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Effect of alpha radiation on the leaching behaviour of nuclear glass

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Abstract

The behaviour of nuclear glass subjected to the stress loading expected in a repository must be investigated to demonstrate that it is capable of durably confining radioactive elements. Because of the minor actinides (Np, Am, Cm) contained in the glass, alpha radiation is one of the stresses that could affect the glass properties. This study focuses on the effect of alpha radiation on the chemical reactivity of R7T7 glass with pure water. Various glass samples doped with ^{237}Np, ^{238}Pu, ^{239}Pu, ^{241}Am or ^{244}Cm were fabricated in the CEA facilities at Marcoule. The content of each actinide was adjusted to cover a range of alpha activity varying from 10^5 to 10^{11} Bq g^{-1} and a range of alpha decay doses up to 4×10^{18} g^{-1}. Inactive glass samples were also subjected to multiple-energy external irradiation by heavy ions to simulate the impact of alpha damage. The initial glass alteration rates, which reflect the chemical reactivity between the glass matrix and pure water, were determined by standard Soxhlet tests together with analysis of the leaching solution by ICP-AES. Comparing the glass leaching rates is indicative of the impact of alpha radiation. The experimental data show that neither the alpha activity nor the alpha decay dose has a significant impact on the initial alteration rate of R7T7 glass.

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1. Introduction

In France, fission products and minor actinides are currently stabilized and immobilized by vitrification; this is the French reference process for industrial management of these high-level wasteforms. 'R7T7' glass, named after the COGEMA La Hague vitrification units, is the reference glass selected to immobilize the radioelements arising from reprocessing light-water reactor fuel. Investigating the effects of radiation on the macroscopic properties of the glass is crucial to assessing its containment performance after disposal. Because of the minor actinide content of the glass, alpha radiation is one of the key parameters: not only is it the main cause of atomic displacement in the glass structure under disposal conditions, but radiolytic processes generated by the field in aqueous solution could affect the glass alteration mechanisms. Despite the numerous studies carried out to assess the impact of radiation on the properties of nuclear glasses, reviewed in [1–3], some issues are still controversial especially

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concerning the effect on the nuclear glass leaching behaviour. Although almost all the data concerning the effects of alpha radiation have been determined by standard Soxhlet leach testing, some discrepancies still exist [4–9]. Estimates of leach rates based on weight loss measurements may have underestimated the effects induced by alpha radiation, so it was generally considered that alpha radiation could increase the leach rate by up to a factor of ten [3]. The aim of this study is to determine the effect of alpha radiation on the leaching behaviour of R7T7 glass by monitoring the release of glass alteration tracer elements during Soxhlet leach testing.

Several stages can be observed during nuclear glass alteration: the first corresponds to congruent dissolution characterized by the forward initial dissolution rate (r_0). Then, in situ recondensation of dissolved species results in the formation of a gel that decreases the alteration rate by several orders of magnitude to a residual alteration rate [10], the underlying mechanisms of which are the diffusion of mobile elements within the solid and the precipitation of secondary phases. Under disposal conditions, the two main stages that control the radionuclide release are the initial and residual alteration rates. This article focuses on the effect of alpha radiation on the initial alteration rate.

2. Experimental

Three types of glasses were considered in this study:

- α-Doped glasses containing 0.85 wt% of either NpO_2, $^{238/239}PuO_2$ or AmO_2 were prepared by melting at a temperature of 1423 K in the CEA's Vulcain facility at Marcoule [11]. Four glass samples were fabricated to cover the range of dose rates for an industrial glass under disposal conditions (Table 1, Fig. 1). The alpha activities of the $^{241}AmO_2$ and $^{238}PuO_2$ glasses were equivalent to fresh glass, whereas the $^{239}PuO_2$ and $^{237}NpO_2$ samples were representative of glasses about 1000 and 100 000 years old, respectively.

