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ARTICLE OPEN



Alpha dose rate and decay dose impacts on the long-term alteration of HLW nuclear glasses

Magaly Tribet¹✉, Caroline Marques¹, Sarah Mougnaud¹, Véronique Broudic¹, Christophe Jegou¹ and Sylvain Peugot¹

In the prospect of deep geological disposal, the long-term behavior of high-level nuclear glasses has to be investigated regarding alpha radiation induced by long-life minor actinides. The present study focuses on the effects of alpha radiation on the long-term chemical reactivity of R7T7-type glasses, by separately considering the alpha dose rate and the alpha decay dose. Old SON68 glasses doped with $^{238/239}\text{PuO}_2$ or $^{244}\text{CmO}_2$ were studied to simulate high alpha dose rates corresponding to an early water ingress and a high level of alpha decay doses corresponding to long-term disposal conditions. A part of the $^{238/239}\text{Pu}$ -doped glass block was annealed to fully recover the irradiation-induced damage accumulated since the glass was fabricated and to dissociate the effect of the alpha dose rate from that of the alpha decay dose. The glasses were then leached under static conditions at 90 °C for several years. The results showed that the residual alteration rate is not affected by the alpha dose rate over a wide range of dose rate values expected under disposal conditions: this glass remained relatively insensitive to the alpha radiolysis phenomena at the glass–water interface. However, over the duration of the experiments, the residual alteration rate of the damaged $^{238/239}\text{Pu}$ -doped glass was enhanced compared to that of the annealed glass. This result is in agreement with those obtained on the ^{244}Cm -doped glass and with reported values in the literature on simplified externally irradiated glasses, indicating that the ballistic effects of the recoil nuclei are responsible for this increase in the residual alteration rate.

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INTRODUCTION

Several countries have chosen to recycle U and Pu in UOX and MOX fuels, and to vitrify the ultimate high-level radioactive waste (HLW) composed of fission products and minor actinides in silicate glasses. In France, the borosilicate glass called R7T7 is currently used to confine the HLW remaining after spent nuclear fuel reprocessing and destined for geological disposal. The safety of such repositories relies on a multi-barrier approach, based on the properties of the glass, metallic containers, and host rock. The physical and chemical stabilities of the glass over a geological timescale must thus be verified by studying the glass response to radiation emitted by the nuclear waste and its behavior when submitted to water dissolution¹.

The alteration of SON68-type glass (which is the non-radioactive surrogate of R7T7 glass) has been extensively studied since the 1980s. The fundamental leaching mechanisms of this type of glass, such as water penetration and interdiffusion^{2–5}, hydrolysis of the bonds of the glass network^{6,7}, condensation of the hydrolyzed species^{7–9}, and precipitation of secondary phases in certain cases^{9,10} are relatively well described. In the long term under disposal conditions, the alteration solution is expected to be poorly renewed, which will lead to an increase of the poorly soluble glass former elements (Si, Al, Zr...) in solution and the formation of a protective alteration layer at the glass surface. The glass will thus dissolve very slowly, by what is called the residual alteration rate regime¹¹. However, the fundamental mechanisms by which the alteration layer forms and the rate-limiting reactions governing this residual alteration rate regime are still debated and two main models are described in the literature^{7,12–18}. First, simultaneous hydrolysis and precipitation mechanisms at the glass–water interface are proposed in the interface-coupled dissolution-precipitation (ICDP) model^{7,13–15}. Such mechanisms lead to inward progress of the leaching front and formation of the

so-called surface alteration layer (SAL). In this model, the residual glass alteration is controlled by this SAL. Second, interdiffusion and ion exchange with water ($\text{H}^+/\text{H}_3\text{O}^+$), followed by progressive in situ hydrolysis and subsequent recondensation^{8,12,16–18} are the proposed mechanisms to explain the formation of the alteration layer. In this last case, the alteration layer region, also called gel, is constantly reorganized over time^{8,19} and acts as a diffusive barrier. Actually, this is the transport-limiting factor of this barrier which explains the residual alteration rate regime.

Furthermore, the specificity of HLW nuclear glasses is their radioactivity lasting over time and which has to be taken into account to accurately describe the glass aging under disposal conditions. Most studies on the radiation impact on long-term leaching behavior focused on the impact of beta and gamma radiation^{1,20–22}. However, some recent results evidenced the predominant role of alpha decay of minor actinides on the long-term radiation component, and assessed its impact on the glass structure and properties^{1,23–25}. Such results thus highlighted the need for improved evaluation of the impact of this kind of radiation on glass leaching.

Due to the various complexities associated with the radioactive specimen handling and characterization, external ion irradiation is commonly used to simulate the effects of self-irradiation damage^{25,26}. However, in such experiments, ion irradiation and leaching cannot occur simultaneously: the glass is first irradiated and then leached, whereby it is observed that the alteration behavior of borosilicate glasses can be modified by prior external irradiation by heavy ions^{24,26–28} specially during the residual alteration rate regime^{24,26,27}. Radiation damage induced by ion irradiation was found to induce the formation of an alteration layer approximately four times thicker than for non-irradiated glass leached under the same conditions²⁷. The increase in the alteration layer thickness with irradiation dose was attributed to

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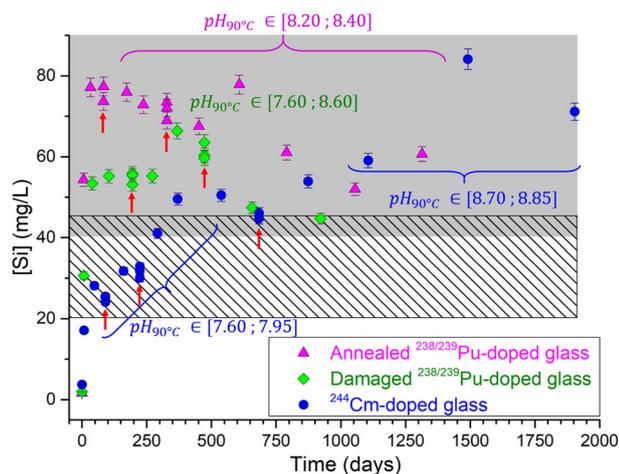


Fig. 1 Si releases and pH evolution versus time for doped glasses leaching tests. Total silicon concentration versus time for annealed and damaged $^{238/239}\text{Pu}$ -doped glass leaching tests (pink triangles and green diamonds, respectively) and ^{244}Cm -doped glass leaching test (blue circles). pH ranges at 90 °C, calculated from measured pH at 25 °C, are detailed for each test in order of magnitude. The gray and hatched areas correspond to saturation values of SON68 glass with respect to orthosilicic acid (H_4SiO_4), based, respectively, on Gin et al.⁴¹ or on Jegou et al.⁵⁰ for a $\text{pH}_{90^\circ\text{C}} \leq 8.97$. Red arrows indicate sampling with filtration and ultrafiltration to check for colloids. Errors bars are of 3%.

the effects of nuclear collisions that change the structural and mechanical properties of the material, enhancing the leach rate^{24,27}. The rate of altered layer growth diminished with time for both irradiated and non-irradiated glasses, with square root of time dependency; this indicates that a diffusive mechanism occurs irrespective of the radiation condition²⁷.

Recent solid-state characterization of irradiated and then altered samples²⁶ shows that radiation damage can accelerate the maturation of the alteration layer, leading to a porous gel-like microstructure. This observation and the kinetics enhancement previously mentioned²⁷ are concomitant, but no link between these two statements is established. Moreover, a higher reactivity in ^{18}O (from enriched water) and ^{16}O (from OH or water contained in the alteration layer) exchanges at 25 °C is also observed in pre-irradiated glasses within the reactive interface, compared to the boron and alkali-depleted silica-rich gel layer (where no higher reactivity is reported). Furthermore, experiments performed on heavily altered glasses²⁹ have shown that ballistic collisions from ion implantation could heal the porous gel part of the altered glasses to create a pore-free homogeneous microstructure. These results demonstrate that the nuclear decay dose affects the alteration layer, and hence, the residual alteration rate, but the precise origin of these effects has not yet been clearly established.

