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**RADIONUCLIDE DECAY EFFECTS ON WASTE GLASS
CORROSION AND WEATHERING**

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RADIONUCLIDE DECAY EFFECTS ON WASTE GLASS CORROSION

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ABSTRACT

The release of glass components into solution, including radionuclides, may be influenced by the presence of radiolytically produced nitric acid, carboxylic acid, and transient water dissociation products such as $\cdot\text{OH}$ and O_2^- . Under batch test conditions, glass corrosion has been shown to increase up to a maximum of three-to five-fold in irradiated tests relative to nonirradiated tests, while in other studies the presence of radiolytic products has actually decreased glass corrosion rates. Bicarbonate groundwaters will buffer against pH decreases and changes in corrosion rates. Under high surface area-to-solution volume (S/V) conditions, 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 high S/V conditions.

Radiation damage to solid glass materials results in bond damage and atomic displacements. This type of damage has been shown to increase the release rates of glass components up to four-fold during subsequent corrosion tests, although under actual disposal conditions, glass annealing processes may negate the solid radiation damage effects.

INTRODUCTION

Radionuclide decay effects on high-level waste (HLW) glasses are an important consideration for radionuclide immobilization because of the potential to influence glass stability. Radiation can influence glass stability through formation of corrosive radiolytic products in the air and liquid water contacting the waste package, and by physically altering the structure of the glass through atomic displacements.

Glass waste forms will exhibit temporal variations in both types and intensities of radioactivity. During the first 500 years after waste vitrification, radiation emissions are expected to be dominated by beta and gamma radiation from the decay of ^{137}Cs , ^{90}Sr , and other fission products [1, 2]. Actinide elements that emit alpha particles (U, Np, Pu, Am, and Cm) generally have much longer half-lives (from hundreds to billions of years) and thus will become the dominant radiation source at longer times. 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 vapor environment of the repository comes in direct contact with the glass.

AIR AND WATER RADIOLYSIS

Ionizing radiation will excite electrons and ionize water molecules and dissolved gases to form reactive radicals and new molecules [3, 4]. 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 the radiolysis of water indicates that gamma radiation produces

TABLE I
Principal Radiolytic Species G-Values for Gamma and 5 MeV Alpha
Radiation of Liquid Water [5]

Species	H ⁺	e ⁻ _{aq}	H•	•OH	HO ₂ •	H ₂	H ₂ O ₂	H ₂ O
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

relatively greater concentrations of e⁻_{aq}, H⁺, •OH, and H•, whereas alpha yields are greatest for HO₂•, H₂, and H₂O₂ molecules (see Table I [5]).

Nitrogen and carbon dioxide dissolved molecular in water may also undergo radiolytic decomposition and recombination of the dissociation products with O₂, water, and other radiolytic products to form nitrogen and carboxylic acids, respectively [5-8]. Because the solubility of N₂ in water is low, the G(NO₃⁻) values for nitric acid production in air-saturated water are small, ranging from 0 to less than 0.2, while the G-values reported for radiolytic production of nitric acid from moist air or two-phase air/liquid water systems are about 2.0 [9-13].

A notable decrease occurs in the pH of irradiated deionized water and air systems due to the formation of nitric acid in the irradiated air above the test solution and its subsequent dissolution in water [6,9,10-13]. Radiolysis of water may also increase the redox potential (Eh) of the irradiated solution. During irradiation of water, equal amounts of reducing and oxidizing species are produced [4,5]. Hydrogen produced during radiolysis is chemically inert toward low-temperature (<100°C) aqueous reactions and has a high diffusional mobility relative to other radiolytic products. Thus, H₂ may separate from the aqueous system, resulting in an increase in the solution Eh. Sunder and Shoosmith [4] noted that with spent fuel radiolysis, O₂⁻ and •OH were the predominant oxidizing agents, followed by H₂O₂ and then O₂. Alpha and gamma radiolysis of brines results in high redox potentials due to the scavenging of OH radicals by halide anions and a resultant increase in the separation of H₂ from the aqueous phase [14]. The presence of ferrous iron and other reduced species may mitigate against oxidization of groundwaters [14].

SOLID PHASE DAMAGE

Radiation damage processes to high-level waste (HLW) glass can be divided into displacement and ionization effects. The type of damage that occurs will depend upon the radiation interacting with the glass and the properties of the glass waste. A number of comprehensive reviews on solid radiation damage exist in the literature and are incorporated into the following discussion [1,2,5,6,15-21].

