RADIONUCLIDE RELEASE FROM HIGH LEVEL WASTE FORMS

UNDER REPOSITORY CONDITIONS IN CLAY OR GRANITE

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Abstract

The behaviour of both fully active and simulated vitrified high level waste (HLW) has been studied under conditions that are likely to occur in future repositories in clay and granite. The simulated HLW was doped with Cs, Sr, Tc and the actinides and the leaching of these elements from the glass has been measured together with their concentrations in the water of the "near-field" and their distribution between the various components of the repository. The diffusion coefficients of several elements in Boom clay has also been measured. The results show that the concentrations of Tc and the actinides in the near-field of a repository will be very low and that the actinides will only diffuse very slowly away from the vicinity of the glass. 24Refs.; 1Figs.; 7Tabs.

1.   Introduction

After vitrification, high-level-waste (HLW) glass is or will be cast into a stainless steel canister which is then closed by welding. After storage until the heat-output of the waste has decayed, the canister may be placed in an "overpack" to delay the time at which water reaches the glass after disposal. This overpack may be of cast-iron or mild steel, say 20cm thick, or of a corrosion resistant metal or alloy, perhaps Ti, a few mm thick. The containers will then be emplaced underground and the space between them and the rock will be "backfilled" with a clay or cementitious material. Various types of rock have been considered for this. Most of the work within the European community has been done on granite (UK and France), clay (Belgium and Italy) and salt (Germany).

The characteristics of a repository in salt are rather different from those in clay or granite. In the absence of large scale water ingress into the salt, release of radioactive material to the environment is impossible. The behaviour of glass in the presence of salt brines is considered in references (1) and (2).

In clay or granite, the rock will usually be saturated with water which will eventually reach the glass and start to react with it, once the overpack, if used, and the canister have corroded. The released radioactive material will then move very slowly away from the glass. This will occur largely by diffusion in a repository in clay where the water flow rates will effectively be zero. In granite, there is normally some water flow which will carry away material in solution but, in a properly chosen repository, the flow rate will be very small - typically 1cm per year.

Initially, the potential hazard of HLW is dominated by Cs-137 and Sr-90 but these isotopes have half-lives of about 30 years and after a few hundred years will have decayed to negligible levels. For times up to a few tens of thousands of years, most of the potential hazard is due to isotopes of Am and Pu and thereafter primarily to Np-237 and Tc-99.

In considering the behaviour of the HLW glass in a repository, two types of data are important. Firstly, the leach-rate must be measured both by weight loss and for individual elements and isotopes in the presence of the various components of the repository and the reaction mechanisms considered. Secondly, the concentrations of the important radioisotopes in solution must be determined because these concentrations are the source terms for the loss of the isotopes from the repository by diffusion or water-flow.

2. Repositories in clay

The enhancing effect of the presence of clay (bentonite, smectite, etc) on waste glass corrosion has been observed and recognised by various authors (ref 3-7). The enhancement is a function of the type of clay considered. Most of the studies considering the effect of clay were directed toward the selection of candidate backfill materials. The Belgian situation, however, is different. A clay layer 100m thick, situated 190m deep, has been selected as a possible geological repository site. The long-term performance of the various candidate waste glasses in clay has to be thoroughly quantified and understood, in order to evaluate the barrier function of the high-level waste glass in the multibarrier disposal concept, and to optimize the other engineered barriers.

Corrosion tests were carried out at Mol on some simulated waste glasses in solutions containing various clay ("Boom" clay) concentrations. The glasses were: SON 68 (the Cogema-AVH reference glass), SM 513 and SM 527 (the DWK-PAMELA reference glasses for the low - and high - enriched waste concentrates resulting from Eurochemic's reprocessing activities).

The reducing and low flow conditions expected in the clay repository were carefully reproduced. This paper focusses on the specific leaching of some radionuclides of interest (Cs, Sr, Pu, Am).

The composition of the waste glasses can be found in the literature (eg ref 8). Glasses SON 68 and SM 513 are HLW borosilicate glasses, but SM 527 has an unusually large Al_2O_3 concentration (about 20wt%.) The glasses used in the active tests were prepared by adding 30 to 50 MBq each of Sr-90 and Cs-134, and about 50 MBq of Pu as solutions simultaneously to about 40g inactive glass pellets. The Pu tracer consisted mainly of Pu-239, but minor fractions of other isotopes, including Pu-241 - producing Am-241 by β decay - were also present.