For radioactive specimens, very few studies that utilize a simplified medium have been reported in the literature^{20,30–35}, and they do not all focus on the residual alteration rate regime nor lead to the same conclusions. In diluted and renewed solutions, neither the alpha dose rate nor alpha decay have been seen to impact actinide-doped SON68 glasses^{30,32–34}, while ‘dramatic’ differences have been recently reported on a simplified Pu-doped glass, subject to a high alpha dose rate ($\sim 8700 \text{ Gy}\cdot\text{h}^{-1}$) compared to the reference experiment on the non-radioactive sample³¹. Only one study on the residual alteration rate regime, which focused on alpha dose rate ($150 \text{ Gy}\cdot\text{h}^{-1}$), has been reported²⁰, and this study concluded that no radiation effect was present.

The current study aimed to assess the impact of alpha radiation on the long-term aqueous behavior of alpha-doped SON68 radioactive glasses by considering the effects of alpha dose rate

and alpha decay dose separately. An old, damaged $^{238/239}\text{Pu}$ -doped SON68 glass was used because of its significant alpha decay dose considering the structural modifications ($14 \text{ MGy}_{\text{nucl}}$)²³ and its alpha dose rate considering its doping in $^{238/239}\text{Pu}$ (a value of $3500 \text{ Gy}\cdot\text{h}^{-1}$ is expected in R7T7-type glass few decades after elaboration). A leaching experiment was also performed under the same conditions on a ^{244}Cm -doped SON68 glass (alpha decay dose of $35 \text{ MGy}_{\text{nucl}}$ and alpha dose rate of $23,500 \text{ Gy}\cdot\text{h}^{-1}$) to complete the alpha radiation description. The dissociation of the radiation parameters (dose rate versus decay dose) on the leaching behavior was achieved by annealing a part of the $^{238/239}\text{Pu}$ -doped glass to fully recover the irradiation-induced damage; the annealed glass had the same alpha dose rate ($3500 \text{ Gy}\cdot\text{h}^{-1}$) as the non-annealed one, but a very low alpha decay dose ($<0.1 \text{ MGy}_{\text{nucl}}$). Actually, the damage on this annealed glass remained low enough for years, which allowed a targeted study of pure radiolytic effects on the long-term glass leaching behavior.

RESULTS AND DISCUSSION

Details of leaching experiments, including reference experiments, are given in the Leaching device and conditions section.

pH and total silicon concentration stabilization in the leachates

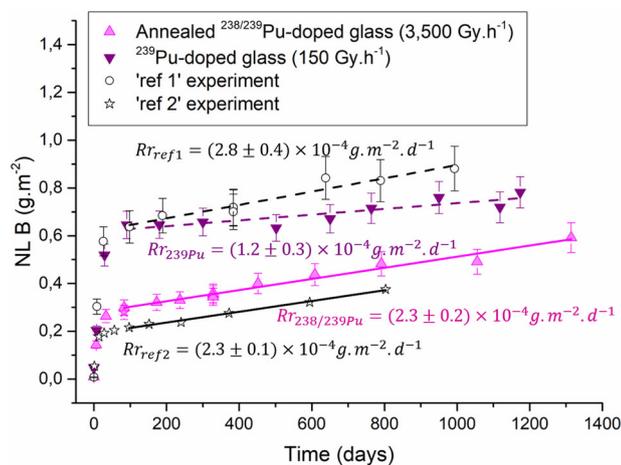
The pH ranges measured in the doped glass leaching tests and then calculated at 90 °C are presented in Fig. 1. They are compared to the $\text{pH}_{90^\circ\text{C}}$ values measured in the reference experiments, which were in the range of 9.25 ± 0.30 (‘ref. 1’ experiment) and 8.95 ± 0.30 (‘ref. 2’ experiment). For these systems under irradiation, the measured pH is around 0.5–1 pH unit lower than those measured in the reference experiment leachates; however, once the silicon releases are stabilized, the pH values also remain stable over time. This acidification of the irradiated glass leachates has already been observed in pure water in previous studies^{36–38} and under environmental conditions^{39,40}. This could be due to radiolysis effects, mainly air radiolysis, which is known to induce nitric acid production in solution³⁶. This could occur when the glass powders were transferred in water from the preparation cell to the leaching cell before the closure of the titanium reactor and the beginning of the experiment. However, in this pH range (8.0–9.5), no effect of the pH value on the residual alteration rate regime was expected, according to the literature⁴¹.

The concentration of silicon first increased in the leachates and then stabilized after less than 100 and 400 days for $^{238/239}\text{Pu}$ -doped glasses and ^{244}Cm -doped glass, respectively. The time necessary to reach this stabilization varied for the ^{244}Cm -doped glass, which may be attributable to its radiological characteristics (Table 1), composition (very slightly different from the other glasses studied here, see Supplementary Table 1 in Supplementary Data), and the particle size distribution of the prepared powder, which could be slightly coarser. The last two factors could cause a slight delay in reaching the residual alteration regime. Thus, the residual alteration rate regime was considered to be reached after 100 and 400 days for the $^{238/239}\text{Pu}$ -doped and ^{244}Cm -doped glasses, respectively.

Once stabilized, the Si concentrations in solution were in agreement with the saturation values of the SON68 glass with respect to orthosilicic acid in solution ($\text{H}_4\text{SiO}_{4\text{aq}}$) proposed by Gin et al.⁴¹ and deduced experimentally under the same leaching conditions (gray area obtained for $\text{pH}_{90^\circ\text{C}}$ ranging from 7 to 9.5, in Fig. 1). Furthermore, no colloids were observed by comparing the filtered and ultrafiltered concentrations in solution (corresponding to various Si concentrations, indicated by red arrows in some samplings in Fig. 1). These data indicate that the altered layer properties, in terms of solubility, are not significantly affected by alpha self-irradiation. The present results are in agreement with

Table 1. Alpha dose rate and cumulative dose values of the doped glasses considered in this study.

Alpha-doped glass	Alpha dose rate (Gy h^{-1})	Alpha cumulative dose at the beginning of leaching experiment
0.4 wt% ^{244}Cm -doped glass	23,500	$\sim 3 \times 10^{18} \alpha \text{ decay.g}^{-1}$ –35 MGy_{nucl}
Damaged $^{238/239}\text{Pu}$ -doped glass	3500	$\sim 1.2 \times 10^{18} \alpha \text{ decay.g}^{-1}$ –14 MGy_{nucl}
Annealed $^{238/239}\text{Pu}$ -doped glass		$< 4 \times 10^{16} \alpha \text{ decay.g}^{-1}$ (negligible)
Previously studied ^{239}Pu -doped glass ²⁰	150	$\sim 3.7 \times 10^{16} \alpha \text{ decay.g}^{-1}$ (negligible)

**Fig. 2** Boron releases versus time for doped glasses leaching test and references experiments. Boron normalized mass loss (NL B) versus time for the $^{238/239}\text{Pu}$ - and ^{239}Pu -doped glass leaching tests (pink triangles and inverted purple triangles, respectively) and reference experiments ('ref. 1' with open circles and 'ref. 2' with open stars). The residual alteration rate value (Rr) associated with each experiment is given. Error bars are of $\pm 10\%$ and their calculation is detailed in the "Solution analyses" section.