Table 1
Alpha specific activity of glasses doped with 0.85 wt% NpO_2, $^{238/239}PuO_2$ or AmO_2

Type of glass	$^{238}PuO_2$	$^{241}AmO_2$	$^{239}PuO_2$	$^{237}NpO_2$
Alpha specific activity (Bq g^{-1})	1.4×10^{9}	1.0×10^{9}	4×10^{7}	2.2×10^{5}

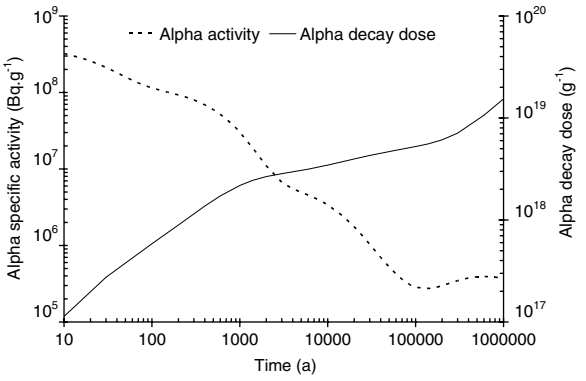

Fig. 1. Evolution of alpha activity and alpha decay dose of a current industrial glass versus time.

- Curium doped glasses with 0.04, 0.40, 1.20 and 3.25 wt% $^{244}CmO_2$ were prepared by melting between 2001 and 2004 in the CEA's Atalante-DHA facility at Marcoule [12] to simulate the alpha decay dose sustained by an industrial glass under disposal conditions. To date these glasses have simulated an alpha decay dose corresponding to around 20 000 years of storage (Fig. 1). Different curium contents were chosen to evaluate the effect of the dose rate on the potential modifications induced by the alpha decay dose.
- Inactive glasses irradiated by heavy ions at CSNCM/CNRS-Orsay were also used to simulate the effect of alpha decay on the glass structure and investigate the consequences on the dissolution rate. This technique is capable in a short time of reaching high doses that would require several years with curium-doped materials. Multiple-energy irradiation by gold ions (Table 2) was used to induce a constant deposited nuclear energy within the first 2 μm of the irradiated samples. Recent results have shown that these irradiation conditions correctly simulate the effect of the alpha decay dose on the glass hardness [13].

The chemical composition of these glasses is indicated in Table 3. The initial glass alteration rates, which reflect the chemical reactivity between the glass matrix and pure water, were determined by Soxhlet-mode dynamic leach testing at 373 K in a stainless steel leaching vessel. A specimen was placed in an overflowing sample holder designed to maintain the glass sample in contact with continuously renewed pure water. Solution samples were taken at regular intervals during the 28-day test for ICP-AES and radiochemical analysis. For

Table 2
Multiple-energy gold ion irradiation conditions ($8 \times 10^{14} <$ flux (m^{-2} s^{-1}) $< 3 \times 10^{15}$)

	Ion energy (MeV)	Ion fluence (m^{-2})	E_{nucl} (eV m^{-3})	E_{elec} (eV m^{-3})
Dose 1	1	1.9×10^{15}	1.6×10^{28}	5.5×10^{28}
	3.5	5.8×10^{15}		
	7	1.4×10^{16}		
Dose 2	1	6.1×10^{15}	5.0×10^{28}	1.7×10^{29}
	3.5	1.8×10^{16}		
	7	4.2×10^{16}		
Dose 3	1	1.1×10^{16}	9.0×10^{28}	3.1×10^{29}
	3.5	3.3×10^{16}		
	7	7.6×10^{16}		
Dose 4	1	2.4×10^{16}	2.0×10^{29}	6.8×10^{29}
	3.5	7.3×10^{16}		
	7	1.7×10^{17}		
Dose 5	1	6.1×10^{16}	5.0×10^{29}	1.7×10^{30}
	3.5	1.8×10^{17}		
	7	4.2×10^{17}		
Dose 6	1	4.6×10^{17}	3.8×10^{30}	1.3×10^{31}
	3.5	1.4×10^{18}		
	7	3.2×10^{18}		

