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Radioactive Waste Storage Materials: Their α-Recoil Aging

Abstract. *Ion implantation experiments suggest that the accumulation of α-recoil damage in radioactive waste storage materials, which behave like solid-state track detectors, plays a drastic role in their long-term degradation. The understanding of α-recoil "aging," overlooked in earlier studies, offers new guidelines for improving waste storage conditions.*

The leach resistance of solidified radioactive waste materials in groundwaters is often invoked as a critical factor for the long-term isolation of high-level radioactive wastes in the environment (*1*). Many phenomena influence leach resistance. This work is concerned with the effects of radiation on the chemical reactivity of solid waste glasses (*2*).

In earlier work designed to evaluate the importance of irradiation effects, the role of α, β, and γ radiation was investigated primarily by loading short-lived radionuclides into the material under evaluation. The experiments simulated in a few years the radiation damage that would occur in the high-level waste form in ~ 1000 years (*3*). Results were reported showing that α, β, and γ radiation do not markedly decrease the materials' leach resistance (*4*). In this report we argue that these simulation experiments clearly overlooked the drastic effects due to heavy recoils emitted during the α-decay of actinide elements (α-recoils) that suddenly appear after ~ 2000 years of storage.

The new consideration underlying our work stems from the realization that most storage materials that have been investigated so far (glasses, ceramics, cements) also register particle tracks, like dielectric minerals exemplified by mica. When such materials are used for the storage of high-level radioactive wastes, most of the damage should result from the accumulation of the very short damage paths of α-recoils. This premise, which neglects the contribution of α, β, and γ radiation, is indeed supported by both experimental observations (*5*) and the predictions of our new model of etchable tracks in dielectric minerals (*6*). Consequently, the alteration of the bulk properties of the α-recoil–irradiated material can be described in terms of the stability of α-recoil damage paths against various environmental parameters. Our predictions are based on our new track model and the results of ion implantation experiments.

These experiments may be schematically described as follows.

1) Over the storage periods of interest (~ 100,000 years), actinide atoms, trapped in the storage material, decay by emitting a single low-energy ($E \sim 0.5$ keV per atomic mass unit), heavy (mass ~ 240 amu) α recoil. This triggers an "internal" ion implantation of the storage material, which should be well simulated by an external beam of 0.5 keV/amu ^{238}U ions. However, in the present work we used lead ions of higher energy ($E \sim 1$ keV/amu). Indeed, these lead ions are much more easily accelerated than uranium nuclei, and we have verified that the increased incident ion energy affects only the depth of the implanted layers and not their etching rates.

2) A polished section of the material under evaluation is covered with an electron microscope grid and then exposed to the beam of lead ions, thus delineating a periodic succession of irradiated and nonirradiated areas. The irradiated areas extending up to a depth of ~ 500 Å (Fig. 1), should be similar to an internal ultrathin slice of the real storage material, where waste elements are homogeneously dispersed. By varying the incident ion fluence (Φ_i) from 10^{10} up to 10^{14} ion cm^{-2}, storage periods (T_s) ranging from 1 to 10^6 years can be continuously simulated (*3*).

3) After a given chemical etching, one can measure depth differences between the two types of areas with an accuracy of ~ 10 Å by probing the etched surface with a diamond stylus device (Fig. 1) and averaging the measurements for a large number of individual areas. These depth differences directly scale the increase in the chemical reactivity of the irradiated material, $\Delta v^* = v^* - v_0$, where v^* and v_0 are the etching rates of the irradiated and nonirradiated material, respectively. The variation in Δv^* can be investigated as a function of several parameters (for example, Φ_i or leaching conditions), that define specific storage conditions.

4) One can then evaluate the variations of v_0 with the leaching conditions by observing with a high-voltage electron microscope the shrinking of micrometer-sized crushed grains or glass fibers, or both, upon chemical etching.

In this work we applied this microscopic approach to three types of glasses: (i) "low" silica (64 percent SiO$_2$) borate glass, similar to a type already in use; (ii) "intermediate" silica (75 percent SiO$_2$) glass; and (iii) "high" silica (100 percent SiO$_2$) glass. The last two of these types of glasses have not as yet been

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Table 1. Values of Δv^* and lifetimes for three types of glasses.

