ANL-93/45

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

**EFFECTS OF RADIONUCLIDE DECAY ON WASTE
GLASS BEHAVIOR -- A CRITICAL REVIEW**

by

David J. Wronkiewicz

Chemical Technology Division

December 1993

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

87B

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.

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	ix
1.0 INTRODUCTION	1
2.0 SOURCES OF RADIONUCLIDE DECAY	2
3.0 SIMULATION TECHNIQUES	4
3.1 Charged Particle Irradiations	4
3.2 Gamma Irradiations	6
3.3 Radionuclide Doping	6
3.4 Pressure Densification	6
4.0 AIR AND WATER RADIOLYSIS	7
5.0 EFFECTS OF SOLID RADIATION DAMAGE	8
5.1 Direct Displacement	8
5.1.1 Volume Effects	9
5.1.2 Bubble Formation	11
5.1.3 Fracture Toughness	11
5.1.4 Latent Energy	13
5.1.5 Summary of Direct Displacement Effects	13
5.2 Ionization Effects	14
5.2.1 Volume Effects for High-Silica Glasses	16
5.2.2 Volume Effects for Low-Silica Glasses	16
5.2.3 Glass Composition Influence on Volume Changes	17
5.2.4 Bubble Formation	18
5.2.5 Alkali Migration Studies	24
5.2.6 Summary of Ionization Effects	26
5.3 Transmutation Effects	26
5.4 Annealing Process	27
6.0 RADIOLYSIS EFFECTS ON GLASS DURABILITY AND RADIONUCLIDE RELEASE	30
6.1 Gamma Radiolysis Tests	30
6.2 Alpha Radiolysis Tests	35
6.3 Simulated Corrosion Tests	36
6.4 Effects of Solid-Phase Radiation Damage	38
6.5 Direct Alpha-Recoil Ejection	40
6.6 Tests with Fully Radioactive Glass	40
6.7 Radiolysis Effects in an Unsaturated Environment	42
7.0 IDENTIFIED FUTURE NEEDS	44
8.0 ACKNOWLEDGMENTS	46
9.0 REFERENCES	47

This page left intentionally blank.

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Cumulative Number of Decay Events per Unit Mass and Per Unit Volume for Commercial and Defense High-Level Waste Forms as a Function of Storage Time in Years	3
2.	Cumulative Ionizing Radiation Dose in Commercial and Defense HLW Forms	5
3.	Cumulative Number of Displacements Per Unit Mass and Per Unit Volume for Commercial and Defense HLW Forms	5
4.	Range of Swelling in Volume Percent for Crystalline and Glass Waste Forms as a Function of Accumulated Dose	10
5.	Hardness, Crack Length at Vickers Indentations, and Crack Probability of the French SON 68 Waste Glass as Function of Alpha Dose	12
6.	Stored Energy in ^{244}Cm -Doped HLW Glasses	13
7.	Gamma Ray-Induced Compaction in Silica and Borosilicate Glasses	15
8.	Absorption Spectra before and after Gamma Irradiation	19
9.	Bubble Density and Total Swelling vs. Dose in Electron-Irradiated Borosilicate Glass	22
10.	Temperature Dependence of Bubble Formation	22
11.	Total Swelling Rate as a Function of Irradiation Temperature in Borosilicate Glasses of Varying Sodium Content	23
12.	Concentration of Oxygen Bubbles Produced in SRL Sodium-Borosilicate Glasses as a Function of Cumulative Gamma Dose	25
13.	Thermal Annealing Trends for (n, α) Irradiation in Four Types of Simulated Borosilicate Waste Glasses	29
14.	Deionized and Deaerated Leachant pH Trends for Gamma Irradiated vs. Nonirradiated Static Leach Tests with PNL 76-68 Glass	31
15.	Deionized and Deaerated Leachant Trends for Na and Si Concentrations in Gamma Irradiated vs. Nonirradiated Static Leach Tests with PNL 76-68 Glass	32
16.	Solution Concentrations for Various Elements Plotted in Four Reaction Environments	34

LIST OF FIGURES (contd.)

<u>No.</u>	<u>Title</u>	<u>Page</u>
17.	Normalized Elemental Release Trends from Borosilicate Glass in MCC-1 Static Leach Tests with Deionized Water as a Function of Time and Alpha Activity	36
18.	Solution Concentrations for Various Elements in Five Reaction Environments	37
19.	Normalized Boron Release from 90°C Batch Tests in EJ-13 Solution for Fully Radioactive and Simulated Savannah River Site Glasses	43

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Cumulative Decay Events and Dose Projections for West Valley and Savannah River Plant Glass	2
2.	Literature Summary of Atomic Displacements in High-Level Waste Glasses	3
3.	Principal Radiolytic Species G Values Resulting from Gamma and 5 MeV Alpha Radiation of Liquid Water	7
4.	Dose Rate and Cumulative Dose Dependence of Ionization-Induced Decomposition	15
5.	Effect of Dose and Temperature on Ionization-Induced Bubble Formation	20

This page left intentionally blank.

EFFECTS OF RADIONUCLIDE DECAY ON WASTE GLASS BEHAVIOR -- A CRITICAL REVIEW

by

David J. Wronkiewicz

ABSTRACT

Both collision and ionization radiation damage to solid glass materials results in bond damage and atomic displacements. This type of damage has been shown to induce minor volume changes in the glass, increase fracture toughness, induce phase separations, and increase the release rates of glass components up to four-fold during subsequent corrosion tests. Solid phase radiation damage may also enhance the release of intermediate decay-series daughter radionuclides from damage tracks in the glass. Under actual disposal conditions, however, glass annealing processes may negate most of the solid radiation damage effects.

The release of glass components into solution, including radionuclides, may be changed by the presence of radiolytically produced nitric acid, carboxylic acid, and transient water dissociation products such as $\bullet\text{OH}$ and O_2^- . Under batch test conditions, glass corrosion has been shown to increase a maximum of three- to five-fold in gamma- and alpha-irradiated tests relative to nonirradiated tests, while in other studies, the presence of radiolytic products has actually decreased the release rates of some glass components. Bicarbonate groundwaters will buffer against pH decreases and resultant corrosion rate increases arising from the formation of radiolytic acids. Under high S/V conditions characteristics of an unsaturated repository setting, the bicarbonate buffering reservoir may be quickly overwhelmed by radiolytic acids that are concentrated in the thin films of water contacting the samples. Glass reaction rates have been shown to increase up to 10- to 15-fold due to radiation exposure under these conditions.

Outstanding information needs associated with radiation effects on waste glass durability include: the extent of selective release of intermediate decay-series radionuclides along damage tracks, repository-relevant testing of glass annealing, radiation-induced phase separation, mechanistic understanding of radiolysis product interaction in glass corrosion, repository-relevant testing of glass under high surface area/volume conditions, the influence of alteration phases in influencing glass dissolution and radionuclide migration, alpha radiation effects on solution composition, and comparisons between simulated and fully radioactive glass reactions.

This page left intentionally blank.

1.0 INTRODUCTION

The Yucca Mountain site (Nevada) is currently under evaluation for geological storage of high-level nuclear waste. Radiation effects on high-level waste glasses and their surrounding repository environment are important considerations for radionuclide immobilization because of the potential to alter the glass stability and thereby influence the radionuclide retentive properties of this waste form. The influence of radionuclide decay on vitrified nuclear waste may be manifested by several changes, including volume, stored energy, structure, microstructure, mechanical properties, and phase separation. Radiation may also affect the composition of aqueous fluids and atmospheric gases in relatively close proximity to the waste form. Changes in many of these features *per se* will not generally influence the release of radionuclides from the waste. What is important to the radionuclide retentive properties of the repository is how these radiation effects collectively or individually influence the durability and radionuclide release from the glass in the event of liquid water contact.

This paper is an extension of a chapter in an earlier report [1] that provides an updated review on the status of radiation damage problems in nuclear waste glasses. This report will focus on radiation effects on vitrified borosilicate nuclear waste glasses under conditions expected in the proposed Yucca Mountain repository. These conditions, although not precisely defined [2], do indicate that geologic waste storage will be in the vadose zone, several hundred meters above the local water table. In the vadose zone, the pore space existing within the geologic medium is occupied by a mixture of liquid water and moist air. In this environment the most likely mode of water contact with the glass waste will be through either water vapor condensation or dripping of limited quantities of liquid water from pore space onto the waste.

The maximum temperatures that the waste will be exposed to have yet to be defined. Waste glass temperatures will initially rise following emplacement of the waste glass in a repository, reach a peak temperature after a few decades, and thereafter decrease slowly until temperatures approach the host rock ambient temperature several thousand years after emplacement. The temperatures that the waste will be exposed to depend on the radionuclide waste loading spacing between the waste containers, age of the waste, the relative proportion of more highly active spent nuclear fuel relative to vitrified waste canisters, and the hydrolysis of the repository environment.

The actual vitrified waste forms will not be exposed to the repository atmosphere until the waste container has been breached by corrosive actions of the repository environment. Current repository criteria call for substantially complete isolation of the waste, by the waste container, during the first 300 to 500 years following disposal. Despite the uncertainties in the temperature range of waste exposure, bounding conditions can be established through consideration of the calculated temperature of spent nuclear fuel at 300 years ($\sim 100^{\circ}\text{C}$) and the ambient temperature of the geologic host rock $\sim 25^{\circ}\text{C}$ [2].

This paper specifically addresses radiation effects on the borosilicate glasses to be fabricated by the Defense Waste Processing Facility (DWPF) and West Valley Demonstration Project (WVDP). However, reports on radiation testing on these glass types are limited; thus, discussion of radiation effects on other glass compositions or crystalline materials will be included where this information provides mechanistic information on radiation effects.

This report discusses the sources and temporal variations in intensities of radiation energy emanating from the DWPF glass; laboratory simulation techniques that mimic radiation damage or accelerate damage effects into reasonably short experimental time frames; effects of radiation on the composition of the atmosphere and/or liquid water that exist in the environment immediately surrounding the waste; solid-phase radiation damage effects in relation to both

displacement (knock-on) and ionizing (electronic) radiation processes; annealing processes that occur in the glass; and the combined effects of radionuclide decay on glass leaching and dissolution properties.

2.0 SOURCES OF RADIONUCLIDE DECAY

Glass waste forms will exhibit temporal variations in types and intensities of radioactivity. During the first 500 years of repository operation, when the source of radiation is most intense, radiation emissions are expected to be dominated by beta and gamma radiation from ^{137}Cs , ^{90}Sr , and other fission product sources (Table 1). Actinide elements that emit alpha particles generally have much longer half-lives (from hundreds to billions of years) and thus will become the dominant radiation source at longer times to the point where the alpha dose exceeds that from combined beta and gamma emissions (Fig. 1). Calculated radiation emissions from 1000-year-old vitrified waste, based on data from Baxter [3], indicate that ~80% of the total activity will be dominated by alpha decay of ^{239}Pu , ^{240}Pu , ^{241}Am , and ^{238}Pu , while ~18% will result from the beta decay of ^{99}Tc , ^{93}Zr , ^{154}Eu , and ^{126}Sn . A small portion of the radionuclides present in the glass may also undergo spontaneous fission, producing neutrons and two intermediate-sized fission atoms. There also are secondary (alpha, n) reactions that may contribute to neutron radiation from the waste. Although spontaneous fission and (alpha, n) reactions will be highly energetic sources for radiation damage (Table 2), their overall contribution to the radiation effects is negligible due to their relatively infrequent occurrence [4].

Because of their low penetrating ability in solids, the alpha and beta particles can interact with the waste package environment only after the waste container has been breached and the air/water environment of the repository comes in direct contact with the glass. Gamma radiation can penetrate the waste canister walls and interact with the environment surrounding the waste package. However, most gamma-emitting sources have relatively short half-lives, thus lessening their importance for radiolysis as the waste glass becomes older [5].

Table 1. Cumulative Decay Events and Dose Projections for West Valley and Savannah River Plant Glass^a

Time, years	Alpha Decays, per cm ³	Beta Decays, per cm ³	Alpha Dose, rad	Beta and Gamma, rad
10 ⁰	5 x 10 ¹⁴	4 x 10 ¹⁷	2 x 10 ⁷	6 x 10 ⁸
10 ¹	5 x 10 ¹⁵	4 x 10 ¹⁸	2 x 10 ⁸	6 x 10 ⁹
10 ²	5 x 10 ¹⁶	7 x 10 ¹⁸	2 x 10 ⁹	6 x 10 ¹⁰
10 ³	3 x 10 ¹⁷	4 x 10 ¹⁹	9 x 10 ⁹	6 x 10 ¹⁰
10 ⁴	8 x 10 ¹⁷	4 x 10 ¹⁹	3 x 10 ¹⁰	8 x 10 ¹⁰
10 ⁵	4 x 10 ¹⁸	4 x 10 ¹⁹	4 x 10 ¹⁰	1 x 10 ¹¹
10 ⁶	3 x 10 ¹⁸	4 x 10 ¹⁹	8 x 10 ¹⁰	1 x 10 ¹¹

^aCalculated from data in Weber [5], assuming a glass density of 2.7 g/cm³.

Fig. 1. Cumulative Number of Decay Events per Unit Mass and Per Unit Volume for Commercial and Defense High-Level Waste (HLW) Forms as a Function of Storage Time in Years (Basis: Commercial HLW -- 3.3% enriched UO_2 fuel, burnup of 33,000 MWd/tonne heavy metal, cooled five years before reprocessing and solidification; defense HLW -- Savannah River Plant borosilicate waste glass, 25 wt % waste loading). Modified from Weber [6].

Table 2. Literature Summary of Atomic Displacements in High-Level Waste Glasses. Data and reference sources from Lutze [4] and Weber and Roberts [7]

Radiation Source	Displacements per Decay		
α -particles (6 MeV)	140	130	180
Recoil nuclei (α -decay)	1500	2000	1200
Fission fragments	-	25,000	4×10^5
Fast neutrons	-	220	-
β -particles	0.13	0.07	~1
Gamma			<<1

Beta decay results in the emission of ~ 0.5 MeV beta particles and for some parent radionuclides additional gamma radiation may be emitted [6]. Beta particles generally produce less than one collisional displacement event per decay (Table 2). Gamma radiation is relatively unimportant in producing displacement events. Both gamma radiation and beta particles lose energy predominantly by ionization events. These electronic excitations can become localized and persist long enough for permanent atomic displacements to occur in a process called "radiolysis." Substantial displacement damage occurs by radiolysis processes in ionic solids such as halides, hydrides, and azides but is relatively uncommon in oxide phases [6].

Alpha decay results in the formation of a high-energy alpha particle (~ 4 to 6 MeV) and a recoil nucleus (~ 0.1 MeV) [6]. Most of the energy associated with the recoil nucleus is lost through "knock-on" collisions and displacements with the glass atoms, producing approximately 1000 to 2000 displacements per decay event (Table 2). Greater than 99% of the energy associated with the alpha particles is lost through ionization processes, while the remainder is dissipated through collision events, producing approximately 100 to 200 displacements per decay event. The ionization dose from the alpha particles is a significant component of the total dose and will exceed the ionization dose from beta and gamma radiation after $\sim 10,000$ years of storage (Fig. 2). The cumulative number of atomic displacement events occurring in glass waste by all radiation processes will be dominated by alpha decay events (Fig. 3). This trend reflects the three orders of magnitude increase in atomic displacements per decay event for alpha decay relative to beta or gamma decay.

3.0 SIMULATION TECHNIQUES

Many simulation techniques have been devised to investigate the effects of long-term radiation damage to glass. The underlying premise for the majority of these tests is to accelerate the damage process that will occur in radioactive waste glass over a period of tens to millions of years, into a laboratory simulation that takes a few years or less. These simulation techniques fall into four major categories: charged particle irradiations, gamma irradiations, doping of glass with short-lived radionuclides, and pressure-induced densification.

3.1 Charged Particle Irradiations

Charged particle irradiations with electrons, protons, or heavy ions offer an advantage in that extensive radiation damage can be induced to specific sample areas in a limited amount of time, without the difficulties associated with the handling of radioactive materials [6]. Studies have found that damage patterns in natural alpha-damaged materials are similar to those of lead-ion implanted crystals and thus indicate that ion implantation may be a useful technique for simulating alpha-recoil damage [8]. Problems associated with this simulation technique may occur where damage effects are concentrated in small surface regions in very short periods of time. Such a damage process may result in excessive damage overlap and radionuclide release rates during subsequent leaching events. This technique also limits the time allowed for annealing processes due to the relatively rapid damage rates.

Weber and Roberts [7] have reviewed a number of assumptions inherent with various charged particle irradiation techniques and their relevance to emissions from decayed radionuclides. Heavy-ion irradiations, typically with lead-, xenon-, or argon-ions, or neutrons, may simulate damage effects from a recoil nuclei with little or no ionization effects. Energetic helium ions produce displacement damage that simulates the effects of alpha particles. These latter techniques, however, also probably include the effects of ionization damage resulting from

Fig. 2. Cumulative Ionizing Radiation Dose in Commercial and Defense HLW Forms. Modified from Weber [6]. See Fig. 1 for description of waste forms.

Fig. 3. Cumulative Number of Displacements Per Unit Mass and Per Unit Volume for Commercial and Defense HLW Forms. Modified from Weber [6].

charged alpha particles. High-energy electron irradiations (>0.5 MeV) can simulate high-energy beta damage and possibly displacement damage associated with alpha decay. Low-energy electron irradiations (<0.5 MeV) will simulate ionization effects associated with beta-gamma irradiation.

3.2 Gamma Irradiations

Gamma radiation is used in a number of solid phase ionization studies but is more commonly used to examine the effects of radiation on atmosphere or groundwater compositions. The advantage to this technique arises from the ability of gamma radiation to penetrate the walls of the test vessels. Thus, samples may be irradiated in environmentally sealed containers without the hazards associated with handling actual radioactive glass samples. Tests are typically performed with the samples being irradiated from external ^{60}Co or ^{137}Cs sources.

3.3 Radionuclide Doping

The effects of long-term radionuclide decay may be accelerated in the laboratory by doping the simulated glass waste with a relatively short-lived isotope. For example, the alpha-decay damage associated with ^{239}Pu ($T_{1/2} = 24,110$ years) may be simulated by doping the glass with ^{238}Pu or ^{244}Cm ($T_{1/2} = 87.74$ and 18.11 years, respectively). The advantages of this technique result from the simultaneous irradiation from the recoil nucleus and alpha particles, thus effectively simulating a realistic waste glass damage exposure scenario. The generation of helium gas, the migration of parent and daughter nuclides in damaged glass regions, and secondary mineral phase incorporation of actinides may also be examined in these studies.

To date, most doping techniques utilize the incorporation of alpha-emitting radionuclides in the glass. This trend has arisen because the majority of damage occurring to radioactive waste glass will result from direct displacements from alpha-recoil nuclei. Surprisingly, damage studies resulting from glass samples doped with beta-emitting radionuclides are nearly nonexistent. A single study investigating transmutation effects on glass was conducted with ^{134}Cs ($T_{1/2} = 2.065$ years) as a surrogate for ^{137}Cs ($T_{1/2} = 30.17$ years) [9], but effects of radiation exposure damage to glass were not investigated. Additional radiation damage investigations have been devised in which ^{235}U or $^{10}\text{B}(n,\alpha)^7\text{Li}$ doped glass samples are neutron irradiated [6]. These tests examine the effects of fission product and alpha decay, respectively, on simulated waste glass. The latter technique also results in high rates of helium gas generation in the glass samples.

3.4 Pressure Densification

A final technique for simulating radiation damage to glass involves the pressure densification of glass samples in high-pressure two-stage anvil cells [10]. This experimental technique produces relatively large-sized ($\sim 0.1 \text{ cm}^3$) samples of compacted fused silica with a density increase of $\sim 20\%$. These samples are thought to reproduce, on a macro-scale, the microscopic effects of radiation damage to glass samples.

4.0 AIR AND WATER RADIOLYSIS

Many studies have been conducted to investigate the effects of radiation on glass leaching in air-water systems. Ionizing radiation will excite electrons and ionize water molecules and dissolved gases to form reactive radicals and new molecules [11-13]. The predominant waste radiolysis species formed (Table 3) include hydrated electrons (e^-_{aq}), hydrogen ions (H^+), hydroxyl ($\bullet OH$), hydroperoxyl ($HO_2\bullet$), hydrogen atoms ($H\bullet$), molecular oxygen anions (O_2^-), molecular hydrogen (H_2), and molecular hydrogen peroxide (H_2O_2). The efficiency of radiation in producing radicals or molecules is expressed as a "G value," which is the average number of radiolytic species created (positive G) or destroyed (negative G) by the absorption of 100 eV of radiation energy. A comparison of the G values for radiolysis of water (Table 3) indicates that gamma radiation produces higher concentrations of radical species like e^-_{aq} , H^+ , $\bullet OH$, and $H\bullet$, whereas alpha yields are greatest for molecular $HO_2\bullet$, H_2 , and H_2O_2 molecules [14].