Table 3
Chemical composition (wt%) of the glasses used in this study

Chemical composition (wt%)					
SiO_2	45.5 ± 1.0	Li_2O	2.0 ± 0.10	P_2O_5	0.3 ± 0.05
B_2O_3	14 ± 0.3	MoO_3	1.7 ± 0.10	TeO_2	0.2 ± 0.05
Na_2O	10 ± 0.2	Cs_2O	1.1 ± 0.10	CdO	0.03 ± 0.05
Al_2O_3	4.9 ± 0.1	BaO	0.6 ± 0.05	Ag_2O	0.03 ± 0.01
CaO	4.0 ± 0.1	Cr_2O_3	0.52 ± 0.05	SnO_2	0.02 ± 0.02
Fe_2O_3	3.0 ± 0.1	NiO	0.4 ± 0.10	Sample specific composition changes	
ZrO_2	2.7 ± 0.1	MnO_2	0.4 ± 0.05	Ln_2O_3	0.9–4.1
ZnO	2.5 ± 0.1	SrO	0.3 ± 0.05	(Np, Pu, Am, Cm)O_2	0.04–4.1[a]

[a] Because of the isotopic composition of the curium used, the glass doped with 3.25 wt% $^{244}CmO_2$ actually contained 4.1 wt% CmO_2.

externally irradiated glasses, because of the two microns of irradiated depth, the duration and sampling were adjusted to evaluate the alteration rate in the irradiated zone.

The initial glass alteration rate was determined by monitoring the release of glass alteration tracer elements (B, Na, Li, Mo). The release of these elements was found to be linear and congruent over time, the leaching rate r_0 was calculated from the following relation:

$$r_0 = \frac{C^{B}_{t_{Max}} V}{F^{B} S t_{Max}}, \quad (1)$$

where $C^{B}_{t_{Max}}$, concentration (g L^{-1}) of boron in the sample taken after 28 days of leaching; V, volume (L) of solution (after 28 days of leaching); F^{B}, conversion factor for boron in the glass (grams of boron per gram of glass); S, surface area (m^2 g^{-1}) of the glass sample; t_{Max}, leaching time (i.e. 28 d).

The uncertainty on the estimated leaching rate is based on the analytical method validation study and the recommendations of the Eurachem guide [14,15]. It takes into account the uncertainty of each parameter used for the calculation of r_0. The uncertainties reported on the figures are expanded uncertainties calculated using a coverage factor of 2.

3. Results and discussion

3.1. Effect of alpha activity on the initial alteration rate

Fig. 2 shows the initial alteration rate versus the alpha activity for the actinide-doped glass samples.

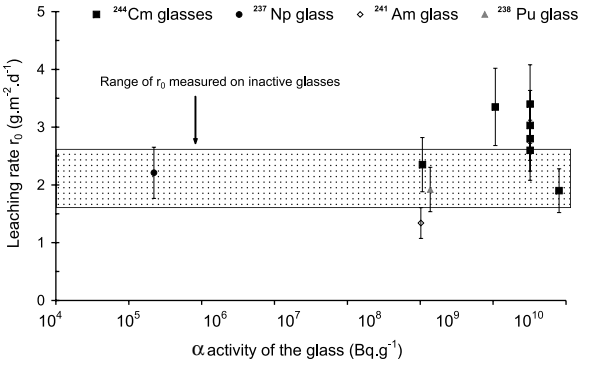

Fig. 2. Effect of alpha activity on the initial alteration rate.

Unfortunately no data are available for the $^{239}PuO_2$ glass. The data obtained with the curium-doped glasses are also reported. The alpha activities of these glasses are higher than those of current industrial glasses but these high dose rates could reveal the potential effect of alpha radiolysis on the glass aqueous alteration rate.

The results reported in Fig. 2 do not show a significant change in r_0 between the glass with the lowest alpha activity ($^{237}NpO_2$) and the glass with the highest activity (3.25 wt% $^{244}CmO_2$). These values are centred in the range of initial dissolution rates of inactive samples. For the alpha activity of fresh glass (about 10^9 Bq g^{-1}), the values measured in Pu, Am and Cm glasses are also consistent with the inactive values. For the glasses doped with 0.4 and 1.2 wt% $^{244}CmO_2$ the measured r_0 values appeared to be higher, although the results of three new measurements performed later on the 1.2 wt% doped glass were in good agreement with the values obtained on inactive samples. Nevertheless, to evaluate the potential effect of the alpha dose rate on the glass alteration rate, the alpha decay dose received by the glass prior to the test should be as low as possible. For the Np-, Pu- and Am-doped glasses the alpha decay doses were very low and can be disregarded. For the curium-doped glasses a potential alpha decay dose effect cannot be neglected.