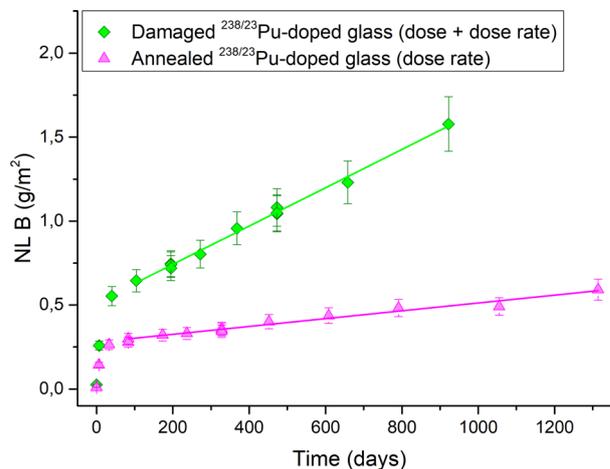
those previously published on the ^{239}Pu -doped glass leachate and are corroborated by SEM/TEM observations of the microstructure of the alteration layer formed on the ^{239}Pu -doped glass, which was similar to that formed on non-radioactive samples²⁰.

Release of tracer elements

Glass alteration can be traced using soluble elements, especially boron, sodium, and lithium, released from the glass into the solution. Supplementary Figs 2–5 in Supplementary Data present the variations in normalized mass losses calculated from these releases for the three radioactive glasses and the reference experiment 'ref. 1' respectively. For each leaching test on actinide-doped glasses, the data show that, similar to non-radioactive experiments (Supplementary Fig. 5), congruence is conserved between the three tracer elements (B, Li, and Na), which indicates that the congruent behavior of these three elements is not affected by alpha self-irradiation. Moreover, the absence of colloids, including B, Li, or Na, was confirmed, and this was in agreement with similar observations in Si as previously described in the last paragraph. Thus, for simplicity, only boron releases are shown in Figs 2, 3, and 4 hereafter.

Impact of the alpha dose rate

The boron releases as a function of time are presented in Fig. 2 for the actinide-doped glasses with very low alpha decay doses, that were subjected to only significant alpha dose rate parameters. The results for the annealed $^{238/239}\text{Pu}$ -doped glass were compared with those of the two reference experiments 'ref. 1' and 'ref. 2' and the previously studied ^{239}Pu -doped glass²⁰.

**Fig. 3** Boron normalized mass loss (NL B) versus time for annealed (pink triangles) and damaged (green diamonds) $^{238/239}\text{Pu}$ -doped glass leaching tests. Solid lines represent residual alteration rate. Error bars are of $\pm 10\%$ and their calculation is detailed in the "Solution analyses" section.

The evolution of the boron releases was very similar for all the experiments: a rate drop was observed after 30–50 days and stationary releases over time attained after ~ 100 days. The boron normalized mass loss values were very close for the experiments on the annealed $^{238/239}\text{Pu}$ -doped glass and non-radioactive glass 'ref. 2' while, by comparison, the boron normalized mass loss values were initially higher for the experiments on the ^{239}Pu -doped glass and reference experiment 'ref. 1'. For glasses of the same composition (the two Pu-doped glasses and the 'ref. 2' glass), this difference could be linked to the absence of the precise knowledge of the specific surface area of the ^{239}Pu -doped glass powder. Indeed, the specific surface area was measured for powders from the non-radioactive glass and the annealed $^{238/239}\text{Pu}$ -doped glass (Table 4). The boron normalized mass loss values were, thus, accurately calculated. Otherwise, the ^{239}Pu -doped glass powder was obtained by re-sieving, between 63 and 125 μm in size, some powder batches prepared in the '1980s' in the Vulcain laboratories at CEA Marcoule. The particle size of this powder was therefore not measured but was assimilated to that of a non-radioactive powder prepared under the same conditions, as detailed in the previous study²⁰. The resulting boron normalized mass loss values were thus less accurate than those of the other experiments. For the reference glass 'ref. 1' boron normalized mass loss values were higher than for the 'ref. 2' experiment, possibly due to the slightly different glass chemical composition (see Supplementary Table 1 in Supplementary Data), which could induce initial releases of tracer elements slightly increased.

It is worth noting that the maximum boron normalized mass loss values (around 1 g.m^{-2}) correspond to an alteration layer thickness of 370 nm. The good correspondence between the thickness expected from the boron releases in solution and the one observed by TEM was previously confirmed on the ^{239}Pu -doped glass²⁰. These TEM characterizations also confirmed that

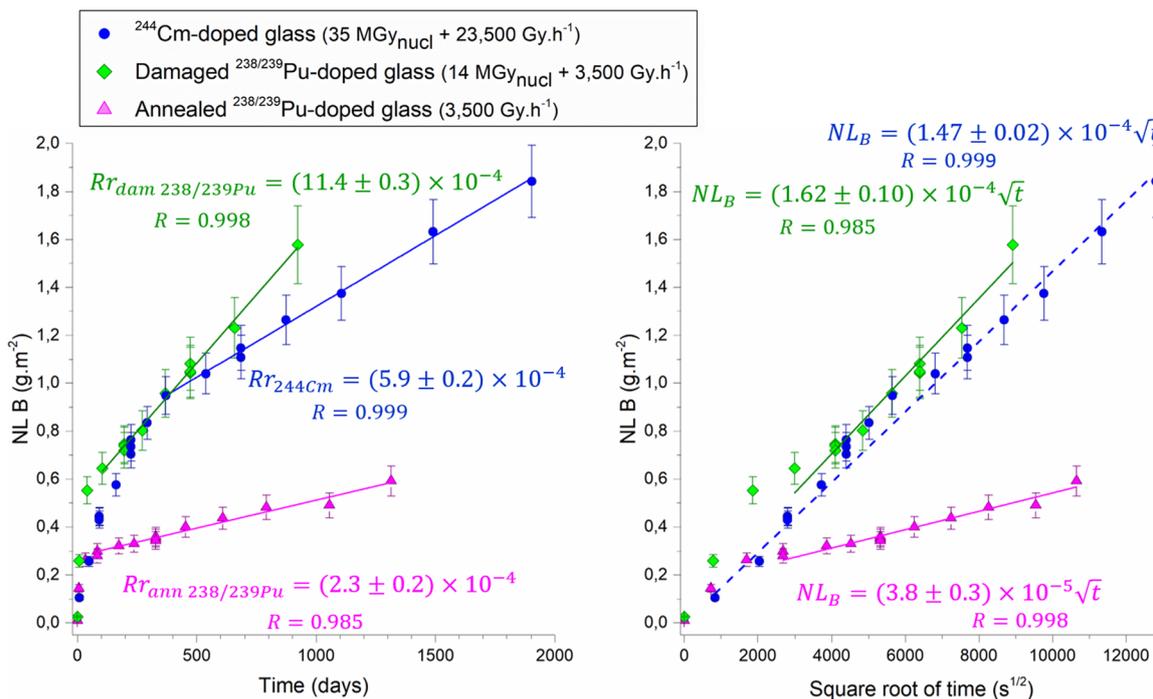


Fig. 4 Time and square root of time dependence of boron releases for the doped glass leaching tests. Boron normalized mass loss (NL B) versus time (a) and square root of time (b), with pink triangles, green diamonds, and blue circles representing annealed $^{238/239}\text{Pu}$ -doped glass, damaged $^{238/239}\text{Pu}$ -doped glass, and ^{244}Cm -doped glass, respectively. In (a), the residual alteration rate values (R) associated with each experiment are given (with the relative Pearson's R-value) and expressed in $\text{g.m}^{-2}.\text{d}^{-1}$. In (b), NL B versus \sqrt{t} can be linearly fitted, either passing through the origin (dashed line) or with a positive y-intercept (solid lines). Error bars are of $\pm 10\%$ and their calculation is detailed in the "Solution analyses" section.

the alteration layer was very adherent to the underlying unaltered glass, as commonly observed on non-radioactive glasses leached under similar conditions (high S/V ratio, no water renewal, for several years).