Dissolved molecular nitrogen and carbon dioxide in the water may also undergo radiolytic decomposition involving a several step recombination of the dissociation products with oxygen, water, and other associated radiolytic products to form nitrogen and carboxylic acids, respectively [14-20]. Because the solubility of nitrogen in water is low, G values for nitric acid production in air-saturated water will also be small. The $G(NO_3^-)$ values reported for irradiated oxidized water systems range from zero to less than 0.2 [21-26]. The G values for radiolytic production of nitric acid from moist air or two phase air/liquid water systems range from ~2.0 to 3.0 for gamma, alpha, electron, and mixed neutron-gamma irradiation studies [24,26-32]. In these systems, nitric acids that formed in the gas phase were concentrated in the liquid [24,32]. The irradiation of solutions containing organic compounds, such as methane, will lead to the formation of methyl radicals that can combine to produce higher molecular weight organic compounds similar to those of carboxylic acid radiolysis [14].

A notable decrease occurs in the pH of deionized water exposed to gamma and alpha radiation because nitric acid forms in the irradiated air above the test solution and subsequently dissolves in water [15,24,26-28,30-33]. Burns et al. [15,16] formulated an equation to predict the molar concentration of nitric acid accumulating in water. This equation requires as input values determined for $G(NO_3^-)$, the concentration of N_2 in the atmosphere, gas/liquid ratio, dose rate, and exposure time. The molar nitric acid concentration can then be used to determine the solution pH in contact with the glass, assuming complete dissociation of the acid. In turn, these pH values can be used to predict the reaction behavior of glass samples in irradiated systems.

Table 3. Principal Radiolytic Species G-Values (Yield, molec/100 ev)
Resulting from Gamma and 5 MeV Alpha Radiation of
Liquid Water [14]

Species	Yield, molec/100 eV							
	H^+	e^-_{aq}	$H\bullet$	$\bullet OH$	HO_2^-	H_2	H_2O_2	H_2O
Gamma	2.7	2.7	0.61	2.86	0.03	0.43	0.61	-4.14
Alpha	0.3	0.3	0.3	0.5	0.10	1.4	1.3	-3.3

Nitrogen acid yields in gamma radiation tests at 90 and 200°C were found to be reduced to ~40% and 10%, respectively, of the levels that characterize tests at 25°C [32]. These results are important from the standpoint of nuclear waste containment in that the highest radiation dose rates will occur early in the life of the repository, when waste package heating due to radioactive decay is also the greatest. Thus, the elevated temperatures expected soon after waste disposal may mitigate against large increases in nitric acid production and resultant pH decreases.

Radiolysis of water may also influence the redox potential (Eh) of the irradiated solution. During irradiation of water, equal amounts of reducing and oxidizing species will be produced [13,14]. The H₂ produced during both alpha and gamma radiolysis is chemically inert toward low-temperature (<100°C) aqueous reactions and has a high diffusional mobility relative to other radiolytic products. The H₂ may thus separate from the aqueous system, thereby increasing the oxidation state of the irradiated groundwater. Sunder and Shoesmith [13] note that during radiolysis with spent fuel, O₂⁻ and •OH are the predominant oxidizing agents, followed by H₂O₂ and then O₂. Alpha and gamma radiolysis of brines results in very high redox potentials due to scavenging of •OH radicals by halide anions and a resultant increase in the separation of H₂ from the aqueous phase [34,35]. Condensation of thin films of fluid on the glass samples may promote the formation of saline brines due to the rapid concentration increase of glass dissolution products in the limited volumes of water. The presence of ferrous iron and other reduced species may impede oxidization of groundwaters [36,37].

5.0 EFFECTS OF SOLID RADIATION DAMAGE

Radiation damage to solid materials such as nuclear waste glass will occur by several processes that depend on the type of radiation interacting with the solid. The chief sources of radiation damage to solid materials are beta and, to a lesser extent, gamma decay of fission products and alpha decay of the actinide elements [4,15,38]. Radiation damage in solid materials will displace atoms from their original sites, primarily through collisions with the recoil nucleus and alpha particles, will transmute parent radionuclides into daughter elements that are no longer stable within the solid structure, and will create ionization effects owing to the electronic excitation of solid materials through collisions with alpha and beta particles and absorption of gamma photons [5,6,39,40].

5.1 Direct Displacement

Radiation damage from alpha decay results from the interaction of the glass with both a high-energy alpha particle and a lower energy alpha-recoil nucleus. Because an alpha particle has an appreciable mass, its ejection will impart ~0.1 MeV of recoil energy to the daughter nucleus. The alpha-recoil nucleus will transfer this energy as it travels through and collides with surrounding atoms, displacing several thousand atoms along an alpha-recoil track in the surrounding glass, as indicated by Table 2 [6,7]. At velocities relatively larger than the Bohr electron velocity ($V_B \sim 2.2 \times 10^8$ cm/s), the emitted alpha particle (~4 to ~6 MeV) dissipates most of its energy in the surrounding medium by electron excitation and ionization [41]. As the velocity of the alpha particle slows, direct displacement events such as Coulomb and hard-sphere interactions are dominant, with enough low-velocity collision events occurring to displace several hundred atoms. Travel distances of alpha particles in glass are ~10,000 to 20,000 nm, while the alpha-recoil nucleus will travel ~10 to 100 nm [41,42]. Beta particles will travel

distances of 10^6 nm [15], while gamma radiation may readily penetrate through the glass waste form and canister walls. Bibler [43] calculates that 80% of the gamma radiation generated by the waste will be absorbed by a glass waste form cylinder with dimensions of 10-ft long (3.0 m) by 2-ft diameter (0.6 m).

Because most of the beta and gamma radiation sources will have largely decayed during the first 500 years of repository operation, solid-phase radiation damage studies have concentrated on direct displacements from alpha particle and alpha-recoil events. The alpha-doped simulation experiments thus emphasize displacements from alpha decay events but do not account for the high ionizing doses of beta and gamma radiation to which the actual waste glass will initially be exposed. The ionizing dose received by the waste from alpha particle sources is also significant, with cumulative dose exposures from alpha sources being expected to exceed those from beta-gamma sources after $\sim 10^6$ years (Fig. 2) [5]. Synergistic effects between alpha-collision and ionization processes may occur in actual vitrified wastes but, with a few exceptions, have not been simulated in short-term radiation experiments [44,45].

5.1.1 Volume Effects

The volume (or density) of glass and crystalline materials may change as a result of atomic displacements that occur after exposure to radiation sources [7,46-48]. For example, crystalline or ceramic waste forms may swell up to 10% after exposure to alpha radiation, due to increasing disorder of the crystalline material (Fig. 4) [49-51]. Volume changes in glass after alpha exposure are generally in the range of $\pm 1.2\%$. Exarhos [52] notes that displacement damage causes marked swelling and eventual amorphization in crystalline materials, while ionization damage causes only slight swelling with no tendency toward amorphization. Neutron irradiation materials display larger volume changes with compactions up to 3% [10,53]. Measurable volume changes are first reported to occur after a cumulative exposure of 1×10^{17} alpha decays/cm³, and saturate after a dose of 5×10^{18} alpha decays/cm³ [51]. A comparison of these damage and saturation levels with the expected cumulative alpha exposure levels for WVDP and DWPF glasses indicates that waste form volume changes may occur after ≤ 1000 years of self-irradiation damage (Table 2) [6,7,14,54].

Glass volume changes observed in alpha decay studies may result from both direct atomic displacements and ionization damage. Ion irradiation studies of Arnold [41,55,56] indicate that ionization processes may be the dominant mechanism for producing volume changes in borosilicate glass, while displacement damage was more important for fused silica glass. A comparison of krypton-, xenon-, and helium-ion irradiations indicates that nuclear collisions rather than ionization are mainly responsible for amorphization of crystalline materials [57]. This conclusion was based on heavy ion damage comparisons with helium ions, the latter of which would have the highest electronic/nuclear energy loss ratio and thus would impart a greater proportion of ionizing radiation to the solid. The helium-ion irradiations gave no indication of amorphization at fluences of up to 1×10^{16} ion/cm². Further discussion of ionization-induced damage effects is presented in Section 6.2.

Primak [58] and Arnold [41,55] subjected vitreous silica and borosilicate glasses to helium-, xenon-, and lead-ion bombardment to simulate the effects of alpha decay damage to glass. Three interactive processes are believed to cause the alternate swelling and shrinking noted in the glasses during irradiation. An initial expansion of 0.1% is associated with the formation of defect centers and valence changes. This was followed by a contraction of 0.1%, associated with the dissipation of particulate radiation, and a second phase of 1% contraction, associated with the intense excitation found in the last fraction of the energy range of a heavy atom. Primak notes that the initial expansion occurs rapidly, saturates, and eventually is

Fig. 4. Range of Swelling in Volume Percent for Crystalline and Glass Waste Forms as a Function of Accumulated Dose (and Repository Storage Time). Modified from McVay [49].

overtaken by the ongoing contraction. Ion bombarded borosilicate and complex nuclear waste glasses also exhibit an initial expansion followed by compaction; however, volume changes appeared to correlate better with ionization rather than direct displacement damage [41].

Owing to damage effects, crystalline materials exposed to natural radiation [8,59] show a progressive development of defect centers that can be attributed to individual, but overlapping damage stages. Stage I is characterized by the development of individual 10 to 40 Å defect centers that represent individual damage tracks. Stage II shows overlap of defect centers and development of amorphous zones surrounded by crystalline material. Stage II is represented by complete amorphization of the solid.

Susman et al. [10] note that an average total volume contraction of ~3% produced during neutron bombardment of vitreous silica actually relates to a contraction of ~20% in the damage tracks, which are then left surrounded by undamaged material. Primak [58] attributes the silicate tetrahedron deformation to a decrease in the silicon-oxygen bond angle that resulted in a rapidly "quenched" compacted structure. In a novel attempt to investigate this damage behavior further, the authors subjected vitreous silica samples to pressures of 16 GPa. The resultant damage was related to extensive intermediate range disorder, although some short-range silicate tetrahedron deformation was also identified. Navrotsky et al. [53] compared the enthalpies of neutron irradiation damaged glasses vs. those that were pressure densified in the manner of Susman et al. Measured enthalpies from the neutron-irradiated silica glass and quartz samples are approximately half those of the pressure-densified samples. This comparison indicates that the extent of local deformation is greater in the neutron-irradiated samples when normalized to the same number of silica tetrahedrons involved.

A significant proportion of crystalline material encapsulated within the glass may be detrimental to the waste form integrity due to differences in the radiation induced volume expansion of glass vs. crystalline waste material (Fig. 4). The more highly ordered crystalline materials will generally show greater amounts of swelling after radiation-induced amorphization than the less structured vitrified materials. Differential volume expansion of crystalline material and glass may result in fracturing and an increase in the surface area of the glass through water access in fracture channels. As an example, Weber and Roberts [7] report microfracturing in ^{244}Cm -doped samples as a result of differential expansion associated with amorphization of crystalline phases after a cumulative exposure of 8×10^{17} alpha decays/cm³.

5.1.2 Bubble Formation

When glass samples are irradiated by neutrons that produce $^{10}\text{B}(n,\alpha)^7\text{Li}$ reactions, the glass expands within the range of 0.12 to 0.6% [60-63]. Sato et al. attributed this glass swelling to the formation of helium bubbles that became entrapped within damaged zones of the glass. When at rest, the alpha particles emitted during actinide fill their valance-electron vacancies to become helium atoms. Matzke [46] indicates that bubbles may form due to a coalescence of radiation-induced thermal vacancies, with the driving force being the surface tension of gas within the bubble. Similar helium-filled microvoids have been observed in naturally occurring metal oxide phases. The accumulation of helium results from either its slow diffusion through the solids or its exclusion from the mineral structure [64].

Inagaki and coworkers [65,66] examined microstructural damage to simulated nuclear waste glass by doping with relatively short-lived actinides of ^{238}Pu and ^{244}Cm . The maximum cumulative number of alpha decays that samples were exposed to was 3.02×10^{19} , representing in excess of 10^6 years of exposure for DWPF waste glass (Table 1). Radiation exposure resulted in the formation of helium bubbles with an average diameter of $0.46 \mu\text{m}$ and a bubble density in the glass of 1×10^{11} bubbles/cm³. The volume of the glass samples was also noted to increase 0.51%. Volume changes in these samples were believed to be controlled primarily through the formation of bubbles.

5.1.3 Fracture Toughness

The fracture properties of glasses being considered for nuclear waste disposal are an important consideration because stress failures induced during handling or by thermoelastic stresses may increase the glass surface area available for leaching, which could then lead to accelerated material degradation.

An increase in fracture toughness, or resistance to fracture, as measured with indentation techniques has been reported for glasses exposed to various radiation sources. Fracture toughness increases up to 80% have been reported for actinide-doped glasses exposed to cumulative alpha exposures of 10^{18} to 10^{19} decays/cm³ [38,66-70], while an increase in fracture toughness was also observed for radiation damage from most ion beams [71], although this positive effect was diminished when the damage beam was induced at glass temperatures above 250°C [72]. Vernaz et al. [70] note that crack lengths and crack probabilities decreased for ^{244}Cm -doped glasses after a cumulative alpha dose of $\sim 3 \times 10^{18}$ decays/cm³ (Fig. 5). Radiation with 77 MeV alpha particles to a fluence of 1.3×10^{15} alpha particles/cm² increases fracture toughness by $\sim 75\%$ [67]. These authors also found that addition of lead to the glass or irradiation with lead ions actually reduced fracture toughness by $\sim 20\%$. This pattern was thought to arise from the replacement of Si-O bonds with weaker Pb-O bonds.

Fig. 5. Hardness, Crack Length at Vickers Indentations, and Crack Probability of the French SON 68 Waste Glass as Function of Alpha Dose. Modified from Vernaz [70].

An increase in fracture toughness of highly damaged crystalline materials is attributed to a more ductile behavior of the solids with increasing disorder and the arresting of tensional fracture growth in regions with residual compressive stresses, such as those that may exist around individual alpha-recoil tracks [73,74]. Evidence for the first condition was found in the decreased elastic modulus of materials subjected to increasing doses, while the latter condition describes compressive strain fields around individual alpha recoil tracks. Increased fracture toughness may provide an enhanced resistance to fracture propagation in vitrified waste. Ewing and Lutze [42] attribute increased fracture toughness in radiation-damaged crystalline phases to crack bowing, crack deflection, internal stresses associated with the coherency of secondary phases, and differences in elastic properties of phases at different stages of the damage process. Some studies [66,69,75] also indicate possible impedance of crack propagation by interaction with radiation-induced voids or bubbles.

5.1.4 Latent Energy

Atoms displaced during atomic decay may have a higher energy level than those in equilibrium positions and will release their latent energy as heat when the waste form is thermally annealed [6,7]. A slow release of latent energy may be beneficial in leading to additional glass annealing, as defect centers may be thermally unstable and will, therefore, anneal as the glass temperature is raised [46,58]. A compilation of saturated latent energy values in waste glass indicates a range from 50 to 125 J/g (Fig. 6). An instantaneous release of this energy would result in a self-sustaining temperature rise of $<130^{\circ}\text{C}$ to the waste [6,7]. Generally, however, the stored energy is released gradually, and the total energy released as a result of annealing will decrease as the temperature of the waste form rises [47,76-78]. A single study that suggests latent saturation energy levels up to 400 J/g is cited by Weber and Roberts [7]. An instantaneous energy release of this magnitude would result in a temperature rise of the waste form of up to 400°C ; however, such an extreme release of energy is unlikely in light of previously described results.

5.1.5 Summary of Direct Displacement Effects

The conclusion from the direct displacement studies is that the limited volume expansions ($\pm 1.2\%$) will not seriously degrade the performance of nuclear waste glass, especially if the glass has not significantly devitrified to form crystalline material. Latent energy released during glass annealing will not produce any detrimental effects on glass stability and may, along with the increase in fracture toughness, actually provide a beneficial influence on glass stability. Implications of direct displacement effects on glass dissolution and radionuclide release from the glass will be discussed in Section 6.0.

Fig. 6. Stored Energy in ^{244}Cm -Doped HLW Glasses. Compositions of PNL glasses given in Weber [7]. Modified from Weber [7].

5.2 Ionization Effects

Solid glass ionization damage results from the excitation and ejection of electrons from the valence orbitals of the target atom by incident radiation. Although ionizing radiation produces few direct displacements, electron excitations, if they are localized and persist long enough, may eventually lead to atomic displacements. This damage effect may manifest itself in several forms, including electron hole pairs, covalent bond rupture, valence changes, H_2O and OH^- decomposition, Compton scattering, photoelectric effects, and decomposition of unstable molecular ions [6,79]. Beta decay will be the principal form of ionizing radiation for the first 10,000 years of repository operation (Fig. 2), with ionizing processes occurring from both the emission of beta particles and gamma radiation. Alpha particles also dissipate most of their energy by ionization processes and will be the dominant ionizing radiation source after 10,000 years of repository operation.

A number of studies have attempted to identify a threshold dose, where damage effects first appear, and a saturation dose for glass materials. These studies are important in that the levels of radiation exposure required for the onset of glass damage may be correlated to the cumulative doses expected for actual waste glass. Howitt et al. [45] note a threshold dose for gamma irradiation damage at $\sim 10^8$ rad and a saturation dose of $\sim 10^9$ rad. Radiation-induced decomposition in these glasses was evidenced by the formation of oxygen bubbles in the glass with average bubble diameters of ~ 5 nm. These bubbles are approximately two orders of magnitude smaller than those reported to occur due to helium accumulation after alpha decay [65].

Weber [38] compared the effects of various types of ionizing radiation on glass decomposition. Results from his tabulation (Table 4) indicate that for a given dose, gamma radiation was most efficient at producing defects, followed by ion, and then electron radiation. Shelby [80] reports that the volume compaction effect per unit dose decreases steadily with increasing gamma dose over the range 10^8 to 10^{10} rad. Saturation doses for volume compaction do not appear to have been reached in Shelby's tests for a variety of different glass compositions after exposure to more than 10^{10} rad (Fig. 7). Combined results from these studies indicate that the glass composition and the type of radiant energy interacting with the glass may influence the resistance of the glass to solid-phase ionization damage.

A comparison of the threshold doses reported above with the dose projections for actual waste (Table 2, Fig. 2) [81] indicates that ionization damage to the waste form may occur in less than ten years of storage for DWPF glasses. Synergistic effects between gamma, beta, and alpha ionization radiation may also influence glass degradation, but studies have yet to be conducted to examine this process. Some of the vitrified French wastes have been in storage since 1978 [82], but to date, studies have not been reported that examine these wastes for ionization damage. An examination of these glasses would be crucial in identifying whether or not ionizing radiation may influence the stability of nuclear waste glass. Ionization doses for WDP and DWPF glasses [54] are lower than those of the European glasses [83], so cumulative dose and/or dose rate effects would be lessened in these glasses relative to the European glasses.

In tests involving glass doped with beta-emitting ^{134}Cs ($T_{1/2} = 2.065$ years), no changes in microstructure were noted after exposure to up to twice the expected decays that would occur in most nuclear waste glasses [9]. An increase in density was noted for these Cs-doped glasses, but no mechanism for this change was reported. Some of the density increase may result from the increased proportion of higher density barium atoms in this glass.

Table 4. Dose Rate and Cumulative Dose Dependence of Ionization-Induced Decomposition. After Weber [38].

Irradiation Method	Dose Rate, rad/hr	Cumulative Dose, rad
Gamma	$10^6 - 10^7$	$10^8 - 10^9$
Ion	$10^{10} - 10^{11}$	$10^9 - 10^{12}$
Electron	$10^{13} - 10^{15}$	$10^{13} - 10^{15}$

Fig. 7. Gamma Ray-Induced Compaction in Silica and Borosilicate Glasses. Modified after Shelby [80].

Approximate Compositions of the Glasses Studied by Shelby [80]

Glass Designation	Composition, mol. %							Other Oxides
	SiO ₂	B ₂ O ₃	Al ₂ O ₃	Na ₂ O	K ₂ O	MgO	CaO	
SiO ₂	100.0	--	--	--	--	--	--	--
CGW-3320	75.0	12.7	2.4	4.6	--	--	--	5.2
CGW-7052	71.0	17.0	4.8	5.7	--	--	--	1.5
CGW-7740	80.8	12.0	2.0	4.2	0.6	0.2	0.2	--
CGW-7913	97.0	2.5	--	0.5	--	--	--	--
GSC-4	85.0	13.3	0.5	1.2	--	--	--	--

5.2.1 Volume Effects for High-Silica Glasses

Changes in volume (and hence density) have been reported for glasses after exposure to ionizing radiation. The composition of a glass can dramatically affect its density response after radiation exposure. Amorphous silica glasses display volume decreases after exposure to gamma radiation. The largest volume decreases are reported by Shelby [80], who notes a maximum compaction of slightly less than $\sim 0.1\%$ for SiO_2 glass after 10^{10} rad of cumulative gamma exposure (Fig. 7). Sato et al. [60] report volume decreases of 0.03 to 0.05% for high-silica glass and quartz exposed to 1.2×10^9 rad of gamma exposure.