The corrosion tests were performed in static media by enclosing the components glass/water/clay in Teflon or Teflon-lined stainless steel cups of about 5×10^{-6} m^3 internal volume. Thin glass plates with a surface area of 5×10^{-4} m^2 and finely ground clay were used. In all experiments, the temperature was kept at 90°C, and the surface area-to-solution volume at 100 m^{-1}. The clay ("Boom" clay sampled at the repository site) - to - water ratio was 10 ("DCSICM") or 500 ("CCSICM") g clay to one liter synthetic interstitial claywater ("SIC"; composition, see ref 9). The 500 gl^{-1} mixture was found earlier to induce a similar corrosion behaviour as in natural, wet clay (ref 5), but still allowed easy chemical analysis of the solution.

All laboratory experiments discussed in this paper were conducted in similar reducing conditions as in the clay repository. Therefore, all test preparations were carried out in glove box conditions, yielding less

than 2 vppm O_2; Eh of the clay media prepared was <-200 mV. In all experiments leachates were high-speed centrifuged (15 x 10^3 rpm) before chemical analysis of the solution. In the case of the radioactive experiments, centrifuged solutions were further ultrafiltered through 10^5 MW cut-off membranes. This is the limit for migration through clay (10) In the case of the inactive tests, concentrations measured in solution were corrected for the blank concentration (ie only clay present).

The analytical procedure followed provided data on the mobile radionuclide inventory leached - ie present in solution, on the clay, and elsewhere (eg on the cup wall). The nuclides concerned were Cs-134, Sr-90, Pu-239 and Am-241. The data for Am-241 are only relevant in terms of mobile concentration and Kd, as no reliable data exist on the initial inventory.

The total Cs, Sr and Pu inventories leached increased with test duration roughly in the same way as the mass losses. Fig 1 shows the time dependence of Pu, Cs and Sr leaching for SON 68 glass. It was found that Sr was leaching congruently with the glass matrix, based on the total Sr inventory leached. Pu and Cs leaching was retarded by comparison with the glass matrix leaching by a factor of two to ten. In addition, the total inventories leached for Cs, Sr and Pu apparently reach maximum values after a few months duration (Figure 1).

The data on the mobile radionuclide inventory leached are summarised in Table 1. The Cs and Sr concentrations increase generally with time. A clear-cut conclusion for Pu and Am is difficult, however, since for both nuclides concentrations are only occasionally above the detection limit (about 1 Bq/ml for both nuclides). This yields upper limits for Pu_{mob} of 10^{-9} mol.l^{-1}, for Am_{mob} of 2.5 x 10^{-7} mol.l^{-1}. Measurement of the total alpha activity in solution showed that at least for glasses SON 68 and SM 513, actinide concentration tended to decrease at the longer times.
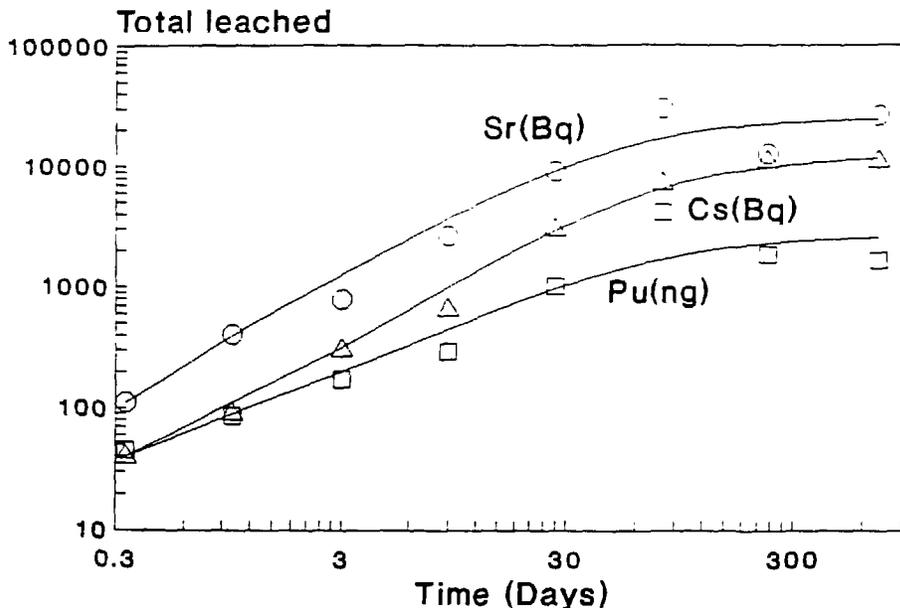

Fig 1. Total inventory of radio-isotopes leached from SON68.