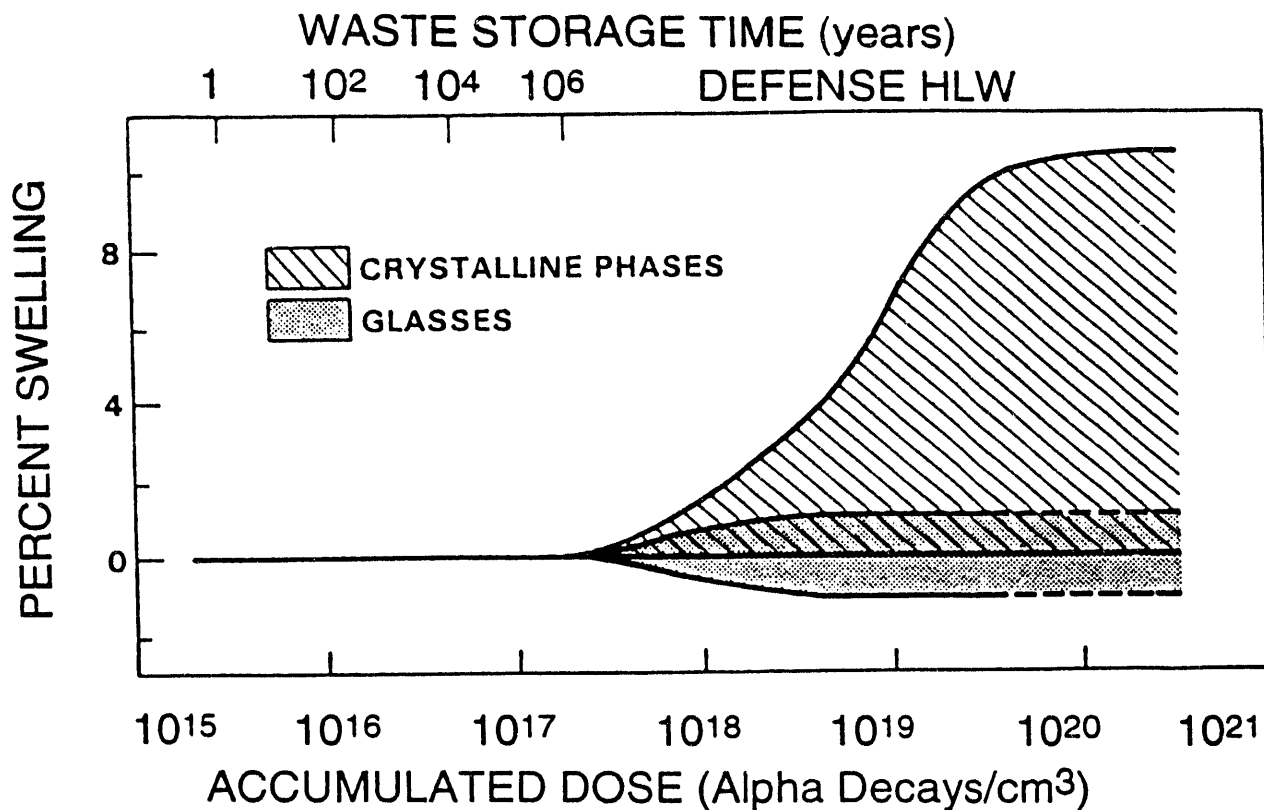


Fig. 1. Range of swelling in volume percent for crystalline and glass waste forms as a function of accumulated dose (and repository storage time) (modified from [24]).

Displacement Damage

The volume (or density) of glass and crystalline materials may change as a result of atomic displacements that occur after exposure to radiation [15, 19, 22, 23]. Crystalline or ceramic waste forms may swell up to 10% after exposure to alpha radiation because of the increasing disorder of the crystalline material (Fig. 1) [16, 24]. Volume changes in glass after alpha exposure are generally $\pm 1.2\%$. Measurable volume changes for glass first occur after a cumulative exposure of 1×10^{17} alpha decays/cm³, and they saturate after a dose of 5×10^{18} alpha decays/cm³ [16]. A comparison of these threshold and saturation levels with the expected cumulative alpha exposure levels for HLW glasses indicates that waste form volume changes may occur after about 1000 years of self-irradiation damage, although annealing processes may limit the damage effects [5, 15, 17].

Radiation damage from alpha decay results from interaction of the glass with both a high-energy alpha particle (about 4 to 6 MeV) and a lower energy alpha-recoil nucleus (about 0.1 MeV). The alpha-recoil nucleus will transfer energy as it travels through and collides with surrounding atoms, displacing several thousand atoms along a 10-nm long alpha-recoil track [15, 25]. The emitted alpha particle dissipates most of its energy in the surrounding medium by an ionization process, but near the end of its ~10,000-nm long track produces enough low-velocity collision events to displace several hundred atoms. Beta radiation is expected to result in less than one direct

displacement per decay event, and direct displacement from gamma radiolysis is negligible.