Using irradiations from helium, xenon, and lead ions, Arnold [55] detected an initial volume increase at low fluences, followed by a volume decrease with larger doses. With these high-silica glasses, the compaction process better correlated with the displacement component of the energy of the ions rather than the ionization energy. The combined gamma- and ion-radiation studies discussed here and in the preceding paragraph indicate that both ionization and displacement processes may cause compaction of glass, with the predominant trend being a slight density increase of irradiated high-silica glasses. Devine et al. [84] found that the formation of oxygen defect centers in amorphous silica glasses irradiated with hydrogen ions varied with temperature. Oxygen vacancies and peroxy radical formation were noted to increase steadily during an increase in reaction temperature from -100°C to 25°C , with a general decline in damage centers occurring as temperatures rose past 25°C .

5.2.2 Volume Effects for Low-Silica Glasses

The diversity of radiation-induced defects and the difficulties in interpreting damage effects on an atomic scale [40] increase with increasing compositional complexity of the glass. Volume changes in irradiated glasses have also been shown to depend on the glass composition. Shelby [80] reports borosilicate glass densification of up to 1% after 10^{10} rad of cumulative gamma exposure, while Bibler [43] indicates compaction of only 0.05% for simulated SRL 131 glass after 8.5×10^{10} rad of gamma exposure. Other studies have indicated increases in glass volume after gamma irradiation. Sato et al. [60] report swelling of 0.2% for low-silica simulated borosilicate waste glass exposed to a cumulative external gamma dose of 5×10^8 rad, while Weber [38] reports 0.07% swelling in PNL 76-68 glass after 6.6×10^8 rad.

In particle irradiation studies, Hall et al. [85] irradiated simulated Magnox waste glass with 0.5 MeV electrons to simulate damage from beta irradiation. No significant volume changes in the glass were detected after the glasses were exposed to a cumulative dose of $10^{25} \text{ e}^-/\text{m}^3$ ($\sim 2.5 \times 10^{11}$ rad) at temperatures of 300°C .

In an examination of irradiation effects from neon, argon, helium, xenon, and lead ions on simulated borosilicate waste, Pyrex, and soda-lime silicate glasses, Arnold [41,55] detected an initial volume expansion at low fluences, followed by a volume decrease at larger doses. These trends were similar to those observed when high-silica glasses were irradiated using the same technique. These studies indicate that compaction processes correlate well with ionization energy for the complex glass compositions. This trend was opposite to that of high-silica glasses, where the compaction process better correlated to the displacement component of the energy lost by the ions. Arnold explained this difference as resulting from the restricted interstitial volume space in the complex glasses, this restriction increased the likelihood that permanent defects will be formed by ionization-induced bond-breaking processes.

5.2.3 Glass Composition Influence on Volume Changes

Data from Shelby [80] indicate that glasses of increasing compositional complexity display more pronounced compaction effects when irradiated to equivalent gamma doses (Fig. 7). Weber [5] also notes a compositional effect that agrees with the general trend reported earlier by Shelby. In a comparison of studies utilizing different glass compositions, Weber noted a general tendency for increasingly greater amounts of swelling in glasses with low alkali/silicon ratios and compaction in glasses with high alkali/silicon ratios.

Cases and Griscom [86] note an alkali content correlation for gamma radiation damage that was induced in potassium silicate glasses. Trapped hole centers were determined to be located on a pure $2p\pi$ orbital of a single nonbridging oxygen atom. In low alkali content silica glasses, existing peroxy radicals (O_2^-) were detected by electron paramagnetic resonance studies on both silicate network and interstitial sites. In high alkali content glasses, peroxy and ozonide (O_3^-) radicals were detected only at interstitial sites. These trends suggest that the amount of unbound oxygen in the glass after irradiation is directly proportional with the number of nonbridging oxygen sites and, hence, is related to the concentration of network-modifying atoms in the glass.

The increased densification of the high alkali glasses may relate to the "phase separated" nature of borosilicate glasses. Regions of alkali-borate rich phases contained within a vitreous silica matrix may react quite differently when exposed to radiation [80]. The degree of compaction for a given dose may be greatly enhanced in the alkali-borate enriched regions due to lower glass transformation temperatures and dual coordination states of boron. When the incident radiation breaks the boron-oxygen bond, then the relaxation of the glass network may occur before the bond is reformed, thus leading to a larger number of broken-bond defects and densification of the overall glass. In glass with 13.3% B_2O_3 , Shelby found that volume compactions were 30 times greater than those for pure silica glasses (Fig. 7). Arnold [41] confirmed this result with a similar study using helium-, xenon-, and lead-ion irradiations on several borosilicate glass compositions. In these tests, the B_2O_3 phase was noted to be more readily compacted than the SiO_2 regions, confirming that phase-separated glasses are more susceptible to radiation damage than homogeneous glasses.

Shelby [80] speculated that irradiation damage in phase-separated glasses may actually involve competing processes from both positive and negative dilations. Experimental results of Arnold [41] provide supportive evidence for this theory with low fluences of helium and xenon ions initially producing expansion of the phase-separated glasses and higher fluences resulting in a dominating compaction process. In a related study, Primak [58] subjected glasses to helium-ion bombardment to simulate the effects of alpha particle damage to glass. Three interactive processes are believed to cause the alternate shrinking and swelling that was noted in the glasses during irradiation. An initial expansion of 0.1% is associated with the formation of defect centers and valence change. This expansion was followed by a contraction of 0.1% associated with the dissipation of particulate radiation and a third phase of 1% contraction associated with the intense excitation found in the last fraction of the range of the helium ion. Primak notes that the initial expansion occurs rapidly, saturates, and eventually is overtaken by the ongoing contraction process in impure silica glasses.

Hydrogen implantation in glass will suppress the formation of optical defects in glasses later being subjected to gamma irradiation [87]. Hydrogen impregnation results in expansion of the glass during irradiation, a process that partially offsets previously described glass densification processes. The rate of glass expansion and the rates of formation of hydroxyl

and hydride formation in the glass were all found to be proportional to the square root of the applied dose. Weeks and Lell [88] found that the formation of defect centers in irradiated silicas also varied directly with the hydroxyl content of the glass.

Several investigators [89,90] have studied gamma radiation damage effects on H₂ implanted silicate, borate, and borosilicate glass. Nonbridging oxygen ions that were either present initially or formed by irradiation damage were suggested to act as hole traps in the glass. Hydrogen in the sample was then able to react with trapped holes and electrons to form hydroxyl and hydride groups that destroy color centers and effectively quench the radiation damage to the glass. Similar studies [91,92] suggest that high OH content silicas are resistant to radiation damage. When these glasses were subjected to irradiation, the radiolytic electrons and holes were trapped by Si-OH, forming atomic hydrogen and nonbridging oxygen hole centers. Any H₂ gas that subsequently forms may undergo a second reaction with the irradiated silica network to produce SiOH and SiH groups that expand upon irradiation.

Acocella et al. [93] note that an increase in water content suppressed optical distortion in sodium-silicate glasses exposed to gamma irradiation. Absorption of visible light was found to decrease substantially as H₂O in the glass was increased from 0 to 11% (Fig. 8). The dissociation of H₂O into OH⁻ and H⁺, as well as their subsequent combination with radiation-damaged color centers to produce colorless SiOH, is suggested as a mechanism for the observed results.

Faile and Roy [89] note that addition of Pb²⁺ or Ti⁴⁺ will retard the previously discussed radiation-enhanced resistance of hydrogen implantations, thus effectively enhancing damage effects in silica glass exposed to gamma radiation. Since DiSalvo and others [90] note that hydrogen impregnation in borate and borosilicate glasses has a similar effect on radiation damage, it may be logical to assume that Pb²⁺ or Ti⁴⁺ will also enhance radiation damage in borate and borosilicate glasses by retarding hydrogen implantation effects.

The addition of aluminum to the glass may reduce radiation damage effects when the bridging oxygen between aluminum and silicon traps a hole during irradiation, thus allowing local charge-compensating alkalis to trap electrons and diffuse away [94]. The resultant hole trapping by the bridging oxygen results in a 50% increase in Al-O bond lengths, thereby offsetting the intensity of the compaction process noted previously for displacement damage in some glasses.

Sato et al. [60] suggest that network modification by irradiation leads to compaction of high-silica samples due to the "loose packing of the glass." With low-silica borosilicate waste glass, network modification by irradiation is less effective in inducing compaction because the silica network structure is already in a highly modified and compacted state prior to irradiation. Primak [58] further explains that the vitreous silica contraction occurs because of a decrease in the normal bond angle of two silicon-oxygen tetrahedra as induced by radiolytic excitation.

5.2.4 Bubble Formation

Numerous studies report the occurrence of oxygen bubbles or spherical voids in glasses irradiated with electrons (Table 5) [60,62,81,95-100]. This bubble formation within the glass is generally associated with a concurrent increase in the volume of the simulated waste form. Sato et al. [60] found that samples exposed to an electron fluence of 2×10^{21} to 3×10^{22} e⁻/cm² swelled to a maximum of ~50% after bubble formation. The amount of glass

Fig. 8.
Absorption Spectra before and after Gamma
Irradiation (5×10^7 rad) of (A) "Dry"
 $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ (~0.015 wt % H_2O),
(B) $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ + 0.49 wt % H_2O , and
(C) $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ + 11.2 wt % H_2O .
Modified after Acocella [93].

Table 5. Effect of Dose and Temperature on Ionization-Induced Bubble Formation

Dose/Fluence	Type Irrad.	Temp.	Glass	Effect	Reference
2.1×10^{10} rad	He	Ambient	Waste glass	Mostly O ₂ bubbles	100
1.3×10^{11} rad	100 keV e ⁻	250°C	PNL 76-68	O ₂ bubbles	100
8.8×10^{11} rad	100 keV e ⁻	Room	PNL 76-68	O ₂ bubbles	100
2.5×10^{21} to 22.5×10^{21} e ⁻ •cm ⁻²	e ⁻ (no energy reported)	100°C	Simulated nuclear waste glass	Phase separation O ₂ bubbles	100
900 sec flux of 4 A•cm ⁻²	e ⁻	200°C	Silicate glass	O ₂ bubbles	98
100-900 sec flux of 4 A•cm ⁻²	e ⁻	100°C	Silicate glass	O ₂ bubbles	98
900 sec 4A•cm ⁻²	e ⁻	240°C	Silicate glass	Coalesced O ₂ bubbles	98
No observed threshold, 4 A•cm ⁻²	0.1 to 1.0 MeV e ⁻	Room to 500°C	76-68 waste glass MCC waste glass	Phase separation	98
150 to 300 C•cm ⁻²	650 keV e ⁻	200 to 600°C	76-68	Phase separation Bubbles	96, 97
Threshold 1×10^{21} e ⁻ •cm ⁻²	1000 keV e ⁻	None reported	Simulated waste glass G-2-30	Voids	60, 99
2×10^{21} to 3×10^{22} e ⁻ •cm ⁻²	1000 keV e ⁻	~60°C	G-2-30	O ₂ Bubbles	60
3.2×10^{22} e ⁻ •cm ⁻²	1000 keV e ⁻	None reported	None reported	O ₂ Bubbles	62
3×10^9 rad	Gamma	Room	PNL 76-68	O ₂ bubbles	100
9.1×10^9 rad	Gamma	≤50°C	PNL 76-68	Bubbles	101
4×10^8 to 3.1×10^{10} rad	Gamma	≤100°C	SRS 165	No phase separation No bubbles	102
Threshold 2×10^8 rad Saturation 10^9 rad	Gamma	None reported	SRL 165, SRL H1A1, SRL Composite, SRL H1 Fe	O ₂ Bubbles	45
Threshold 2×10^8 rad Saturation 1.3×10^9 rad	Gamma	None reported	SRP glass	O ₂ Bubbles	Heuer MS. Thesis Ref. in [38]
4.0×10^8 to 3.6×10^{10} rad	Gamma	None reported	SRP 165	No effect	103
5×10^8 to 1×10^9 rad	Gamma	None reported	P0504, P0500	Slight swelling/ No bubbles	60
1.2×10^9 rad	Gamma	None reported	Quartz glass Pyrex	Slight shrinking/ No bubbles	60

swelling in these tests appeared to initially stabilize at ~20% after a fluence of $1 \times 10^{22} \text{ e}^-/\text{cm}^2$, but then increased again after a fluence of $2 \times 10^{22} \text{ e}^-/\text{cm}^2$. Manara et al. [104] noted ~50% volume expansion swelling after an electron fluence of $\sim 7 \times 10^{20} \text{ e}^-/\text{cm}^2$. At this stage, the damage effects were saturated and no further increases in volume were noted for fluences of up to $\sim 9 \times 10^{20} \text{ e}^-/\text{cm}^2$, even though the bubble density still continued to increase (Fig. 9). Helium ion irradiations, which simulate both collision and ionization effects induced by alpha-particle damage, also result in the formation of gas bubbles within the glass [100].

The presence of a gas phase in the bubbles has been confirmed by Heuer et al. [100], who employed a thin carbon film coating to trap gases being emitted from the glass during electron irradiation-induced damage. Todd et al. [105] have confirmed, using mass spectrometry analysis, that oxygen constitutes >95% of the gas evolved during the irradiation of glass with 20 keV electrons.

Radiation-enhanced sodium mobility, and subsequent bubble formation, during beam irradiation studies may also be caused by the electric field set up during implantation. Since the damage features are generally not observed in glasses doped with short-lived radionuclides, they are not likely to occur in actual waste glass under real disposal conditions [72].

The mechanism of the bubble damage process has been interpreted to involve the disruption of ionic bonds and electron capture by migrating cations, such as Na^+ , under an electric field generated across the glass [45,98,106]. Continued ionization of the glass in the absence of Na^+ will lead to the formation of Si-O-Si bonds, O_2 , and electrons, with the O_2 gas accumulating as bubbles within the glass. Bubble formation and gas evolution depend on the glass composition, with high-silica glasses displaying the lowest outgassing rates, while the addition of other oxides increased the oxygen evolution rate [98,104,105]. The probability of bond breaking varies conversely with bond strength and thus increases from network-forming elements to network modifiers [107]. Hall et al. [85] indicate that high-lithium glasses are the most susceptible to ionization-induced bubble formation.

Manara et al. [95,104] observed a marked increase in the electron flux required to induce bubble formation concurrent with increasing irradiation temperature between ~50 and 300°C. DeNatale and Howitt [98] examined the effect of cumulative dose vs. temperature in inducing bubble formation over a range of temperatures from ambient to 450°C. These authors observed a minimum in the total dose required to form bubbles located at approximately 250°C, with an increase in the threshold dose at both higher and lower temperatures (Fig. 10). The increasing ease at which bubbles occur when temperatures are increased to 250°C has been used to support a diffusion behavior model for the formation of bubble- or void-like defects, although the increasing dose required to induce bubble formation between 250 and 450°C is not readily explained by a diffusion model.

Manara et al. [104] examined the complex interdependence of both temperature and glass composition on oxygen bubble formation in sodium silicate glasses. In these tests, the largest swelling rates were detected for glasses with lower silica concentrations (Fig. 11). The temperature at which the peak swelling occurred also shifted from ~125°C for glasses with 48% SiO_2 , to ~150°C at 53% SiO_2 , to ~325°C at 80% SiO_2 . No bubbles were observed in 100% silica glasses for temperatures of up to ~725°C and electron fluences of up to $\sim 9 \times 10^{20} \text{ e}^-/\text{cm}^2$.

Fig. 9. Bubble Density and Total Swelling vs. Dose in Electron-Irradiated Borosilicate Glass: (•) total swelling %; (□) bubble density (bubbles/ m^3). Modified after Manara et al. [104].

Fig. 10. Temperature Dependence of Bubble Formation. Modified 76-68 waste glass (10% waste loading by weight). Constant flux of $4 \text{ A} \cdot \text{cm}^{-2}$. After DeNatale and Howitt [98].

Fig. 11. Total Swelling Rate as a Function of Irradiation Temperature in Borosilicate Glasses of Varying Sodium Content. After Manara et al. [104].

A second effect of electron irradiation seen in the glasses is phase segregation, where the glass separates into silica-rich and silica-poor amorphous "phases" [96-98,100]. The tendency for phase separation and/or bubble formation does not appear to be directly related to the glass composition, and the same regions may experience bubble formation, phase separation, or both types of damage. The high concentration of heavy metals associated with the silica-poor regions may increase the likelihood of glass devitrification in these regions during further irradiation [98].

The regression or disappearance of bubbles in regions where metal-rich, separated phases are present is used as evidence to support an oxygen diffusion model. Greater diffusivity of oxygen through high-silica regions allows the interior gas to escape from the glass and the bubble to regress under the influence of its own surface tension [98]. The observation that bubbles did not form in regions of the glass that had phase separated first supports this interpretation. The evolution of oxygen bubbles from the glass has been identified during electron irradiation studies that trapped the evolving gas in a thin carbon surface film [100], although the extent of phase separation within these oxygen-evolved glasses was not reported. These authors also note that oxygen may recombine with waste components in glass to produce silicon-poor phase-separated regions. These silicon-poor regions were noted to form when the glass phase separated during irradiation and the bubbles regressed.

Several studies of gamma irradiation effects have noted bubble formation after a threshold dose of $\sim 10^8$ rad and a saturation dose of $\sim 10^9$ rad for a variety of different glass compositions (Table 5 and Fig. 12) [38,45,81,100,101]. Although bubble density appeared to saturate, bubble growth by coalescence did continue with increasing dose. The G-value for the formation of oxygen in gamma-irradiated glass was determined to be ~ 0.1 [101].

Both a dose rate effect and a cumulative dose effect exist for ionization-induced decomposition of glass (Table 4) [38], with ionization-induced decomposition occurring for both the lowest dose rate (flux) and lowest cumulative dose (fluence) for gamma irradiation, followed by ion irradiation, and then electron irradiation. The dose rates tabulated in Table 4 represent a summarization of experimental results; thus, while cumulative dose effects have been systematically examined, dose rates have not. The formation of bubbles was most pronounced during gamma irradiation, followed by ion irradiation, and then electron irradiation, and can also be correlated directly with the Na_2O content of the glass [101]. A synergistic effect is also observed where oxygen decomposition can be produced more readily in electron microscopy specimens that previously have been gamma irradiated [45]. DeNatale and Howitt also observed that, unlike electron irradiation where bubble formation was most easily produced at $\sim 250^\circ\text{C}$ (Fig. 10), gamma irradiation was more efficient at producing damage bubbles at temperatures of $\sim 50^\circ\text{C}$.

Tosten [103] and Bibler et al. [102] have confirmed the process of bubble formation for e^- irradiation, but dispute the occurrence of gamma-induced bubble formation and phase separation in glasses. Tosten [103] gamma irradiated glasses identical in composition to those of Howitt et al. [45], at doses of up to 3.6×10^{10} rad, without noting any associated bubble formation. He suggests that bubble formation may have been induced during the ion milling sample preparation of Howitt et al. Similarly, Bibler et al. [102] gamma-irradiated borosilicate glass up to a cumulative dose of 3.1×10^{10} rad, without observing any bubble formation. These authors suggest that bubble formation in other studies may result from electron beam damage.

The disagreement on whether or not gamma irradiation may induce bubble formation may be irrelevant in light of the expected temporal variations in radiation emissions emanating from the glass waste (Table 1). Beta, not gamma, will be the dominant ionizing radiation source interacting with the waste for the first 10^5 years of waste disposal (Fig. 2). Therefore, electron irradiations that simulate beta decay effects may be a more realistic scenario for bubble formation in actual glass waste. Synergistic effects between beta, gamma, and alpha ionization may also influence bubble formation but have been rarely addressed in the literature [45], although Townsend [106] does report synergistic effects between collision and electronic energy deposition processes in developing imperfections in insulators. Contrasting this later study, Soileau et al. [108] note an antagonistic effect where the pre-irradiation of fused silica glass with 10^8 rad of gamma irradiation reduced subsequent laser-induced breakdown thresholds.

5.2.5 Alkali Migration Studies

Electron and ion-beam irradiations may also directly influence the glass composition in a field-induced migration process [45,68,109,110]. This process occurs when the formation of excess secondary electrons on an irradiated solid surface leaves the center of the irradiated region with a positive charge. This charged region will result in migration of positively charged ions from the irradiated region of the solid. This type of migration is

Fig. 12. Concentration of Oxygen Bubbles Produced in SRL Sodium-Borosilicate Glasses as a Function of Cumulative Gamma Dose. Dose rate to samples was 2.5×10^6 rad/h. Modified from Howitt [45].

artificially produced by the polarized nature of the impinging ion beam and, therefore, is not a process expected to occur in nuclear waste glasses [72]. Despite their artificial origin, these types of ion irradiation studies are important for identifying the mechanistic development of defect centers in glass.