Type of glass	Composition (% by weight)	Δv^*† (Å/hour)	Lifetime of a rod 0.5 m in diameter‡ (years)
Low silica	SiO_2, 64 B_2O_3, 12 Na_2O, 24	2700	105
Intermediate silica	SiO_2, 75 Na_2O, 11 CaO, 9 MgO, 3	200	1.4×10^3
High silica	SiO_2, 100	0.2	1.4×10^6

†These Δv^* values refer to glass etched in a NaCl solution (250 g liter^{-1}) heated to 100°C. ‡In this evaluation we have only taken into account the α-recoil-induced enhancement of the etching rate after a storage period of ~2000 years corresponding to a fluence of 10^{13} lead ions per square centimeter.

used for storage purposes. Our preliminary findings and conclusions are:

1) The etching rates of all irradiated glasses undergo a drastic > 20-fold increase when the α-recoil damage paths start overlapping, for ion fluences in excess of a critical value, $\Phi_c \sim 5 \times 10^{12}$ ion cm^{-2}, which corresponds to an "equivalent" storage time (T_c) of ~ 2000 years (*3*). On the other hand and in agreement with earlier investigators (*4*), we find that $\Delta v^* = 0$ when $T_s < T_c$. This unexpected variation of Δv^*, which then steadily increases from Φ_c up to 10^{14} ion cm^{-2} ($T_s \sim 10^6$ years), should considerably shorten the lifetime of glasses already stored for a period $T_s \gtrsim T_c \sim 2000$ years (Table 1).

2) After a thermal annealing of 2 hours at 400°C, the Δv^* values decrease to negligible values in the three glasses as a result of the annealing of α-recoil damage paths. However, this laboratory annealing temperature is already too high to allow the improvement of storage conditions by relying on the natural annealing of α-recoil damage in the storage site (temperatures can hardly be higher than 70°C).

3) The complex effects of the composition of the leaching solutions were not sufficiently investigated before, and the extrapolation of the results of previous leaching experiments to natural environments is highly questionable for several reasons. (i) The highly damaged material produced in the storage glasses when $T_s > T_c$ is much more chemically reactive than the nonirradiated material and thus behaves like a gigantic nuclear particle track in insulators. Consequently, the etching rate of such a "track" is expected to be extremely sensitive to the presence of trace elements, including those released in the leaching solution by the storage glass itself and the metallic container. Indeed, we have observed that the Δv^* value of the intermediate-silica glass is about 15 times lower in seawater than in distilled water containing the same concentration of NaCl. Furthermore, the etching rate of the high-silica glass is at least 1000-fold higher in a solution of carnallite (250 g liter^{-1}) than in a NaCl solution of the same concentration. (ii) The leaching of alkali-rich glass in a confined environment triggers an increase in the *p*H of groundwater solution in contact with the glass. As we noted a 10-fold increase in Δv^* when the *p*H of the NaCl solution varied from 6 to 10.7, we wonder whether such confined environments should not be avoided, for example, by showering storage glasses in a controlled way in order to prevent the formation of high-*p*H spots on their surfaces. (iii) A 10-fold increase in the Δv^* value is observed when the concentration of NaCl varies from 30 to 250 g liter^{-1}. Thus salt mines, where such high-salinity waters could accidentally evolve, are probably not as safe storage sites as was previously thought.

The simulation experiments discussed in this report are only directly relevant to storage materials where the radioactive elements are homogeneously dispersed and not heterogeneously embedded into the host matrix as "remnants" of oxide particles. (Such heterogeneous matrices are possibly more stable than the homogeneous ones, because α-recoil damage would be limited to an ultrathin skin of glass surrounding the oxide grains that would thus be efficiently shielded in an unirradiated matrix.) Furthermore, one major limitation of these experiments is that we did not consider the contribution of other important effects such as the formation of helium bubbles, the fracturing of glass, and the devitrification of glass (*7*). For example, if the specific area of fractures reaches a plausible upper limit of 0.20 m^2 g^{-1} (*8*) at the end of the glass-casting process, then the lifetimes reported in Table 1 should be further reduced by a factor of 100. Nevertheless, the extreme sensitivity and versatility of our microscopic approach are unique advantages that should greatly help in identifying "best choice" characteristics, when one considers possible combinations of storage material (glass, cement, thorianite, synthetic rock) and storage conditions in natural environments.