Primak [18] and Arnold [26] subjected vitreous silica and borosilicate glasses to He-, Xe-, and Pb-ion bombardment to simulate the effects of alpha-particle damage to glass. An initial expansion of 0.1% was associated with the formation of defect centers and valence changes. This initial expansion was followed and eventually overtaken by a contraction of ~1% associated with the dissipation of particulate radiation and the intense excitation found in the last fraction of the energy range of a heavy atom [18]. The compacted structure is attributed to silicate tetrahedron deformation where the silicon-oxygen bond angle was decreased. Borosilicate and complex high-level waste glasses display ion bombardment stresses that correlate with ionization processes, whereas high silica samples have stresses associated with displacement damage [26].

Glass samples irradiated by neutrons that produce $^{10}\text{B}(n, \alpha)^7\text{Li}$ reactions expanded within the range of 0.12 to 0.6%. Sato et al. [27,28] attributed this swelling to the formation of He bubbles that became entrapped within damaged zones of the glass. When at rest, the alpha particles (He-ions) emitted during actinide decay fill their valence-electron vacancies to become He atoms. The accumulation of He in bubbles may result from the slow diffusion of He through solids, exclusion of He from mineral structures, or by capture of thermal vacancies with the driving force being the surface tension between the gas and the bubble walls [22].

Susman et al. [29] suggests that an average total volume contraction of about 3% produced during neutron bombardment of vitreous silica actually relates to a contraction of 20% in the damage tracks which were surrounded by undamaged material. To investigate this damage behavior further, the authors subjected vitreous silica samples to pressures of 16 GPa in a diamond anvil cell. The resultant damage was related to extensive intermediate-range disorder, although some short-range silicate tetrahedron deformation was also identified. Navrotsky et al. [30] compared the enthalpies of neutron irradiation damaged samples vs. those that were pressure densified in the manner of Susman et al. Measured enthalpies from irradiated silica glass and quartz samples are approximately half those of the pressure densified samples, indicating that the extent of local deformation is greater in the neutron-irradiated samples when normalized to the same number of silica tetrahedron involved.

A significant proportion of crystalline material contained within the glass may be detrimental to waste form integrity because the more highly ordered crystalline materials show a greater amount of swelling than the less structured vitrified materials (Fig. 1). Weber and Roberts [15] reported microfracturing in ^{244}Cm -doped samples as a result of differential expansion associated with amorphization and swelling of crystalline phases after a cumulative exposure of 8×10^{17} alpha decays/cm³.

Transmutation of fission products results in changes of both valence and ionic size of the daughter atom relative to its parent radionuclide. Transmutations that produce decay product nuclei that are insoluble in the glass may result in the nucleation of crystalline material, provided that sufficiently large solid state diffusion rates occur [16,31]. For example, the transmutation of ^{90}Sr to ^{90}Zr involves a change from a parent nuclide that is a network modifier to a decay product that may be a

network former. If the production of additional Zr by transmutation results in a total ZrO_2 concentration of >2.3 wt.%, then the glass may become saturated with respect to Zr and crystalline phases will begin to nucleate. Differential volume expansions exhibited by radiation-damaged glass and crystalline solids could eventually contribute to fracturing of these waste forms [15]. Although most HLW glass will contain combined $ZrO_2 + SrO$ concentrations of <2.3 wt.%, other waste glasses, most notably the West Valley WV205 and the French R7T7 compositions, contain >2.3 wt.% $ZrO_2 + SrO$.

Increases in fracture toughness or resistance to fracture propagation of up to 80% have been reported for glasses exposed to cumulative alpha exposures of 10^{18} to 10^{19} decays/cm³ [17,21,32,33] or ion beams [34]. Fracture toughness increases in radiation-damaged crystalline materials have been attributed to more ductile behavior of the solids, arresting of tensional fracture growth in compressed alpha-recoil track regions, crack bowing, crack deflection, internal stresses associated with the coherency of secondary phases, differences in elastic properties of phases at different stages of the damage process, and impedance of crack propagation by interaction with voids [25,35,36].

Displaced atoms that have a higher energy level than those in equilibrium positions may release their latent energy as heat when the waste form is thermally annealed [29,30]. A compilation of saturated latent energy values in waste glass indicates a range of 50 to 125 J/g. An instantaneous release of this energy would result in a self-sustaining temperature rise of $<130^\circ C$ in the waste [15]. Generally, however, the stored energy is released over a broad temperature range. A slow release of latent energy may be beneficial in inducing additional glass annealing because defect centers may be thermally unstable and will, therefore, anneal more rapidly as the temperature is raised slightly [18,22].