Miotello and Toigo [111] envision an ionic transport process in electron-irradiated glasses where the radiant energy breaks cation bonds in the glass, creating an electronic field and defects that recombine to form relaxed structural units. Cation migration can occur only through these relaxed units, with initiation of migration only occurring when the concentration of relaxed units exceeds a critical value of $\sim 1/3$ to form a random network. Matzke et al. [68] also note that alkali diffusion occurs along radiation-induced defects or due to mobile defects formed by radiation. In this study, the authors found that sodium diffusivity exceeds that of rubidium and cesium in irradiation-damaged glass. Calmon and Serruys [112] also report the diffusion of calcium and sodium, with metallic elements such as lead also migrating, especially in regions of the glass that had been depleted in sodium. Several researchers have noted that ion-damaged glasses that have been annealed display reduced sodium- and helium-ion diffusion rates relative to virgin glass [68,113]. This reduced diffusion is due to implanted ions in the glass that retard the subsequent diffusion of glass components.

5.2.6 Summary of Ionization Effects

A conclusion from these ionization studies is that the limited magnitude of non-bubble-induced volume changes associated with ionization damage does not appear to pose any direct problems for the safe storage of nuclear waste glass. When ionization-induced damage leads to oxygen bubble nucleation in the glass, large volume increases may occur and thus the potential to induce glass fracturing exists. There is no agreement in the scientific community on the potential for gamma radiation to induce bubble formation; however, it is widely accepted that electron irradiation under an induced electronic field will eventually lead to bubble segregation from the glass. Since electron irradiation simulates beta decay reactions, the potential for bubble formation in nuclear waste glass exists. Several questions remain to be answered relating to volume expansions in irradiated glass. Will synergistic effects occur between ionization energy from gamma, beta, and alpha radiation? Will bubble formation occur when glass is doped with a beta-emitting radionuclide as opposed to a polarized ion beam source, with the former representing a more realistic repository scenario? What levels of ionizing doses from gamma and alpha sources will be required to induce bubble formation? What is the effect of dose or fluence rate on bubble formation and phase segregation in glass?

Regardless of the magnitude of the volume changes, radiogenically induced microstructural and bonding changes associated with ionization damage have the potential to influence radionuclide release rates during exposure to aqueous fluids [114]. Potential radiogenic processes that have received little attention include glass devitrification and phase separation. For example, the radiolytic disruption of the Si-O-Si bonds to form the SiOH and SiH groups discussed previously [92] is also analogous to the network hydrolysis process [115] and may therefore enhance glass dissolution upon exposure of the glass to aqueous solutions. A clear mechanistic understanding of ionization damage to glasses has not been reached, partially due to the limited number of studies to date and partially due to the complexities arising from tests with different glass compositions (and structures), radiation sources, and test conditions. Implications of ionization damage effects on glass dissolution and radionuclide release from the glass will be discussed further in Section 6.0.

5.3 Transmutation Effects

Transmutation of fission products changes both the valence and ionic size of the daughter atom relative to its parent radionuclide. Most radionuclide transmutations are unlikely to directly affect the durability of waste glass due to the low production rates and wide range of elements acceptable in the glass matrix [9,51]. In a study of ^{134}Cs -doped glass, the effect of cesium transmutation to barium resulted in limited physical changes to the glass. The most obvious change was an increase in glass density, which can be attributed, at least in part, to conversion of cesium to more dense barium atoms. Glass samples with ~30 wt % cesium exhibited density increases of ~1 to 3%. These changes are of interest because the density increases may exceed volume changes that arise due to direct displacement and ionizing radiation damage alone (see Fig. 4).

Transmutations that produce daughter nuclei that are insoluble in the glass matrix may result in the formation of crystalline products within the glass waste. With nuclear waste glass, the most commonly occurring beta-decay transmutations and their associated half-lives are

The transmutation of cesium to barium should not alter the waste glass behavior because both of these elements occupy similar structural sites as network modifiers in the bulk glass [79]. The transmutation of strontium to zirconium involves a change from a parent nuclide that is a network modifier to a daughter that may be a network former. If the production of additional zirconium by transmutation results in a total ZrO_2 concentration of ~ 2.3 wt % in the glass, then the glass may become saturated with respect to zirconium. Crystalline phases may begin to nucleate only if solid-state diffusion rates are sufficiently large enough to allow the excess zirconium to agglomerate and exsolve from the glass structure. Although DWPF glass compositions will have considerably less than 2.3 wt% combined $\text{SrO} + \text{ZrO}_2$, several other waste glass compositions, including West Valley WV205 and the French R7T7 glasses, will contain >2.3 wt% $\text{SrO} + \text{ZrO}_2$ [1,116,117].

The nucleation of crystalline phases, combined with the differential volume expansions exhibited by radiation-damaged glass and crystalline solids, could eventually contribute to fracturing of the waste form [6,7]. This fracturing can increase the surface area of the glass by providing fluid channels to interior portions of the glass, although the narrow dimensions expected for fractures may not contribute greatly to glass corrosion [70,118].

Transmutation also generally involves a change in the valence of an atom as it decays from a parent to a daughter isotope [119]. Conservative calculations indicate that a maximum excess of $1.5 \times 10^{20} \text{ e}^-/\text{cm}^3$ will be generated due to fission product decay after 10^6 years of glass storage. Such changes are not expected to seriously affect the waste, but systematic investigations have not been conducted.

5.4 Annealing Process

The accumulation of radiation damage in glass partly depends on the energy barrier of glass to repair or anneal the radiation-damaged regions. A large increase in leach rates resulting from solid radiation damage will occur only after damage zones overlap and provide interconnected fluid and/or solid diffusion channelways between the interiors of the samples and the surface. If individual damage zones anneal in relatively short times, the damage zones will not overlap and significant increases in leach rates will not be realized. In laboratory experiments, dose rates may be increased several orders of magnitude above levels that are pertinent to actual waste to accelerate glass damage processes into reasonably short time periods. If the radiation exposure accelerates damage overlap relative to the annealing process, then an artificially accelerated leach rate may result.

Weber [38] has summarized experimental dose rate and cumulative dose conditions under which ionization-induced glass decomposition has been observed (Table 4). Weber concludes that a dose rate effect may exist for ionization-induced decomposition of glass, and therefore, glasses irradiated at high dose rates will not accurately reflect the behavior of actual waste glasses at realistic exposures.

The process of annealing has been addressed in numerous studies with crystalline materials [for example, 59,120-123], but in relatively few studies with glass. The retention of alpha-decay damage in solids depends on the energy barrier of the solid to recrystallization. If the barrier is low enough, the radiation damage will readily anneal and significant damage accumulation will not occur. Burns et al. [16] estimate that a mean recovery time for damage tracks in glass will be 3 hours and 110 days at 200 and 25°C , respectively. With critical damage zone overlaps occurring for alpha-simulated tests only after ~ 1200 days, these recovery rates suggest that alpha-recoil damage tracks in the glass will readily anneal and, therefore, will not significantly affect the stability of the waste form. This low-energy barrier to annealing is one of

the more positive attributes of glass as a radionuclide-immobilizing waste form. The low-energy barrier of glass can be related to the bond energy and/or disordered structure of the glass. In studies of crystalline materials, Ewing et al. [59] report that disordered alloys have the lowest energy barrier to recrystallization because of the nondirectional bonding and equivalence of crystallographic sites. This feature may also explain the relatively rapid rates of annealing observed in vitrified waste.

Sato et al. [60] have determined isochronal annealing changes as a function of temperature and isothermal annealing changes as a function of time for alpha-damaged waste glass. Their results indicate that annealing processes will readily diminish glass expansion damage within days after heating to 400 to 450°C, with lower recovery rates indicated at lower temperatures (Fig. 13). Eyal and Ewing [124] also note complete annealing of alpha-track damage effects on thorium leaching after a 24-hour anneal at 650°C.

Mark and Ritter [125] and Walder and Mark [126] studied the annealing process in sodium-silicate glass and obsidian after fission-product, alpha-decay, and electron beam-induced damage. Mark and Walder [127] also note that leach rates from natural and artificial obsidians can be influenced by annealing processes occurring during testing. In this study, the leach rate of sodium in deionized water from irradiated samples at 60°C was 2 times larger than unirradiated samples, whereas at 90°C the observed leach rates were similar. The authors attributed the lack of leach rate differences at higher temperatures to more rapid annealing of damage tracks at 90°C. These authors note an Arrhenius temperature dependence of annealing rates, which was generally independent of the source of the radiation damage. These residual density changes should not significantly affect the glass properties due to the relatively small density changes expected for radiation damage in the glass (see Fig. 4). These relationships suggest that radiation damage buildup will not occur in glass due to the relatively low dose rates and rapid annealing rates expected in vitrified waste.

Marples [48], however, indicates that at moderate temperatures (130 to 300°C) glass densities only followed an exponential annealing curve for a short time, with ~20 to 70% residual density change remaining even after long annealing periods. Marples also notes that actinide-doped glass may undergo some partial annealing of damage during radiation testing, while at the high dose rates characteristic of ion-bombardment tests, almost no annealing will occur.

Inagaki et al. [128] note a compositional dependence on annealing rates of gamma-irradiated glasses, with glasses with a few weight percent Fe₂O₃ being more resistant to radiation damage. The authors suggest that ferric ions will form ferrous iron after trapping an electron, and ferrous ions can form ferric iron after trapping a hole. These processes will thus reduce damage accumulation in irradiated glasses.

Bubble formation resulting from alpha decay and/or ionization processes may occur during waste storage [65,100]. The formation of these bubbles has the potential to increase the available surface area of the glass and may, therefore, affect leach rates [104]. Inagaki et al. [65] examined annealing effects on helium bubbles that formed as a result of alpha decay processes. The average diameter of the helium bubbles in glass was noted to decrease ~50% during annealing at 400°C for periods of up to 6 hours. In additional tests, glass samples were annealed at temperatures of 300 to 450°C for periods of up to 48 hours. Results indicate near complete recovery of many of the physical properties of the glass (hardness, fracture toughness, and Young's modulus) after annealing for ten hours at 400°C [66].

Fig. 13. Thermal Annealing Trends for (n,α) Irradiation in Four Types of Simulated Borosilicate Waste Glasses. (a) Isochronal annealing changes as a function of temperature and (b) isothermal annealing changes as a function of time. From Sato [62]. Glass compositions for "PO" prefix glasses given in Sato et al. [61].

6.0 RADIOLYSIS EFFECTS ON GLASS DURABILITY AND RADIONUCLIDE RELEASE

The radiation effects on glass reactions are quite complex due to interactions between the glass components dissolved in the leachate, radiolysis products, and the buffering capacity of bicarbonate and/or silicate groundwaters against radiolytically produced acids. Changes in microstructure and bonding in the solid glass also have the potential to affect the integrity of waste glass and its ability to retain radionuclides. Alpha tracks, phase changes, bubble formation, phase separation, and associated microfracturing [5,120,129] also can increase the corrosion rate of glass and other solids by providing access channels for water entry, thereby increasing the surface area of the solid waste. The influence of annealing processes in limiting the cumulative radiation damage to solids also complicates interpretations of solid damage effects on glass alteration properties.

Most of the following discussion on the radiolysis effects on glass durability focuses on experimental investigations that were conducted under relatively low SA/V conditions. Although these tests are not necessarily representative of conditions expected for an unsaturated repository setting, they do, however, provide important insight into radiolysis effects on glass. Low SA/V conditions may influence radiolysis effects on glass primarily by providing a larger pH buffering reservoir to lessen the impact of radiolytically produced acids, and attenuating alpha and beta particles emitted from the waste. As a result, the proportion of water radiolysis products increases while atmospheric radiolysis products decrease.

6.1 Gamma Radiolysis Tests

Both the formation of nitric acid in air above an aqueous solution and the formation of water disassociation products can influence glass reaction rates. McVay et al. [49] conducted experiments with glass samples immersed in deaerated and deionized water at 50 to 90°C at 20 m^{-1} to examine the effects of water dissociation products in the absence of air irradiation products like nitric acid. The leachates irradiated in the absence of air were found to increase in pH more rapidly and reach a higher "steady-state" pH than their nonirradiated analogues (Fig. 14) [130]. The rapid increase in pH of the deaerated leachate solutions indicates a greater degree of reaction between water radiolysis products and the glass. The increase in pH occurs as the reacting glass releases hydroxide during reactions that neutralize water radiolysis products. Furthermore, the difference in pH values between the irradiated and nonirradiated tests was lowest in the 90°C tests, indicating that the radiolysis-enhanced leaching effects are lessened with increasing temperatures.

With tests in both deaerated and deionized water at 20 m^{-1} [131] and deaerated brines at 10, 100, and 1000 m^{-1} [132], the effects of radiation on release rates of sodium, silicon, and boron were progressively diminished as the reaction temperatures were increased from 50 to 90°C (Fig. 15). The decreased difference in elemental release rates between irradiated and nonirradiated tests at higher temperatures also corresponds with the reduction in hydroxide release, as previously discussed. McVay et al. [49] also note that elemental release rates exhibited a dose rate dependence, where a 20% increase in silicon release at 70°C and $\text{SA/V} = 10 \text{ m}^{-1}$ results from a 200-fold increase in the dose rate.

In tests conducted with borosilicate waste glass and gamma-irradiated deionized water systems, dissolution rates of boron, aluminum, silicon, alkalis, and actinides from the glass generally increase from 3- to 5-fold over nonirradiated tests, but may vary for individual elements from less than 1- to 12-fold [17,18,49,130,131,133-135]. McVay et al. [49]

Fig. 14. Deionized and Deaerated Leachant pH Trends for Gamma Irradiated vs. Nonirradiated Static Leach Tests with PNL 76-68 Glass. (a) 50°C trends, (b) 70°C trends, and (c) 90°C trends. Modified from McVay [130].

Fig. 15. Deionized and Deaerated Leachant Trends for Na and Si Concentrations in Gamma Irradiated vs. Nonirradiated Static Leach Tests with PNL 76-68 Glass. (a) 50°C trends, (b) 70°C trends, and (c) 90°C trends. Test SA/V ratio at 20 m⁻¹. Modified from Pederson [131].

sequentially irradiated glass samples in the presence of air + water, deaerated water, or preirradiated solid glass samples prior to immersion in water at $SA/V = 10 \text{ m}^{-1}$ (Fig. 16). In these tests conducted at 50°C , the largest release rate increases for alkalis, alkaline earths, silicon, and boron were recorded for samples irradiated in the presence of air + water. The exposure to gamma irradiation accelerated release rates of these elements an average of 6-fold relative to the release rates from nonirradiated tests otherwise run under identical conditions. These increases are attributed to the combined effects that atmospheric and water radiolysis products have on glass reactions. When air was excluded from the irradiated tests, elemental release rates increased only ~3.5-fold over the rates displayed by the nonirradiated tests. This comparison indicates that water radiolysis products appear to be responsible for ~60% of the increased release rate attributed to radiolysis effects, while radiolytically produced acids account for the remainder. Gamma irradiation of the solid glass samples prior to immersion in deionized water did not cause any measurable increase in elemental release.

Irradiation-enhanced release rates were even further increased when air + water systems were irradiated at 90°C [49]. In these tests, release rates of boron and silicon were increased 7.0- and 8.4-fold, respectively, relative to the release rates from nonirradiated tests in 90°C deionized water. These increases were approximately twice as large as those that characterized boron and silicon release (4.2- and 4.1-fold, respectively) from the 50°C irradiation tests previously discussed. By contrast, radiation-induced increases in the release rate of the alkali and alkaline earths, especially the higher atomic weight elements, were relatively unchanged between the two test temperatures.

These combined results suggest that, in deionized water systems, release rates of most glass components are increased due to radiolytic product formation. This radiolysis effect is noticeably enhanced at high temperatures (90°C) for silicon and boron, while release rates of alkalis and alkaline earths show little change with temperature. The enhanced silicon release in the air + water tests at high temperature was opposite to the decreased rates observed in similar tests with deaerated water systems [131]. The increased silicon release is unexpected in light of the decreased $G(\text{HNO}_3)$ values detected in high temperature tests [20; see Section 4.0] and the lower reaction rates detected for glass samples reacted in deaerated deionized water systems at high temperature [130].

Examinations of 90°C MCC-1 test elemental release rates from gamma-irradiated and nonirradiated brines indicate an increase in silicon release of less than two times after a total exposure of $8.5 \times 10^{10} \text{ rad}$ [43]. Release rates of silicon are also 2 to 4 times lower in the brines compared to deionized water for both the irradiated and nonirradiated systems.

Significant changes in the leachate pH and glass leach rates were not observed when glass samples were irradiated in the presence of groundwater equilibrated with tuff under MCC-1 conditions, at a temperature of 90°C , and SA/V ratios of 30 and 100 m^{-1} . Changes in solution pH of these systems are either buffered by bicarbonate in solution or reactions with the tuff rock, and/or the radiogenic acids are diluted under the relatively low glass surface area/liquid volume (SA/V) conditions of some of the tests [19,136-143]. In a few tests, glass corrosion rates were actually reduced when the glass samples were exposed to irradiated solutions [138]. Van Iseghem et al. [144,145] note a decrease in corrosion that correlates with a decrease in pH, from 8.5 to 7.5, for glasses being reacted in the presence of clay at a temperature of 90°C and a SA/V ratio of 100 m^{-1} . The reduced pH led to a decrease in total silicon solubility and, consequently, to a reduction in the release rate of other glass matrix components. Hench et al. [146] also indicate that the effects of radiation are negligible in the presence of granite, bentonite, and silicate waters.

Fig. 16.

Solution Concentrations for Various Elements Plotted in Four Reaction Environments. All tests performed with 76-68 glass reacted in gold tubes, for five days, in DIW, at $SA/V = 10 \text{ m}^{-1}$. Explanation of legend: "Air," DIW equilibrated with air and no radiation exposure; "Pre-Irrad.," glass sample subjected to gamma irradiation at dose rate of $2.4 \times 10^6 \text{ R/h}$ prior to leach testing; "Irrad. Ar," glass plus DIW leachant gamma irradiated in argon atmosphere at $2.4 \times 10^6 \text{ R/h}$; "Irrad. Air," glass plus DIW leachant gamma irradiated in air atmosphere at $2.4 \times 10^6 \text{ R/h}$. (a) Cumulative B release, 50°C; (b) cumulative Na release, 50°C; (c) cumulative Si release, 50°C; (d) cumulative B release, 90°C; (e) cumulative Na release, 90°C; and (f) cumulative Si release, 90°C. Plots from data of McVay et al. [49].

6.2 Alpha Radiolysis Tests

Tests conducted with alpha-emitting transuranic-doped glass under a variety of different test procedures and conditions, but without any external gamma exposure, showed increased dissolution rates by up to a factor of four relative to nonirradiated tests [6,7,16,54,147,148]. Weber [5] notes that dissolution rates from these studies were determined from weight loss from the solids and, therefore, may underestimate the radiation-induced release rates by a factor of three to four if reprecipitation of leached components has occurred.

Weber et al. [149] presented dissolution data for high alpha dose rates (^{238}Pu -doped glass) vs. low alpha dose rates (^{239}Pu - and ^{232}Th -doped glass) and found that the higher alpha radiation levels led to release rates of Pu and Si from the glass that are about a factor of two to three higher in both brines and deionized water at 10 m^{-1} and 40°C (Fig. 17). Weber [54] identified a correlation between release rate increases and volume changes in the solids, suggesting a mechanistic relationship between leaching and solid-phase radiation damage. These types of tests simulate a long-term scenario in a saturated repository environment where alpha-radiolysis predominates, and the alpha decay process is affecting both the properties of the solid glass and the chemistry of the surrounding solution.

By contrast, Bibler [43] compared actinide release rates in 23°C deionized water from high-activity ^{244}Cm -doped glass (4×10^{18} alpha decays/ cm^3) with relatively low-activity ^{239}Pu -doped glass (2×10^{14} alpha decays/ cm^3). Both glasses displayed comparable release rates at 10 m^{-1} (^{244}Cm vs. ^{239}Pu release), suggesting that alpha decay has had no effect on glass dissolution. Vernaz et al. [70] note that silicon concentrations in solution were actually decreased slightly with increasing alpha dose, while boron, calcium, and aluminum concentrations were unaffected for glasses leached in 150°C solutions after exposures of 10^{18} to 10^{19} alpha decays/ cm^3 .

In a similar study, Mark and Walder [127] compared release rates of sodium from alpha-track damaged natural and artificial obsidians that were leached in deionized water, under static conditions, at temperatures of 60 and 90°C . The authors note that sodium release rates at 60°C were two times larger for the irradiated relative to the unirradiated specimens, whereas at 90°C the observed release rates were similar. The authors attributed the lack of release rate differences at higher temperatures to rapid annealing of damage tracks in the glass. Thermal annealing may also be responsible for the differences observed in radiation-induced release rate changes between the previously discussed tests at 40°C by Weber et al. [149] and at 150°C by Vernaz et al. [70]. The differences between the studies of Weber and Bibler [43] remain unresolved as both tests were conducted under relatively low-temperature conditions.

For most radiolysis leaching studies, the leachant was simultaneously irradiated with the glass, thus making it difficult to differentiate the effects of solid radiation damage from those of solution radiolysis. Mendel et al. [14] devised experiments to separate the two effects by exposing borosilicate glass covered with a $25\text{ }\mu\text{m}$ layer of deionized water to an electroplated ^{238}Pu film. While the solution covering the glass was exposed to alpha radiation during testing, the glass was shielded from the alpha particles by the layer of water. No enhancement was noted in the growth rate of the hydrolyzed layer after 24 hours, as determined by secondary ion mass spectrometry depth profiling. Nevertheless, tests run for longer time intervals would clearly be of interest.