The residual alteration rates were calculated after stabilization of the tracer element releases in solution, that is, after ~ 100 days for these experiments. They are of the same order of magnitude as the considered experiment, ranging from $(1.2 \pm 0.3) \times 10^{-4} \text{g.m}^{-2}.\text{d}^{-1}$ to $(2.8 \pm 0.4) \times 10^{-4} \text{g.m}^{-2}.\text{d}^{-1}$. Moreover, the mean residual alteration rate values determined from the reference experiments on the non-radioactive glasses were close or even higher compared to those determined from the two Pu-doped glass leaching experiments. It should be noted that the residual alteration rate values with their associated uncertainties are very close in the powders for which the specific surface area has been measured (i.e., all but the ^{239}Pu -doped glass). The slightly lower residual alteration rate value calculated from the boron releases of the ^{239}Pu -doped glass is due to the uncertainty in the glass powder specific surface value and does not reflect any beneficial effect of the low alpha dose rate of this glass. An impact of radiolytic species created by alpha radiation of the leachate close to the glass surface was suspected in the literature to explain higher leaching rates^{34,37}, when the leaching tests were performed in static conditions. By focusing on the results obtained here from glass powders for which the specific surface area has been measured (i.e., all, but the ^{239}Pu -doped glass), as the residual alteration rate of the most radioactive Pu-doped glass (3500Gy.h^{-1}) was not higher than the residual alteration rates of the two reference experiments, it can be concluded that radiolytic phenomena at the glass–solution interface do not seem to modify the overall mechanisms and kinetics of glass alteration. Thus, even under these conditions where radiolytic species can accumulate with time, no impact of alpha radiolysis is expected. Therefore, this result is still in agreement with previous results on the residual

alteration rate regime²⁰, which did not show any alpha dose rate value effect on the kinetics of ^{239}Pu -doped glass. We can therefore deduce that an alpha dose rate of up to 3500Gy.h^{-1} has no impact on the alteration kinetics of a R7T7-type glass in the residual rate regime. The present results allow us to further elaborate on the conclusion drawn in a previous paper²⁰ where the alpha dose rate had no impact on glass leaching behavior. The present study indicates that this is also the case for a higher dose rate value, and therefore, this behavior can be determined to cover a wide range of the alpha dose rate values expected under disposal conditions, even with early water ingress. The present results are also in agreement with those obtained for SON68 glasses altered under gamma irradiation²¹, which means that whatever the irradiation field and related energy deposition values at the glass–water interface⁴², the SON68-type glass remained relatively insensitive to the mechanism by which radiolysis of both the materials (glass, alteration layer) and the water was induced. The hypothesized protective role of pore water in limiting and/or healing the radiation defects created by radiolysis of the solid, as discussed in the literature concerning gamma external radiation of nanoporous glasses^{43,44} and electron external irradiation of simplified glasses and corresponding alteration layers²², is invoked here to explain the absence of a dose rate impact on the alteration behavior of the glass in the residual alteration rate regime. In such conditions, the alteration layer remained very thin ($< 400 \text{nm}$), adherent to the glass and thus, was protecting the glass from further alteration as observed on the non-radioactive glasses altered in the same conditions. Furthermore, these results did not support the 'dramatic' impact of the alpha dose rate reported in one study³¹, which could instead be related to the leaching conditions chosen in that study (aerated conditions, very low S/V, water renewal, and TeflonTM vessel) combined with a different glass composition (higher content of Na) rather than to the alpha dose rate value. Indeed,

the alteration layer developed on that ^{238}Pu -doped glass was thick (10 μm), mechanically unstable, and probably composed of aluminum hydroxide, therefore very different from that expected in this study or the related one²⁰. No data concerning the pH was specified in that publication³¹ and the glass leaching was monitored in solution by the Pu releases, which could not be considered as a tracer element without any experimental comparison with B and Na.

Impact of the alpha decay dose

Since there was no discernible impact of the dose rate for the annealed $^{238/239}\text{Pu}$ -doped glass, the results obtained on the annealed glass were, therefore, taken as a reference for comparison with the doped glasses with a significantly higher alpha decay dose. Indeed, this annealed glass has the same composition as the higher dose damaged glass, and all experiments were performed under exactly the same conditions (shielded cell, titanium leach reactors, radiolysis of glass–water interface).

The evolution of the boron normalized mass losses as a function of time is presented in Fig. 3 for both the damaged and annealed $^{238/239}\text{Pu}$ -doped glasses. The two followed the same trend; the boron release initially greatly increased with time and then tended to stabilize after around 100 days, which indicates the beginning of the residual rate regime with the formation of a protective alteration layer¹. Once the residual alteration rate regime was reached, both the normalized mass loss and residual alteration rate values were significantly higher for the leaching experiment on the damaged glass than those of the annealed glass. This could be due to the alpha decay dose, as this is the only difference between these two experiments (same glass block before annealing and same leaching conditions).

However, in order to complete the reasoning, the results for the annealed and damaged $^{238/239}\text{Pu}$ -doped glasses were compared to those of the ^{244}Cm -doped glass (Fig. 4). The boron release values, as well as the residual alteration rates (slopes), remained higher for the two doped glasses having a significant alpha decay dose (Fig. 4a) than those of the annealed $^{238/239}\text{Pu}$ -doped glass, considered as the reference here. The cumulative dose, prior to the leaching experiment, induced some modifications in the alteration behavior of the glass, which was manifested by an increase in the residual alteration rate values.

Furthermore, a slight decrease in the boron release rate could be observed for the ^{244}Cm -doped glass (Fig. 4). The evolution of the normalized mass loss values was plotted as a function of the square root of time (Fig. 4b). For the three doped glasses considered here, the evolution is linear versus \sqrt{t} either from the beginning of the leaching experiment (^{244}Cm -doped glass) or after a period of time ($^{238/239}\text{Pu}$ -doped glasses). This time period lasted about 90 days (around 2750 $\text{s}^{1/2}$), which corresponds to the period of establishment of the residual alteration rate regime. The non-linearity with \sqrt{t} within the first 90 days could thus be due to the predominance of another mechanism inducing a greater glass alteration for this $^{238/239}\text{Pu}$ -doped glass (annealed and damaged) before the residual regime was established.

Then, as described in the literature, the evolution of the altered glass thickness is consistent with a residual alteration rate regime governed by a global diffusive mechanism^{27,45–47}. Thus, the apparent diffusion coefficient, D_{app} , was calculated from the altered thickness by applying Eq. (1), which was derived from Fick's second law by considering a semi-infinite medium. This apparent diffusion coefficient (in $\text{m}^2\cdot\text{s}^{-1}$) is an overall value, which integrates different mechanisms such as the mobility and reactivity of the species. The D_{app} values, derived from the plots displayed in Fig. 4b, are given in Table 2.

A D_{app} value of $(1.5 \pm 0.2) \times 10^{-22} \text{m}^2\cdot\text{s}^{-1}$, calculated from the leaching experiment on the annealed $^{238/239}\text{Pu}$ -doped glass

Table 2. Apparent diffusion coefficient (D_{app}) calculated from the linear regression obtained by fitting NL B versus \sqrt{t} in Fig. 4b.

