0.99	0.70	1.77	1.77
BaO	0.96	0.96	0.54	0.49	0.96	0.96
La ₂ O ₃	1.97	--	0.51	0.40	1.97	1.97
CeO ₂	3.98	--	1.15	0.81	3.95	3.95
Pr ₆ O ₁₁	0.41	--	0.51	0.39	0.41	0.41
Nd ₂ O ₃	1.40	--	1.50	4.13	1.40	1.40
Sm ₂ O ₃	0.25	--	0.32	0.01	0.25	0.25
Eu ₂ O ₃	0.06	--	0.07	0.05	0.06	0.06
Gd ₂ O ₃	0.17	--	0.05	0.03	0.17	0.17
<u>Actinides</u>						
U ₃ O ₈	--	--	4.39	4.67	--	--
Cm ₂ O ₃	1.0	8.2	3.0	3.0	1.0	1.0
<u>Others (a)</u>						
Na ₂ O	--	--	4.84	2.31	--	--
Fe ₂ O ₃	0.93	0.93	9.38	1.08	0.93	0.93
Cr ₂ O ₃	0.21	0.21	0.40	0.02	0.21	0.21
NiO	0.09	0.09	0.20	0.01	0.09	0.09
P ₂ O ₅	0.41	0.41	0.46	2.08	0.41	0.41
MnO ₂	--	--	--	0.09	--	--
Gd ₂ O ₃	--	--	--	9.11	--	--
ZrO ₂	--	--	--	0.12	--	--

(a) Includes corrosion products, nuclear poisons, process chemicals, and cladding residues.

made on ~3-g test specimens by the buoyancy technique. The density changes (percent) as a function of accumulated dose for these waste glass compositions are shown in Figure 6.4. The glasses either expanded (density decrease) or contracted (density increase), depending on composition. The density changes tend to follow an exponential behavior as a function of dose, as described by the following relation:

$$\Delta\rho/\rho = A[1 - \exp(-\delta D)] \quad (1)$$

where ρ is the density of the glass, D is the dose (alpha decays/cm³), and A and δ are material-dependent parameters (A is the density change at saturation

FIGURE 6.4. Density Changes in ²⁴⁴Cm-Doped Waste Glasses (Roberts, Turcotte, and Weber 1981)

and B determines the rate of density change). The values of A and B, as determined by regression analyses of the data, for the different waste glasses are given in Table 6.2. From the results, the volumetric changes in these waste glasses should not exceed approximately $\pm 1\%$; a volume change on this order can be tolerated by present canister designs (Mendel 1978).

Bibler and Kelley (1978) have evaluated the effects of internal alpha decay on the density of a borosilicate glass (52.5 wt% SiO_2 , 10 wt% B_2O_3 , 22.5 wt% Na_2O , 10 wt% TiO_2 , and 5 wt% CaO) for long-term storage of Savannah River Plant (SRP) radioactive waste. Two glasses, each containing 45 wt% of a simulated dry waste [50 mole% $\text{Fe}(\text{OH})_3$ and 50 mole% MnO_2], were prepared by actinide doping. One was doped with 0.49 wt% ^{244}Cm , and the other with 0.97 wt% ^{238}Pu . A third glass, containing no simulated waste, was also prepared by doping with 0.81 wt% ^{238}Pu . Measurements were made over a period of 420 days to an accumulated dose of $\sim 1.2 \times 10^{18}$ alpha decays/ cm^3 for the ^{244}Cm -doped glass and $\sim 6 \times 10^{17}$ alpha decays/ cm^3 for the ^{238}Pu -doped glasses. Density measurements (performed at $22 \pm 1^\circ\text{C}$ by weighing in air and carbon tetrachloride) of all three glasses showed a volume expansion that increased linearly with dose over the range studied. The maximum volume change observed

TABLE 6.2. Values of Constants A and B, for Exponential Dependence of Density Change in PNL Glasses (adapted from Roberts 1980)

<u>PNL Glass Composition</u>	<u>A(a)</u>	<u>B, cm^3</u>
72-68-a	8.33×10^{-3}	6.7×10^{-19}
72-68-b	10.0×10^{-3}	7.7×10^{-19}
76-68	1.33×10^{-3}	5.3×10^{-19}
77-260 (vitreous)	not measurable	not measurable
77-260 (small crystals)	-4.5×10^{-3}	11.0×10^{-19}
77-260 (large crystals)	-10.2×10^{-3}	6.6×10^{-19}
E-G	-9.75×10^{-3}	8.7×10^{-19}
P-G	-4.36×10^{-3}	9.3×10^{-19}

(a) Predicted density change at saturation.

(^{244}Cm -doped glass) is about 0.55%. Since the changes in volume in all three glasses show no signs of approaching saturation, larger volume expansions can be expected at higher doses. (Data at higher doses have not been reported.) The two waste glasses containing simulated waste and doped with ^{244}Cm or ^{238}Pu are very similar in their rates of volume change with dose. In the glass containing no simulated waste and doped with ^{238}Pu , the rate of volume change with dose was significantly less than in the other two glasses that contained simulated waste.

In a collaborative program to characterize waste forms undertaken by the Centre de Marcoule (CEA-France), the Hahn-Meitner Institut (Berlin), and the Atomic Energy Research Establishment (Harwell, UK), four borosilicate glasses and one phosphate glass were doped with $^{238}\text{PuO}_2$, and the effects of radiation damage studied (Malow, Marples, and Sombret 1980). The four borosilicate glasses, designated SON 58.30.20.U2 (French), VG 98/3 (German), UK-209 and UK-189 (British), were doped with 2.5 wt% $^{238}\text{PuO}_2$. The Pamela phosphate glass was doped with 5 wt% $^{238}\text{PuO}_2$ because of the higher solubility of PuO_2 in this glass. The changes in density as a function of accumulated dose in these glasses are shown in Figure 6.5. The Pamela phosphate glass and the French glass, SON 58.30.20.U2, show an increase in density with dose (volume contraction), while in the other three borosilicate glasses the density decreases (volume expansion). All the glasses are showing signs of saturation in density change and fit the exponential relation given by Eq. 1. The values of the constants, A and B, for these glasses are given in Table 6.3. The results predict that the volume expansion for three of the glasses will saturate at less than 1.0%, while the volume contraction of SON 58.30.20.U2 will saturate at about 1.2%. The values of B for these glasses are smaller than the values of B for the PNL glasses (Table 6.2). This indicates that the European glasses will saturate at a slightly slower rate (per unit dose) and, hence, higher dose than the PNL glasses.

Two other studies on the effects of alpha decay on glass volume have also been carried out. At Harwell, Hall et al. (1976) measured length changes in a borosilicate glass developed to immobilize Magnox fuel reprocessed waste and

FIGURE 6.5. Density Changes in ^{238}Pu -Doped European HLW Glasses (adapted from Malow, Marples and Sombret 1980)

TABLE 6.3. Values of Constants A and B for Exponential Dependence of Density Change in European Glasses (adapted from Malow, Marples and Sombret 1980)

Glass Composition	A(a)	B, cm ³
SON 58.30.20.U2	12.0×10^{-3}	3.5×10^{-19}
VG 98/3	-8.8×10^{-3}	1.3×10^{-19}
UK-209	-9.0×10^{-3}	1.0×10^{-19}
UK-189	-4.9×10^{-3}	3.0×10^{-19}

(a) Predicted density change at saturation.

doped with 5 wt% $^{238}\text{PuO}_2$. At 50°C storage temperature, the length increased by 0.02% after 2×10^{18} alpha decays/cm³; whereas, in specimens stored at 170°C the length increased by 0.4% after 0.27×10^{18} alpha decays/cm³ and then slowly decreased with dose. Unfortunately, initial density measurements were not made; therefore, density data is not available as a function of dose. After a dose of 2×10^{18} alpha decays/cm³, the specimens were annealed and density recovery measured. The specimens stored at 50°C showed a 0.15% increase in density after heating to 460°C, while the specimens stored at 170°C exhibited a decrease in density of 0.23% after heating to 480°C. The disparity between the dilatometer and density measurements was not resolved. In the other study, Bonniaud et al. (1979, 1980) observed no density changes in either a ^{241}Am doped glass or a ^{238}Pu doped glass after $\sim 1 \times 10^{18}$ alpha decays/cm³.

6.2.1.2 Neutron Irradiations

Uranium doping followed by neutron irradiation has been used in a simulation experiment by Antonini et al. (1980) to study density changes as a function of displacements per atom (dpa) in a borosilicate glass representative of the glasses commonly taken into consideration in Europe for high-level waste vitrification. They doped samples of the borosilicate glass waste form with different amounts of ^{235}U , encapsulated test specimens in a cadmium shield to eliminate the thermal neutrons and irradiated the specimens in the high-flux reactor at Petten to induce damage by the fissioning of the ^{235}U (Antonini, Lanza and Manara 1979). The specimens were irradiated to doses ranging from 0.0012 dpa (1×10^{15} fissions/cm³) to 0.36 dpa (4×10^{17} fissions/cm³), reported to represent equivalent alpha-decay doses of $\sim 3 \times 10^{16}$ alpha decays/cm³ to 9.4×10^{18} alpha decays/cm³, respectively. Density measurements were carried out in hot cells by the traditional Archimedian method using tetrachloroethylene (density = 1.67 g/cm³) as the reference fluid. The results show a definite decrease in density (volume expansion), but the functional dependence of density change on dose is uncertain due to large scatter in the data. The maximum volume expansion measured was 0.80%. (Note: There is an error in the dose values given in Table 1 of Antonini et al. 1980; the last two dose entries should be increased by a factor of 10.)