Ionization Damage

Glass ionization damage results from the excitation and ejection of electrons from valence orbitals of atoms 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 [29]. This ionizing damage may manifest itself in several forms, including electron hole pairs, covalent bond ruptures, valence changes, structural water decomposition, and decomposition of unstable molecular ions [15]. Although the ionizing radiation dose will initially be dominated by beta and gamma sources, the dose received from alpha particle sources is also significant, with cumulative dose exposures from alpha sources expected to exceed those from beta-gamma sources after about 10^5 years [17]. Synergistic effects between collision and ionization processes may occur in actual vitrified wastes, but such effects are generally not simulated in short-term radiation experiments.

The largest volume changes associated with gamma irradiation have been reported by Shelby [37], who noted a maximum compaction of about 1% for silica and borosilicate glasses. Sato et al. [27] determined maximum swelling of 0.2 and 0.04% for borosilicate glass exposed to cumulative external gamma doses of 1×10^9 and 5×10^8 rad, respectively, and densification of 0.003 to 0.005% for high silica glass at

1.2×10^9 rad. Bibler [38] noted a density change of <0.05% for borosilicate glass exposed to cumulative doses of 8.5×10^{10} rad. Comparisons with combined beta and gamma doses expected for the HLW glasses suggest that these levels of radiation exposure may be readily attainable within the first 10 years after glass fabrication.

The amount of structural damage incurred by glass may also be influenced by the glass composition. The addition of B, an increase in the alkali/Si ratio, and an increase in compositional complexity have all been noted to enhance the rate of densification in gamma- and electron-irradiated glasses [1,18,20,37,39,40], whereas glass samples implanted with hydrogen expanded during irradiation [41]. Several studies note a suppression of the amount of ionizing radiation-induced damage, coloration, and leaching as a function of increasing Al, Ce, and water content [42-46].

Ruller and Friebele [47] suggested that when natural and synthetic high-silica glasses containing more than 150 ppm OH are irradiated, the radiolytic electrons and holes are trapped by the Si-OH, forming atomic hydrogen and non-bridging oxygen hole centers. The H_2 gas that subsequently forms may undergo a second reaction with the silica network, breaking the Si-O-Si bonds to produce SiOH and SiH groups that inhibit densification of the glass [41]. This radiolytic disruption of the Si-O-Si bonds is also analogous to the network-hydrolysis process that results from aqueous corrosion processes.

Damage from gamma irradiation may also manifest itself in bubble formation and phase separation. The mechanism of this bubble formation involves the disruption of nonbridging ionic bonds and electron capture by migrating cations such as Na^+ under an electric field generated across the glass [39]. Continued ionization of the glass in the absence of Na^+ leads to the formation of Si-O-Si bonds, O_2 , and e^- , with the O_2 gas accumulating as bubbles. The formation rate of bubbles can be correlated directly with the Na_2O content of the glass; and is most pronounced under the influence of gamma irradiation, followed by ion irradiation, and then electron irradiation [48]. Heuer et al. [49] have confirmed the presence of generated gas in the bubbles by trapping gases escaping from irradiated glass with a carbon coating, while Todd et al. [50] have confirmed, using mass spectrometry analysis, that oxygen constitutes >95% of the gas evolved during the irradiation of glass.

Tosten [51] and Bibler et al. [52] irradiated glasses identical in composition to those of Howitt et al. [39] at doses of up to 3.6×10^{10} rad but did not note any associated bubble formation; Tosten [51] suggests that Howitt et al. may have induced bubble formation during their ion-milling sample preparation process. If true, then oxygen bubbles are not expected to form under actual disposal conditions since bubble formation in these tests may have been induced by polarizing fields.

Annealing Processes

A large increase in corrosion rates resulting from solid radiation damage will occur only if damage zones overlap and provide interconnected channel ways between the interior and the surface of the glass. If individual damage zones anneal in relatively short times, then significant damage zone overlap will not occur and increases in corrosion rates will not be realized. Most laboratory irradiation experiments accelerate glass reactions by increasing dose rates several orders of

magnitude above levels that are pertinent for actual waste glass disposal. This exposure promotes excessive damage overlap relative to annealing rates, such that an artificially accelerated corrosion rate may result. [23].

The process of annealing has been addressed in numerous studies with crystalline materials but in relatively few studies with glass [53-55]. 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 anneal as it occurs. For alpha-damaged waste glass, Sato et al. [27] have determined that annealing will diminish glass expansion damage within days after heating to 400 to 450°C, with longer recovery times at lower temperatures. Burns et al. [6] estimated annealing rates in glass of about three hours to 110 days, at 200 to 25°C, respectively. With critical damage zone overlaps occurring for alpha-simulated tests only after 1200 days, these rates suggest that alpha-recoil tracks will readily anneal in the vitrified waste and, therefore, will not significantly affect the stability of the waste form.