Moreover, it is also important to check whether the dynamic leaching test can conceal the alpha radiolysis effect by diluting the radiolytic species. For this reason, the dissolution rates of the Np-, Pu- and Am-doped glasses altered for three days under static conditions at 363 K with a surface-to-volume ratio of 50 m^{-1} were compared with one other. The glass alteration under these conditions is mainly controlled by the initial alteration stage. The values reported in Table 4 do not show significant dependence of the dissolution rate on the sample alpha activity.

The data thus suggest that the alpha activity in the range covered by the studied glasses, i.e. the whole range of alpha activity of a glass package under disposal conditions, does not significantly affect the initial dissolution rate of the glass.

3.2. Effect of alpha decay dose on the initial alteration rate

Fig. 3 shows the initial alteration rate of the curium-doped glass samples versus the alpha decay dose.

The measurements on the three glass doped with 0.04, 0.4 and 1.2 wt% $^{244}CmO_2$ are all comparable within the experimental uncertainty. Nevertheless, a slight increase of r_0 could be suspected up to an alpha dose of 2×10^{17} g^{-1}, followed by a decrease of same amplitude between alpha doses of 2×10^{17} and 3×10^{18} g^{-1}. Because the surface area of the samples must be known to determine r_0, it is important to check if such variations could reflect the variation of the surface area of the glass samples with the alpha decay dose. First, it is important to note that all the glass samples were cut at the same time just after fabrication, i.e. prior to any change in the mechanical properties induced by alpha decay 0. Second, even if density measurements in the same alpha decay dose range 0 show a slight decrease of around 0.5% between 2×10^{17} and 3×10^{18} g^{-1}, this slight monotonic evolution could not induce a surface area variation affecting r_0 by about 20–40%. Finally, no change in the glass microstructure (microcracking) was observed in this alpha decay dose range that could have increased the leach rate. Despite these elements, the signification of this potential increase followed by a decrease in the leaching rate is difficult to evaluate.

Nevertheless, the results show that the alpha decay dose does not modify the initial dissolution

Table 4
Alteration rate of doped glasses after 3 days of leaching under static conditions

Type of glass	$^{238}PuO_2$	$^{241}AmO_2$	$^{239}PuO_2$	$^{237}NpO_2$	Inactive glass
Alteration rate (g m^{-2} d^{-1})	0.73 ± 0.14	0.75 ± 0.15	0.76 ± 0.15	0.87 ± 0.18	0.88 ± 0.18

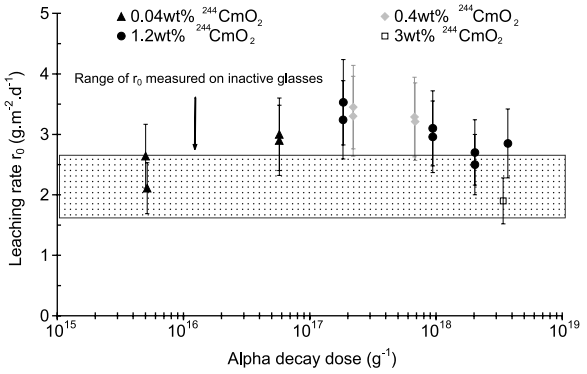

Fig. 3. Effect of alpha decay dose on the initial alteration rate.

rate significantly, considering a measurement uncertainty of 20%. Most published findings are based on rates determined from sample mass losses (by weighing before and after leaching), which can underestimate the actual alteration rate because of the formation of an alteration film. For this reason, it is generally noted that alpha damage could affect the leaching rate by up to a factor of 10 [3]. The rates indicated here were determined from the release into solution of glass alteration tracer elements that are not retained in the alteration film formed during the test, and thus correspond precisely to the leach rate of the glass network. These results clearly show that an alpha decay doses of up to $4 \times 10^{18}\,g^{-1}$ does not significantly increase the initial alteration rate. These findings are also consistent with the results recently reported by Wellman et al. [16] for plutonium-doped glass over a similar dose range.