	D_{app} ($\text{m}^2\cdot\text{s}^{-1}$)
^{244}Cm -doped glass	$(2.23 \pm 0.05) \times 10^{-21}$
Damaged $^{238/239}\text{Pu}$ -doped glass	$(2.70 \pm 0.30) \times 10^{-21}$
Annealed $^{238/239}\text{Pu}$ -doped glass (acts as reference)	$(1.5 \pm 0.2) \times 10^{-22}$

considered as a reference, is of the same order of magnitude as that reported in the literature for non-radioactive SON68 powders ($1.4 \times 10^{-22} \text{m}^2\cdot\text{s}^{-1}$)⁴⁸ and 5–10 times lower than that obtained on the ISG glass^{27,48}. It is worth noting that this value of $(1.5 \pm 0.2) \times 10^{-22} \text{m}^2\cdot\text{s}^{-1}$ is on the order of magnitude of the values expected for diffusion in solids but still ~ 3 orders of magnitude lower than the water diffusion values previously determined in borosilicate glasses and extrapolated at $\text{pH} = 9$ ⁵, and ~ 50 times lower than the interdiffusion coefficient value calculated in the literature⁴⁹ and used to fit the experimental data on pre-altered SON68 glasses in saturated Si conditions⁵⁰ (90 $^{\circ}\text{C}$, $\text{pH}_{90^{\circ}\text{C}} = 9$, $S/V = 10 \text{cm}^{-1}$). These observations indicate that various mechanisms are involved in this apparent diffusion coefficient.

$$\text{Altered thickness} = \frac{NL_B}{\rho} = 2\sqrt{\frac{D_{\text{app}} \times t}{\pi}} \quad (1)$$

However, D_{app} is 15 to 18 times higher in the damaged radioactive glasses compared to the reference value (Table 2). This increased value calculated for damaged actinides doped glasses is similar to that ($\times 20$) calculated from a leaching experiment performed on gold ion-damaged ISG glasses²⁷. Moreover, the nuclear doses induced by the alpha decays in the damaged $^{238/239}\text{Pu}$ and ^{244}Cm -doped glasses were 14 and 35 MGy_{nuc} , respectively (Table 1), at the beginning of the leaching experiments, and these values are similar to that needed to reach the plateau (i.e., around 14 MGy_{nuc}) in the alteration enhancement described for gold ion-damaged ISG glasses^{24,27}. These similarities suggest that the ballistic effects of the recoil nuclei are responsible for this increase in residual alteration rate observed for the damaged radioactive glasses. However, this increase was slightly lower in the case of the doped glasses than for externally irradiated simplified glasses. This could be explained either by differences in the glass composition and the higher sensitivity of simplified glass compositions toward irradiation²³ or by the partial annealing effect of the alpha particles in the case of alpha decay^{51–54} as described in the literature for various borosilicate glass compositions. Moreover, the slightly lower boron release values seen in the case of the ^{244}Cm -doped glass compared to the damaged $^{238/239}\text{Pu}$ -doped glass were not inconsistent with a higher cumulative alpha decay dose value because the saturation value of 14 MGy_{nuc} ²⁷ was reached for both doped glasses. This observation could, thus, be explained by either the slightly different glass composition or the fact that the specific surface area is not accurately known for the ^{244}Cm -doped glass and could be slightly overestimated.

Origin of the higher alteration kinetics of the damaged glasses

It should be noted that the alpha decay dose and the heavy ion irradiations^{24,27} lead to similar changes in long-term glass alteration behavior. As proposed in the literature^{24,27}, this can be related to the changes in glass structure and properties. This link between glass structure and leaching behavior was also reported recently for glasses with simplified compositions whose structure was modified either by fast quenching^{55,56} or by external irradiation by high-energy heavy ions²⁸. Some authors have

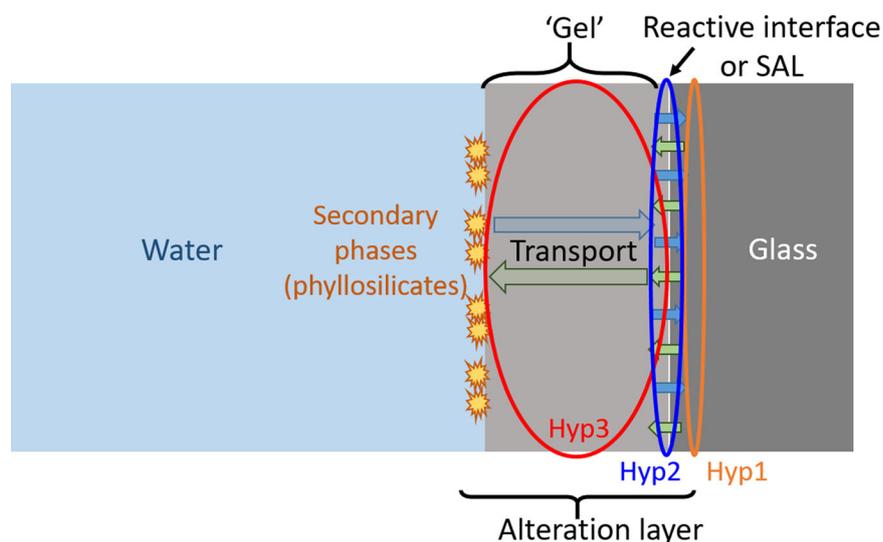


Fig. 5 Schematic of glass alteration layer and three hypotheses detailed in text. The first hypothesis concerns the glass because it involves an initial water penetration. Then, the interdiffusion process induces the transformation of the glass in what is called the ‘reactive interface’.

highlighted the role of the B(III) content in glass to explain the decrease in glass chemical durability^{55,56}. However, no significant impact of the nuclear dose was identified during the initial alteration rate regime of both actinide-doped borosilicate glasses^{30,32–34} and glasses externally irradiated with heavy ions³², as measured by dynamic leaching tests. This initial alteration rate regime, occurring in very diluted solutions, is well known to be governed by the hydrolysis of the silicate network. These results, compared to the present one, suggest that, depending on the main mechanism(s) involved in a given medium (very diluted or more concentrated solutions), the chemical durability of a borosilicate glass is more or less impacted by its structure.

Based on these results, we developed three hypotheses to explain the impact of the nuclear contribution of the alpha decay dose on the long-term chemical durability of borosilicate glasses occurring during the residual alteration regime, with the formation of the protective alteration layer. Each hypothesis was related to a specific zone (glass, interfacial zone, and gel) and the corresponding possible mechanism(s) that could control the alteration during the residual alteration rate regime^{7,8,12–18}. A schematic of the glass alteration profile is proposed in Fig. 5 to better illustrate the hypotheses described below.

1. Under irradiation, the glass is restructured, which led (among other effects) to a modification of the free volumes²³ and could induce an increase in the mobility of water in this irradiated glass close to the reactive interface^{18,57} and consequently, an increase in the alteration kinetics of the interdiffusion mechanism. Depending on whether the most important mechanism affecting the glass structure is solely water penetration or the overall interdiffusion mechanism, including alkali migration and subsequent glass reorganization and boron release³, this first hypothesis could be closely linked to the second one.
2. The internal energy of the damaged glass is known to increase under irradiation; the alpha decay dose in an R7T7-type glass led to a stored energy of $\sim 110 \text{ J.g}^{-1}$ ^{23,58} due to the formation of defects in its structure and the resulting increased disorder. A damaged glass could thus be seen as a glass having higher energy and entropy than pristine glass (i.e., non-irradiated glass). A possible higher reactivity of the glass at the reactive interface in contact with water could thus be hypothesized due to the higher energetic state of the damaged glass⁵⁹. Indeed, it could be schematically seen

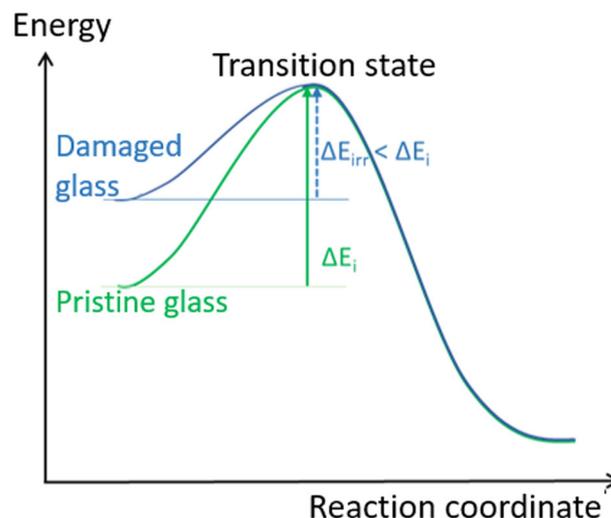


Fig. 6 Schematic of hypothesis 2, which describes energy of system (glass) as a function of reaction coordinate. This implies that the transition states of reactions occurring from the pristine and damaged glasses are similar.