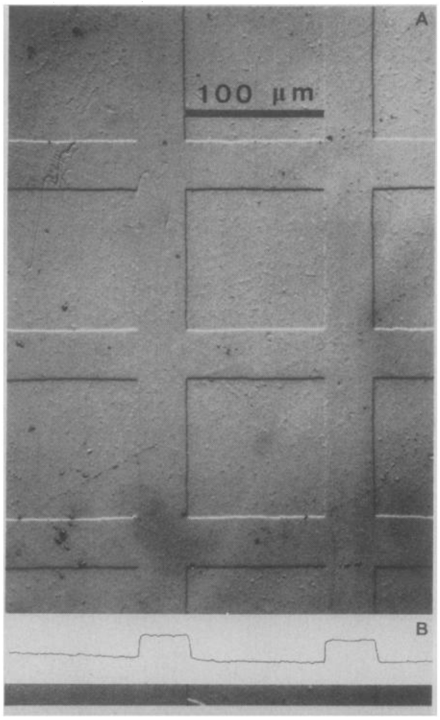

Fig. 1. (A) Micrograph of a glass surface obtained with the phase-contrast attachment of an optical microscope. This surface was covered with an electron microscope grid, irradiated with 10^{13} lead ions per square centimeter, and subsequently etched for 2 hours at 100°C in a NaCl solution (250 g liter^{-1}). The print of the electron microscope grid reflects the enhancement of the etching rate of the irradiated square areas of the glass with sizes of ~ 100 μm^2. (B) The corresponding depth profile obtained with the diamond stylus device. Each step corresponds to a depth difference of ~ 500 Å.

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2. As we are strongly encouraged by the French Atomic Energy Commission, which presently relies on glass for storing high-activity wastes, our preliminary work was aimed at glass.
3. The evaluation of the equivalent storage time, T_s, reported in the present work is relevant to wastes originating from a pressurized water reactor after a 3-year period of operation at 1 GW. These wastes are stored in a glassy matrix where the number of α decays per gram of storage material reaches a level of ~ 1.2×10^{18} g^{-1} after 10,000 years.

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8. An extensive fracturing of the storage glass probably results from the cold-water showering of their host metallic containers, which is intended for decontamination purposes. We have evaluated an upper limit for the contribution of this effect by dropping into cold water a hot (500°C) chunk of glass loaded with a 0.5 percent (by weight) uranium. The use of a scanning electron microscope to both measure the size distribution of the residual fragments and evaluate their degree of residual fracturating yields the value of 0.20 $m^2 g^{-1}$.
9. We thank Dr. R. Klapisch, G. Goutière, and J. Chaumont for their active interest. Supported by the Commissariat à l'Energie Atomique.

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A New Irradiation Effect and Its Implications for the Disposal of High-Level Radioactive Waste

Abstract. *Materials containing alkali metals or alkaline earths are sensitized by bombardment with either ions, electrons, or photons to chemical attack by atmospheric moisture. The implications of this effect on the proposed immobilization and long-term storage of high-level nuclear waste in glass or similar materials is discussed.*

Recent observations in this laboratory have led to the recognition of a new mechanism, through which a large range of materials containing alkali metals or alkaline earths can be rendered susceptible to chemical attack and breakdown by atmospheric moisture. As reported in (*1*, *2*), this degradation process can be induced by particle bombardment or by irradiation with energetic photons, and the effect has been shown to occur both in ionic crystals and in glasses. Although the breakdown mechanism was discovered in the course of experiments quite unrelated to the problem of nuclear waste disposal, the fact that it is effective in vitreous as well as in crystalline materials has obvious implications for the current proposal to incorporate high-level radioactive waste in massive glass blocks for permanent storage. It is the purpose of this report to draw attention to these implications and to point out the need for further investigation before this disposal technique is adopted.