6.2.1.3 Charged-Particle Irradiations

Hall et al. (1976) simulated radiation damage from beta decay in simulated Magnox waste glass by irradiating with 0.5-MeV electrons from a Van de Graaff accelerator. The irradiations were carried out at 300°C to a dose of 10^{19} electrons/cm² ($\sim 2.5 \times 10^{11}$ rad). Density measurements revealed no significant volume change.

6.2.1.4 Gamma Irradiations

There have been no gamma irradiation experiments performed on glass waste forms that measured volumetric changes. Shelby (1980), however, has measured density changes in several commercial borosilicate glasses irradiated with ⁶⁰Co gamma radiation over the dose range from 10^8 to 10^{11} rad. The radiation-induced densification increased with dose and apparently with boron content. The maximum volume change observed was $\sim 1.0\%$.

6.2.1.5 Transmutation Simulation

As discussed previously (Section 6.2.2.5), there is currently only one transmutation simulation experiment being carried out. In that study (Chick et al. 1980; Weber, Wald and Gray 1980), three glasses are being studied: A simulated waste glass, a high-cesium glass, and a high-silica glass. The high-cesium glass was prepared in two forms, with and without ²⁴⁴Cm (~ 2 wt%). Density measurements after about 3% of the total cesium transmuted to barium indicate no significant volume changes in either the simulated waste glass or the high-silica glass. The two forms of the high-cesium glass have both shown volume contractions of about 0.8%. This study is continuing, and future data should establish whether these trends continue.

6.2.2 Leach Rate Changes

The leach rate of a high-level nuclear waste solid is the rate at which the components of the waste form are attacked and dissolved by a contacting liquid and is, therefore, a measure of the chemical durability of the material. The leach rate of a waste form is important in geologic disposal because the primary pathway of radionuclide migration to the biosphere begins with ground water leaching of the waste form. Radiation damage may affect the leach rate

by producing physical and chemical changes in the waste form or by producing chemical changes in the surrounding environment (mainly the ground water).

6.2.2.1 Actinide Doping Data

Of the several waste glass compositions doped with ^{244}Cm at the Pacific Northwest Laboratory (Table 6.1), only two of the compositions, PNL 72-68-a and 77-260, have been studied for changes in leach rate (Mendel et al. 1976; Mendel et al. 1977; Weber et al. 1979; Roberts 1980). Mendel et al. (1976 and 1977) measured the leach rate of curium-doped PNL 72-68-a as a function of time by a static leach test in distilled water at 25°C. The leach rates were determined from both potassium and curium in solution. The results, based on average values from seven different specimens, are shown in Figure 6.6 along with the leach rate (based on potassium) of a similarly prepared but undoped sample of PNL 72-68-a. The leach rates based on potassium are significantly higher (two orders of magnitude) than those based on curium. This suggests that curium leaches at a much lower rate than the more soluble alkali ions, such as potassium, or that the solubility of the curium in the solution is low enough to control the curium release rates. A comparison of the leach rates, based on potassium, of the curium-doped and undoped samples shows that the curium-doped sample has a slightly higher leach rate (factor of two) but does not significantly change with time (or dose). The difference between the doped and undoped samples may be a solution radiolysis effect from the alpha particles at the sample-solution interface in the curium-doped study. Similar behavior from gamma radiolysis has been reported by McVay and Pederson (1981) and McVay, Weber and Pederson (1980) and will be described in more detail below (Section 6.2.2.4). Roberts (1980) measured the leach rate change of PNL 72-68-a as a function of dose using the dynamic Soxhlet test described by Mendel et al. (1977). The leach rate, determined by weight loss, did not increase significantly (less than factor of two) as shown in Figure 6.7 after a dose of 10×10^{18} alpha decays/cm³; this is a factor of two beyond where the structural damage saturated. The increase is well within the experimental error of the tests.

Weber et al. (1979) performed leach testing on three forms of PNL 77-260, one vitreous and two partially devitrified (see Section 6.2.1.1), using both

FIGURE 6.6. Static-Test Leachability at 25°C ^{244}Cm -Doped PNL 72-68-a (adapted from Mendel et al. 1976)

FIGURE 6.7. Soxhlet-Test Leachability of ^{244}Cm -Doped PNL 72-68-a HLW Glass (adapted from Roberts 1980)

dynamic Soxhlet and acid-base tests (Mendel et al. 1977). The leach rates calculated from both overall weight loss and from the ^{244}Cm concentration in the leachant are shown in Figure 6.8. The results obtained by weight loss were significantly higher than the results based on ^{244}Cm in solution, except in the pH 4 test, where the results are comparable. The amount of ^{244}Cm in solution increases as the leachant goes from basic (pH 9) to acid (pH 4), which directly follows the solubility behavior of actinides as a function of pH. The ^{244}Cm is apparently retained to a higher degree by the glass and devitrification products than the more soluble elements (alkali, boron), in agreement with the PNL 72-68-a results discussed above, but leach rates based on a single species in solution should be suspect. In general, the results based on weight loss are more indicative of actual behavior, and in the case of PNL 77-260 the results show no significant change in leach rate after a dose of 4.4×10^{18} alpha decays/cm³, which is the dose where saturation of structural changes was nearly complete. The results also showed that amorphization of a crystalline phase within the two partially devitrified glasses did not significantly affect the leach rates.

In the study by Bibler and Kelley (1978) discussed in Section 6.2.1.1, the actinide leachabilities of the two ^{244}Cm - and ^{244}Pu -doped borosilicate glasses containing simulated radioactive waste were determined by leach testing in stirred, distilled water at 25°C (the leach water was changed daily). The leachabilities were calculated based on the measured alpha activity in the water. The calculated leachabilities did not significantly change with dose. The maximum dose attained was 1.1×10^{18} alpha decays/cm³ in the ^{244}Cm -doped glass and 4.4×10^{17} alpha decays/cm³ in the ^{238}Pu -doped glass. The leachability of the ^{238}Pu ($\sim 4.0 \times 10^{-4}$ g/m² · d) in the glass was consistently higher than for the ^{244}Cm ($\sim 0.5 \times 10^{-4}$ g/m² · d). This suggests that either the ^{244}Cm is more strongly bound in the matrix than is the ^{238}Pu , or the solubility of ^{244}Cm is less than the solubility of ^{238}Pu is in the solution. These results, however, provide data only on actinide leachability (or solubility) and, as discussed above, are not easily extrapolated to the actual leach rate (or change in leach rate) of the glass waste form being tested.

FIGURE 6.8. Leachability in ^{244}Cm -Doped PNL 77-260 HLW Glass (Weber et al. 1979)

Several studies of changes in leach rates of actinide-doped waste glasses have been carried out abroad. Bonniaud, Jacquet-Francillon, and Sombret (1980) measured the change in leach rate for a ^{244}Cm -doped glass, a ^{241}Am -doped glass, and a ^{238}Pu -doped glass by static leach test with tap water. The leach rates were calculated from the actinide activity of the leachant; consequently (as previously discussed), they are the leachabilities (or solubilities) of only the individual actinides and may not provide information on the actual leach rate changes of the glass. The data show little change in actinide leachability as a function of increasing dose. Scheffler and Riege (1977) also measured leach rate changes in a ^{242}Cm -doped borosilicate glass by static leach tests at 23°C. They observed no significant changes in leach rate with increasing dose up to a dose of $\sim 4 \times 10^{18}$ alpha decays/cm³.

Boult et al. (1979) measured the change in leach rate of UK glass 189 doped with 5 wt% ^{238}Pu . Samples were stored at 20°C between the leach tests. The leach rates, based on weight loss, were measured by the Soxhlet leach test. Initial leach rates were not measured. The leach rate did increase by about 50% between 1 year (2.4×10^{18} alpha decays/cm³) and 2 year (4.7×10^{18} alpha decays/cm³) storage. No significant, further increases were observed after 3-year storage (7.1×10^{18} alpha decays/cm³).

The most complete work on European glasses is the collaborative effort reported by Malow, Marples, and Sombret (1980) and referred to in Section 6.2.1.1. In that study, the leach rates were determined initially and after 3.3×10^{18} alpha decays/cm³ by using the Soxhlet technique and calculated from the weight loss. Samples were stored at 50°C and 170°C during the self-radiation. The leach test results are given in Table 6.4. All the glasses show an increase in leach rate. The changes are not considered significant, except for SON 58.30.20.U2; in this glass, however, the alumina content, which improves leach resistance, was only one-tenth of that normally specified for this glass.

TABLE 6.4. Leach Rates Based on Weight Loss and Measured by the Soxhlet Technique for European HLW Glasses Doped with 2.5 wt% ^{238}Pu (adapted from Malow, Marples and Sombret 1980)

Glass	Storage Temp., °C	Initial Leach Rate, g/m ² · d	Final(a) Leach Rate, g/m ² · d
UK 189	50	13.3	19.1
UK 189	170	10.9	17.9
UK 209	50	2.1	2.3
UK 209	170	2.3	2.8
SON 58.30.20.U2	50	22.6	69.0
SON 58.30.20.U2	170	21.9	35.6
VG 98/3	50	22.1	29.1
VG 98/3	170	21.8	23.3

(a) Final leach rate measured after a cumulative dose of 3.3×10^{18} alpha decays/cm³.