	Duration (days)	Cs	Sr	Pu	Am
SON 68	9	2.7×10^{-13}	1.35×10^{-13}	$<1.0 \times 10^{-9}$	$<2.5 \times 10^{-11}$
	80	9.2×10^{-13}	9.7×10^{-13}	$<1.0 \times 10^{-9}$	2.5×10^{-11}
	720	25×10^{-13}	10.5×10^{-13}	$<1.0 \times 10^{-9}$	$<2.5 \times 10^{-11}$
SM 513	9	3.3×10^{-13}	4.5×10^{-13}	1.0×10^{-9}	$<2.5 \times 10^{-11}$
	80	3.8×10^{-13}	17×10^{-13}	0.3×10^{-9}	$<2.5 \times 10^{-11}$
	720	$<1.8 \times 10^{-13}$	13×10^{-13}	$<1.0 \times 10^{-9}$	$<2.5 \times 10^{-11}$
SM 527	9	$<1.8 \times 10^{-13}$	nd	$<1.5 \times 10^{-9}$	1.5×10^{-11}
	80	$<1.8 \times 10^{-13}$	nd	$<0.7 \times 10^{-9}$	2.0×10^{-11}
	240	3.6×10^{-13}	16×10^{-13}	$<1.5 \times 10^{-9}$	$<2.5 \times 10^{-11}$

nd = no data

Table 1: Concentration of the mobile nuclide fraction (in $mol.l^{-1}$)

Distribution coefficients, Kd, were calculated from the relative isotope concentrations in solution ($< 10^5$ MW) and those sorbed on the clay. Since for Pu and Am only upper limits could be given in most cases for the mobile fraction, Kd data are approximate only. The definition of Kd in the present corrosion tests is justified because reversible ion exchange reactions are limited to the solution/clay system.

	Duration (days)	Cs	Sr	Pu	Am
SON 68	9	130	170	> 420	> 360
	80	470	203	1140	940
	720	207	209	> 870	>1380
SM 513	9	150	50	> 170	> 65
	80	445	275	1360	> 180
	720	>1010	450	>1170	> 580
SM 527	9	40	nm	>1230	740
	80	390	nm	>9840	3130
	240	1361	85	>7400	>5600
Pure tracer (ref 11)	60	–	–	2470	>1300

nm = not measured

Kd = $(X_S/M) / (X_A/V)$ with X_S and X_A the quantity of nuclide X in the solid and aqueous phase, respectively, V the volume of the aqueous phase (in ml), and M the amount of solid phase (in g).

Table 2: Distribution coefficients, Kd (in ml g^{-10}) for the various radioisotopes upon corrosion of the waste glass in a clay solution.

The following tendencies can be deduced from the data in Table 2.
- Kd values for Cs, Sr, Pu and Am generally increase at the longer times.
- Kd values for the most relevant nuclides, Pu and Am, show that after some minimum test duration (about 80 days), at the most 0.2% of the leached nuclide is in a mobile form, ie is able to migrate through the clay rock.
- Kd data for Cs and Sr are comparable for all three glasses; for Pu and Am, data for SM 527 are systematically larger (up to ten times) than for SM 513 or SON 68. This may be because of competition in the case of SM 527 with other glass constituents for sorption onto the clay.
- Comparison with data from reference (11) obtained with pure Pu or Am tracers instead of the complex waste glass is difficult, as those interaction experiments were performed at room temperature but with similar contact times, clay/water ratio and ultrafiltration (11).

The cumulative releases of Pu and Am appear to reach limiting values. But, even more important, the nuclide inventory leached in a mobile form is below 0.2% of the total inventory leached. The remainder is immobile, eg sorbed on the clay.