(Fig. 6) as a decrease in the activation energy necessary for the chemical reactions to hydrolyze the glass bonds⁶⁰ in this confined medium, assuming that the transition state remained similar in both cases (for pristine and damaged glasses). As no impact of the alpha decay dose was observed in the literature in a dilute medium governed by a total hydrolysis of the silicate network^{30,32–34}, we can consider that the confined nature of the medium where hydrolysis reactions could occur here is a crucial point. This hydrolysis could affect either weakly linked elements such as alkalis or former elements such as boron or silicon, which is preferentially hypothesized. For example, in the case of the damaged glass, despite a constant chemical composition, the B(III)/B(IV) ratio is higher than that of pristine glass^{23,24}. Moreover, the preferential reactivity of boron (III) was recently shown and explained by the observation that B (III) acts as a Lewis acid, whereas water acts as a Lewis base⁶¹. This hypothesis of increased reactivity does not presume the partial/total ability of the involved hydrolyzed

reactions in the case of the silicate network hydrolysis, which could be partial and progressive (for example, one to three of the four Si–O bonds impacted in SiO₄) or total (all four Si–O bonds broken).

3. The gel could preserve the structure of the parent glass from which it was formed if its formation involved progressive hydrolysis-condensation reactions of the former elements⁸. In this case, one could think that the gel formed from a glass damaged by recoil nuclei could have different structures and thus different protective properties than that formed from a non-irradiated glass.

Some recent experimental and simulation studies can provide further information to discuss these three hypotheses. First, Jan et al.⁶² explored the direct impact of a modified glass structure (boron coordination, Q_n species distribution, strength of Si–O–Si linkages) on leachability using a Monte-Carlo method coupled with molecular dynamics. They concluded that these modifications of the glass short-range order have a limited impact and indicated that, potentially, the medium-range order may more significantly affect the leachability of the glass⁶². They also used molecular dynamics to explore the mobility of water by building glasses containing 10 mol% H₂O and reproducing the recoil nuclei impact by ultrafast quenching⁶³. They qualitatively showed that the water mobility (i.e., diffusion) increased with the glass disorder.

Additional characterizations were recently carried out on irradiated and altered ISG glasses²⁷. First, the evolution of the gel porosity was observed by TEM in cryogenic mode as a function of the history of the parent glass²⁶. The authors showed no observable porosity in the gel obtained from a non-irradiated glass leached for 2 months and from an irradiated sample leached for a few days, whereas a porosity with average pore sizes of (1.5 ± 0.2) nm was observed on the pre-irradiated and 2 months leached ISG samples. The appearance of porosity during the alteration was recently reported in the literature^{8,19}, and this would indicate a slow reorganization of the gel over time (several years), with a tendency to develop a more porous but also more protective structure with respect to glass dissolution by water. It seems possible, based on the current state of knowledge, that the microstructure of the irradiated glass gel would evolve faster than that of the non-irradiated glass, without making any link between this early “maturation” and the increased alteration kinetics of pre-irradiated glasses. In addition, the healing of pores was evidenced in simplified glass compositions by irradiating with low-energy heavy ions and monitoring by TEM in real time²⁹, demonstrating the ability of the gel to reorganize itself. This healing ability of the gel material could be hypothesized in the case of radioactive glasses that are subject to their own irradiation fields. However, as these radioactive glasses behave as externally irradiated glasses in terms of chemical dissolution²⁷, the low impact of gel porosity on glass chemical behavior could be hypothesized. Furthermore, ¹⁸O enriched water penetration in the alteration layer and the associated exchanges involving the pore water and the silanol entities were explored at room temperature²⁶. The ¹⁸O/¹⁶O exchanges were similar within the uncertainty limits in the major part of the gel, regardless of the parent glass history (irradiated or not), suggesting that the two gels had similar transport and exchange properties with respect to water regardless of their microstructures observed by TEM. However, in the reactive interface, the relative ¹⁸O/¹⁶O exchanges were significantly higher in the pre-irradiated glass compared to the non-irradiated one, suggesting that the previous irradiation modified the properties and reactivity of the glass and/or the reactive interface.

All these recent studies favor hypotheses 1 and 2 but not hypothesis 3. They also strongly suggest the need to refine our knowledge and description of the interfacial zone in order to identify the mechanism(s) responsible for the increase in glass alteration due to the nuclear impact of the alpha decay dose.

Finally, concerning the impact of the present results on long-term behavior prediction of nuclear glasses under disposal conditions, the level of alpha decay accumulated in a nuclear glass will exceed the dose required to significantly damage it (several 10¹⁸ α.g⁻¹, i.e., 12 MGy_{nuc}) before water arrival, expected after several thousand years¹. Therefore, the glass damage has to be taken into account on the leaching studies in order to predict as accurately as possible the glass long-term chemical durability²⁴. As described in the present work, it is expected that the residual alteration rate value at a given time would be increased. But, the alteration rate evolution with square root of time indicates that the alteration rate still diminishes with time. Consequently, the impact of the alpha decay dose on the leaching rate will diminish with time under disposal conditions and the alteration rate of the damaged glass will become as low as the one observed on non-damaged glasses.

To conclude, actinide-doped SON68 glass powders were leached at 90 °C and at an S/V ratio ranging from 23 to 76 cm⁻¹ for up to 5 years to study the residual alteration rate regime. A part of an old ^{238/239}Pu-doped glass block was annealed to fully recover the irradiation-induced damage for more than 30 years. Thus, the effect of the alpha dose rate parameter on leaching behavior could be dissociated from the effect of the alpha decay dose parameter on this old ^{238/239}Pu-doped glass (14 MGy_{nuc}). A complementary study concerning a 0.4 wt% ²⁴⁴Cm-doped SON68 glass displaying a significant alpha decay dose (35 MGy_{nuc}) and two reference experiments on non-radioactive glasses were also performed.

The annealed ^{238/239}Pu-doped glass showed similar behavior in water to the corresponding non-radioactive glasses and also similarly to a previously studied ²³⁹Pu-doped glass²⁰. Thus, the residual alteration rate value is not affected by the alpha dose rate, and this conclusion is demonstrated for the wide range of dose rate values expected under disposal conditions (≤3500 Gy.h⁻¹), even in the eventuality of an early water ingress. This result is also in agreement with the one obtained for SON68 glasses altered under gamma irradiation (up to 10,000 Gy.h⁻¹), which means that, irrespective of the irradiation fields and related energy depositions at the glass–water interface, SON68-type glass remains relatively insensitive to a medium inducing radiolysis of the materials (glass, alteration layer) and water. The protective role of pore water can be hypothesized to explain this result.

The residual alteration rate of the damaged ^{238/239}Pu-doped glass was clearly enhanced compared to that of the annealed glass (i.e., having a very low level of damage). This was also observed for the damaged ²⁴⁴Cm-doped glass and is in agreement with that of ISG glasses externally irradiated with gold ions^{24,27}, indicating that the nuclear effects of the recoil nuclei are responsible for this increase in the residual alteration rate due to the alpha decay accumulation. The present results and recent studies from the literature^{28,55,56} demonstrate a link between the glass structure and its leaching behavior. Although no mechanisms are clearly proposed to explain such a link, the role of the reactive interface is strongly suspected.

Further studies and characterizations should focus on this layer to provide a better understanding of the precise mechanisms underlying it. Indeed, the solid characterization of the actinide-doped altered glasses by SEM and TEM, which compares the microstructures of the alteration layers formed as a function of the parent glass history (with or without an alpha decay dose), will provide valuable information to complete the description of the alpha decay dose impact and the suspected involved mechanism(s). The consideration of damaged glasses provides an opportunity to focus on different glass structures with the same chemical composition and can greatly improve our understanding of long-term leaching mechanisms. The healing

ability of the gel formed under self-irradiation will also be investigated. On externally irradiated simplified glasses, fully leached fine glass powders can be characterized by CPMA NMR in order to complete a possible correlation between elements in the glass (^{11}B , ^{29}Si) and water species (^1H)⁶⁴ in the alteration layer and specifically at the reactive interface.