Most data on the change in leach rate in actinide-doped HLW glasses have been measured using the Soxhlet technique and calculated based on weight loss. In general, this has occurred because the Soxhlet technique gives fairly reproducible results, the calculations based on weight loss give a better indication of actual leach rates than calculations based on a single species in solution, and only changes in leach rates were of interest and not absolute values. All the data obtained by the Soxhlet technique on HLW glasses and discussed above are summarized in Table 6.5. This probably represents the best current state-of-the-art understanding of changes in leach rate due to radiation-induced changes in the chemical durability of HLW glasses. (This is to be distinguished from radiation-induced changes induced by radiolysis of the leachant discussed below.) The maximum change in leach rate is 205% (factor of 3), but in general, the increase in leach rate is less than 100% (factor of 2), and in some instances (PNL 77-260) small decreases in the leach rate are measured.

TABLE 6.5. Summary of Leach Rate Changes in HLW Glasses Obtained by the Soxhlet Technique and Based on Weight Loss

Simulated HLW Glass	Storage Temp., °C	Maximum Dose, alpha decays/cm ³	Leach Rate Change at Maximum Dose, %	Reference
PNL 77-260 (vitreous)	23	4.4×10^{18}	-10	Weber et al. 1979
PNL 77-260 (700°C, 1 wk)	23	4.4×10^{18}	-33	Weber et al. 1979
PNL 77-260 (6°C/hr)	23	4.4×10^{18}	-5	Weber et al. 1979
PNL 72-68-a	23	10.2×10^{18}	+100	Roberts 1980
UK 189	20 ^(a)	7.1×10^{18}	+44	Boult et al. 1979
UK 189	20 ^(b)	7.1×10^{18}	+73	Boult et al. 1979
UK 189	23	3.3×10^{18}	+44	Malow et al. 1980
UK 189	170	3.3×10^{18}	+64	Malow et al. 1980
UK 209	23	3.3×10^{18}	+10	Malow et al. 1980
UK 209	170	3.3×10^{18}	+22	Malow et al. 1980
SON 58.30.20.U2	23	3.3×10^{18}	+205	Malow et al. 1980
SON 58.30.20.U2	170	3.3×10^{18}	+63	Malow et al. 1980
VG 98/3	23	3.3×10^{18}	+32	Malow et al. 1980
VG 98/3	170	3.3×10^{18}	+7	Malow et al. 1980

(a) Stored at 50°C for 1 yr (2.4×10^{18} alpha decays/cm³).

(b) Stored at 170°C for 1 yr (2.4×10^{18} alpha decays/cm³).

6.2.2.2 Neutron Irradiation Data

There have been no neutron irradiation experiments reported to date on HLW glasses which measured irradiation-induced changes in leach rate. However, Rauscher and Tischer (1964) reported increased solubility of some commercial borosilicate glasses after neutron irradiation. The solubilities increased by no more than a factor of three after fluences of $1.4 \times 10^{19} \text{ n/cm}^2$.

6.2.2.3 Charged-Particle Irradiation Data

Dran et al. (1980) have irradiated a simple borosilicate glass (64 wt% SiO_2 , 12 wt% B_2O_3 , and 24 wt% Na_2O) and several simulated European HLW glasses with low-energy ($\sim 1 \text{ KeV/amu}$) lead ions in an effort to quickly evaluate the effect of irradiation on leach rate. Their premise is that the low-energy lead ions simulate the recoil nuclei generated by alpha decay. Polished sections of the material to be irradiated are covered with an electron microscope grid and then exposed to the beam of lead ions. The result is a periodic succession of irradiated and unirradiated areas. The irradiated areas extend to a depth of $\sim 50 \text{ nm}$ ($500 \text{ \AA}$). The irradiated specimens are then leached in a NaCl solution (250 g/l) at 100°C . The change in leach rate due to irradiation is inferred from the difference of depth between the irradiated and unirradiated areas with a diamond stylus device (accuracy reported to be $\sim 10 \text{ \AA}$). Their results suggest irradiation-enhanced changes in leach rates on the order of factors of 25 to 500. Such increases in leach rate are in sharp contrast to the results from actinide decay (Section 6.2.2.1); however, the technique employed is open to question as to its ability to predict actual changes in bulk leach-rate behavior as a result of alpha decay. This is currently the subject of much debate, and questions concerning surface damage versus bulk damage and such effects as irradiation texturing of the surface, the small damage depth, the role of alpha particles (which are not present in the lead-irradiation studies), different leachants, dose rate, etc. will need to be answered by more fundamental studies before data from such studies of ion irradiation can be applied to the evaluation of nuclear waste forms.

Araki (1981) has reported irradiation studies of several Japanese simulated HLW glasses using 2-MeV electrons from a Cockcroft-Walton type accelerator to simulate beta-gamma damage. The irradiations were carried out to

$\sim 10^{10}$ rad, and no measurable changes in leach rates were observed. Bonniaud (1977) also performed electron irradiations on a number of HLW glasses using 3 MeV electrons at doses as high as 1.2×10^{11} rad. No changes were observed in the cesium or strontium leach rates.

6.2.2.4 Gamma Irradiation Data

Grover (1973) irradiated borosilicate and phosphate glasses in the Gamma Irradiation Facility at Mol to a dose of $\sim 1 \times 10^{11}$ rad over the temperature range from 350 to 800°C. For the borosilicate glass there was a slight increase in the leach rate (based on cesium and strontium in solution) between 600 and 650°C. There is a much larger increase in the leach rate (about a factor of 10) of the phosphate glass at temperatures above 550°C. In another study, Kelley (1975) irradiated two borosilicate waste glasses with gamma radiation from a ^{60}Co source to 10^{10} rad at $\sim 65^\circ\text{C}$. No changes in leachabilities were observed. Mendel et al. (1977) also reported no significant changes in the leach rates of full-level borosilicate waste glasses after doses of 1 to 4.6×10^{11} rad.

In a different type of study, McVay and Pederson (1981) and McVay et al. (1980) reported significant increases in the leach rate of PNL 76-68 in the presence of ^{60}Co gamma radiation at a dose rate of 2.4×10^6 R/hr. Some of the increased leaching was due to the generation of nitric acid from air radiolysis in the leach vessel. Nitric acid appeared to preferentially attack zinc and lanthanides, both of which normally build up on the surface of the glass when leached in nonacidic solutions. Increased rates were also observed for samples irradiated while leaching, but with air excluded to eliminate nitric acid formation, which indicated that water radiolysis products may also be important. Samples irradiated with gamma radiation prior to leaching showed dissolution rates indistinguishable from those of unirradiated specimens. These results may explain the factor of ~ 2 higher leach rates observed by Mendel (1973) in waste glasses containing up to 90 Ci/cm^3 of fission products than in nonradioactive waste glasses of similar composition.

6.2.2.5 Transmutation Simulation Data

Data are not currently available on leach rate changes in the only transmutation simulation experiment currently under way (Chick et al. 1980; Weber, Wald and Gray 1980).

6.2.3 Stored Energy Changes

Stored energy is the latent energy stored in a glass matrix (or crystal lattice) by radiation, generally through the displacement of atoms. The stored energy is released as heat when the irradiated material is thermally annealed. Although stored energy is now generally believed to be unimportant in solid nuclear waste forms, an understanding of the amount of energy involved and of the annealing behavior is, however, useful for evaluation of the potential hazards. If the quantity of stored energy is large and the release rate high, an uncontrolled release could produce sudden excessively high waste-form temperatures. Such high temperatures could affect the physical and chemical properties of the waste forms and the integrity of the waste-form canister.

6.2.3.1 Actinide Doping Data

Radiation-induced changes in stored energy have been studied for several different waste-glass compositions doped with ^{244}Cm at the Pacific Northwest Laboratory (Mendel et al. 1976; Mendel et al. 1977; Mendel 1978; Roberts, Jenks and Bopp 1976; Roberts, Turcotte and Weber 1981; Ross et al. 1978; Turcotte and Roberts 1977; Weber et al. 1979). The stored energy release was measured by differential scanning calorimetry (DSC) on specimens weighing 25 to 60 mg at a heating rate of 20°C/min, as described in detail by Roberts, Jenks, and Bopp (1976). One of the PNL waste glass compositions (PNL 72-68) has been studied more extensively than any other glass composition in this country or abroad. The rates of energy release in PNL 72-68-a as a function of temperature and cumulative dose are shown in Figure 6.9 (Roberts, Jenks and Bopp 1976). The release occurs over a broad temperature range, and a two-stage release mechanism is suggested. The stored energies as a function of cumulative dose for PNL 72-68-a (1 wt% ^{244}Cm) and PNL 72-68-b (8 wt% ^{244}Cm) are shown in Figure 6.10 (Turcotte and Roberts 1977; Mendel et al. 1977); these results suggest that dose rate effects (factor of eight) are not significant.

FIGURE 6.9. Stored Energy Release Rates in ²⁴⁴Cm-Doped PNL 72-68-a HLW Glass (adapted from Roberts, Jenks and Bopp 1976)

FIGURE 6.10. Effect of Dose Rate on Stored Energy in ²⁴⁴Cm-Doped PNL 72-68 HLW Glass (adapted from Turcotte and Roberts 1977)

The stored energy of PNL 72-68-b as a function of cumulative dose (and equivalent storage time, assuming commercial HLW) at very high dose levels is shown in Figure 6.11 (Ross et al. 1978; Mendel 1978). The stored energy shows a maximum at a value of ~ 120 J/g. The effect of storage temperature on the buildup of stored energy in PNL 72-68-a is shown in Figure 6.12 for a cumulative dose of 1.7×10^{18} alpha decays/cm³ (Roberts, Jenks and Bopp 1976). The results show that stored energy is inversely proportional to storage temperature and is completely absent in PNL 72-68-a when stored at 350°C.