Walder and Mark [56] noted an Arrhenius temperature dependence of annealing rates that was generally independent of the source of radiation damage. Marples [23], however, indicated that, at 130 to 300°C, glass densities followed an exponential annealing curve for only a short time, with ~20 to 70% residual density change remaining even after long annealing periods.

EFFECTS ON GLASS DURABILITY AND RADIONUCLIDE RELEASE

Evaluations of radiolytic effects on glass reactions are quite complex due to interactions between the dissolving glass components, radiolytic products, and buffering capacity of silicate groundwater against radiolytically produced acids. Alpha tracks, phase changes, bubble formation, annealing, phase separation, and microfracturing [1,53,57] also can influence the alteration rate of glass materials.

In experiments conducted with PNL 76-68 glass samples immersed in deaerated and deionized water at 50 and 90°C, and at a S/V of 20 m⁻¹, the gamma irradiated leachates displayed a larger increase in pH relative to their nonirradiated tests due to release of hydroxide from the glass [58]. Furthermore, the difference in pH values and release rates of Na, Si, and B between the irradiated and nonirradiated tests were lowest at the highest temperature tests, indicating that the effects of radiolysis on the corrosion rate become less important at higher temperatures (see Fig. 2; B not shown) [58]. Similar results were noted for brines at 10, 100, and 1000 m⁻¹ [59], although comparative MCC-1 tests indicate that dissolution rates of Si are three or four times lower in irradiated brines relative to irradiated DIW [38].

In tests conducted with gamma-irradiated borosilicate waste glass in aerated and deionized water systems, release rates of B, Al, Si, alkalis, and actinides generally increased three- to five-fold over nonirradiated tests [7,24,58,60]. McVay et al. [24] sequentially irradiated PNL 76-68 glass samples in the presence of air + water or deaerated water prior to immersion in water at a S/V of 10 m⁻¹. In these tests, the largest release rate increases for alkalis, Si, and B were recorded for samples irradiated in the presence of air + water, with slightly larger increases at 90°C than at 50°C. Irradiation of the deaerated water, where the formation of nitric acid has been

eliminated, accelerated glass reaction rates to about 60% of the level that characterized the aerated water. McVay et al. [24] also exposed glass samples to a nonirradiated deionized water + nitric acid solution prepared at S/V ratios of 10 to 20 m⁻¹ and pH 3.5. Elemental release rates were again about half as large as those of irradiated air + water systems. These combined results indicate that nitric acid and water radiolytic products were equally responsible for the enhanced corrosion observed in the irradiated tests in aerated water.

In studies where glasses were exposed to gamma irradiation for cumulative doses from 10⁷ to 4.6 x 10¹¹ rad prior to being immersed in a leachant solution, no significant increases were noted in release rates of alkalis, B, and Si over those of nonirradiated samples [24,38,52,61,62]. Other studies, however, have noted increases in dissolution rates up to four-fold after preirradiated samples at doses of up to 10¹¹ rad [63, 64].

Significant changes in leachate pH and glass dissolution rates were not observed when glass samples were irradiated in the presence of bicarbonate groundwater [8,65-67]. In some instances, glass dissolution rates were actually reduced in the irradiated tests relative to nonirradiated tests due to a decrease in pH and a subsequent decrease in Si solubility [68,69].

In tests conducted with alpha-emitting transuranic-doped glass, but without external gamma exposure, glass dissolution rates increased up to three-fold relative to nonirradiated tests [1,6,15,61,70,71]. Weber [1] notes that the dissolution rates determined from these studies were primarily determined from weight loss of the solids and, therefore, may underestimate the true dissolution rates if reprecipitation of corrosion products has occurred. Vernaz et al. [33] noted that Si concentrations in solution decreased slightly, whereas B, Ca, and Al concentrations were unaffected for glasses leached in 150°C solutions after exposures to 10¹⁸ to 10¹⁹ alpha decays/cm³.

Weber et al. [71] tested high alpha dose rate (²³⁸Pu-doped) vs. low alpha dose rate (²³⁹Pu- and ²³²Th-doped) glasses and found that the higher radiation levels led to increased release rates of both Pu and Si, by about a factor of two to three in both brines and deionized water at 10 m⁻¹ and 40°C (Fig. 3). Weber [17] also identified a correlation between release rate increases and volume changes in the solids, suggesting a mechanistic relationship between glass dissolution and solid phase radiation damage.

By contrast, Bibler [38] compared actinide release rates in deionized water from high-activity ²⁴⁴Cm-doped glasses (4 x 10¹⁸ alpha decays/cm³) with relatively low-activity ²³⁹Pu-doped glass (2 x 10¹⁴ alpha decays/cm³). Both glasses displayed comparable release rates at 10 m⁻¹ (²⁴⁴Cm vs. ²³⁹Pu release), suggesting that alpha decay damage had no effect on actinide release rates from the glass.