The various chemical reactions in the breakdown process will occur only if they are promoted at catalytically active centers on the surface of the material. These centers are activated by the irradiation at sites of suitable structural irregularity, such as may occasionally be produced by incidental mechanical surface damage. In crystalline materials the sites are primarily associated with crystallographic ledges (*1*), whereas in vitreous substances they are usually found at the boundary between separated phase particles and the main matrix of the glass (*2*). To achieve activation, the sites must receive a minimum irradiation dose *D*, enabling them to act as locations for electron transfer, so that a cation M^+, which diffuses from its normal position in the solid to an active center, can there be neutralized to an atom M.

I shall illustrate the degradation mechanism by discussing the breakdown of a simple sodium silicate glass. As a first step, let us consider Na^+ associated with a nonbridging terminal structure of the well-known type $[\text{-Si-O-Si-O}^-Na^+]$ within the silica network. Even at room temperature Na^+ is fairly readily detached by the application of heat, although detachment can also be effected by irradiation, which may thus act in a second role, additional to its function in the activation of catalytic centers.

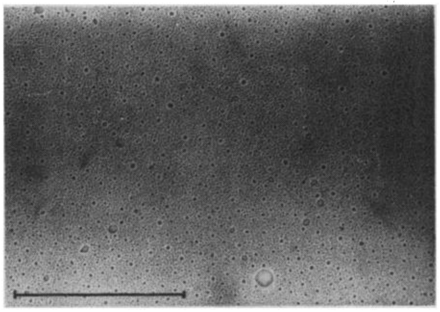

Fig. 1. Corrosion sites on crown glass (Schott type B 270). The photograph was taken 24 hours after exposure to laboratory air, following bombardment by 1.6-keV Ar ions. The bombardment intensity was 2.5 × 10^{14} ions per square centimeter per second; the total ion dose was 1.5 × 10^{17} ions per square centimeter. Scale bar, 100 μm.

After electron transfer at an active site, to which the ion has diffused, the now neutral Na atom will react with atmospheric moisture according to the reaction

$$Na + H_2O \rightarrow NaOH + H \uparrow \qquad (1)$$

yielding H_2 as a gaseous reaction product. The terminal structure, now truncated by removal of the Na^+, acts effectively as a cation that dissociates another H_2O molecule in the reaction

$$[\text{-Si-O-Si-O}^-] + H_2O \rightarrow [\text{-Si-O-Si-OH}] + OH^- \qquad (2)$$

At a suitable surface site the OH^- radical formed in this way is able to break a siloxane bond in the continuous network of the glass, a reaction represented by

$$[\text{-Si-O-Si-}] + OH^- \rightarrow [\text{-Si-OH}] + [\text{-Si-O}^-] \qquad (3)$$

The $[\text{-Si-O}^-]$ thus produced now reacts with another H_2O molecule in the manner of Eq. 2, so that a cyclically repeated corrosion reaction is set into motion.

A similar process takes place with alkali metals other than Na and, with a slight modification, also with the alkaline earths. Apart from the evolution of H_2, the overall result is the formation of products that are not only water soluble but also readily detachable from the bulk of the glass. This is clearly undesirable; particularly since, when we are dealing with a waste storage glass, among the major constituents of these soluble degradation products will be substances such as ^{137}Cs and ^{90}Sr, whose immobilization the glass is intended to ensure and which contribute a large portion of the total radioactivity within the waste during the first 100 years or so of its storage (*3*).

To illustrate the degradation effect, Fig. 1 shows the accumulation of corrosion sites on the surface of a crown glass (Schott type B 270). As discussed in (*2*), the decomposition occurs preferentially at the location of minority phase particles, and since in the multiconstituent glasses now under investigation for waste storage, phase separation is very pronounced (*4*-*9*), the irradiated glass surface is likely to be rich in areas susceptible to attack. One important class of phases known to exist in these materials is the molybdates, arising from the reac-

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