METHODS

Glass materials

Two Pu-doped glasses were fabricated in a glove box in the Vulcain facility at CEA Marcoule in 1985 by means of the melting pot process³⁵. A nitric acid solution containing the radionuclides was first added to a simulated inactive fission product solution and then mixed with the glass frit prepared in the form of sludge. No reducing components were added. The mixture was then heated at 1150 °C for 3 h. The glass was then annealed for 1 h at 525 °C and cooled at a rate lower than 50 °C.h⁻¹. Under these fabrication conditions and with a loading factor of 0.85 wt%, Pu was expected to be homogeneously dissolved in the glass matrix⁶⁵.

The chemical compositions of the Pu-doped glasses were determined after hot acidic dissolution of glass specimens and ICP-AES analyses of the non-radioactive elements and were consistent with the calculated compositions. They are detailed in Supplementary Data (Supplementary Table 1). The Pu concentrations in the glasses were determined from the thermal power measurement of glass samples by isothermal calorimetry, and the Pu isotopic composition was determined. The two Pu-doped glasses both included ~0.85 wt% of PuO₂ but differed in their isotopic distribution; they were thus called ^{239}Pu and $^{238/239}\text{Pu}$ -doped glasses because of their isotopic composition, as detailed in Table 3. The glass that was more enriched in ^{239}Pu has already been extensively studied^{20,42} and is used for comparison with the results presented here. The second glass was mainly enriched in ^{238}Pu compared to ^{239}Pu to provide a greater alpha dose rate (Tables 1 and 3, in bold).

0.4 wt% $^{244}\text{CmO}_2$ -doped glass (called ^{244}Cm -doped glass) was fabricated in the high-level waste laboratory (DHA) of the Atalante facility at CEA Marcoule in 2004. The fabrication and initial characterization of this glass have already been described in detail⁶⁶. The glass sample was produced by melting oxides, carbonates, and nitrates. The first step, prior to initiating each glass melt, consisted of dissolving curium oxide in a 3 mol.L⁻¹ nitric acid solution and measuring the Cm concentration by isothermal calorimetry in order to adjust the solution volume to obtain the desired concentration in the glass. The isotopic composition of the curium used for glass fabrication is shown in Table 3. The content of the main isotope, ^{244}Cm , is written in bold. The curium-doped nitric acid solution was then added to the oxides in a platinum crucible. This method was selected rather than a dry route to promote curium solubilization in the glass. The mixture was melted for 3 h at 1200 °C without stirring, then quenched to a temperature slightly above the glass transition point (600 °C), from which it was cooled more slowly to release the residual stresses from the glass. The

theoretical chemical composition of this ^{244}Cm -doped glass is detailed in Supplementary Data (Supplementary Table 1).

The aim of this study was to assess the impact of alpha self-irradiation on long-term aqueous behavior by dissociating the impact of the alpha dose rate and the impact of the alpha decay dose.

The radioactive glasses studied here, doped with short-lived actinides (^{244}Cm , ^{238}Pu), were subjected to self-radiation, inducing varying alpha dose rate values. Consequently, after several years, they reached alpha decay doses equivalent to those sustained by the R7T7-type glass several thousand years after fabrication. The alpha dose rate values and the alpha cumulative dose of these glasses are presented in Table 1. The characteristics of these two glasses were compared to those of the previously studied ^{239}Pu -doped glass^{20,42}. The alpha cumulative dose values of the annealed $^{238/239}\text{Pu}$ -doped glass and of the ^{239}Pu -doped glass previously studied are considered as negligible because they induced <5% modifications to the solid structure and properties, compared to the modifications expected at the saturation dose value²³.

The alpha dose rate values of the two Pu-doped glasses (i.e., $^{238/239}\text{Pu}$ and ^{239}Pu -doped glasses) covered a wide range of the alpha dose rate values expected for a typical R7T7 glass over thousands of years²¹. Moreover, it was previously demonstrated by calculation⁴² that the mean dose rates calculated from the glass composition were a good approximation of the local dose rate values both in the glass side and in the water side in contact with the glass powder.

Concerning the alpha decay dose values, at the beginning of the leaching tests, the $^{238/239}\text{Pu}$ -doped and ^{244}Cm -doped glasses were already highly damaged regarding the doses needed to induce the evolution of the glass structure and properties, whose evolution becomes significant after around 12 MGy_{nucl} and saturates at around 40 MGy_{nucl}²³.

In order to dissociate the alpha dose rate parameter from the alpha decay dose parameter, the $^{238/239}\text{Pu}$ -doped glass block was cut into two equal parts, and two monoliths were also separated from this block and polished to obtain a surface roughness of <1 μm on one side (see Fig. 7). One part of the cut block and one polished monolith were annealed for 3 h at 545 °C, that is, 30 °C higher than the T_g temperature of this glass. Then, the cooling was slow (15 °C.h⁻¹ between 545 °C and 350 °C) in order to allow the glass to relax and recover its initial structure immediately after fabrication (see Supplementary Fig. 1 in Supplementary Data). This annealing efficiency was checked by measuring the hardness of both the annealed and damaged polished monoliths. An increase of 29% in the hardness value was measured after annealing, which was in agreement with the expected hardness difference (30%) between the pristine and damaged glasses at a saturation value given in the literature²³.

To obtain a high glass surface to water volume ratio and then quickly reach the residual alteration regime during the leaching experiment, glass samples were ground and sieved to recover the 63–125 μm size fraction. Then, they were washed in water to remove the finest particles. The specific surface area of the annealed and damaged $^{238/239}\text{Pu}$ -doped glass powder samples was measured by krypton adsorption using the BET method⁶⁷, and the values are given in Table 4. The ^{244}Cm -doped glass powder was too highly radioactive to be manipulated in glove boxes and to perform such a specific surface area measurement. Thus, the specific

Table 3. Isotopic compositions of the doped glasses at the beginning of the leaching tests (normalized to the Pu and Cm contents).

wt%	^{239}Pu -doped glass	$^{238/239}\text{Pu}$ -doped glass	^{244}Cm -doped glass
^{238}Pu	0.1	21.8	
^{239}Pu	75.3	47.8	0.2
^{240}Pu	21.7	18.7	36.7
^{241}Pu	0.7	1.0	
^{242}Pu	0.6	5.0	
^{241}Am	1.5	5.6	
^{243}Cm			0.6
^{244}Cm			45.3
^{245}Cm			8.1
^{246}Cm			8.3
^{247}Cm			0.4
^{248}Cm			0.4

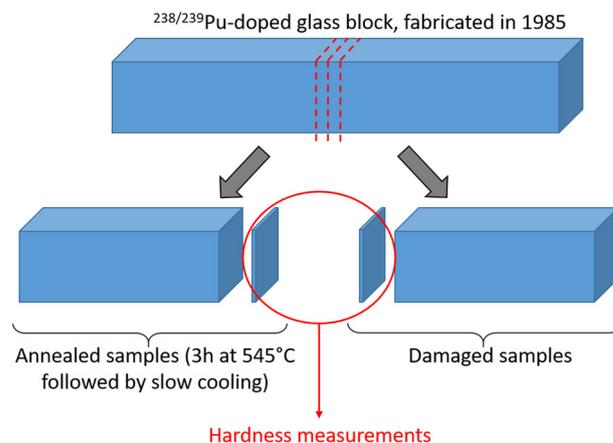


Fig. 7 Schematic view of the annealing of a part of the $^{238/239}\text{Pu}$ -doped glass. The monoliths were polished to micron range roughness on one face.

Table 4. Glass powder samples and leaching conditions descriptions.