Fig. 17. Normalized Elemental Release Trends from Borosilicate Glass in MCC-1 Static Leach Tests with Deionized Water as a Function of Time and Alpha Activity. Sample dopant levels (in oxide weight %) as follows: DRG-T1, 1.0% $^{232}\text{ThO}_2$; DRG-P1, 1.0% $^{239}\text{PuO}_2$; DRG-P2, 0.9% $^{239}\text{PuO}_2$ + 0.1% $^{238}\text{PuO}_2$; DRG-P3, 1.0% $^{238}\text{PuO}_2$. (a) Pu release trends and (b) Si release trends. Modified from Weber [54].

6.3 Simulated Corrosion Tests

Several experiments have been devised to separately evaluate the influence of radiolytically produced nitric acid, carboxylic acid, and water dissociation products on glass corrosion. In tests where nitric acid and carboxylic acid production was eliminated by vacuum degassing and argon sparging, the amounts of boron, silicon, and alkalis released were slightly reduced relative to release rates from glass irradiated in the presence of an air-water system (Fig. 16) [49,131]. McVay et al. [49] also exposed glass samples to a 50°C nonirradiated solution of deionized water + HNO_3 prepared to pH of 3.5 at SA/V ratios of 10 to 20 m^{-1} (Fig. 18). This test simulated the glass exposure to radiolytically produced nitric acid without the exposure to water radiolysis products. Elemental release rates from these experiments were

Fig. 18.
Solution Concentrations for Various Elements in Five Reaction Environments. All tests performed with 76-68 glass reacted in gold tubes, for five days, at 50°C, in DIW, at SA/V = 10 m⁻¹. Explanation of legend: "Air," DIW equilibrated with air and no radiation exposure; "Irrad. Air," glass plus DIW leachant gamma irradiated in air atmosphere at 2.4 x 10⁶ R/h; "HNO₃ soln.," glass plus HNO₃ solution at pH = 3.5; "H₂O₂ soln.," glass plus 300 ppm H₂O₂ solution; "HNO₃ + H₂O₂," glass with HNO₃ plus 300 ppm H₂O₂ solution at pH = 3.5. (a) Cumulative B release, (b) cumulative Na release, and (c) cumulative Si release. Plots from data of McVay et al. [49].

about half as large as those of the irradiated air + water systems. These combined results indicate that both water radiolysis products and pH changes arising from acid production may be equally responsible for the enhanced corrosion of glass observed in irradiated air + water experiments.

With experiments where H₂O₂ was added in concentrations similar to levels expected during radiolysis, no measurable increase was noted in glass dissolution rates at 50°C (Fig. 18) [49]. Furthermore, elemental release rates in solutions where both HNO₃ and H₂O₂ were added were indistinguishable from those where HNO₃ was added alone. Burns et al. [15,16] suggest that the two most likely transient water radiolysis products responsible for accelerated glass corrosion are the hydroxyl radical ($\cdot\text{OH}$) and the molecular oxygen anion (O_2^-). The former is

avored as the dominant water radiolysis species responsible for accelerated glass corrosion, since gamma radiolysis favors both radical species production and accelerates glass dissolution more than an equivalent dose exposure of alpha radiation [16,131].

The effects of $\text{OH}^\bullet$ and O_2^- radicals in glass dissolution processes need to be addressed from an experimental standpoint. Sunder and others [13,150] recently devised an experimental configuration to identify the radiolytic species controlling the chemistry of UO_2 dissolution, and these tests could be readily adapted to examine the glass dissolution processes. These authors examined the influence of N_2O saturated solutions, which favor the formation of $\text{OH}^\bullet$ radicals because N_2O scavenges solvated electrons to form $\text{OH}^\bullet$ radicals according to

and formate or t-butanol $[(\text{CH}_3)_3\text{COH}]$ ions, which favor the formation of O_2^- radicals by scavenging $\text{OH}^\bullet$

Increases in the redox potential of irradiated solutions may also lead to solubility changes in redox sensitive elements, such as actinides and some transition metals [14,36], while even release rates of non-redox sensitive elements like lithium and boron have been increased slightly under more oxidizing conditions, indicating that redox conditions may have a small effect on overall glass durability [36]. Nash et al. [133] investigated the redox controls on plutonium and americium dissolution and found that, for solutions that were externally gamma irradiated, plutonium and americium release rates in an $\sim 25^\circ\text{C}$ deionized water solution were 5 times higher than for corresponding tests without external irradiation. When glass disks were exposed to nonirradiated dilute HNO_3 solutions, the release rates increased only by a factor of two over the tests with nonirradiated deionized water. Speciation studies indicate that most of the plutonium was present in V and VI oxidation states in the leachates. The increase in transuranic release is, therefore, attributed to a combination of radiolytically produced HNO_3 , oxidation of the leachant, and increased oxidation state of the transuranics.

6.4 Effects of Solid-Phase Radiation Damage

Boult et al. [151] irradiated alpha-doped glasses at 20°C for periods of one, two, and three years prior to their being exposed to leaching solutions in a Soxhlet test. Results indicate that corrosion rates, based on sample total weight loss, increased $\sim 50\%$ for glasses irradiated for a total of two years ($\sim 4.7 \times 10^{18}$ cumulative alpha decays/ cm^3) relative to glasses irradiated for one year ($\sim 2.5 \times 10^{18}$ cumulative alpha decays/ cm^3). No additional increase in weight loss was observed for glasses subjected to three years of irradiation ($\sim 7 \times 10^{18}$ cumulative alpha decays/ cm^3), an observation consistent with the solid damage saturation dose of 5×10^{18} alpha decays/ cm^3 observed by Weber [50,51]. Malow et al. [152] similarly noted minor increases in weight loss for samples exposed to temperatures of 50 to 170°C and cumulative doses of up to 3.3×10^{18} alpha decays/ cm^3 . Wald and Roberts [153] reacted thermally annealed and alpha damaged glasses in 90°C deionized water after a cumulative exposure of 8×10^{18} alpha decays/ cm^3 and found no significant effect of alpha decay damage on leaching behavior. In

related studies, Ram et al. [154] and Cousens et al. [77] neutron irradiated boron-containing glasses to produce the $^{10}\text{B}(n, \alpha)^7\text{Li}$ reaction, while Cousens and coworkers [155] neutron irradiated UO_2 -containing glasses with neutrons to produce (n, α) and (n, f) events. The Ram et al. tests simulated a total exposure of $\sim 3 \times 10^{19}$ alpha decays/cm³, without any observed increase in glass corrosion rates, while the results from the two Cousens tests displayed 2- to 4-fold release rate increases for lithium, strontium, and silicon.

In glasses exposed to a gamma irradiation source prior to being immersed in a leachant solution, no significant increases were noted in release rates of alkalis, boron, and silicon over those of nonirradiated samples for cumulative doses from 10^7 to 4.6×10^{11} rad (Fig. 16) [43,49,102,147,156-158]. Other studies, however, have noted increases in dissolution rates up to a factor of four after gamma irradiation doses up to 10^{11} rad [159,160].

Ion irradiation studies have shown variable effects on glass corrosion rates. Dran et al. [161,162] irradiated several types of glasses with low-energy lead ions to simulate the damage effects of recoil nuclei generated by alpha decay. In subsequent etching tests, they noted increases in etch pit development in damaged glass by factors of up to 50 or more. In similar studies, Primak [163] and Manara et al. [95] irradiated glasses with xenon, argon, neon, helium, and deuterium ions but only noted etch rate increases of 2- to 4-fold. Burns et al. [15,16] suggest that the ion irradiation studies of Dran et al. did not simulate a realistic scenario for repository leaching because the ion irradiation produced excessive damage overlap zones, and the glass did not have time to thermally anneal during the few minutes that the ion irradiation dose was applied. It is possible that the Dran et al. experiments may have simulated the release rates to be expected from alpha-recoil damage tracks rather than release rates from the bulk glass samples. The effect of annealing on elemental release rates was examined by Mark and Walder [127], who note a 2-fold increase in sodium leachate concentrations for glasses subjected to induced ^{235}U fission at 60°C, while similar tests conducted at 90°C did not yield any increase in leach rates. The difference between the results at the two temperatures was attributed to the more rapid annealing that occurred at 90°C.

Arnold et al. [164] and Petit et al. [165] also note near-surface compositional changes in hydrogen, lithium, silicon, sodium, and neodymium in lead-ion irradiated glasses and crystals, but no increases in release rates were observed after damaged samples were immersed in deionized water at 90 to 100°C. Manara et al. [95] note a 4-fold increase in each pit development on amorphous silica after neon- and nickel-ion bombardment. Bibler [43], however, irradiated Savannah River Plant reference waste glass with either 160 keV xenon ions or 50-250 keV lead ions at a cumulative fluence of 3×10^{13} ion/cm². In subsequent tests at 90°C in deionized water, no significant increase in corrosion rates was detected in irradiated relative to the nonirradiated glass.

Model simulations of ion bombardment predict an increase in leaching as a result of spatial saturation effects at fluences of 10^{12} and 10^{14} ion/cm² [166]. The growth of stress is also found to be greatest for ion tracks impinging on a planar surface, relative to an equivalent fluence resulting from internal alpha doping [167]. This induced increase in stress during ion irradiation may offer an additional explanation for the large increase in dissolution observed in the ion irradiation tests by Dran and co-workers [161,162].

Structural modifications of glass have also been noted to occur at depths greater than the corresponding projected ion ranges [106,168]. This observation suggests that damaged volumes may exceed the areas directly affected by the daughter radionuclides. If these regions are more susceptible to attack from corrosive fluids, then enhanced dissolution of the damage track regions may occur.

Several studies have utilized both 2 to 3 MeV and 0.5 MeV electrons to simulate the damage to waste glass as a result of high- and low-beta irradiation, respectively [15,47,119,169]. Studies at the upper energy range used a maximum cumulative dose of 1.2×10^{11} rad, whereas tests at the lower part of the range were exposed to a cumulative dose of 3×10^{11} rad. Where ionization energy from electron and/or gamma irradiation leads to the formation of bubbles in the glass, an increase in the glass surface area is expected to lead to increased release rates of glass components during subsequent corrosion events. In addition to the changes in the surface area, the radiation-induced mobility of cations within the glass may also contribute to increased corrosion rates [100]. DeNatale and Howitt [98] report that the concentrations of potassium, calcium, lithium, barium, and sodium were continually depleted in electron-irradiated regions of the glass, with depletion being most pronounced for sodium.

In dissolution tests of electron-irradiated glass samples, there were no significant increases in elemental release rates for the irradiated relative to the nonirradiated glasses [47,119,169]. Maximum release rate increases, as measured by weight loss, were less than a factor of two after a total fluence of 10^{19} e-/cm² and a cumulative dose of 3×10^{11} rad. These measured weight losses may underestimate true release rates since the weight measurements do not account for the reprecipitation of corrosion components in alteration phases. (Marples unpublished data, referenced in Burns et al. [15].)

Eyal and coworkers [129,170-176] have compared isotopic release rates of ²³⁸U and ²³²Th with their decay series daughters ²³⁴U, ²³⁰Th, and ²²⁸Th for a variety of naturally occurring silicate, phosphate, and oxide crystalline phases. Release rates of ²²⁸Th and, to a lesser extent, ²³⁴U were enhanced for most phases relative to the release rates of parent nuclides during leach tests in a 25°C bicarbonate solution. Enhanced daughter nuclide release is attributed to increased chemical reactivity along alpha-recoil damage tracks and recoil ejection across the liquid-solid interface. No fractionation of ²³⁴U from ²³⁸U was observed in monazite, probably because the relatively long half-life of ²³⁴U allows the damage tracks to anneal prior to ²³⁴U decay. Although annealing reduced overall release rates of U and Th, enhanced ²²⁸Th/²³²Th was detected, probably due to the rejection of ²²⁸Ra from the mineral structure. For these samples, it appears that ²²⁸Ra diffusion was enhanced during lattice repair. A single study examining the preferential release of decay series daughter isotopes from a 17-year-old glass sample has been conducted by Eyal and Ewing [124]. In this example, ²²⁸Th leach rates at 25°C were enhanced by a maximum of 45% relative to the release of the ²³²Th parent isotope.

6.5 Direct Alpha-Recoil Ejection

Eyal and Olander [174] indicate that less than 4% of the total radium released from monazite samples over a 6.8-year test period will be ejected from the solid directly by alpha-recoil processes. Burns et al. [15] have calculated the contribution of alpha-recoil atoms leaving the solid from near-surface regions of glass (~0.1 μm) relative to the total number of alpha decay events. Results indicate that direct recoil release atoms will represent only 1.5×10^{-21} times the total alpha decays in the glass.

6.6 Tests with Fully Radioactive Glass

Several issues need to be addressed by comparing the dissolution of fully radioactive versus simulated (nonradioactive) glass, including

1. Do both glass types react through the same controlling mechanism?
2. Is there an atmospheric solution or solid-phase radiation or annealing effect that is not accounted for in tests with simulated glass, and are the radiation conditions applied to evaluate the initial rate of glass reaction or long-term conditions similar to the conditions that will prevail under repository-relevant conditions?
3. Is there an element composition difference between the two glass types?
4. Is there a difference in secondary phases produced on the two glass types?
5. Is there a difference in durability between the two glass types?
6. What is the correspondence between the glass production, sample preparation, and test configurations used in the comparative tests?

Comparative tests between fully radioactive and simulated glasses were performed with an extensive test matrix that evaluated glass dissolution as a function of time (through one year), groundwater composition, temperature, flow rate, and the presence of engineered barrier system components [177-179]. Results for the simplest test comparison (deionized water, argon atmosphere, static, SA/V ratio of 1100 m^{-1}) showed that the boron and silicon release rate was about 50% greater from the fully radioactive glass (JSS/A) than from the simulated glass (ABS-118) after 91 to 180 days of reaction, although the difference in release rates diminished after 365 days. These differences are less than the factor of two reported for systematic errors with this data set, indicating that radiation did not have any significant effect on glass reactions under the argon atmosphere conditions of these tests. In a second comparison with an SA/V of 10 m^{-1} , the fully radioactive JSS/A glass was reacted at 90°C and the simulated ABS-118 glass at 110°C . Based on the temperature difference, the simulated glass was expected to react about four times faster than the radioactive glass (for every 10°C increase in temperature, the reaction rate is estimated to double) [180]. Although this expectation was met through 90 days, the boron release rate for the simulated glass decreased significantly between 182 and 365 days, whereas the release rate for the fully radioactive glass continued to increase linearly with time. When water flow was included as a test parameter, the general release trends were similar for both glasses, but there was a 40-day delay in the onset of release from the radioactive glass. Additionally, the boron release after 200 days appeared to be less than that of the radioactive glass.

Comparative results are also available for tests in which 1 g of magnetite was included in the test vessel to simulate metal corrosion products. Through 182 days, the release rates for relatively insoluble elements such as aluminum, calcium, and strontium from the radioactive glass were similar to, or significantly less than, those of the simulated glass. Tests were also done under static conditions with an SA/V ratio of 1100 m^{-1} , and the results were even closer between the fully radioactive and simulated glasses than in the tests at an SA/V ratio of 10 m^{-1} .

In the U.K., the release rates of the radionuclides technetium, neptunium, plutonium, and americium were compared for fully radioactive glasses and actinide-doped simulated glasses with compositions representative of Magnox and THORP processes [181-183]. The differences in release rates were between two (for technetium) and 75 times (for americium), with the highest release rates from the fully radioactive glass.

To evaluate the dissolution of fully radioactive glass under variable SA/V conditions, Bates and coworkers compared reaction patterns for simulated versus fully radioactive glass in static conditions at 90°C and SA/V ratios of 340, 2000, and $20,000 \text{ m}^{-1}$ [184-187]. These SA/V

values were chosen to span a range that may be expected if only limited amounts of water were available for glass reactions. The tests were performed with both fully radioactive and simulated 131/11 and 165/42 glasses that were previously studied by Bibler, as well as 200 composition glass which had been evaluated in short-term product consistency tests [102,188]. Differences in release rates for silicon, lithium, boron, and sodium were less than a factor of two to three between the simulated and fully radioactive tests run for reaction periods up to 182 days. The differences were attributed to the effect of radiation on the solution pH and dominant rate-controlling mechanism. For example, the SRL 165/42 glass displayed a slower pH rise than other glasses, with the fully radioactive SRL 165/42 glass showing a slightly lower initial pH relative to the simulated glass. The lower pH values would favor an ion-exchange mechanism for glass corrosion, and thus, the fully radioactive glass would be expected to release more alkali and alkaline earth components. This pattern was observed, with a larger increase in alkali release occurring for the radioactive glass relative to the simulated glass, based on normalized release values (Fig. 19).

With the 131/11 and 200 glasses, the solution pH is expected to be more basic, favoring a hydrolysis process for glass reactions. The more basic solutions result from the less-durable nature of the 131/11 and 200 glasses and the correspondingly higher release rates of alkali components when compared to the 165/42 glass [185,187]. The more basic the solution, the more rapid the expected reaction, and thus, the simulated glass may react faster than the radioactive glass when radiolytic acids result in a lowering of the solution pH in the latter tests. The differences in reaction rates between the simulated and fully radioactive glass were initially relatively small, and an examination of the reacted glass structure indicates that the composition of the reacted layers is similar. This comparison suggests that, although there is a difference in reaction rates between simulated and fully radioactive glass, the reaction processes are similar, and the glass performance can be modeled with confidence using data generated from simulated glass.

Over longer time intervals, a major difference in reactivity was observed for the 200 glasses. As shown in Fig. 19c, the simulated glass undergoes rapid reaction in the period between 182 and 364 days [189]. This increase in release of soluble components (e.g., boron) was matched by the formation of distinct secondary crystalline silicate phases. However, the fully radioactive glass did not show a concomitant increase. This may be due to the slightly lower solution pH in the radioactive test, which inhibits onset of the rapid reaction, or due to solution differences in alkali or silicon concentrations that inhibit nucleation of secondary phases.

The conclusion from this work to date is that models to predict glass performance can adequately be generated using results of tests with simulated glass [177], but such models must account for the effects of using fully radioactive glass (solid radiation damage and solution composition effects) and must be validated using tests done with fully radioactive glass [189].

6.7 Radiolysis Effects in an Unsaturated Environment

Radiation exposure of glasses under relatively high SA/V conditions, such as those expected to exist in an unsaturated repository setting, will lead to rapid concentration of radiolytic products in the relatively limited amounts of water condensed on the glass surface [20,190]. In such an environment, the bicarbonate present in the small volume of condensate may be neutralized by nitric acid produced in radiolysis reactions. Any nitric acid that subsequently accumulates on the glass surface is likely to react with the glass, significantly accelerating the glass dissolution process. Previous tests with both alpha and gamma radiation sources have demonstrated that nitrogen acids form in high gas/liquid systems (gas/liquid = 100), and becomes concentrated in the small volumes of water present [32].

Fig. 19.
Normalized Boron Release from 90°C Batch Tests in EJ-13 Solution for Fully Radioactive (R) and Simulated (S) Savannah River Site Glasses (modified from Bates [185] and Feng [187]). (a) 165/42 glass, SA/V = 2000 m⁻¹; (b) 131/11 glass, SA/V = 2000 m⁻¹; (c) 200 glass, SA/V = 20,000 m⁻¹.

The resultant effect of these radiolytic products on glass reactions in relatively high SA/V conditions have been examined by Wronkiewicz et al. [20,31,191]. Tests were run with glass doped with americium, plutonium, neptunium, and technetium, with the glass exposed to a saturated air-vapor environment in an external gamma field of about 5×10^3 rad/h. This combination of alpha/gamma fields is similar to that expected during the early stages of storage; however, the integrity of the waste container is expected to isolate glass waste from the repository environment until the radiation levels are considerably lower than those used in these tests. These values thus represent an upper bound for radiation exposure. In these tests, alteration layer development was observed to occur 10 to 15 times faster for SRL 202 glasses reacted at 200°C [20] and 4 times faster for SRL 131 glass reacted at 150°C [191] relative to corresponding tests run without radiation exposure. Both the diversity and total quantity of secondary alteration products on the glass surface also increased in high SA/V tests conducted with radiation exposure [20,31,191,192].