The stored energies as a function of cumulative dose for all the PNL waste-glass compositions studied to date are shown in Figure 6.13 (Roberts, Turcotte and Weber 1981). In general, the buildup of stored energy follows exponential behavior similar to the change in density (Eq. 1) and saturates at a value in the range of 80 to 130 J/g. In the case of PNL 77-260, the vitreous form (data in Figure 6.13) exhibited a higher release rate than the two partially devitrified forms (data not shown), but this is attributed in part to volume effects and an insufficient temperature to anneal all the damage out of

FIGURE 6.11. Stored Energy in ²⁴⁴Cm-Doped PNL 72-68-b HLW Glass at Very High Doses (adapted from Mendel 1978)

FIGURE 6.12. Effect of Storage Temperature on Stored Energy in PNL 72-68-a HLW Glass (adapted from Roberts, Jenks and Bopp 1976)

FIGURE 6.13. Stored Energy in ²⁴⁴Cm-Doped HLW Glasses (Roberts, Turcotte and Weber 1981)

the crystalline phases (Weber et al. 1979). The recovery of the radiation-induced stored energy in the waste glasses of Figure 6.13 was investigated by 7-day isochronal anneals (Roberts 1980; Chick et al. 1980). The fractional recovery of these glasses at each annealing step is shown in Figure 6.14. The results show a single continuous recovery stage for all the waste-glass compositions which is complete at 360°C.

Several studies of stored energy in actinide-doped waste glasses have also been carried out abroad. At Harwell, Hall et al. (1976) measured stored energy release in a borosilicate waste-glass composition doped with 5 wt% $^{238}\text{PuO}_2$. The stored-energy release was measured by differential thermal analysis (DTA) at a constant heating rate of 1°C/min. The total energy release from specimens self-irradiated at 50°C for 1 year (2×10^{18} alpha decays/cm³) was 97 J/g. The energy release from specimens self-irradiated at 170°C to the same dose was 82 J/g. This reduction in energy release at elevated storage temperatures supports the data in Figure 6.12. At the Nuclear Research Center in Karlsruhe (Scheffler, Riege and Hild 1976; Scheffler and Riege 1977) three

FIGURE 6.14. Thermal Recovery of Stored Energy in ^{244}Cm -Doped HLW Glasses (Roberts 1980)

HLW glasses were doped with ^{242}Cm and the stored energy measured as a function of dose out to $\sim 6.6 \times 10^{18}$ alpha decays/cm³. The stored energy for the three waste glasses saturated at values ranging from 264 to 395 J/g after a dose of $\sim 3 \times 10^{18}$ alpha decays/cm³. In the collaborative European Communities research program, Malow, Marples and Sombret (1980) measured the stored energy of four borosilicate glasses doped with $^{238}\text{PuO}_2$. The energy release was measured using a DSC on samples weighing ~ 30 mg at a constant heating rate of $2^\circ\text{C}/\text{min}$. The stored energies ranged from values of 43 to 78 J/g at a dose of 3.3×10^{18} alpha decays/cm³.

All the currently available data on stored energy release in actinide doped waste glasses are summarized in Table 6.6. The results in Table 6.6 show that stored energy ranges from about 50 to 400 J/g, or 50 to 125 J/g if the data of Scheffler and Riege (1977) are excluded. Since the specific heat of the waste glasses is usually about $1 \text{ J/g} \cdot ^\circ\text{C}$, the maximum temperature rise that could occur from the sudden release of the stored energy is 50 to 400°C ,

TABLE 6.6. Summary of Stored Energy Measurements in Actinide-Doped Simulated HLW Glasses

Simulated HLW Glass	Storage Temp., $^\circ\text{C}$	Maximum Dose, alpha decays/cm ³	Maximum Stored Energy, J/g	Reference
PNL 72-68-a	23	4.4×10^{18}	98	Roberts et al. 1976
PNL 72-68-b	23	30.0×10^{18}	121	Ross et al. 1978
PNL P-G	23	3.6×10^{18}	36	Ross et al. 1978
PNL S-G	23	3.6×10^{18}	125	Ross et al. 1978
PNL 76-68	23	3.6×10^{18}	83	Ross et al. 1978
PNL 77-260 (vitreous)	23	4.8×10^{18}	120	Weber et al. 1979
PNL 77-260 (700 $^\circ\text{C}$, 1 wk)	23	4.8×10^{18}	90	Weber et al. 1979
PNL 77-260 (6 $^\circ\text{C}/\text{hr}$)	23	4.8×10^{18}	86	Weber et al. 1979
UK 189	50	2×10^{18}	97	Hall et al. 1976
UK 189	170	2×10^{18}	82	Hall et al. 1976
Basic "98"	23	5.2×10^{18}	254	Scheffler and Riege 1977
HLW "98"	23	5.5×10^{18}	347	Scheffler and Riege 1977
HLW-GD "98"	23	6.1×10^{18}	395	Scheffler and Riege 1977
UK 189	23	3.3×10^{18}	78	Malow et al. 1980
UK 209	23	3.3×10^{18}	73.5	Malow et al. 1980
SON 58.30.20.U2	23	3.3×10^{18}	76	Malow et al. 1980
VG 98/3	23	3.3×10^{18}	55	Malow et al. 1980

or only 50 to 125°C if data of Scheffler and Riege (1977) are excluded. Temperature excursions of this magnitude should present no serious problems after several thousand years' storage, the amount of time required to reach these stored energy values.

6.2.3.2 Neutron Irradiation Data

Roberts, Jenks and Bopp (1976) measured the stored energy release in two borosilicate waste glass compositions irradiated at ~100°C with fast neutrons ($E > 1$ MeV) to two different fluence levels: 1.45×10^{20} n/cm² and 3.48×10^{20} n/cm². The results indicate that the stored energy has saturated at these fluences. The stored energies are ~98 J/g for one glass and ~88 J/g for the other glass (PNL 72-68). The neutron irradiation data for PNL 72-68 (~88 J/g) is in close agreement with the results shown in Table 6.6.

Antonini, Lanza and Manara (1979) measured stored energy in a borosilicate waste glass doped with ²³⁵U and irradiated with fast neutrons to induce damage by the fissioning of the ²³⁵U. The stored energy was measured with a differential scanning calorimeter at a constant heating rate of 10°C/min on samples irradiated to doses ranging from 1×10^{15} fissions/cm³ to 4×10^{17} fissions/cm³ (the upper dose is reported to correspond to 9.4×10^{18} alpha decays/cm³). The maximum stored energy observed was ~82 J/g, which is in agreement with stored energy values measured in other actinide-doped waste glasses.

6.2.3.3 Charged-Particle Irradiation Data

Antonini et al. (1979; 1980) irradiated two borosilicate waste glasses and SiO₂ with 46.5 MeV Ni⁶⁺ ions to ~1 dpa (reportedly corresponds to 2.6×10^{19} alpha decays/cm³). The maximum stored energy for the two borosilicate glasses was ~165 J/g, whereas in the SiO₂ the maximum stored energy was ~210 J/g. These stored energy values are slightly higher than those observed from actinide decay, perhaps a result of the much higher displacement rates.

6.2.3.4 Gamma Irradiation Data

There have been no gamma irradiation experiments reported on glass waste forms that measured stored energy.

6.2.3.5 Transmutation Simulation Data

Stored energy is not being measured in the only currently reported transmutation study under way (Chick et al. 1980; Weber, Wald and Gray 1980).

6.2.4 Other Property Changes

The data available on other property changes (besides volume, leach rate, and stored energy) are very limited. For instance, no radiation-induced devitrification (crystallization) has ever been observed in HLW glasses; however, amorphization of crystalline phases has been observed in partially devitrified HLW glasses (Weber et al. 1979). This section reviews the remaining radiation effects data available on HLW glasses. These limited data cover mechanical strength/microcracking, helium buildup/release, and structural/ microstructural changes.

6.2.4.1 Mechanical Strength/Microcracking

Radiation can potentially affect the mechanical strength of a waste form by producing embrittlement or microcracking, which may lead to increased fracturing in the event of an accident during transportation and handling. Fracturing will produce fine particles that can be inhaled and also increases surface area; this can, in turn, increase the waste form's susceptibility to leaching.

Weber et al. (1979) performed impact tests on a vitreous and two partially devitrified forms of ^{244}Cm -doped PNL 77-260 waste glass. The results indicate that the impact performance was not adversely affected by the self-radiation; however, one of the partially devitrified forms of these glass compositions (containing large crystals from a slow cool at 6°C/hr) exhibited extensive microcracking associated with the amorphization of the crystalline devitrification product $[\text{Ca}_3\text{Gd}_7(\text{SiO}_4)_5(\text{PO}_4)\text{O}_2]$. No microcracking was observed in the other partially devitrified glass (smaller crystals from anneal at 700°C for 1 week), even though the same phase was present and also underwent amorphization. This same partially devitrified glass did, however, show microcracking after immersion in room temperature water for 3 weeks. Bibler and Kelley (1978) also observed microcracking in the actinide-doped HLW glasses they studied, but did not perform any mechanical strength tests. No other investigators have reported microcracking in irradiated HLW glasses.

Bonniaud et al. (1979; 1980) reported a slight decrease in the microhardness of actinide-doped HLW glasses as a result of radiation damage, and Scheffler and Riege (1977) reported that the mechanical properties of ^{242}Cm -doped HLW glasses were slightly altered after $\sim 5 \times 10^{18}$ alpha decays/cm³.