	0.4 wt% ²⁴⁴ CmO ₂ -doped glass	Damaged ^{238/239} Pu-doped glass	Annealed ^{238/239} Pu-doped glass	²³⁹ Pu-doped glass ²⁰	'ref. 1' experiment	'ref. 2' experiment ⁴¹
<i>S</i> _{spe} (cm ² g ⁻¹)	645 ± 50 (theoretical)	720 ± 68 (measured)	2340 ± 230 (measured)	645 ± 50 (theoretical)	885 ± 62 (measured)	860 ± 40 (measured)
Initial <i>S/V</i> (cm ⁻¹)	~26	23 ± 3	76 ± 7	~20	38 ± 3	50 ± 3
<i>m</i> _{glass powder} (g)	11.8	9.6	9.6	9.4	13.2	4.651
<i>V</i> (L)	0.297	0.298	0.307	0.305	0.310	0.080
Leaching duration	>5 years	~3 years	>3.5 years	3.2 years	2.7 years	2.2 years

surface area of this ²⁴⁴Cm-doped glass powder sample was estimated at about 645 ± 50 cm²·g⁻¹ based on the tests performed with a ground and sieved inactive SON68 glass powder (detailed in Rolland et al.²⁰). To ensure this specific surface area value, the grain size was qualitatively checked by timing the settling rate of this ²⁴⁴Cm-doped glass powder in water. Using Stokes' law, it was determined that more than 80% of the glass grains were larger than 60 ± 7 μm. In Table 4, uncertainties in the initial *S/V* ratio are specified only when the *S*_{spe} has been experimentally measured.

It is worth noting that the higher than expected specific surface value, *S*_{spe}, measured for the annealed glass powder sample was probably due to less efficient washing of the powder in water. The smallest particle size was estimated to be <1.4 μm by using Stokes' law in water and measuring the maximum settling rate (>7 h in 5 cm water).

Leaching device and conditions

Radioactive glass leaching tests were performed in a shielded cell in the Atalante facility at CEA Marcoule in titanium reactors. Before entering the shielded cell, each titanium reactor was annealed for 3 h at 450 °C to form a passivating TiO₂ film to minimize the possible interactions between the species generated by water radiolysis and the experimental setup. In the literature, it was shown that finely divided titanium oxides were capable of decomposing H₂O₂ through redox reactions⁶⁸. In the present case, the titanium surfaces in the reactors were polished and thus, we assume that these surfaces covered by TiO₂ were not sufficient to significantly affect the H₂O₂ concentration produced by alpha radiolysis under anoxic conditions in the present systems. Indeed, this was experimentally demonstrated in a previous study with small titanium containers under gamma radiation²¹, where H₂O₂ experimental concentrations were reproduced by calculations with CHEMSIMUL⁶⁹ for a homogeneous closed system of pure water.

For each experiment, about 10 g of glass powder was first mixed with 30 mL of ultrapure water to allow it to be easily transferred into the leaching reactor, and the leachate volume was adjusted to ~300 mL by adding ultrapure water. The leaching tests were thus carried out under static conditions at an initial glass-surface-area-to-solution volume (*S/V*) ratio of ~23 to 76 cm⁻¹, as described in Table 4.

After reactor closure, the solution was degassed by argon bubbling for 3 h (argon purity = 99.9999%). Then, an argon overpressure of 4 bars was applied to prevent any ingress of air into the reactor and to allow leachate sampling at regular intervals. Finally, the temperature was adjusted to 90 °C. The total duration of each radioactive glass leaching test was at least 3 years.

Two reference experiments, called 'ref. 1' and 'ref. 2', were performed under similar conditions (90 °C, *S/V* values) and were used to compare the present results obtained for Pu and Cm-doped glasses to those obtained for non-radioactive glasses. The 'ref. 1' experiment was performed in a titanium reactor similar to the one used for radioactive glasses, but the SON68 glass had a slightly different composition (see Supplementary Table 1 in Supplementary Data), whereas the 'ref. 2' experiment was performed on the same glass composition compared to the Pu-doped glasses, but in a 120 mL PFA SavillexTM reactor. PFA reactors are commonly used for leaching experiments in a non-radioactive environment. This second reference experiment, already described in detail⁴¹, also provided a reference in terms of leaching devices.

Solution analyses

The leachate pH was measured in an aliquot at room temperature using either a combination gel-filled pH electrode (Checker) in the hot cell or an ISFET probe (Metrohm) if the measurements were performed in glove boxes. The measurement uncertainty was ±0.1 pH unit. The pH at 90 °C was calculated to be about 0.4 pH units lower than the pH measured at 25 °C, according to both CHESS calculations⁷⁰ and experimental measurements on non-radioactive solutions⁷¹. The uncertainty of the calculated pH_{90°C} was ±0.3 pH unit.

For each experiment, most of the leachate samples were analyzed directly, except for the annealed ^{238/239}Pu-doped glass where the leachate was systematically filtered (0.45 μm) to prevent the presence of small glass grains. However, for all experiments, some samples were filtered (0.45 μm) and ultrafiltered (10,000 Dalton) to check for colloids, as previously described by Rolland et al.²¹. Both fractions were then acidified with nitric acid to reach a pH ranging from 0.5 to 1. Cation analyses were performed using a Horiba Jobin Yvon JY46 ICP-AES system. The analytical uncertainty was ±3% for concentrations above 10 mg·L⁻¹, ±5% between 1 and 10 mg·L⁻¹, and ±20% for concentrations below 1 mg·L⁻¹. The releases in solution were expressed in terms of normalized mass losses (NL in g·m⁻²) for element *i* and were calculated as follows for a leachate sample taken at time *t*:

$$NL_i^t = \frac{m_i^t}{x_i \times S} \quad (2)$$

where

$$m_i^t = C_i^t \times \left(V - \sum_{j=1}^{t-1} v^j \right) + \sum_{j=1}^{t-1} C_i^j \times v^j \quad (3)$$

*m*_{*i*}^{*t*} represents the amount of element *i* released in solution at time *t* (in g), *C*_{*i*}^{*t*} is the measured concentration of element *i* at time *t* (in g·L⁻¹), *C*_{*i*}^{*t-1*} is the concentration measured in the previous leachate sample (*t-1*) for which the sampled volume was *v*^{*t-1*}, *x*_{*i*} is the mass fraction of element *i* in the glass, *S* is the glass surface area (corresponding to *S*_{spe} × *m*_{glass powder}, in m²), and *V* is the initial volume of the solution (L). For tracer elements such as B, Na, and Li, this parameter (NL) represents the amount of altered glass. The relative uncertainty calculated on NL is ~10%, with major contributions coming from the specific area measurements/estimations (see Table 4), cation analyses (see above), and the glass formula (3% for B, Na, Li, and Si). Error bars are specified in each figure.

When the glass grain size was much greater than the glass altered thickness, this altered thickness can be directly calculated from the normalized mass losses of boron by dividing it by the density of the glass ρ (g·cm⁻³). This density is taken as 2.75 for all the glasses studied here.

$$\text{Altered thickness} = \frac{(NL_B)_t}{\rho} (\mu\text{m}) \quad (4)$$

The residual alteration rate for element *i* (*R_{r,i}*) corresponds to the slope of the *NL_i* evolution versus time (in days) in a given time range, and can be described by Eq. (5).

$$R_{r,i} = \frac{d(NL_i)}{dt} (\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}) \quad (5)$$

It was calculated using the linear fit function in the Origin software using 'direct weighting' mode. This mode takes into account the entire uncertainty dataset with the same 'weight'.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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AUTHOR CONTRIBUTIONS

M.T. supervised the entire study and wrote the paper. C.M. and V.B. were responsible for the experimental analysis of the leachates. S.M. was responsible for the leaching experiment on the ²⁴⁴Cm-doped glass; M.T., S.M., C.J., and S.P. were involved in data interpretation. All authors helped to edit the paper.

COMPETING INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

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