7.0 IDENTIFIED FUTURE NEEDS

Several conclusions were reached from the above literature review. Radiation damage to solid glass materials under simulated waste exposure scenarios results in molecular bond damage and atomic displacements, with a maximum attributable increase in released components during subsequent leach tests of a factor of four. Glass annealing processes may negate most of the alpha-radiation damage effects to the glass structure, thereby eliminating damage overlap processes that may influence glass stability. Studies on the effects of radiation on glass leaching indicate that corrosion rates of glass components, including radionuclides, may be increased or decreased by the presence of radiolytically produced nitric acid, carboxylic acid, and transient water molecules, such as $\bullet\text{OH}$ and O_2^- . Bicarbonate in groundwaters may buffer against leach rate increases arising from radiolytic acid formation. Release rates of boron, aluminum, silicon, alkalis, alkaline earths, and actinides are increased a maximum of 3- to 5-fold, when glass samples are submerged in irradiated deionized water solutions at relatively low SA/V conditions relative to the leach rates of nonirradiated tests. These rates are significantly reduced when the glass is submerged in irradiated bicarbonate or silicate groundwater, and in some instances, silicon release has decreased in the presence of an irradiated solution. An increase in reaction layer thicknesses, by a factor of ~ 10 to 15 times for SRL 202 glass and 4 times for SRL 131 glass, is observed during irradiation at high SA/V conditions, where the radiolytic products are concentrated in small volumes of liquid water contacting the glass.

Outstanding information needs related to radiolysis effects on glass durability are as follows:

- (1) Alpha-recoil direct displacement processes associated with "knock-on" collisions have been studied in detail, with maximum attributable release rate increases from glass samples being approximately four times. Most of these tests either compared weight losses from the damaged solids, or compared leach rates of glass matrix components like silicon or actinide elements.

What is surprising, is that few of these studies address release rates of the daughter recoil radionuclides that will exist in the damage tracks of the glass, and none of these studies includes the release of daughter radionuclides derived from transuranic elements. During the decay of transuranic elements, ^{239}Pu for example, the decay process is likely to result in the formation of a recoil damage track in which the daughter product of this decay, ^{235}U will exist; ^{235}U is an intermediate decay product and will itself eventually decay to ^{231}Th , and so on. Tests that measure dissolution rates of Pu or Si from the glass will only record the overall dissolution rate from the glass matrix and may, therefore, not accurately measure preferential dissolution rates of daughter radionuclides from damaged regions of the glass. If fluid channel pathways are formed in recoil damaged tracks and/or if damaged regions of the surrounding glass are less resistant to the corrosiveness of solution, then release rates of daughter radionuclides, such as ^{235}U , will be accelerated relative to the dissolution of the bulk glass. Isotopic measurements of release rates of daughter radionuclides need to be investigated to address this concern.

- (2) Annealing rates of a variety of glass radiation damage processes have not been adequately investigated, especially at repository-relevant temperatures. However, because overall glass dissolution increases resulting from radiation damage are relatively low (typically <5 times), annealing rates appear to be relatively unimportant, as they will only reduce the already low rates of radionuclide

release. If release rates of daughter radionuclides are significantly larger than the bulk dissolution rate of the glass (as described in comment #1) then glass annealing may be an important parameter in limiting this release.

- (3) The formation of ionization-induced phase segregations and bubble defects needs to be addressed from several viewpoints, including the dose rate dependence, the effect of a polarized field influencing bubble formation during charged particle irradiation, and the effects of phase segregation and bubble formation on glass leachability. Most of these concerns can be adequately addressed by examining both solid-phase damage and leach rate effects resulting from the doping of glass with a β -emitting radionuclide such as ^{90}Sr , ^{137}Cs , or ^{134}Cs . The issue on whether gamma radiation can result in bubble formation is relatively unimportant since the radiation exposure to the glass is expected to be dominated by beta sources for the first 500 years and alpha sources for longer time periods. Synergistic effects between beta, alpha, and gamma ionizing sources may, however, be important from a glass stability viewpoint.
- (4) The identification of the relative influences of various air and water radiolysis products has received a significant amount of attention, most notably in studies by McVay and co-workers [49]. Unresolved issues include the identification of water radiolysis species responsible for glass corrosion and the mechanism involved in this corrosion process. Radical species such as O_2^- and $\text{OH}^\bullet$ have been implicated as being responsible for as much as 50% of radiation damage to glasses under a restricted range of test conditions (Section 6.3). The influence of these species could be even more important when environmental parameters such as temperature, SA/V ratio, and type of radiation source interacting with the sample.
- (5) Most radiolysis tests on glass dissolution have been performed at relatively low temperature and SA/V conditions. The issue of maximum temperature exposures that the glass may be subjected to in the repository depend on waste loading and repository spacing considerations between spent nuclear fuel and vitrified waste canisters. It is not unreasonable to assume, however, a temperature range of 25 to 100°C for exposure of the glass to the repository environment, given a required 300-year service life of the nuclear waste container. In this respect, most radiation tests have accurately simulated potential repository temperature conditions.

In an unsaturated repository setting, the most likely contact mode of water with glass will be condensation of limited amounts of condensed water vapor, or intermittent dripping of small amounts of water onto the sample. It is also conceivable that when the waste container is eventually breached, the canister walls will be simultaneously penetrated in many locations. Given these considerations, it is likely that water contact with glass will be under relatively high SA/V conditions. Most radiolysis tests on glass leaching effects, however, have been conducted with the glass samples fully immersed in liquid water under relatively low SA/V conditions. The limited number of high SA/V radiation tests that have been completed were also performed at temperatures and dose rates that exceed those expected for actual waste glass exposure.

The amount of liquid water contacting the glass samples may have an important influence on glass reactions by controlling the solution composition. Both radiolytic and glass dissolution products will become rapidly concentrated in the limited quantities of solution present under high SA/V conditions. Under this scenario, the rapid concentration of radiolytic acids may create solutions that have a detrimental effect on glass durability. The rapid concentration of glass dissolution products may also accelerate the precipitation of alteration minerals, which then deplete the leachate of certain elements, such as silicon and aluminum. This situation may result in the rapid dissolution of the glass as its constituent elements are transferred via solution to secondary alteration products.

- (6) Because the formation of secondary phases may influence the process of glass dissolution and radionuclide migration, knowledge of the stability of secondary minerals under a variety of environmental conditions is important with respect to radionuclide retentive properties of the waste package. The influence of radiolysis and radiolytic products on the stability and genesis of secondary mineral phases needs to be addressed and compared to modeled results of mineral phase formation.
- (7) Most radiolysis studies on solution composition have been performed under gamma radiation exposure. Because the long-term waste will be dominated by long-lived alpha sources, alpha radiation effects on solution composition need to be better characterized, especially under high gas/liquid ratio conditions characteristic of an unsaturated repository setting.
- (8) Tests using simulated glass compositions appear to simulate the behavior of fully radioactive glass samples, although more tests are needed to better understand the long-term effects of radiation on glass corrosion.

8.0 ACKNOWLEDGMENTS

The author wishes to acknowledge reviews of this manuscript by J. K. Bates, W. L. Ebert, and J. E. Harmon. This work was supported by the U.S. Department of Energy, Office of Environmental Restoration and Waste Management, under Contract W-31-109-ENG-38.

9.0 REFERENCES

1. J. C. Cunnane et al., High-Level Waste Borosilicate Glass: A Compendium of Corrosion Characteristics, Volume I, Appendix A, Argonne National Laboratory Report (in press).
2. Site Characterization Plant, U.S. Department of Energy, Office of Civilian Radioactive Waste Management, DOE Report DOE/RW-0199 (1988).
3. R. G. Baxter, Description of Defense Waste Processing Facility Reference Waste Form and Canister, Savannah River Laboratory Report DP-1606, Rev. 1 (1983).
4. W. Lutze and R. C. Ewing, "Silicate Glasses," in Radioactive Waste Forms for the Future, North-Holland, Amsterdam, Netherlands, pp. 66-93 (1988).
5. W. J. Weber, "The Effect of Radiation on Nuclear Waste Forms," J. Min. Metals and Mat. Soc., pp. 35-39 (1991).
6. W. J. Weber, "A Review of the Current Status of Radiation Effects in Solid Nuclear Waste Forms," Mat. Res. Soc. Symp. Proc. 15, 407-414 (1983).
7. W. J. Weber and F. P. Roberts, "A Review of Radiation Effects in Solid Nuclear Waste Forms," Nucl. Technol. 60, 178-198 (1983).
8. T. J. Headley, G. W. Arnold, and C. J. M. Northrup, "Dose-Dependence of Pb-Ion Implantation Damage in Zirconolite, Hollandite, and Zircon," Sci. Basis for Nucl. Waste Mgmt. V, 379-388 (1982).
9. W. J. Gray, "Fission Product Transmutation Effects on High-Level Radioactive Waste Forms," Nature 296, 547-549 (1982).
10. S. Susman, K. J. Volin, R. C. Liebermann, G. D. Gwanmesia, and Y. Wang, "Structural Changes in Irreversibly Densified Fused Silica: Implications for the Chemical Resistance of High Level Nuclear Waste Glasses," Phys. Chem. Glasses 31, 144-159 (1990).
11. P. Cohen, "Radiation Chemistry and the Behavior of Gases in Reactor Systems," in Water Coolant Technology of Power Reactors, Gordon and Breach Science Publishers, pp. 89-141 (1969).
12. J.-C. Tait, D. L. Wilkin, and R. F. Hamon, Gamma-Radiolysis Effects on Leaching of Nuclear Fuel Waste Forms: Influence of Groundwater and Granite on Gaseous Radiolysis Products, Atomic Energy of Canada, Ltd., Report AECL-8731 (1986).
13. S. Sunder and D. W. Shoesmith, Chemistry of Uranium Dioxide Fuel Dissolution in Relation to the Disposal of Used Nuclear Fuel, Atomic Energy of Canada, Ltd., Report AECL-10395 (1992).
14. J. E. Mendel (compiler), "Radiation Effects," in Final Report of The Defense High-Level Waste Leaching Mechanisms Program, Chapter 5.0, Pacific Northwest Laboratory Report PNL-5157 (1984).

15. W. G. Burns, A. E. Hughes, J. A. C. Marples, R. S. Nelson, and A. M. Stoneham, "Effects of Radiation on the Leach Rates of Vitrified Radioactive Waste," *J. Nucl. Mater.* 107, 245-270 (1982).
16. W. G. Burns, A. E. Hughes, J. A. C. Marples, R. S. Nelson, and A. M. Stoneham, "Radiation Effects and the Leach Rates of Vitrified Radioactive Waste," *Nature* 295, 130-132 (1982).
17. Aa. Barkatt, Al. Barkatt, and W. Sousanpour, "Effects of Gamma Radiation on the Leaching Kinetics of Various Nuclear Waste-Form Materials," *Nature* 300, 339-341 (1982).
18. Aa. Barkatt, Al. Barkatt, and W. Sousanpour, "Gamma Radiolysis of Aqueous Media and Its Effects on the Leaching Processes of Nuclear Waste Disposal Materials," *Nucl. Technol.* 60, 218-227 (1983).
19. N. E. Bibler, "Leaching Fully Radioactive SRP Nuclear Waste Glass in Tuff Groundwater in Stainless Steel," *Adv. Ceram.* 20, 619-626 (1986).
20. D. J. Wronkiewicz, L. M. Wang, J. K. Bates, and B. S. Tani, "Effects of Radiation Exposure on Glass Alteration in a Steam Environment," *Mat. Res. Soc. Symp. Proc.* 294, 183-190 (1993).
21. L. Dolle and J. Rozenberg, "Radiolytic Yields in Water Reactor System and Influence of Dissolved Hydrogen and Nitrogen," in Water Chemistry of Nuclear Reactor Systems, British Nuclear Society, London, p. 291 (1978).
22. D. Rai, R. G. Strickert, and J. L. Ryan, "Alpha Radiation Induced Production of HNO_3 During Dissolution of Pu Compounds," *Inorg. Nucl. Lett.* 16, 551-555 (1980).
23. H. K. Rae, G. M. Allison, A. R. Bancroft, W. Makintosh, J. F. Palmer, E. E. Winter, J. E. Lesurf, and S. R. Hatcher, "Experience with the Chemistry of Water in Moderator and Coolant Systems," *Third Proc. of Int. Conf. on Peaceful Uses for Atomic Energy*, Geneva, Vol. 9, p. 318 (1985).
24. J. K. Linacre and W. R. Marsh, The Radiation Chemistry of Heterogenous and Homogenous Nitrogen and Water Systems, UKAEA Harwell Laboratory, Oxfordshire, AERE Report R-10027 (1981).
25. W. J. Gray and G. L. McVay, Nitric Acid Formation During Gamma Irradiation of Air/Water Mixtures, Pacific Northwest Laboratories Report PNL-SA-12309 (1984).
26. D. T. Reed and D. L. Bowers, "Alpha Particle-Induced Formation of Nitrate in the Cm-Sulfate Aqueous System," *Radiochim. Acta* 51, 119-125 (1990).
27. W. Primak and L. H. Fuchs, "Nitrogen Fixation in a Nuclear Reactor," *Nucleonics* 13, 38-41 (1955).
28. A. R. Jones, "Radiation-Induced Reactions in the $\text{N}_2\text{-O}_2\text{-H}_2\text{O}$ System," *Radiation Res.* 10, 655-663 (1959).
29. D. T. Reed and R. A. Van Konynenburg, "Effect of Ionizing Radiation on Moist Air Systems," *Mat. Res. Soc. Symp. Proc.* 112, 393-404 (1987).

30. D. T. Reed and R. A. Van Konynenburg, "Effect of Ionizing Radiation on the Waste Package Environment," Am. Nucl. Soc. Proc., High Level Radioactive Waste Management Conf., Las Vegas, Nevada, pp. 1396-1403 (1991).
31. D. J. Wronkiewicz, J. E. Young, and J. K. Bates, "Effects of Alpha and Gamma Radiation on Glass Reaction in an Unsaturated Environment," Mat. Res. Soc. Symp. Proc. 212, 99-106 (1991).
32. D. J. Wronkiewicz and J. K. Bates, "Alpha and Gamma Radiation Effects on Air-Water Systems with High Gas/Liquid Ratios," submitted to *Nuclear Technology* (1993).
33. S. L. Nicolosi, "A General Model for the Analysis of Groundwater Radiolysis," Mat. Res. Soc. Symp. Proc. 44, 631-640 (1985).
34. W. J. Gray and S. A. Simonson, "Gamma and Alpha Radiolysis of Salt Brines," Mat. Res. Soc. Symp. Proc. 44, 623-630 (1985).
35. H. Jain, T. M. Ahn, and P. Soo, "The Effects of Gamma Radiolysis on the pH of WIPP Brine A," Nucl. Chem. Waste Mgmt. 5, 345-348 (1985).
36. C. M. Jantzen and N. E. Bibler, "The Role of Groundwater Oxidation Potential and Radiolysis on Waste Glass Performance in Crystalline Repository Environments," Mat. Res. Soc. Symp. Proc. 50, 219-230 (1985).
37. W. J. Gray, "Effects of Radiation on the Oxidation Potential of Salt Brine," Mat. Res. Soc. Symp. Proc. 112, 405-413 (1988).
38. W. J. Weber, "Radiation Effects in Nuclear Waste Glasses," Nucl. Inst. Meth. in Phys. Res. B32, 471-479 (1988).
39. D. H. Day, A. E. Hughes, J. W. Leake, J. A. C. Marples, G. P. Marsh, J. Rae, and B. O. Wade, "The Management of Radioactive Wastes," Rep. Prog. Phys. 48, 101-169 (1985).
40. N. E. Bibler and D. G. Howitt, "Radiation Effects in Silicate Glasses - A Review," Mat. Res. Soc. Symp. Proc. 125, 263-284 (1988).
41. G. W. Arnold, "Ion Implantation Damage Processes in Nuclear Waste Glass and Other Silicate Glasses," Mat. Res. Soc. Symp. Proc. 44, 617-622 (1985).
42. R. C. Ewing and W. Lutze, "Radiation Damage Effects: Comparison of Borosilicate Glass to Synrock Phases," Ceram. Trans. 9, 33-44 (1990).
43. N. E. Bibler, "Effects of Alpha, Gamma, and Alpha-Recoil Radiation on Borosilicate Glass Containing Savannah River Defense High-Level Nuclear Waste," Mat. Res. Soc. Symp. Proc. 6, 681-687 (1982).
44. F. P. Roberts, R. P. Turcotte, and W. J. Weber, Materials Characterization Center Workshop on the Irradiation Effects in Nuclear Waste Forms. Summary Report, Pacific Northwest Laboratory Report PNL-3588 (1981).
45. D. G. Howitt, H. W. Chan, J. F. DeNatale, and J. P. Heuer, "Mechanism for the Radiolytically Induced Decomposition of Soda-Silicate Glasses," J. Am. Ceram. Soc. 74, 1145-1147 (1991).

46. HJ. Matzke, "Radiation Damage in Crystalline Insulators, Oxides, and Ceramic Nuclear Fuels" Rad. Effects 64, 3-33 (1982).
47. International Atomic Energy Agency, "Radiation," in Chemical Durability and Related Profentics of Solidified High-Level Waste Forms, Chapter 4.4, IAEA Technical Reports Series No. 257, pp. 69-143 (1985).
48. J. A. C. Marples, "Dose Rate Effects in Radiation Damage to Vitrified Waste," Nucl. Instr. Meth. in Phys. Res. B32, 480-486 (1988).
49. G. L. McVay, W. J. Weber, and L. R. Pederson, "Effects of Radiation on the Leaching Behavior of Nuclear Waste Forms," Nucl. Chem. Waste Mgmt. 2, 103-108 (1981).
50. W. J. Weber, R. P. Turcotte, and F. R. Roberts, "Radiation Damage from Alpha Decay in Ceramic Nuclear Waste Forms," Radioact. Waste Mgmt. 2, 295-319 (1982).
51. W. J. Weber, L. R. Pederson, W. J. Gray, and G. L. McVay, "Radiation Effects on Nuclear Waste Storage Materials," Nucl. Instr. Meth. in Phys. Res. B1, 527-533 (1984).
52. G. H. Exarhos, "Induced Swelling in Radiation Damaged $ZrSiO_4$," Nucl. Instr. Meth. in Phys. Res. B1, 538-541 (1984).
53. A. Navrotsky, Y. Wang, and R. C. Liebermann, "Energetics of Pressure Densified and Neutron Irradiated Amorphous Silica," Amer. Geophys. Union Fall 1992 Mtg., San Francisco, CA (abstract), p. 581 (1992).
54. W. J. Weber, J. W. Wald, and G. L. McVay, "Effects of Alpha-Radiolysis on Leaching of a Nuclear Waste Glass," J. Am. Ceram. Soc. 68, C253-C255 (1988).
55. G. W. Arnold, "Ion Implantation-Induced Stress In Glasses; Variation Of Damage Mode Efficiency With Changes In Glass Structure," Nucl. Instr. Meth. Phys. Res. B32, 504-507 (1988).
56. G. W. Arnold, "Ion Implantation in Glasses: Mechanical Modifications," in Modifications Induced by Irradiation in Glasses, ed., P. Mazzoldi, Elsevier, Amsterdam, pp. 39-52 (1992).
57. L. M. Wang and R. C. Ewing, "Detailed in Situ Study of Ion Beam-Induced Amorphization of Zircon," Nucl. Instr. Meth. Phys. Res. B65, 324-329 (1992).
58. W. Primak, "Radiation Effects in Silicate Glasses Pertinent to Their Application as a Radioactive Waste Storage Medium," Nucl Technol. 60, 199-205 (1983).
59. R. C. Ewing, B. C. Chakoumakos, G. R. Lumpkin, T. Murakami, R. B. Gregor, and F. W. Lytle, "Metamict Minerals: Natural Analogues for Radiation Damage Effects in Ceramics Nuclear Waste Forms," Nucl. Instr. Meth. in Phys. Res. B32, 487-497 (1988).
60. S. Sato, H. Furuya, K. Asakura, K. Ohita, and T. Tamai, "Radiation Effect on Simulated Waste Glass Irradiated with Ion, Electron, and Gamma Ray," Nucl. Instr. Meth. in Phys. Res. B1, 534-537 (1984).