6.2.4.2 Helium Buildup/Release

Helium, which results from the capture of two electrons by the alpha particles emitted in alpha decay, must either be accommodated interstitially, or diffuse to internal voids or the plenum of the canister. Helium buildup in waste forms can potentially produce embrittlement, swelling from bubble formation, or pressurization of the canister.

Turcotte (1976) made a detailed study of helium diffusion in ^{244}Cm -doped PNL 72-68. The diffusion of helium at short times and low fractional release values followed Arrhenius behavior; at longer times and higher fractional release values, the apparent diffusion coefficient is decreased by about one order of magnitude due to trapping effects at radiation-induced defects. The helium solubility was also measured and determined to be 1.5×10^{16} atoms/cm³ at 400°C and 730 Torr helium. This leads to the conclusion that >99% of the helium generated in HLW glass will not remain in solution, but will diffuse to internal voids or pores, or to the canister plenum. There was insufficient experimental evidence to determine whether or not helium bubbles will form at ambient temperatures. In addition, helium pressurization of the canister containing waste from UO₂ fuel reprocessing was shown to be negligible, but canister pressurization may exceed 1 atmosphere if the sealed canisters contain waste from plutonium recycle fuel reprocessing.

Malow and Andresen (1979) investigated helium generation and diffusion in the same waste glass composition as Turcotte (1976); but instead of actinide doping, utilized the high ^{10}B (n, α) cross section by irradiating the waste glass (PNL 72-68) specimens in the thermal neutron flux of a reactor for 2 to 20 hr. At the maximum fluence (9.4×10^{18} n/cm²), 1.5×10^{19} helium atoms/cm³ were produced in the glass. The waste glass specimens were subsequently analyzed for fractional helium release at various temperatures. Evaluation of the results indicated that a nonideal diffusion process had occurred that was

probably due to trapping of the helium at irradiation-induced defects. The apparent diffusion coefficient was found to decrease with dose, in agreement with the results of Turcotte (1976). The activation enthalpy increased with dose and saturated at a value of 110 kJ/mole at a dose of ~ 0.1 dpa (equivalent to $\sim 2.5 \times 10^{18}$ alpha decays/cm³), which is approximately the dose where saturation of volume changes and stored energy are observed (see Sections 6.2.1 and 6.2.3). Scanning electron microscopy (SEM) revealed the apparent formation of helium bubbles at $\sim 750^\circ\text{C}$, suggesting another possible helium transport mechanism that could delay helium release.

Malow, Marples and Sombret (1980) measured helium release in three borosilicate waste glasses and a phosphate waste glass, all doped with ²³⁸Pu and stored at 170°C . Estimates of the diffusion coefficient (at 170°C) were also made for the three borosilicate waste glasses. They concluded that only a small fraction of the helium will be released from a glass monolith at lower temperatures (noting that most alpha decay events will occur after the glass has returned to ambient temperature). Similar results were obtained by Hall et al. (1976), who measured helium release in a ²³⁸Pu-doped borosilicate waste glass. No helium release was measured in a specimen stored at 50°C . Measurable helium release was found in a specimen stored at 170°C and a diffusion coefficient and activation energy measured. Bonniaud, Jacquet-Francillon and Sombret (1980) measured helium release in ²⁴⁴Cm, ²⁴¹Am and ²³⁸Pu-doped waste glasses and observed higher fractional release in the ²⁴⁴Cm-doped glass. No explanation for this observation or estimates of diffusion coefficients and activation energies were given. Scheffler and Riege (1977) also investigated helium release in ²⁴²Cm-doped waste glass stored at room temperature to $\sim 4.7 \times 10^{18}$ alpha decays/cm³, but observed no helium release within the detectability range of their equipment.

6.2.4.3 Structural/Microstructural Changes

Radiation-induced (or enhanced) structural changes (such as devitrification, phase separation, lattice expansions, crystal structure changes, and crystalline to amorphous transformations) and radiation-induced microstructural changes (such as the formation of bubbles, voids, and other extended defects and point defects) can affect volume, leach rate, stored energy, mechanical

strength/microfracturing, and helium buildup/release. Although a fundamental understanding of these structural/microstructural effects could help to more confidently predict the long-term stability and chemical durability of HLW forms, little information is presently available.

Weber et al. (1979) investigated structural changes in ^{244}Cm -doped PNL 77-260 glass by x-ray diffraction techniques. Radiation-induced devitrification was not observed. In the two partially devitrified forms of this waste glass composition, the crystal phase, $\text{Ca}_3\text{Gd}_7(\text{SiO}_4)_5(\text{PO}_4)\text{O}_2$ with an apatite structure, transformed from a crystalline to an x-ray amorphous state as a result of concentrated alpha decay in this phase. Accurate lattice parameter measurements were not possible during this transformation. The amorphization of this crystal phase resulted in the microcracking (discussed above) observed in the glass specimens containing large crystals (slow cooled at 6°C/hr). The other major phase in both partially devitrified glasses, a Gd-titanate, was reported to be stable with respect to radiation damage. It has since been observed (unreported results of W. J. Weber at PNL) that this phase is unstable and does become x-ray amorphous at higher doses than covered in the initial work.

Kelley and Bibler (1978) observed the formation of blisters in ^{238}Pu -doped glass after exposure to the electron beam of a SEM and postulated that this effect may be due to helium agglomeration by electron beam heating. Dé et al. (1976) implanted 50 keV helium into a simulated borosilicate glass with an accelerator and observed bubble formation and surface blistering after heating the specimens to 600°C . They also observed this same behavior at room temperature when the helium was implanted through the $^{10}\text{B}(n, \alpha)$ reaction by irradiating a glass-boron foil sandwich in a nuclear reactor. As noted above, Malow and Andresen (1979) observed helium bubble formation in neutron-irradiated PNL 72-68 after heating to 750°C .

Hall et al. (1976) observed no microscopic changes in a borosilicate waste glass irradiated at 300°C with 0.5 MeV electrons from a Van de Graaff accelerator; however, when the irradiations were carried out in a high-voltage electron microscope (HVEM), bubbles were observed to form at 200°C and above. The bubbles were postulated to contain oxygen.

6.3 RADIATION DAMAGE IN CERAMIC WASTE FORMS

As alternatives to glass waste forms, several ceramic waste forms have been proposed that are tailored to produce specific crystalline phases as hosts for radioactive waste products. Generally, fission products (such as cesium and strontium) are confined to one or more crystalline phases, and the actinides (uranium, neptunium, plutonium, americium, curium) to another set of phases. Three ceramic waste forms have received considerable attention: Supercalcine (McCarthy 1977), SYNROC (Ringwood et al. 1979), and glass ceramics (Dé et al. 1976). There has, however, been very little radiation damage work done to date on these or other ceramic waste forms. The data that are available are presented below.

6.3.1 Supercalcine (SPC-2)

The only radiation damage study that has been performed to date on one supercalcine formulation, SPC-2, was carried out at the Pacific Northwest Laboratory (PNL) and has been summarized by Rusin, Gray and Wald (1979). In that study the SPC-2 formulation was doped with 3 wt% Cm_2O_3 (2 wt% ^{244}Cm). X-ray diffraction, stored energy, and density measurements were made initially and at ~3-month intervals out to a total cumulative dose of $\sim 7 \times 10^{18}$ alpha decays/cm³. Initial characterization of this supercalcine formulation showed it to consist of three major phases: fluorite, apatite, and a tetragonal phase. Subsequent analysis suggested that the curium predominantly entered the apatite and tetragonal phases.

X-ray diffraction analysis of the curium-doped supercalcine as a function of dose showed a gradual transformation of the apatite phase from a crystalline to amorphous state. An expansion in the unit cell of this phase was also observed with increasing dose. There was a slight increase in the intensity of the reflections associated with the tetragonal phase, but changes in the tetragonal unit cell were indeterminable. The fluorite peak was used as a standard, since this phase did not appear to accept the curium dopant and was unaffected by external radiation.

Stored energy and density measurements were also made as a function of dose for the curium-doped supercalcine. The stored energy reached a maximum value of about 42 J/g at a dose of $\sim 2 \times 10^{18}$ alpha decays/cm³.

and then decreased slightly with further increases in dose. The data indicate that energy release is not complete at 600°C (the upper limit of the calorimeter used); therefore, additional energy release may occur at higher temperatures (>600°C). The density decreased exponentially with dose from ~4.185 g/cm³ to 4.120 g/cm³ at 7×10^{18} alpha decays/cm³ (Rusin, Gray and Wald 1979). Roberts at PNL reports density measurements out to $\sim 26 \times 10^{18}$ alpha decays/cm³ with little additional change. The density change as a function of dose in SPC-2 is shown in Figure 6.15. The volume expansion at saturation (~1.5%) is partially attributed to the unit cell expansion observed in the apatite phase.

No leach testing of the ²⁴⁴Cm-doped supercalcine formulation was performed. Rusin (1980), however, has suggested that leach rate changes in the supercalcine may be minimal since radiation damage effects are observed for

FIGURE 6.15. Density Changes in Ceramic Waste Forms

the apatite phase only and Weber et al. (1979) have shown that amorphization of a similar apatite phase does not significantly affect leach rates.

The effects of Cs $\rightarrow$ Ba transmutation in this same supercalcline formulation (SPC-2), but undoped, and in pollucite, the cesium host phase in SPC-2, are currently being investigated by Gray of PNL (Chick et al. 1980). Initial results (Weber, Wald, and Gray 1980) show no significant changes in density or leach rate. This study is continuing, and future data should establish whether these trends continue.