In order to cover the entire range of alpha decay doses sustained by an industrial glass under disposal conditions, external irradiations with heavy ions were performed on inactive samples. These irradiation conditions correctly reproduced the effect on the glass hardness and showed that nuclear interactions could be responsible for this effect (Fig. 4, [13]). The initial alteration rates of the six irradiated glasses were consistent with the rate determined on a nonradioactive glass sample leached under the same conditions (Fig. 5). These results show that neither the electronic nor the nuclear interaction induced by these irradiations affect the glass leach rate. Because these irradiations simulate ranges of deposited electronic and nuclear energies equivalent to about 10^{18} and 2×10^{19} alpha decays per gram of glass, this could mean that the slight r_0 variations suspected on the curium-doped glasses are not

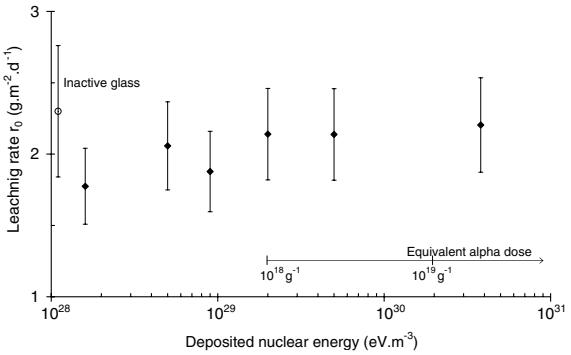

Fig. 5. Effect of gold ion irradiation on the initial alteration rate.

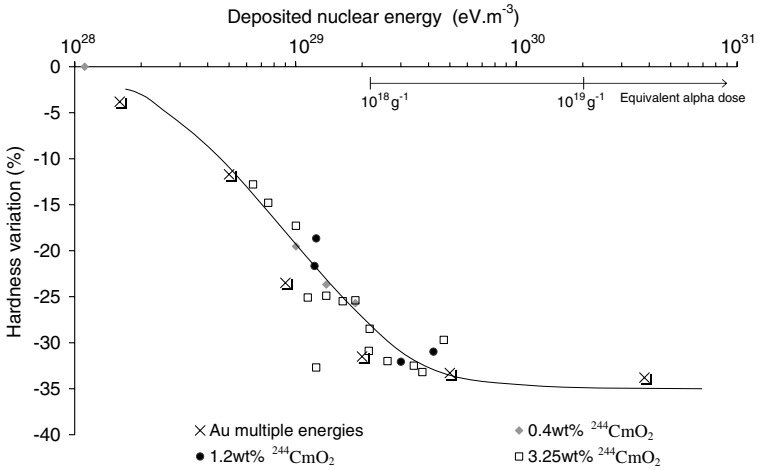

Fig. 4. Comparison of hardness variations of curium-doped glasses and glasses irradiated by gold ions, Hardness variations between irradiated and pristine glasses obtained by Vickers indentation [13].

significant. Additional measurements on the glass doped with 0.04 wt% $^{244}CmO_2$ at an alpha decay dose of about 2×10^{17} g^{-1} sand on the glasses doped with 0.4 and 1.2 wt% $^{244}CmO_2$, just after heat treatment to restore the glass structure should help to clarify this point.

4. Conclusion

Experiments performed on actinides-doped glasses and on externally irradiated glasses have concerned the effect of alpha radiation on the initial glass dissolution rate (r_0). The studied glasses cover the ranges of alpha activity and alpha decay dose of the current industrial glass under disposal conditions. The initial glass alteration rate was determined by monitoring the release of glass alteration tracer elements (B, Na, Li, Mo) in Soxhlet leaching tests.

The results have shown that alpha activity has no significant impact on the glass alteration rate. Moreover, the results obtained on the doped and externally irradiated glasses do not show any change induced by the accumulation of alpha decay in the glass structure exceeding the test uncertainty. Nevertheless, some data may suggest a slight increase (around 40%) of r_0 up to an alpha dose of 2×10^{17} g^{-1}, followed by a decrease of the same amplitude between alpha doses of 2×10^{17} and 3×10^{18} g^{-1}. Additional measurements will be performed to clarify this issue.

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