Eyal and coworkers [52,72,73] compared release rates of ²³⁸U and ²³²Th with their intermediate daughter decay products ²³⁴U, ²³⁰Th, and ²²⁸Th, for ~1 μm powdered samples produced from a variety of naturally occurring silicate, phosphate, and oxide crystalline phases. Release rates of ²²⁸Th and, to a lesser extent, ²³⁴U were typically enhanced relative to the release rates of parent nuclides during corrosion tests in a bicarbonate solution at 25°C. Enhanced daughter product release was attributed to increased chemical reactivity along alpha-recoil damage tracks and recoil ejection across the liquid-solid interface. A single study examining

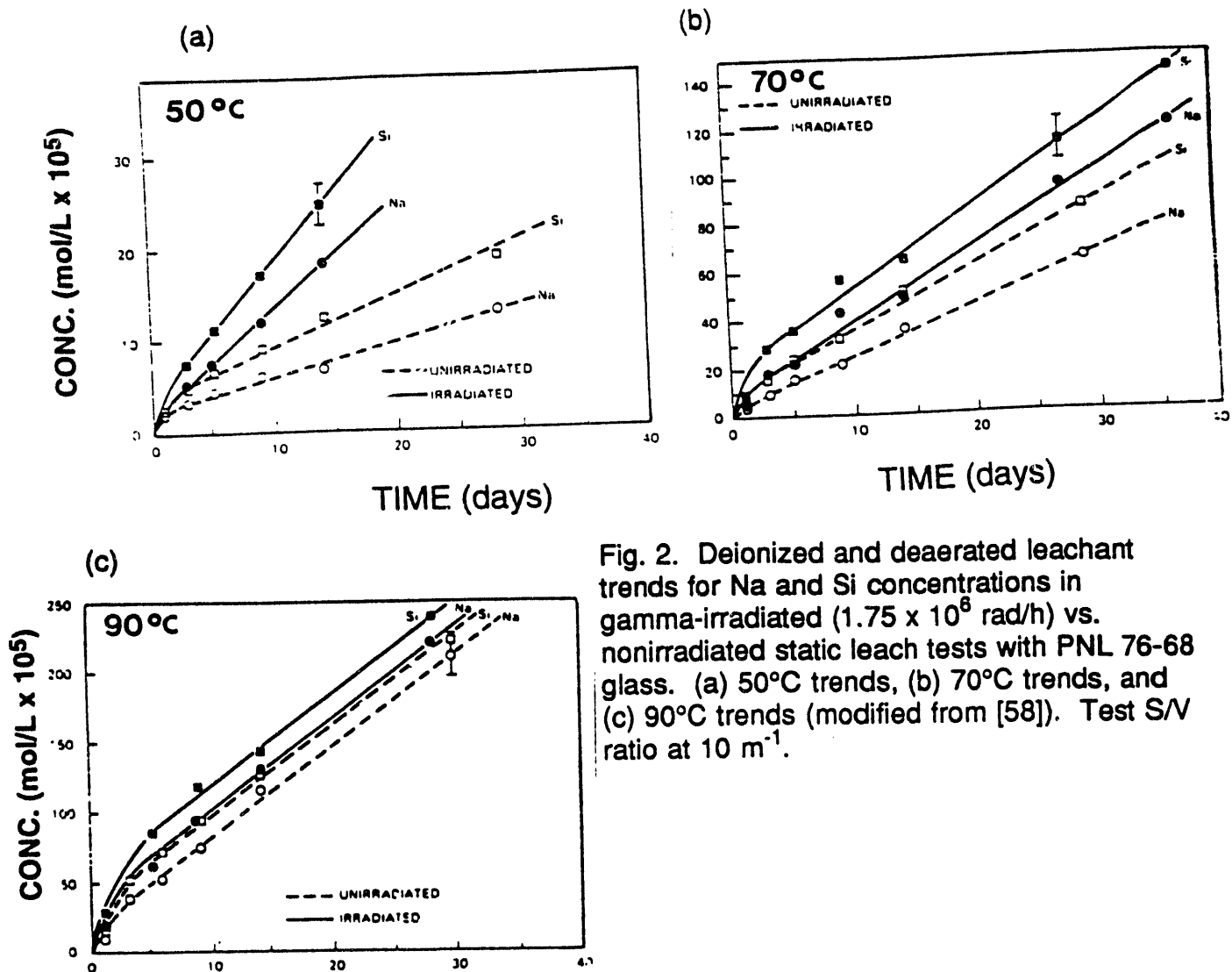


Fig. 2. Deionized and deaerated leachant trends for Na and Si concentrations in gamma-irradiated (1.75×10^6 rad/h) vs. nonirradiated static leach tests with PNL 76-68 glass. (a) 50°C trends, (b) 70°C trends, and (c) 90°C trends (modified from [58]). Test S/V ratio at 10 m^{-1} .

the preferential release of decay products from glass samples has also indicated preferential release of ^{228}Th relative to the ^{232}Th parent isotope [55].