6.3.2 SYNROC

Ringwood, Oversby and Sinclair (1980) have argued that SYNROC is stable with respect to alpha decay damage, based on an assessment of natural minerals of uranium- and/or thorium-bearing perovskite and zirconolite, which are the actinide host phases of SYNROC. As stated earlier in this report (Section 6.1.3), such data can provide only qualitative results, and since zirconolite is observed to become metamict, the rate of metamictization (amorphization) or any other radiation damage effect may change with slight modifications in chemistry. Therefore, quantitative evaluation of SYNROC as a waste form requires radiation-damage testing of actual or simulated waste forms.

A limited amount of accelerated irradiation damage testing has been performed on SYNROC and its constituent phases by Reeve et al. (1980, 1981) using fast neutrons. Specimens of SYNROC B, SYNROC C, and their constituent minerals hollandite, perovskite and zirconolite were irradiated in the fast-neutron flux of the HIFAR reactor at Lucas Heights, for different lengths of time. The longest irradiation to date on the SYNROC specimens has been 13.4×10^{19} n/cm² ($E > 1$ MeV), which reportedly represents an equivalent SYNROC storage time of 1.2×10^5 years and corresponds to 0.36 dpa or $\sim 20.5 \times 10^{18}$ alpha decays/cm³. Measurements of volume, density, open-porosity and lattice parameter changes were made. The volume expansion of SYNROC B is greater than that of perovskite, which in turn is greater than that of hollandite. The results, also illustrated in Figure 6.15 (neutron dose has been converted to an equivalent alpha decay dose), indicate that the volume expansion of SYNROC B will saturate at $\sim 6.5\%$. Initial data at only a single dose for zirconolite and SYNROC C

suggest that the volume expansion for zirconolite falls between perovskite and hollandite and that the volume of SYNROC C may expand slightly more than SYNROC 8.

No leach testing has been performed on these irradiated specimens.

6.3.3 Celsian Glass Ceramic

A glass ceramic is the ceramic product derived from a homogeneous glass by annealing the glass at the temperature of maximum nucleation rate, followed by a high-temperature anneal to yield maximum growth rate. Through proper choice of the glass composition, crystalline phases may be tailored into the glass-ceramic product that are resistant host phases for the long-lived radionuclides (Dé et al. 1976). The celsian glass ceramic, developed at the Hahn-Meitner Institut (Berlin) and named for the predominant crystalline phase, is easy to fabricate, is homogeneously crystallized, and contains a variety of chemically resistant host phases for the radionuclides. Celsian glass ceramic as a waste form has been studied for potential radiation effects both at PNL (Ross et al. 1979; Weber, Wald and Gray 1980), in cooperation with the Hahn Meitner Institut, and as part of a collaborative research program within the European Community (Malow, Marples and Sombret 1980).

R. P. Turcotte and coworkers at PNL and W. Lutze of Hahn-Meitner Institut recently studied the effects of radiation damage in ^{244}Cm -doped celsian glass ceramic. As shown in Figure 6.15, density was observed to decrease exponentially with dose, saturating at a dose of $\sim 3 \times 10^{18}$ alpha decays/cm³ (Roberts, Turcotte and Weber 1981). Volume expansion at saturation is about 0.5%. Stored energy also increased exponentially with dose to a value of ~ 80 J/g (saturation also occurred at $\sim 3 \times 10^{18}$ alpha decays/cm³). X-ray diffraction data revealed that a curium-rich, rare-earth titanate phase in this waste form underwent a small volume expansion with dose and eventually became amorphous at the same saturation dose of $\sim 3 \times 10^{18}$ alpha decays/cm³ (equivalent to $\sim 5 \times 10^{19}$ alpha decays/cm³ in the rare-earth titanate phase, if all the curium concentrated in this phase). No leach testing was performed on this material.

In the study of Malow, Marples and Sombret (1980), the celsian glass ceramic was doped with 2.5 wt% ^{238}Pu . The density changed exponentially

with dose, as shown in Figure 6.15, and the results suggest saturation will occur at $\sim 5 \times 10^{18}$ alpha decays/cm³ with a corresponding volume expansion of $\sim 0.5\%$, in good agreement with the results of Turcotte and coworkers above. The stored energy was measured to be 43 ± 5 J/g after a dose of $\sim 3.3 \times 10^{18}$ alpha decays/cm³. This is approximately the value reported by Turcotte and coworkers, but it is not known whether saturation has occurred in this material. Changes in leach rates were measured for specimens stored at 23 and 170°C to a cumulative dose of $\sim 3.3 \times 10^{18}$ alpha decays/cm³. The leach rate decreased by $\sim 19\%$ in the specimen stored at 23°C, while the leach rate decreased by only $\sim 4\%$ in the specimen stored at 170°C. The fractional helium release was also determined to be $\sim 3\%$ after storage at 170°C to a cumulative dose of $\sim 3.3 \times 10^{18}$ alpha decays/cm³.

6.3.4 Other Materials

There have been several studies reported of pure actinide compounds or actinide-doped phases that contribute to the understanding of radiation effects from alpha decay in nuclear waste solids. Much of this work has been recently reviewed by Weber and Turcotte (1980). Of particular importance is the data on self-damage from alpha decay in the actinide dioxides: PuO₂ ... (Chikalla and Turcotte 1973; Noe and Fuger 1974; Mendelssohn et al. 1967), AmO₂ (Mendelssohn et al. 1967; Hurtgen and Fuger 1977) and CmO₂ (Noe and Fuger 1971; Mosley 1971). All these compounds have the same fluorite structure as UO₂, which is a potential crystalline phase in some ceramic formulations proposed as waste forms. The most accurate available data from x-ray diffraction studies are summarized in Figure 6.16. The unit cell expansions all increase exponentially with dose and at saturation vary with the ionic radius of the constituent actinide, as would be expected. The important point is the relative constancy of the behavior over several orders of magnitude in the dose rates (proportional to the half-lives, which are ²⁴⁰Pu 6580 years; ²³⁹Pu 24,400 years; ²³⁸Pu 87.7 years; ²⁴¹Am 458 years; and ²⁴⁴Cm 18.1 years). No tendency toward amorphization is reported for any of the actinide dioxides.

Several single-crystal and polycrystalline materials have been irradiated at room temperature with alpha particles emitted from a thick ²³⁸PuO₂ source

FIGURE 6.16. Lattice Expansions from Self-Radiation Damage in Several Actinide Dioxides

($E_{\max} = 5.5$ MeV) to simulate the alpha-particle flux incident on the nonactinide-containing phases in nuclear waste solids (Weber, Wald and Gray 1980; Weber and Turcotte 1980; Chick et al. 1980). The relative changes in lattice parameters, measured by x-ray diffraction techniques, as a function of alpha dose are shown in Figure 6.17. The observed damage ingrowth follows the same exponential relationship observed for alpha decay. The results indicate that nonactinide-containing phases may undergo significant lattice expansion as a result of alpha bombardment from adjacent actinide host phases.

Clinard and Hurley (1979) summarized studies of general radiation effects and their potential application to nuclear waste forms. At the long-term damage levels expected for ceramic waste forms (1 to 10 dpa), some materials show little effect while others undergo major structural changes. They concluded that there are several major material characteristics that seem to enhance irradiation stability: cubic crystal structure, high helium permeability,

FIGURE 6.17. Lattice Expansions for Several Cubic Structures Irradiated with Alpha Particles Emitted from a ²³⁸PuO₂ Source (Weber and Turcotte 1980)

large internal surface area, high fracture toughness, high ionic bonding character, dense atomic packing, and low propensity for absorption of water. There are inevitable contradictions, but knowledge of these factors should help in the identifying of waste forms having high stability characteristics.

Naguib and Kelly (1975) examined several criteria that may be useful in predicting if a ceramic material will be subject to irradiation-induced amorphization. Using available data for energetic heavy-ion bombardment of 72 nonmetallic solids, they deduced both a temperature-ratio criterion and a bond-type (ionicity) criterion that successfully predict the occurrence of amorphization or crystallization. The temperature-ratio criterion, based on a physical model involving thermal spikes, predicts that amorphization should occur whenever the ratio, crystallization temperature/melting point, exceeds 0.3. The bond-type criterion states that amorphization should occur whenever the ionicity is ≤ 0.47 .

Stored energy in ceramic waste forms may potentially reach higher values than observed in glass waste forms. Some irradiated crystalline materials are known to exhibit rather large energy releases when the radiation damage is thermally annealed. A notable example is neutron-irradiated graphite, which undergoes enthalpy changes greater than 2400 J/g (Woods, Bupp, and Fletcher 1956). Neutron-irradiated refractory oxides are more typical of the expected behavior of crystalline phases in ceramic waste forms. Stored energy values for several materials are shown in Table 6.7. The maximum observed values lie between 100 and 350 J/g.

Roberts, Jenks and Bopp (1976) measured stored energy in neutron-irradiated simulated PW-4m calcine, PW-4m calcine on alumina spheres, and a compact made by hot-pressing PW-4m calcine mixed with quartz sand. The compact gave a maximum stored energy value of 134 J/g, while the calcine and calcine on alumina stored energy values were substantially lower at 60 to 75 J/g.

Radiolysis from both gamma and alpha irradiation in concrete containing simulated Savannah River Plant waste was studied by Bibler (1978). With gamma radiolysis, hydrogen was the only significant product. With alpha radiolysis, hydrogen and oxygen were produced. Tingey and Felix (1977) also studied radiolysis from both gamma and alpha irradiation, but in a calcine (PW-7-2).