61. S. Sato, H. Furuya, T. Kozaka, Y. Inagaki, and T. Tamai, "Volumetric Changes of Simulated Radioactive Waste Glass Irradiated by the $^{10}\text{B}(\text{n},\alpha)^7\text{Li}$ Reaction as a Simulation of Actinide Irradiation," *J. Nucl. Mater.* 152, 265-269 (1988).
62. S. Sato, Y. Inagaki, H. Furuya, and T. Tamai, "Radiation Effects on Volumetric Change and Corrosion for Simulated Radioactive Waste Glass," in *Joint Int. Waste Mgmt. Conf.*, Am. Soc. of Mech. Eng., ed., F. Feizollahi, Vol. 2, pp. 323-328 (1989).
63. S. Sato, H. Furuya, K. Morikawa, M. Sugisaki, and Y. Inagaki, "Behavior of Helium Released from Simulated Radioactive Waste Glasses," *J. Nucl. Sci. Tech.* 27, 343-349 (1990).
64. T. J. Headley, R. C. Ewing, and R. F. Haaker, "Amorphous Structure of Metamict Minerals Observed by TEM," *Nature* 293, 449-450 (1981).
65. Y. Inagaki, H. Furuya, and K. Idemitsu, "Microstructure of Simulated High-Level Waste Glass Doped with Short-Lived Actinides, ^{238}Pu and ^{244}Cm ," *Mat. Res. Soc. Symp. Proc.* 257, 199-206 (1992).
66. Y. Inagaki, H. Furuya, Y. Ono, and K. Idemitsu, "Effects of α -Decay on Mechanical Properties of Simulated Nuclear Waste Glass," *Mat. Res. Soc. Symp. Proc.* 294, 191-198 (1993).
67. J. L. Routbort and H. J. Matzke, "The Effect of Composition and Radiation on the Fracture of a Nuclear Waste Glass," *Mat. Sci. Eng.* 58, 229-237 (1983).
68. H. J. Matzke, E. Toscano, and G. Linker, "Alkali Diffusion and Radiation Effects in the Waste Glass VG 98/12," *Nucl. Inst. Meth. in Phys. Res.* B32, 508-511 (1988).
69. H. J. Matzke, H. G. Scheibel, and V. Friehmelt, "Characterization of Waste Glasses Using Vickers Indentation, Short Rod Fractometry and Drop Tests," *Mat. Res. Soc. Symp. Proc.* 127, 173-180 (1989).
70. E. Y. Vernaz, A. Loida, G. Malow, J. A. C. Marples, and H. J. Matzke, Long-Term Stability of High-Level Waste Forms, Third EC Conf. on Radioactive Waste Management and Disposal, Luxembourg, September 17-21, 1990, EUR-13389, pp. 302-315 (1991).
71. H. J. Matzke and G. Linker, "Fracture Toughness and Leaching Behavior of Ion Bombarded Waste Glasses," *Nucl. Inst. Meth. in Phys. Res.* B1, 569-580 (1984).
72. H. J. Matzke, G. Della Mea, J. C. Dran, V. Rigato, and A. Bevilacqua, "Chemical and Physical Modifications in Waste Glass Ion Implanted at Different Temperatures," in Modifications Induced by Irradiation in Glasses, ed., P. Mazzoldi, Elsevier, Amsterdam, pp. 25-31 (1992).
73. B. C. Chakoumakos, T. Murakami, G. P. Lumpkin, and R. C. Ewing, "Alpha-Decay-Induced Fracturing in Zircon: The Transition from the Crystalline to the Metamict State," *Science* 236, 1556-1559 (1987).
74. B. C. Chakoumakos, W. C. Oliver, G. R. Lumpkin, and R. C. Ewing, "Hardness and Elastic Modulus of Zircon as a Function of Heavy-Particle Irradiation Dose: I. *In Situ* α -Decay Event Damage," *Rad. Effects and Defects in Solids* 118, 393-403 (1991).

75. F. W. Clinard, Jr., D. S. Tucker, G. F. Hurley, C. D. Kise, and J. Rankin, "Irradiation-Induced Reduction of Microcracking in Zirconolite," *Mat. Res. Soc. Symp. Proc.* 44, 663-670 (1985).
76. F. P. Roberts, G. H. Jenks, and C. D. Bopp, Radiation Effects in Solidified High-Level Wastes. Part I. Stored Energy, Pacific Northwest Laboratory Report BNWL-1944 (1976).
77. D. R. Cousens, R. A. Lewis, S. Myhra, R. L. Segall, R. St. C. Smart, and P. S. Turner, "The Chemical Durability of Some HLW Glasses: Effects of Hydrothermal Conditions and Ionizing Radiation," *Mat. Res. Soc. Symp. Proc.* 11, 163-171 (1982).
78. G. Malow, "The Mechanisms for Hydrothermal Leaching of Nuclear Waste Glasses: Properties and Evaluation of Surface Layers," *Mat. Res. Soc. Symp. Proc.* 11, 25-36 (1982).
79. J. L. Means, E. D. Spinsosa, A. J. Markworth, J. K. McCoy, N. E. Miller, R. E. Kurth, and G. C. Taylor, Long-Term Performance of High-Level Glass Waste Forms, Nuclear Regulatory Commission Report NUREG/CR-4795 (1987).
80. J. E. Shelby, "Effect of Radiation on the Physical Properties of Borosilicate Glasses," *J. Appl. Phys.* 51, 2561-2565 (1980).
81. J. F. DeNatale and D. G. Howitt, "Importance of Ionization Damage to Nuclear Waste Storage Glasses," *Am. Ceram. Soc. Bull.* 66, 1393-1396 (1987).
82. Hanford Waste Vitrification Plant Foreign Alternatives Feasibility Study, U.S. Department of Energy Report DOE/RL-90-09, Rev. 1 (1990).
83. H. J. Matzke, "Radiation Damage Effects in Nuclear Materials," *Nucl. Instr. Meth. in Phys. Res.* B32, 455-470 (1988).
84. R. A. B. Devine, A. Grouillet, and J. Y. Berliuet, "Temperature Dependence of Radiation Induced Defect Creation in α -SiO₂," *Nucl. Instr. Meth. Phys. Res.* B32, 307-310 (1988).
85. A. R. Hall, J. T. Dalton, B. Hudson, and J. A. C. Marples, "Management of Radioactive Wastes from the Nuclear Fuel Cycle, Vol. II," International Atomic Energy Agency Report IAEA-SM-207/24, p. 3 (1976).
86. R. Cases and D. L. Griscom, "On the Structure of Defect Centers in Gamma Irradiated Alkali Silicate Glasses," *Nucl. Instr. Meth. Phys. Res.* B1, 503-510 (1984).
87. J. E. Shelby, "Radiation Effects in Hydrogen Impregnated Vitreous Silica," *J. Appl. Phys.* 50, 3702-3706 (1979).
88. R. A. Weeks and E. Lell, "Radiation Between E' Centers and Hydroxyl Bonds in Silica," *J. Appl. Phys.* 35, 1932-1938 (1964).
89. S. P. Faile and D. M. Roy, "Mechanism of Color Center Destruction in Hydrogen Impregnated Radiation Resistant Glasses," *Mater. Res. Bull.* 5, 385-389 (1970).
90. R. DiSalvo, D. M. Roy, and L. N. Mulay, "EPR Studies of Radiation Damage in Hydrogen-Impregnated Glass," *J. Am. Ceram. Soc.* 55, 536-537 (1972).

91. E. J. Friebele, R. E. Jager, G. H. Siegel, and M. E. Gingerich, "Effect of Ionizing Radiation on the Optical Attenuation in Polymer-Clad Silica Fiber-Optic Waveguides," *Appl. Phys. Lett.* 32, 95-97 (1978).
92. J. A. Ruller and E. J. Friebele, "The Effect of Gamma-Irradiation on the Density of Various Types of Silica," *J. Non-Cryst. Sol.* 136, 163-172 (1991).
93. J. Acocella, M. Takata, M. Tomozawa, E. B. Watson, and J. T. Warden, "Effect of Gamma Radiation on High-Water-Contact Glasses," *J. Am. Ceram. Soc.* 65, 407-410 (1982).
94. D. L. Griscom, "ESR Studies of an Intrinsic Trapped-Electron Center in X-Irradiated Alkali Borate Glasses," *J. Chem. Phys.* 55, 1113-1122 (1971).
95. A. Manara, P. N. Gibson, and M. Antonini, "Structural Effects of Radiation Damage in Silica Based Glasses," *Mat. Res. Soc. Symp. Proc.* 11, 349-356 (1982).
96. J. F. DeNatale, D. K. McElfresh, D. G. Howitt, "Radiation Effects in Nuclear Waste Glass," *Mat. Res. Soc. Symp. Proc.* 6, 697-702 (1982).
97. J. F. DeNatale and D. G. Howitt, "Radiation Damage in a Nuclear Waste Glass," *Am. Ceram. Soc. Bull.* 61, 582-584 (1982).
98. J. F. DeNatale and D. G. Howitt, "A Mechanism for Radiation Damage in Silicate Glasses," *Nucl. Inst. Meth. in Phys. Res.* B1, 489-497 (1984).
99. S. Sato, K. Asakura, and H. Furuya, "Microstructure of High-Level Radioactive Waste Glass Heavily Irradiated in a High-Voltage Electron Microscope," *Nucl. Chem. Waste Mgmt.* 4, 147-151 (1983).
100. J. P. Heuer, H. W. Chan, D. G. Howitt, and J. F. DeNatale, "An Accurate Simulation of Radiation Damage in a Nuclear Waste Repository," *Adv. Ceram.* 20, 175-180 (1986).
101. J. F. DeNatale and D. G. Howitt, "The Gamma-Irradiation of Nuclear Waste Glass," *Rad. Effects* 91, 89-96 (1985).
102. N. E. Bibler, M. H. Josten, and D. C. Beam, "Recent Results on the Effect of Gamma Radiation on the Durability and Microstructure of DWPF Glass," *Proc. of High-Level Radioactive Waste Mgmt. Conf., American Nuclear Society*, Vol. 2, pp. 1103-1109 (1990).
103. M. H. Tosten, TEM Examination of Irradiated Waste Glass, Memorandum, M. H. Tosten to N. E. Bibler, Westinghouse Savannah River Company Report WSRC-RP-89-584 (1989).
104. A. Manara, M. Antonini, P. Camaghi, and P. N. Gibson, "Radiation Damage in Silica-Based Glasses: Point Defects, Microstructural Changes and Possible Implications on Etching and Leaching," *Nucl. Inst. Meth. in Phys. Res.* B1, 475-480 (1984).
105. B. J. Todd, J. L. Linweaver, and J. T. Kerr, "Outgassing Caused by Electron Bombardment of Glass," *J. Appl. Phys.* 31, 51-55 (1960).

106. P. D. Townsend, "Optical Modifications in Ion Implanted Glasses," in Modifications Induced by Irradiation in Glasses, ed., P. Mazzoldi, Elsevier, Amsterdam, pp. 73-84 (1992).
107. J. C. Dran, "Chemical Modifications Induced by Ion Implantation in Glasses," in Modifications Induced by Irradiation in Glasses, ed., P. Mazzoldi, Elsevier, Amsterdam, pp. 1-9 (1992).
108. M. J. Soileau, N. Mansour, E. Canto, and D. L. Griscom, "Effects of Ionizing Radiation on Laser-Induced Damage in SiO₂," Nucl. Instr. Meth. in Phys. Res. B32, 311-314 (1988).
109. G. Arnold, G. Battaglin, G. Della Mea, G. DeMarchi, P. Mazzoldi, and A. Miotello, "Enhanced Diffusion Processes During Heavy Ion Irradiation of Glasses," Nucl. Instr. Meth. Phys. Res. B32, 315-317 (1988).
110. D. L. Medlin and D. G. Howitt, "Radiation Damage Processes Affecting Electron Beam Lithography of Inorganic Materials," Scanning 14, 86-90 (1992).
111. A. Miotello and F. Toigo, "Radiation Enhanced Diffusion in Glasses," Nucl. Instr. Meth. Phys. Res. B32, 258-263 (1988).
112. P. Calmon and Y. Serruys, "Irradiation Effects on the Diffusion in Silicate Glasses," in Modifications Induced by Irradiation in Glasses, ed., P. Mazzoldi, Elsevier, Amsterdam, pp. 39-52 (1992).
113. G. Malow, "Thermal and Radiation Effects in the Range of Glass Transition Temperature T_g," Mat. Res. Soc. Symp. Proc. 127, 153-162 (1989).
114. W. J. Weber and F. R. Roberts, Radiation Effects in MCC A State-of-the-Art Review of Materials Properties of Nuclear Waste Forms, Pacific Northwest Laboratory Report PNL-3802, pp. 6.1-6.52 (1981).
115. T. A. Abrajano, J. K. Bates, and J. J. Mazer, "Aqueous Corrosion of Natural and Nuclear Waste Glasses; II. Mechanisms of Vapor Hydration of Nuclear Waste Glasses," J. Non-Cryst. Solids 108, 269-288 (1989).
116. J. L. Nogues, E. Y. Vernaz, and N. Jacquet-Francillon, "Nuclear Glass Corrosion Mechanisms Applied to French LWR Reference Glass," Mat. Res. Soc. Symp. Proc. 44, 89-98 (1985).
117. R. W. Geldart and C. H. Kindle, The Effects of Composition on Glass Dissolution Rates: The Application of Four Models to a Data Base, Pacific Northwest Laboratory Report PNL-6333 (1988).
118. J. M. Perez, Jr., and J. H. Westsik, Jr., "Effects of Cracks on Glass Leaching," Nucl. Chem. Waste Mgmt. 2, 165-168 (1981).
119. International Atomic Energy Agency, "Effects of Radiation," in Characteristics of Solidified High-Level Waste Products, Chapter 6, IAEA Technical Reports Series No. 187, pp. 85-110 (1979).

120. G. R. Lumpkin, R. C. Ewing, and Y. Eyal, "Preferential Leaching and Natural Annealing of Alpha-Recoil Tracks in Metamict Betafite and Samarskite," *J. Mater. Res.* 3, 357-368 (1988).
121. G. R. Lumpkin and R. C. Ewing, "Alpha-Decay Damage and Annealing Effects in Natural Pyrochlores: Analogues for Long-Term Radiation Damage Effects in Actinide, Pyrochlore, Structure Types," *Mat. Res. Soc. Symp. Proc.* 127, 253-260 (1989).
122. D. R. Olander and Y. Eyal, "Dissolution Mechanisms of Thorium and Uranium Isotopes from Monazite," in *Int. Waste Mgmt. Conf.*, S. C. Slate et al., eds., Am. Soc. of Mechanical Engs., Vol. 2, pp. 367-373 (1989).
123. W. J. Weber, "Radiation Induced Defects and Amorphization in Zircon," *J. Mater. Res.* 5, 2687-2697 (1990).
124. Y. Eyal and R. C. Ewing, "Impact of Alpha-Recoil Damage on Dissolution of Thoriated Glass," in Low and Intermediate Level Radioactive Waste Management, Proc. 1993 Internat. Conf. Nucl. Waste Mgmt. and Env. Remed. 1, 191-196 (1993).
125. T. D. Mark and W. Ritter, "Radiation Damage and Its Annealing in Sodium Silica Glass," *Mat. Res. Soc. Symp. Proc.* 84, 659-669 (1987).
126. G. Walder and T. D. Märk, "Annealing Kinetics of Radiation Damage in Artificial Obsidian Glass," *Nucl. Inst. Meth. in Phys. Res.* B32, 303-306 (1988).
127. T. D. Mark and G. Walder, "Annealing and Leaching Studies with Natural Glass and Artificial Obsidian Glass," *Mat. Res. Soc. Symp. Proc.* 112, 693-701 (1988).
128. Y. Inagaki, H. Furuya, T. Kikuchi, and K. Idemitsu, "Electron Spin Resonance Studies of Gamma-Irradiation Damage in Simulated Nuclear Waste Glass," *J. Nucl. Sci. Technol.* 28, 314-320 (1991).
129. Y. Eyal and D. R. Olander, "Impact of Alpha-Decay on Incongruent Actinide Isotope Leaching from Monazite," *J. Nucl. Mater.* 170, 117-120 (1990).
130. G. L. McVay, "Effects of Gamma Irradiation on Leaching," Unpublished Proceedings, Workshop on Testing of High Level Waste Forms under Repository Conditions, October 17-28, 1981.
131. L. R. Pederson and G. L. McVay, "Influence of Gamma Irradiation on Leaching of Simulated Nuclear Waste Glass: Temperature and Dose Rate Dependence in Deaerated Water," *J. Am. Ceram. Soc.* 66, 863-867 (1983).
132. L. R. Pederson and G. L. McVay, "Effect of Gamma Radiolysis on Waste Glass Leaching in Brines," *Adv. Ceram.* 8, 76-85 (1984).
133. G. L. McVay and C. Q. Buckwalter, "The Nature of Glass Leaching," *Nucl. Technol.* 51, 123-129 (1980).
134. K. L. Nash, S. Fried, A. Friedman, N. Susak, P. Rickert, J. C. Sullivan, D. P. Karim, and D. J. Lam, "The Effect of Radiolysis on Leachability of Plutonium and Americium from 76-101 Glass," *Mat. Res. Soc. Symp. Proc.* 6, 661-666 (1982).

135. K. L. Nash, S. Fried, A. Friedman, N. Susak, P. Rickert, and J. C. Sullivan, "Radiation Effects in Solution and on the Solid/Liquid Interface," Nucl. Technol. 60, 257-266 (1983).
136. N. E. Bibler, G. G. Wicks, and V. M. Oversby, "Leaching of Savannah River Plant Nuclear Waste Glass in a Saturated Tuff Environment," Mat. Res. Soc. Symp. Proc. 44, 247-456 (1985).
137. R. A. Van Konynenburg, Radiation Chemical Effects in Experiments to Study the Reaction of Glass in an Environment of Gamma-Irradiated Air, Groundwater, and Tuff, Lawrence Livermore National Laboratory Report UCRL-53719 (1986).
138. J. K. Bates, D. F. Fischer, and T. J. Gerding, The Reaction of Glass During Gamma Irradiation in a Saturated Tuff Environment, Part I: SRL 165 Glass, Argonne National Laboratory Report ANL-86-62 (1986).
139. T. A. Abrajano, J. K. Bates, W. L. Ebert, and T. J. Gerding, "The Effect of Gamma Radiation on Groundwater Chemistry and Glass Leaching as Related to the NNWSI Repository Site," Adv. Ceram. 20, 609-618 (1986).
140. T. A. Abrajano, Jr., J. K. Bates, T. J. Gerding, and W. L. Ebert, The Reaction of Glass During Gamma Irradiation in a Saturated Tuff Environment, Part III: Long-Term Experiments at 1×10^4 Rad/Hour, Argonne National Laboratory Report ANL-88-14 (1988).
141. W. L. Ebert, J. K. Bates, T. J. Gerding, and R. A. Van Konynenburg, "The Effects of Gamma Radiation on Groundwater Chemistry and Glass Reaction in a Saturated Tuff Environment," Mat. Res. Soc. Symp. Proc. 84, 613-622 (1987).
142. W. L. Ebert, J. K. Bates, and T. J. Gerding, The Reaction of Glass during Gamma Irradiation in a Saturated Tuff Environment, Part 4: SRL 165, ATM-1c, and ATM-8 Glasses at $1\text{E}3$ R/h and 0 R/h, Argonne National Laboratory Report ANL-90/13 (1990).
143. W. L. Ebert, J. K. Bates, T. A. Abrajano, Jr., and T. J. Gerding, "The Influence of Penetrating Gamma Radiation on the Reaction of Simulated Nuclear Waste Glass in Tuff Groundwater," Ceram. Trans. 9, 155-164 (1990).
144. P. Van Iseghem, K. Berghman, and W. Timmerman, "The Interaction between Nuclear Waste Glasses and Clay-II," Mat. Res. Soc. Symp. Proc. 176, 291-298 (1990).
145. P. Van Iseghem, C. Cantale, M. Coquerelle, J. L. Dussossoy, G. Malow, and H. Roggendorf, "Corrosion Mechanisms of Vitrified High-Level Waste," in Radioactive Waste Management and Disposal, ed., L. Cecille, Elsevier, New York, pp. 275-286 (1991).
146. L. L. Hench, D. E. Clark, and A. B. Harker, "Review Nuclear Waste Solids," J. Mater. Sci. 21, 1457-1478 (1986).
147. J. E. Mendel (compiler), "Thermal Radiation Effects on Borosilicate Waste Glasses," Proc. Symp. Management of Radioactive Wastes from the Nuclear Fuel Cycle, Vienna, Austria, IAEA-SM-207, Vol. 2, p. 49 (1976).

148. R. P. Turcotte, "Radiation Effects in High-Level Radioactive Waste Forms," *Radioac. Waste Mgmt.* 2, 169-177 (1981).
149. W. J. Weber, J. W. Wald, and G. L. McVay, "Effects of Alpha-Radiolysis on Leaching of a Nuclear Waste Glass," *J. Am. Ceram. Soc.* 69(9), C253-C255 (1985).
150. S. Sunder, "UO₂ Fuel by the Products of Gamma Radiolysis of Water," *J. Nucl. Mater.* 190, 78-86 (1992).
151. K. A. Boulton, J. T. Dalton, A. R. Hall, A. Hough, and J. A. Marples, The Leaching of Radioactive Waste Storage Glasses, UKAEA Harwell Laboratory, Oxfordshire, AERE-R9188; HAWSWP/P177, (1978).
152. G. Malow, J. A. C. Marples, and S. Sombret, "Thermal and Radiation Effects on Properties of High-Level Waste Products," in Radioactive Waste Management and Disposal, eds., R. Simon and S. Orlowski, Harwood Academic, Luxembourg, Switzerland, p. 341 (1980).
153. J. W. Wald and W. J. Weber, "Effects of Self-Irradiation Damage on the Leachability of Actinide-Host Phases," *Adv. Ceram.* 8, 71-75 (1984).
154. L. Ram, G. A. Vaswani, M. S. Kumra, and R. N. S. Sunder, Progress Report Presented at the Co-ordinated Programme Meeting for the International Atomic Energy Agency, Richland, Washington, May 1983.
155. D. R. Cousens and S. Myhra, "The Effects of Ionizing Radiation on HLW Glasses," *J. Non-Cryst. Sol.* 54, 345-365 (1983).
156. J. A. Kelley, Evaluation of Glass as a Matrix for Solidification of Savannah River Plant Waste, *Radioactive Studies*, Savannah River Laboratory Report DP-1382 (1975).
157. A. Barkatt, J. H. Simmons, and P. B. Macedo, "Corrosion Mechanisms and Chemical Durability of Glass Media Proposed for the Fixation of Radioactive Wastes," *Nucl. Chem. Waste Mgmt.* 2, 3-23 (1981).
158. G. L. McVay and L. R. Pederson, "Effect of Gamma Radiation on Glass Leaching," *J. Am. Ceram. Soc.* 64, 154-158 (1984).
159. J. R. Grover, "Glasses for the Fixation of High-Level Radioactive Wastes," in Management of Radioactive Wastes from Fuel Reprocessing, Organization for Economic Cooperation and Development, Paris, France, p. 593 (1973).
160. N. E. Bibler and J. A. Kelley, Effect of Internal Alpha Radiation on Borosilicate Glass Containing Savannah River Plant Waste, Savannah River Laboratory Report DP-1482 (1978).
161. J.-C. Dran, M. Maurette, and J.-C. Petit, "Radioactive Waste Storage Materials: Their α -Recoil Aging," *Science* 209, 1518-1520 (1980).
162. J.-C. Dran, M. Maurette, J.-C. Petit, and Vassent, "Radiation Damage Effects on the Leach Resistance of Glasses and Minerals: Implications for Radioactive Waste Storage," in Scientific Basis for Nuclear Waste Management Vol. 3, ed., J. G. Moore, Plenum Press, New York, pp. 449-456 (1981).