Eyal and Olander [57] showed that less than 4% of the total Ra released from monazite samples over a 6.8-year test period was directly ejected from the $\sim 1 \mu\text{m}$ solid particles directly by alpha-recoil processes. Burns et al. [6] have also calculated that the number of atoms released by direct recoil represent a negligible fraction (1.5×10^{-21}) of the total alpha decays in the glass.

In experiments where H_2O_2 was added in concentrations similar to levels expected during radiolysis, no measurable increase was noted in glass dissolution rates [24]. Burns suggested that the two most likely transient water radiolytic products responsible for accelerated glass leaching are the hydroxyl radical ($\cdot\text{OH}$) and the molecular oxygen anion (O_2^-) with the former being favored as the dominant species because gamma radiolysis favors both radical species production and accelerates glass dissolution more than an equivalent dose exposure of alpha radiation [6,58].

Increases in redox potential may also lead to solubility changes for redox-sensitive elements such as actinides and some transition metals [5]. Nash et al. [60]

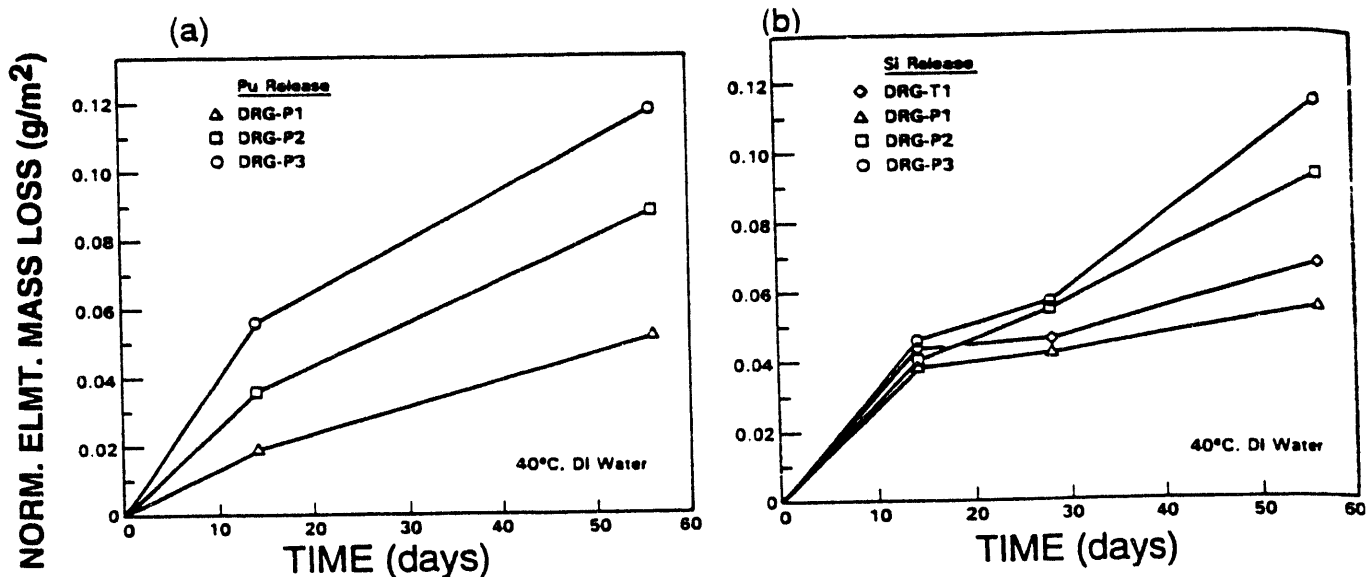


Fig. 3. Normalized elemental mass loss from borosilicate glass in deionized water MCC-1 static leach tests as a function of time and alpha activity. Sample dopant levels (in oxide wt.%) as follows: DRG-T1, 1.0% $^{232}\text{ThO}_2$; DRG-P1, 1.0% $^{239}\text{PuO}_2$; DRG-P2, 0.9% $^{239}\text{PuO}_2$ + 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 [71]).

investigated the redox controls on Pu and Am dissolution and found that for irradiated tests, Pu and Am release rates in deionized water at 25°C were two- to three-fold greater than for corresponding tests where glass disks were exposed to nonirradiated, dilute nitric acid solutions.