TABLE 6.7. Stored Energy in Several Neutron-Irradiated Ceramics

Material	Maximum Observed Stored Energy, J/g	Reference
SiO ₂ (amorphous)	176	Roux et al. 1971
Al ₂ O ₃	117	Roux et al. 1971
MgO	105	Roux 1969
BeO	334	Heur and Stolarski 1966
Steatite (MgO·SiO ₂)	250	Bopp and Towns 1964
Cordierite (2 MgO·2 Al ₂ O ₃ ·5 SiO ₂)	176	Bopp and Towns 1964

They reported that gas generation rates for both gamma and alpha radiolysis appeared to be about the same; however, there was a clear distinction in the gases generated. The gamma radiolysis yielded nearly 100% O₂, while a wide range of products were observed from alpha radiolysis.

REFERENCES

- Antonini, M., P. Camagni, F. Lanza, and A. Manara. 1980. "Atomic Displacements and Radiation Damage in Glasses Incorporating HLW." In Scientific Basis for Nuclear Waste Management, Vol. 2. C. J. M. Northrup, Jr., ed., pp. 127-133. Plenum Press, New York.
- Antonini, M., F. Lanza, and A. Manara. 1979. "Simulations of Radiation Damage in Glasses." In Ceramics in Nuclear Waste Management, T. D. Chikalla and J. E. Mendel, ed., pp. 289-293, CONF-790420, NTIS, Springfield, Virginia.
- Araki, K. 1981. "Methods for Testing High-Level Waste Forms in Japan." Paper presented at the Third IAEA Research Coordinating Meeting on Evaluation of Solidified High-Level Waste Products, February 23-27, 1981, Bhabha Atomic Research Center, Trombay, India.
- Bibler, N. E. 1978. Radiolytic Gas Production from Concrete Containing Savannah River Plant Waste. DP-1464, Savannah River Laboratory, Aiken, South Carolina.
- Bibler, N. E. and J. A. Kelley. 1978. Effect of Internal Alpha Radiation on Borosilicate Glass Containing Savannah River Plant Waste. DP-1482, Savannah River Laboratory, Aiken, South Carolina.
- Bonniaud, R. A. 1977. "La Vitrification en France des Solutions de Produits de Fission." Nucl. Technol. 34:449-460.
- Bonniaud, R. A., N. R. Jacquet-Francillon, F. L. Laude, and C. G. Sombret. 1979. "Glasses as Materials Used in France for Management of High-Level Wastes." In Ceramics in Nuclear Waste Management, T. D. Chikalla and J. E. Mendel, ed., pp. 57-61, CONF-790420, NTIS, Springfield, Virginia.
- Bonniaud, R. A., N. R. Jacquet-Francillon, and C. G. Sombret. 1980. "The Behavior of Actinides in α -Doped Glasses as Regards to the Long Term Disposal of High Level Radioactive Materials." In Scientific Basis for Nuclear Waste Management, Vol. 2, C. J. M. Northrup, Jr., ed., pp. 117-125, Plenum Press, New York.
- Bopp, C. D. and R. L. Towns, 1964. "Thermal Analysis of Irradiated Ceramics." In Reactor Chemistry Division Annual Progress Report for Period Ending January 31, 1964. ORNL-3591, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

- Boult, K. A., J. T. Dalton, A. R. Hall, A. Hough, and J. A. Marples. 1979. "The Leaching of Radioactive Waste Storage Glasses." In Ceramics of Nuclear Waste Management, T. D. Chikalla and J. E. Mendel, ed., pp. 248-255, CONF-790420, NTIS, Springfield, Virginia.
- Burns, W. G. and P. B. Moore, 1976. "Water Radiolysis and Its Effect Upon In-Reactor Zircaloy Corrosion." Radiation Effects 30:233.
- Chick, L. A., G. L. McVay, G. B. Mellinger, and F. P. Roberts. 1980. Annual Report on the Development and Characterization of Solidified Forms for Nuclear Wastes. PNL-3465, Pacific Northwest Laboratory, Richland, Washington.
- Chikalla, T. D. and R. P. Turcotte, 1973. "Self-Radiation Damage Ingrowth in $^{238}\text{PuO}_2$." Radiation Effects 19:93-98.
- Clinard, F. W. and G. F. Hurley. 1979. "Effects of Irradiation on Structural Properties of Crystalline Ceramics." In Ceramics in Nuclear Waste Management, T. D. Chikalla and J. E. Mendel, ed., pp. 300-304, CONF-790420, NTIS, Springfield, Virginia.
- Dé, A. K., B. Luckscheiter, W. Lutze, G. Malow and E. Schiewer. 1976. "Development of Glass Ceramics for the Incorporation of Fission Products." Ceramic Bulletin 55(5):500-503.
- Dé, A. K., B. Luckscheiter, W. Lutze, G. Malow, E. Schiewer, and S. Tymochowicz. 1976. "Fixation of Fission Products in Glass Ceramics." In Proceedings of Symposium on Management of Radioactive Wastes from the Nuclear Fuel Cycle, Vol. 2, pp. 63-73, IAEA, Vienna, Austria.
- Draganic, I. V. and Z. D. Draganic. 1971. The Radiation Chemistry of Water. Academic Press, New York.
- Dran, J. C., Y. Langeuin, M. Maurette, and J. C. Petit. 1980. "A Microscopic Approach for the Simulation of Radioactive Waste Storage in Glass." In Scientific Basis for Nuclear Waste Management, Vol. 2, C. J. M. Northrup, Jr., ed., pp. 135-140, Plenum Press, New York.
- Dran, J. C., M. Maurette, and J. C. Petit. 1980. "Radioactive Waste Storage Materials: The α -Recoil Aging." Science 209(26):1518-1520.
- Dran, J. C., M. Maurette, J. C. Petit, and B. Vassent. 1980. "Radiation Damage Effects on the Leach Resistance of Glasses and Minerals: Implications for Radioactive Waste Storage." Paper presented at the Third International Symposium on the Scientific Basis for Nuclear Waste Management, November 16-21, 1980, Boston, Massachusetts.
- Ewing, R. C. 1981. Radiation Damage in Natural Materials: Implications for Radioactive Waste Forms. PNL-SA-9227, Pacific Northwest Laboratory, Richland, Washington.

- Ewing, R. C. and R. F. Haaker. 1980. "The Metamict State: Implications for Radiation Damage in Crystalline Waste Forms." Nuclear and Chemical Waste Management 1:51-57.
- Gilmour, B. A. and W. F. Heenan. 1965. Radiation Effects on Glass: An Annotated Bibliography. REIC Memorandum 26, Radiation Effects Information Center, Battelle Memorial Institute, Columbus, Ohio.
- Grover, J. R. 1973. "Glasses for the Fixation of High Level Radioactive Wastes." In Management of Radioactive Wastes From Fuel Reprocessing, pp. 593-612, Organization for Economic Cooperation and Development, Paris, France.
- Hall, A. R., J. T. Dalton, B. Hudson, and A. C. Marples. 1976. "Development and Radiation Stability of Glasses for Highly Radioactive Wastes." In Proceedings of Symposium on Management of Radioactive Wastes from the Nuclear Fuel Cycle, Vol. 2, pp. 3-13, IAEA, Vienna.
- Heur, P. M. and G. Z. A. Stolarski. 1966. "Stored Energy in Neutron-Irradiated Beryllium Oxide." J. Nucl. Mater. 19:70-78.
- Hobbs, L. W. 1976. "Point Defect Stabilization in Ionic Crystals at High Defect Concentrations." Journal De Physique 37(7):3-26.
- Hurtgen, C. and J. Fuger. 1977. "Self-Irradiation Effects in Americium Oxides." Inorg. Nucl. Chem. Letters 13:179-188.
- International Standards Organization. 1980. DRAFT Standard Method for Testing the Irradiation Stability of Solidified Radioactive Waste. ISO/DIS 6962.
- Jenks, G. H. and C. D. Bopp. 1973. Energy Storage in High-Level Radioactive Waste and Simulation and Measurement of Stored Energy with Synthetic Wastes. ORNL-TM-3781, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- Jones, A. R. 1959. "Radiation-Induced Reactions in the N₂-O₂-H₂O System." Radiation Research 10:655-663.
- Kelley, J. A. 1975. Evaluation of Glass as a Matrix for Solidification of Savannah River Plant Waste. DP-1382, Savannah River Laboratory, Aiken, South Carolina.
- Malow, G. and H. Andresen. 1979. "Helium Formation from α -Decay and Its Significance for Radioactive Waste Glasses." In Scientific Basis for Nuclear Waste Management, Vol. 1, G. J. McCarthy, ed., pp. 109-115, Plenum Press, New York.
- Malow, G., J. A. C. Marples, and C. Sombret. 1980. "Thermal and Radiation Effects on Properties of High Level Waste Products." In Radioactive Waste Management and Disposal, R. Simon and S. Orłowski, ed., pp. 341-359, Harwood Academic Publishers, Chur, Switzerland.