163. W. Primak, "Radiation-Enhanced Saline Leaching of Silicate Glasses," Nucl. Sci. Eng. 80, 689-699 (1982).
164. G. W. Arnold, C. J. M. Northrup, and N. E. Bibler, "Near-Surface Leaching Studies of Pb-Implanted Savannah River Waste Glass," Mat. Res. Soc. Symp. Proc. 11, 357-368 (1982).
165. J.-C. Petit, J.-C. Dran, G. Della Mea, and A. Paccagnella, "Dissolution Mechanisms of Silicate Minerals Yielded by Intercomparison with Glasses and Radiation Damage Studies," Chem. Geol. 78, 219-227 (1989).
166. A. M. Ougouag and A. J. Machiels, "Modeling of Ion-Bombardment Effects on Nuclear Waste Glass Leaching," Adv. Ceram. 8, 76-85 (1984).
167. A. M. Ougouag and A. J. Machiels, "Effects of Radiation-Induced Stress on the Chemical Durability of Nuclear Waste Glass," Mat. Res. Soc. Symp. Proc. 44, 609-616 (1985).
168. G. Battaglin, A. Boscolo-Boscoletto, F. Caccavale, G. DeMarchi, P. Mazzoldi, and G. W. Arnold, "Etching Effects in Ion Implanted SiO₂," in Modifications Induced by Irradiation in Glasses, ed., P. Mazzoldi, Elsevier, Amsterdam, pp. 91-96 (1992).
169. R. A. Bonniaud, "La Vitrification en France des Solutions de Produits de Fission," Nucl. Technol. 34, 449-460 (1977).
170. Y. Eyal and R. L. Fleischer, "Preferential Leaching and the Age of Radiation Damage from Alpha Decay in Minerals," Geochim. Cosmochim. Acta 49, 1155-1164 (1985).
171. Y. Eyal, G. R. Lumpkin, and R. C. Ewing, "Alpha-Recoil Effect on the Dissolution of Betatite: Rapid Natural Annealing of Radiation Damage within a Metamict Phase," Mat. Res. Soc. Symp. Proc. 50, 379-392 (1985).
172. Y. Eyal, G. R. Lumpkin, and R. C. Ewing, "Natural Annealing of Alpha-Recoil Damage in Metamict Minerals of the Thorite Group," Mat. Res. Soc. Symp. Proc. 84, 635-643 (1987).
173. Y. Eyal and D. R. Olander, "Mechanisms of Actinide Leaching from Monazite," Mat. Res. Soc. Symp. Proc. 127, 169-276 (1989).
174. Y. Eyal and D. R. Olander, "Leaching of Uranium and Thorium from Monazite: I. Initial Leaching," Geochim. Cosmochim. Acta 54, 1867-1877 (1990).
175. D. R. Olander and Y. Eyal, "Leaching of Uranium and Thorium from Monazite: II. Elemental Leaching," Geochim. Cosmochim. Acta 54, 1879-1887 (1990).
176. D. R. Olander and Y. Eyal, "Leaching of Uranium and Thorium from Monazite: III. Leaching of Radiogenic Daughters," Geochim. Cosmochim. Acta 54, 1889-1896 (1990).
177. L. Werme, I. K. Bjorner, G. Bart, H. U. Zwicky, B. Grambow, W. Lutze, R. C. Ewing, and C. Magrabi, "Chemical Corrosion of Highly Radioactive Borosilicate Nuclear Waste Glass under Simulated Repository Conditions," J. Mater. Res. 5, 1130-1146 (1990).

178. JSS-Project Phase IV: Final Report. Experimental and Modeling Studies of HLW Glass Dissolution in Repository Environments, Japanese Swiss Swedish Project Technical Report JSS-87-01 (1987).
179. JSS Project Phase V: Final Report. Testing and Modelling of the Corrosion of Simulated Nuclear Glass Powders in a Waste Package Environment, Japanese Swiss Swedish Project Technical Report JSS-88-02 (1988).
180. J. E. Mendel et al., A State-of-the-Art Review of Materials Properties of Nuclear Waste Forms, Pacific Northwest Laboratory Report PNL-3802 (1981).
181. A. R. Hall, A. Hough, and J. A. C. Marples, Leach Testing of Fully Active MW Glass, Harwell Laboratory, Oxfordshire, AERE-R-13071 (1988).
182. K. A. Boulton, J. T. Dalton, A. Hough, J. A. C. Marples, G. P. Robertson, and R. I. Wilkins, Radionuclide Release from Solidified High Level Waste, Task 3. Characterization of Radioactive Waste Forms. A Series of Final Reports, No. 19, UKAEA Harwell Laboratory, Oxfordshire, EUR 13604 (1991).
183. J. A. C. Marples, N. Godon, F. Lanza, and P. Von Iseghem, "Radionuclide Release from High Level Waste Forms Under Repository Conditions in Clay or Granite," in Radioactive Waste Management and Disposal, ed., L. Cecille, Elsevier, Amsterdam, pp. 287-301 (1991).
184. J. K. Bates, C. R. Bradley, J. P. Bradley, N. L. Dietz, W. L. Ebert, J. W. Emery, T. J. Gerding, J. C. Hoh, J. J. Mazer, and J. E. Young, Unsaturated Glass Testing for DOE Program in Environmental Restoration and Waste Management. Annual Report, October 1989-September 1990, Argonne National Laboratory Report ANL-90/40 (1991).
185. J. K. Bates, W. L. Ebert, X. Feng, and W. L. Bourcier, "Issues Affecting the Prediction of Glass Reactivity in an Unsaturated Environment," J. Nucl. Mater. **190**, 198-227 (1992).
186. J. K. Bates, J. P. Bradley, A. Teetsov, C. R. Bradley, and M. Buchholtz ten Brink, "Colloid Formation during Waste Form Reaction: Implications for Nuclear Waste Disposal," Science **256**, 649-651 (1992).
187. X. Feng and J. K. Bates, "Initial Comparison of Leach Behavior Between Fully Radioactive and Simulated Nuclear Waste Glasses Through Long-Term Testing. Part 1. Solution Analysis," Am. Nucl. Soc. Proc. of High-Level Radioactive Waste Mgmt. Conf., Las Vegas, NV, pp. 925-933 (1992).
188. N. E. Bibler and J. K. Bates, "Product Consistency Leach Tests of Savannah River Site Radioactive Waste Glass," Mat. Res. Soc. Symp. Proc. **176**, 327-338 (1990).
189. J. K. Bates, X. Feng, C. R. Bradley, and E. C. Buck, "Initial Comparison of Leach Behavior between Fully Radioactive and Simulated Nuclear Waste Glasses through Long-Term Testing. Part 2. Reacted Layer Analysis," in Waste Management '92, Tucson, Arizona, pp. 1047-1053 (1992).
190. D. K. McElfresh, J. F. DeNatale, D. G. Howitt, and E. P. Butler, "Direct Observations of the Leaching of a Simulated Nuclear Waste Glass in a Radiation Environment," Rad. Effects **79**, 285-290 (1983).

191. D. J. Wronkiewicz, C. R. Bradley, J. K. Bates, and L. M. Wang, "Effects of Radiation Exposure on SRL 131 Composition Glass in a Steam Environment," Mat. Res. Soc. Symp. Proc., in press (1994).
192. H. Yokomama, H. P. Hermansson, H. Christenson, I. K. Bjorner, and L. Werme, "Corrosion of Simulated Nuclear Waste Glass in a Gamma Radiation Field," Mat. Res. Soc. Symp. Proc. 44, 601-608 (1985).

Distribution for ANL-93/45Internal:

J. K. Bates (35)	J. E. Harmon	J. Laidler
J. E. Battles	J. E. Helt	D. J. Wronkiewicz
J. C. Cunnane	T. R. Johnson	TIS Files

External:

DOE-OSTI (2)

ANL-E Library (2)

ANL-W Library

Manager, Chicago Operations Office, DOE

A. Bindokas, DOE-CH

J. Haugen, DOE-CH

Chemical Technology Division Review Committee Members:

E. R. Beaver, Monsanto Company, St. Louis, MO

D. L. Douglas, Consultant, Bloomington, MN

R. K. Genung, Oak Ridge National Laboratory, Oak Ridge, TN

J. G. Kay, Drexel University, Philadelphia, PA

G. R. St. Pierre, Ohio State University, Columbus, OH

J. Stringer, Electric Power Research Institute, Palo Alto, CA

J. B. Wagner, Arizona State University, Tempe, AZ

T. Ahn, U. S. Nuclear Regulatory Commission, Washington, DC

D. H. Alexander, USDOE, Civilian Radioactive Waste Management, Washington, DC

J. Allison, USDOE, Office of Waste Operations, Germantown, MD

S. Bates, Idaho Falls, ID

H. Benton, B&W Fuel Company, Las Vegas, NV

A. Berusch, USDOE, Civilian Radioactive Waste Management, Washington, DC

N. E. Bibler, Westinghouse Savannah River Company, Aiken, SC

J. M. Boak, USDOE, Yucca Mountain Site, Las Vegas, NV

K. Boomer, Westinghouse Hanford Company, Richland, WA

W. Bourcier, Lawrence Livermore National Laboratory, Livermore, CA

E. Bramlitt, Defense Nuclear Agency, Kirtland Air Force Base, Kirtland, NM

A. Brandstetter, Science Applications International Corp., Las Vegas, NV

J. Bucher, Lawrence Berkeley Laboratory, Berkeley, CA

J. Canepa, Los Alamos National Laboratory, Los Alamos, NM

K. A. Chacey, USDOE, Office of Waste Management, Germantown, MD

D. Chesnut, Lawrence Livermore National Laboratory, Livermore, CA

G. R. Choppin, Florida State University, Tallahassee, FL

S. Clark, University of Georgia, Aiken, SC

P. Cloke, Science Applications International Corp., Las Vegas, NV

M. O. Clonger, Mac Technical Services, Inc., Richland, WA

D. Codell, U. S. Nuclear Regulatory Commission, Washington, DC
 G. Colton-Bradley, U.S. Nuclear Regulatory Commission, Rockville, MD
 C. Colter, Los Alamos National Laboratory, Los Alamos, NM
 S. Coplan, U. S. Nuclear Regulatory Commission, Washington, DC
 S. P. Cowan, USDOE, Office of Waste Operations, Germantown, MD
 J. Davidson, U. S. Environmental Protection Agency, Washington, DC
 J. Docka, Roy R. Weston, Inc., Washington, DC
 R. Dresser, Roy F. Weston, Inc., Washington, DC
 R. S. Dyer, Yucca Mountain Project Office, Las Vegas, NV
 R. Erickson, USDOE, Office of Waste Operations, Germantown, MD
 E. Essington, Los Alamos National Laboratory, Los Alamos, NM
 F. M. Estes, Idaho State University, Pocatello, ID
 R. C. Ewing, University of New Mexico, Albuquerque, NM
 D. Farr, Los Alamos National Laboratory, Los Alamos, NM
 R. Fish, B&W Fuel Company, Las Vegas, NV
 J. Gauthier, Sandia National Laboratories, Albuquerque, NM
 F. Gelbard, Sandia National Laboratories, Albuquerque, NM
 C. P. Gertz, USDOE, Yucca Mountain Project Office, Las Vegas, NV
 S. E. Gomberg, USDOE, Civilian Radioactive Waste Manage., Washington, DC
 W. Gray, Battelle Pacific Northwest Laboratory, Richland, WA
 D. Harrison, Yucca Mountain Project Office, Las Vegas, NV
 P. Hart, USDOE, Office of Waste Operations, Germantown, MD
 B. Hastings, TRW Environmental Safety Systems, Fairfax, VA
 J. Hennessey, USDOE, Office of Waste Operations, Germantown, MD
 J. Herzog, Westinghouse Idaho Nuclear Company, Idaho Falls, ID
 D. Hobart, LANL-TTISO/USDOE Headquarters, Germantown, MD
 J. Hunt, University of California, Berkeley, CA
 D. Hutchins, Martin Marietta Systems, Inc., Oak Ridge, TN
 C. Interrante, U. S. Nuclear Regulatory Commission, Washington, DC
 V. J. Jain, West Valley Nuclear Services, West Valley, NY
 C. Jantzen, Westinghouse Savannah River Company, Aiken, SC
 L. J. Jardine, Lawrence Livermore National Laboratory, Livermore, CA
 P. Karl, Oak Ridge National Laboratory, Grand Junction, CO
 J. Keith, Daniel B. Stephens & Associates, Albuquerque, NM
 J. Kerrisk, Los Alamos National Laboratory, Los Alamos, NM
 W. S. Ketola, USDOE, West Valley Project Office, West Valley, NY
 D. A. Knecht, Westinghouse Idaho Nuclear Company, Idaho Falls, ID
 W. L. Kuhn, Battelle Pacific Northwest Laboratory, Richland, WA
 K. S. Kung, Los Alamos National Laboratory, Los Alamos, NM
 W. Lee, Environmental Evaluation Group, Albuquerque, NM
 W. W. Lee, University of California, Berkeley, CA
 J. C. Lehr, USDOE, Office of Environmental Restoration, Germantown, MD
 H. Leider, Lawrence Livermore National Laboratory, Livermore, CA
 W. Lemons, Los Alamos National Laboratory, Los Alamos, NM
 S. Levy, Los Alamos National Laboratory, Los Alamos, NM
 D. Livingston, USDOE, Yucca Mountain Site, Las Vegas, NV

R. Lopez, Los Alamos National Laboratory, Los Alamos, NM
 J. J. Lorenz, USDOE, Yucca Mountain Site, Las Vegas, NV
 R. Luce, Nuclear Waste Technical Review Board, Arlington, VA
 W. Lutze, University of New Mexico, Albuquerque, NM
 H. Manaktala, Southwest Research Institute, San Antonio, TX
 S. Martin, Lawrence Livermore National Laboratory, Livermore, CA
 J. M. Matuszek, JJM Consulting, Del Mar, NY
 J. McCarthy, Oak Ridge National Laboratory, Oak Ridge, TN
 L. McDowell-Boyer, Oak Ridge National Laboratory, Grand Junction, CO
 T. W. McIntosh, USDOE, Office of Waste Management, Germantown, MD
 A. Meijer, Jacobs Engineering, Albuquerque, NM
 J. Meldrum, University of Nevada, Las Vegas, NV
 A. Mitchell, Los Alamos National Laboratory, Los Alamos, NM
 R. Morissette, Science Applications International Corp., Las Vegas, NV
 D. Morris, Los Alamos National Laboratory, Los Alamos, NM
 P. K. Nair, Southwest Research Institute, San Antonio, TX
 S. Nelson, M & O Woodward-Clyde, Las Vegas, NV
 B. Newman, Los Alamos National Laboratory, Los Alamos, NM
 C. Novak, Sandia National Laboratories, Albuquerque, NM
 E. Nuttall, University of New Mexico, Albuquerque, NM
 W. O'Connell, Lawrence Livermore National Laboratory, Livermore, CA
 G. Ordaz, USDOE, Office of Technology Development, Washington, DC
 C. Palmer, Lawrence Livermore National Laboratory, Livermore, CA
 R. Palmer, West Valley Nuclear Services, West Valley, NY
 H. Papenguth, Sandia National Laboratories, Albuquerque, NM
 U-S. Park, Science Applications International Corp., Las Vegas, NV
 W. D. Pearson, Savannah River Laboratory, Aiken, SC
 D. Peeler, Battelle Pacific Northwest Laboratories, Richland, WA
 C. Peterson, U. S. Nuclear Regulatory Commission, Washington, DC
 T. H. Pigford, University of California, Berkeley, CA
 M. J. Plodinec, Westinghouse Savannah River Company, Aiken, SC
 W. Polzer, Los Alamos National Laboratory, Los Alamos, NM
 W. G. Ramsey, Westinghouse Savannah River Company, Aiken, SC
 P. Reimus, Los Alamos National Laboratory, Los Alamos, NM
 B. Robinson, Los Alamos National Laboratory, Los Alamos, NM
 P. Rogers, Los Alamos National Laboratory, Los Alamos, NM
 R. Rundberg, Los Alamos National Laboratory, Los Alamos, NM
 C. G. Russomanno, USDOE, Civilian Radioactive Waste Manage., Washington, DC
 J. Ryan, University of Colorado, Boulder, CO
 R. Schulze, Los Alamos National Laboratory, Los Alamos, NM
 W. C. Schutte, USDOE, Office of Technology Development, Washington, DC
 R. Sherman, Los Alamos National Laboratory, Los Alamos, NM
 M. Siegel, Sandia National Laboratories, Albuquerque, NM
 R. Silva, Lawrence Livermore National Laboratory, Livermore, CA
 M. Silva, Environmental Evaluation Group, Albuquerque, NM
 A. Simmons, USDOE, Las Vegas, NV

E. Springer, Los Alamos National Laboratory, Los Alamos, NM
 J. Sproull, Westinghouse Savannah River Company, Aiken, SC
 D. Stahl, M&O/B&W Fuel Company, Las Vegas, NV
 W. Steinkampf, U.S. Geological Survey, Lakewood, CO
 L. Stetzenbach, University of Nevada, Las Vegas, NV
 R. B. Stout, Lawrence Livermore National Laboratory, Livermore, CA
 D. Strachan, Battelle Pacific Northwest Laboratories, Richland, WA
 D. Stucher, USDOE, Las Vegas, NV
 M. Tomozawa, Rensselaer Polytechnic Institute, Troy, NY
 I. Triay, Los Alamos National Laboratory, Los Alamos, NM
 V. Trice, USDOE, Office of Waste Management, Germantown, MD
 D. Turner, Southwest Research Institute, San Antonio, TN
 B. Viani, Lawrence Livermore National Laboratory, Livermore, CA
 J. Wan, New Mexico Tech, Socorro, NM
 L. Wang, University of New Mexico, Albuquerque, NM
 R. Weiner, Environmental Evaluation Group, Albuquerque, NM
 M. Whitbeck, Desert Research Institute, University of Nevada, Reno, NV
 C. N. Wilson, Westinghouse Hanford Company, Richland, WA
 J. Wilson, New Mexico Tech, Socorro, NM
 M. Wilson, Sandia National Laboratories, Albuquerque, NM
 A. Wistrom, Los Alamos National Laboratory, Los Alamos, NM
 J. H. Wolfram, Montana State University, Bozeman, MT
 Kurt Wolfsberg, Los Alamos National Laboratory, Los Alamos, NM
 A. Wollerman, Science Applications International Corp., Germantown, MD
 A. Yang, U.S. Geological Survey, Denver, CO
 M. P. Gardiner, Harwell Laboratory, Didcot, Oxon, UNITED KINGDOM
 N. C. Garisto, Atomic Energy of Canada, Pinawa, Manitoba, CANADA
 B. Grambow, Kernforschungszentrum Karlsruhe, GmbH, GERMANY
 L. Johnson, Atomic Energy of Canada, Pinawa, Manitoba, CANADA
 J. Kim, Kernforschungszentrum Karlsruhe, GmbH, GERMANY
 H. Nitsche, Forschungszentrum Rossendorf e.V., Institut für Radiochemie, GERMANY
 T. Payne, Australian Nuclear Science and Technology Organization, AUSTRALIA
 P. Van Iseghem, Boerecamp, BELGIUM
 E. Vernaz, Centre d'Etudes Nucleaires de la Vallée du Rhône, Marcoule, FRANCE
 P. Vilks, Atomic Energy of Canada, Pinawa, Manitoba, CANADA
 L. Werme, Svensk Kärnbränslehantering AB, Stockholm, SWEDEN