Boult et al. [74] irradiated alpha-doped glasses at 20°C for periods of one, two, and three years prior to their being exposed to leachant solutions in a Soxhlet leach test. Results indicate that total sample weight loss increased about 50% for glasses irradiated for two years (about 4.7×10^{18} cumulative alpha decays/cm³) relative to glasses irradiated for one year (about 2.5×10^{18} cumulative alpha decays/cm³). No additional weight loss was observed for glasses subjected to three years of irradiation (about 7×10^{18} cumulative alpha decays/cm³), an observation consistent with a solid damage saturation dose of 5×10^{18} alpha decays/cm³ [16].

Dran et al. [75] irradiated several types of glass with low-energy Pb ions to simulate the damage effects of recoil nuclei generated by alpha decay. In subsequent etching tests, pit development increased in damaged glass by a factor of 50-fold or more over undamaged glass. Burns et al. [6] noted that the ion-irradiation studies of Dran et al. did not simulate a realistic waste form scenario because the intense ion beam produced overlapping zones of excessive damage and the glass did not have time to thermally anneal during the few minutes that the tests were run. Also, the growth of stress has been found to be greater for ion tracks that act on a planar surface, relative to an equivalent fluence resulting from internal alpha decay [76].

Several studies have utilized both 2-3 MeV electrons and 0.5 MeV electrons to simulate the damage to waste glass as a result of beta irradiation [6,77,78]. Subsequent corrosion tests did not show any detectable increase in elemental release rates for the irradiated samples relative to nonirradiated glasses. A single exception was reported for the high cumulative dose (3×10^{11} rad), low-energy electron-irradiated samples, where relative weight loss increases were less than two-fold after a total fluence of 10^{19} e-/cm² (Marples, unpublished data; referenced in Burns et al. [6]).

Comparative tests between fully radioactive and simulated glasses were evaluated as a function of time (through one year), leachant composition, temperature, leachant flow, and the presence of engineered barrier system components [79,80]. Results for the simplest test comparison (deionized water, Ar atmosphere, static, S/V ratio of 1100 m⁻¹) showed that the B and Si release rates were about 50% greater from the fully radioactive glass than from the simulated glass 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 Ar-atmosphere conditions of these tests. The release rates of the radionuclides Tc, Np, Pu, and Am were compared for fully radioactive glasses and actinide-doped simulated glasses with compositions representative of Magnox and THORP processes [81-83]. The differences in release rates were between two (Tc) and 75 times (Am), with the higher release rates from the fully radioactive glass.

To evaluate the behavior of fully radioactive glass under variable S/V conditions, the reaction of simulated vs. fully radioactive glasses were compared under static conditions at 90°C at S/V ratios of 340, 2000, and 20,000 m⁻¹ [84]. The differences in reaction rates between the simulated and fully radioactive glass were initially small, but beyond 182 days, the simulated 200 composition glass displayed an increase in release of soluble components (B) and the formation of distinct set of secondary mineral phases. During this period, the radioactive glass did not show any concomitant increase in B release or secondary phase nucleation. These results may be due to a slightly lower pH in the fully radioactive tests, which lowers the solubility of silica in solution and inhibits the onset of rapid glass reaction.

Radiation exposure of glasses under the high S/V conditions that exist when glass is exposed to saturated air-steam leads to rapid concentration of radiolytic products in the relatively limited amounts of water condensed on the glass surface [13,85]. Wronkiewicz et al. [13] performed irradiated tests to examine the effect of both gamma and alpha radiation at bounding levels that would exist during HLW glass storage. Alpha radiation effects were studied by exposing a saturated air-vapor environment to an alpha field of about 5×10^3 rad/h generated by an inert metal foil doped with ²⁴¹Am, while gamma tests were performed with an external ⁶⁰Co source. These studies demonstrate that both gamma and alpha fields are effective in radiolytically producing nitrogen acids in moist air, and these acids become concentrated in the small volume of liquid present.

The resultant effect of radiolytic products on glass weathering has been examined by Wronkiewicz et al. [86,87]. Tests were conducted using glass doped with Am, Pu, and Np, and the glass being exposed to a saturated air-steam

environment in an external gamma field of about 5×10^3 rad/h. In these tests, the bicarbonate present in the small volume of condensed water was quickly overwhelmed by nitric acid produced in radiolytic reactions. Any nitric acid that subsequently accumulated on the glass surface reacted with the glass, significantly accelerating the glass corrosion process. Alteration layer development was observed to occur four times faster for irradiated SRL 131 glasses [87] and 10 to 15 times faster for irradiated SRL 202 glasses [86], relative to corresponding tests run without radiation. The total quantity of secondary alteration products on the glass surface increased and the paragenetic sequence development was also accelerated due to radiation exposure [86-88]. Similar effects of acidic species accelerating glass reaction under weathering conditions have also been observed in controlled atmosphere studies of historical window glass [89].

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