- Materials Characterization Center. 1981. DRAFT Standard Procedure MCC-6 Method for Testing Alpha-Decay Effects in Radioactive Waste Forms. Pacific Northwest Laboratory, Richland, Washington.
- McCarthy, G. J. 1977. "High-Level Waste Ceramics: Material Considerations, Process Simulation, and Product Characterization." Nucl. Technol. 32:92-105.
- McVay, G. L. and L. R. Pederson. 1981. "Effect of Gamma Radiation on Glass Leaching." J. Am. Ceram. Soc. 64(3/4).
- McVay, G. L., W. J. Weber, and L. R. Pederson. 1980. "Effect of Radiation on the Leaching Behavior of Nuclear Waste Forms." PNL-SA-8951, Pacific Northwest Laboratory, Richland, Washington. Presented at the ORNL Conference on the Leachability of Radioactive Solids, December 9-12, 1980, Gatlinburg, Tennessee.
- Mendel, J. E. 1973. "Measurements on Core-Drilled Samples." In Quarterly Progress Report, Research and Development Activities, Waste Fixation Program, April through June 1973. BNWL-1761, pp. 16-18, Pacific Northwest Laboratory, Richland, Washington.
- Mendel, J. E. 1978. The Storage and Disposal of Radioactive Waste as Glass in Canisters. PNL-2764, Pacific Northwest Laboratory, Richland, Washington.
- Mendel, J. E. et al. 1976. "Thermal Radiation Effects on Borosilicate Waste Glasses." In Proceedings of Symposium on Management of Radioactive Wastes from the Nuclear Fuel Cycle, Vol. 2, pp. 49-60, IAEA, Vienna, Austria.
- Mendel, J. E. et al. 1977. Annual Report on the Characteristics of High-Level Waste Glasses. BNWL-2252, Pacific Northwest Laboratory, Richland, Washington.
- Mendelsohn, K., E. King, J. A. Lee, M. H. Rand, C. S. Griffin, and R. S. Street. 1967. "Self Irradiation Damage in Transuranic Elements and Compounds." In Plutonium 1965, A. E. Kay and M. B. Waldron, ed., pp. 189-204, Chapman and Hall, London.
- Mosley, W. C. 1971. "Self-Radiation Damage in Curium-244 Oxide and Aluminate." J. Amer. Ceram. Soc. 54(10):475-479.
- Naguib, H. M. and R. Kelley. 1975. "Criteria for Bombardment-Induced Structural Changes in Non-Metallic Solids." Rad. Effects 25:1-12.
- Noe, M. and J. Fuger. 1971. "Self-Radiation Effects on the Lattice Parameter of $^{244}\text{CmO}_2$." Inorg. Nucl. Chem. Letters 7:421-430.
- Noe, M. and J. Fuger. 1974. "Self-Radiation Effects on the Lattice Parameter of $^{238}\text{PuO}_2$." Inorg. Nucl. Chem. Letters 10:7-19.

- Primak, W. 1977. "Notes on Radiation Effects in Glasses Pertinent to Solid Storage of Radioactive Wastes." In Ceramic and Glass Radioactive Waste Forms, pp. 157-173, USERDA CONF-770102, NTIS, Springfield, Virginia.
- Rauscher, H. E. and R. E. Tischer. 1964. The Effect of the $^{10}\text{B}(n,\alpha)^7\text{Li}$ Reactions of the Solubility of Borosilicate Glasses. Report L-241, Corning Glass Works, Corning, New York.
- Reeve, K. D., D. M. Levins, E. J. Ramm, J. L. Woolfrey, W. J. Buykx, R. K. Ryan, and J. F. Chapman. 1981. "The Development and Testing of SYNROC for High-Level Radioactive Waste Fixation." Paper presented at Waste Management '81, February 23-26, 1981, Tucson, Arizona.
- Reeve, K. D., D. M. Levins, and J. L. Woolfrey. 1981. "Properties of Waste Forms in the AAEC Research Establishment's SYNROC R and D Program." Paper presented at Third Meeting of the IAEA Coordinated Research Program on Evaluation of Solidified High Level Waste Forms, February 23-27, 1981, Trombay, India.
- Reeve, K. D. and J. L. Woolfrey. 1980. "Accelerated Irradiation Testing of SYNROC Using Fast Neutrons. I. First Results on Barium Hollandite, Perovskite and Undoped SYNROC 8." J. Aust. Ceram. Soc. 16:10-15.
- Riley, W. C., W. G. Coppins, and W. H. Duckworth. 1958. The Effect of Nuclear Radiation on Glass. AD-207701, Radiation Effects Information Center Technical Memorandum No. 9, Battelle Memorial Institute, Columbus, Ohio.
- Ringwood, A. E., S. E. Kesson, N. G. Ware, W. O. Hibberson, and A. Major. 1979. "The SYNROC Process: A Geochemical Approach to Nuclear Waste Immobilization." Geochemical Journal (Japan) 13:141-165.
- Ringwood, A. E., V. M. Oversby, and W. Sinclair. 1980. "The Effects of Radiation Damage on SYNROC." In Scientific Basis for Nuclear Waste Management, Vol. 2, C. J. M. Northrup, Jr., ed., pp. 273-280, Plenum Press, New York.
- Roberts, F. P. 1980. "Irradiation Effects on Borosilicate Glasses." Paper presented at the 10th ASTM International Symposium on Effects of Radiation on Materials, June 3-5, 1980, Savannah, Georgia.
- Roberts, F. P., R. P. Turcotte and W. J. Weber. 1981. Materials Characterization Center Workshop on the Irradiation Effects in Nuclear Waste Forms, Summary Report. PNL-3588, Pacific Northwest Laboratory, Richland, Washington.
- Roberts, F. P., G. H. Jenks, and C. D. Bopp. 1976. Radiation Effects in Solidified High-Level Wastes - Part I, Stored Energy. BNWL-1944, Pacific Northwest Laboratory, Richland, Washington.

- Ross, W. A. et al. 1978. Annual Report on the Characterization of High-Level Waste Glasses. PNL-2625, Pacific Northwest Laboratory, Richland, Washington.
- Ross, W. A. and J. E. Mendel. 1979. Annual Report on the Development and Characterization of Solidified Forms for High-Level Wastes: 1978. PNL-3060, Pacific Northwest Laboratory, Richland, Washington.
- Ross, W. A., R. P. Turcotte, J. E. Mendel, and J. M. Rusin. 1979. "A Comparison of Glass and Crystalline Waste Materials." In Ceramics in Nuclear Waste Management, T. D. Chikalla and J. E. Mendel, ed., pp. 52-56, CONF-790420, NTIS, Springfield, Virginia.
- Roux, A. 1969. "Energie Emmagasinee dans les Oxydes BeO, MgO, Al₂O₃, et SiO₂ Irradies aux Neutrons." Thesis, University of Lyon, Report No. CEA-N-4171.
- Roux, A., J. Elston, P. Gerard, and J. Cheipps. 1971. "Etude Comparative de l'energie Wigner de BeO, MgO, Al₂O₃ et SiO₂ Vitreous." Comp. Rend., Vol. 272, Series C, pp. 812-815.
- Rusin, J. M. 1980. A Review of High-Level Waste Form Properties. PNL-3035, Pacific Northwest Laboratory, Richland, Washington.
- Rusin, J. M., W. J. Gray, and J. W. Wald. 1979. Multibarrier Waste Forms Part II: Characterization and Evaluations. PNL-2668-2, Pacific Northwest Laboratory, Richland, Washington.
- Scheffler, K., U. Riege, and W. Hild. 1976. Energiespeicherung in Borosilikatglassern. KfK 2333, Kernforschungszentrum, Karlsruhe, Germany.
- Scheffler, K. and U. Riege. 1977. Investigations on the Long-Term Radiation Stability of Borosilicate Glasses Against Alpha Emitters. KfK 2422, Kernforschungszentrum, Karlsruhe, Germany.
- Shelby, J. E. 1980. "Effect of radiation on the physical properties of borosilicate glasses." J. Appl. Phys. 51:2561-2565.
- Tingey, G. L. and W. D. Felix. 1977. Radiolytic Gas Generation from Cal-cined Nuclear Waste. BNWL-2381, Pacific Northwest Laboratory, Richland, Washington.
- Turcotte, R. P. 1976. Radiation Effects in Solidified High-Level Wastes. Part 2 - Helium Behavior. BNWL-2051, Pacific Northwest Laboratory, Richland, Washington.
- Turcotte, R. P. and F. P. Roberts. 1977. "Phase Behavior and Radiation Effects in High Level Waste Glass." In Ceramic and Glass Radioactive Waste Forms, D. W. Readey and C. R. Cooley, ed., pp. 65-81, CONF-770102, NTIS, Springfield, Virginia.

- Weber, W. J. 1981. "Ingrowth of Lattice Defects in Alpha Irradiated UO_2 Single Crystals." J. Nucl. Mater. 98 (in preparation).
- Weber, W. J., R. P. Turcotte, L. R. Bunnell, F. P. Roberts, and J. H. Westsik, Jr. 1979. "Radiation Effects in Vitreous and Devitrified Simulated Waste Glass." In Ceramics in Nuclear Waste Management, T. O. Chikalla and J. E. Mendel, ed., pp. 294-299, CONF-790420, NTIS, Springfield, Virginia.
- Weber, W. J. and R. P. Turcotte. 1980. "Radiation Damage in Nuclear Waste Ceramics." Paper presented at the Fall Meeting of the American Ceramic Society, October 26-29, 1980.
- Weber, W. J., J. W. Wald, and W. J. Gray. 1980. "Radiation Effects in Crystalline High-Level Nuclear Waste Solids." Paper presented at the Third International Symposium on the Scientific Basis for Nuclear Waste Management, November 16-21, 1980, Boston, Massachusetts.
- Woods, W. K., L. F. Bupp, and J. F. Fletcher. 1956. "Irradiation Damage in Artificial Graphite." In Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Vol. 7, pp. 455-462, United Nations, New York.