The glass composition does seem to influence the distribution coefficients for Pu and Am and, as a consequence, one might conclude that the waste glass itself contributes in a non-negligible way to the safety of geological disposal in clay.

At JRC, Ispra, a series of tests have been carried out to measure simultaneously the leach-rate of glass in contact with Boom clay and the diffusion rates of the released elements (12). The tests were performed in an apparatus in which a cylinder of wet clay was pressed by a piston against a glass surface (13). Three series of tests were carried out with a maximum duration of 6 months. The first two were at 50 and 75°C using the glass I117 and the third was at 75°C on the glass SON 68. The compositions of the glasses have been reported (12).

At the end of the experiments, the glass weight losses were determined after removing the surface layer. The clay cylinders were cut into slices 1mm thick which were analysed for the various elements using neutron activation analysis.

The glass leaching data showed that the weight-loss leach-rates were constant with time. No saturation effects were found, at least for the durations investigated. This was probably due to the fact that the clay adsorbed the silica released from the glass, preventing any silica saturation at the glass/clay interface. A linear regression analysis for the two glasses gave the following leach-rates:

For I117 at 50°C 2.6 x 10^{-5} g.cm^{-2} day^{-1}
For I117 at 75°C 8.6 x 10^{-5} g.cm^{-2} day^{-1}
For SON 68 at 75°C: 4.2 x 10^{-5} g.cm^{-2} day^{-1}

The latter value compares to 10^{-6} g.cm^{-2} day^{-1} in dilute interstitial clay water and 1 x 10^{-5} in concentrated interstitial clay water (14) and to 2.1x10^{-5} at 60°C for MW glass in the presence of Boom clay – see Section 3.

In order to calculate the effective diffusion of the different elements, it is necessary to classify them according to their solubility limits. Two classes can be defined:
(a) Elements forming compounds of high solubility which, once freed from the glass matrix, dissolve in the water. Their release rate will be proportional to the degradation rate of the glass (eg Cs, Co). Their diffusion rates were fairly rapid eg for I117 at 75°C, the concentration of Cs after 106 days was 125ppm at the glass/clay interface and 80ppm at 1cm distance.

(b) Elements whose concentration in the solution is defined by the solubility product of their most stable phase so that their release does not depend on the degradation rate. Once freed from the glass matrix, they stay on the surface, either adsorbed on the gel-layer or in a reprecipitated form (eg U, Ce, Eu, La). Their diffusion rates are much slower: eg for U from I117 at 75°C the concentration after 84 days was 100ppm close to the glass but only about 1ppm 1cm away.

In the first case, for an infinite column, the concentration variation was given by the following equation:

$$C = 2\phi_i \sqrt{(t/D)} \text{ ierfc } (x/2\sqrt{(Dt)})$$

where ϕ, the constant flux of the diffusing element, is proportional to the leach-rate. In the second case, assuming that the diffusion coefficient does not depend on the concentration and that the column can be considered infinite, the concentration variation was of the type:

$$C = C_0 \text{ ierfc } (x/2\sqrt{(Dt)})$$

Starting from the experimental values, the effective diffusion coefficients for the different elements were calculated using a best fitting routine. The results obtained are given in Table 3. A similar study has also been conducted for a column of sea sediments (15).

The diffusion coefficients have quite large errors which can be ascribed to various reasons. First the degradation rate of the glass, which acts as a continuous source, has a large variation from test to test.

Element	I117 (50°C)	I117 (75°C)	SON 68 (75°C)
Cs	$(2.3 \pm 0.5)10^{-11}$	$(3.3 \pm 0.7)10^{-11}$	$(4.5 \pm 0.7)10^{-11}$
U	$(1.1 \pm 0.2)10^{-12}$	$(1.4 \pm 0.2)10^{-12}$	$(1.3 \pm 0.6)10^{-11}$
Co	$5.9 \cdot 10^{-13}$	$(4.2 \pm 0.6)10^{-13}$	$4.6 \cdot 10^{-13}$
Ce		$(0.9 \pm 0.2)10^{-13}$	$(1.7 \pm 0.7)10^{-13}$
Eu	$5 \cdot 10^{-14}$	$(3.6 \pm 0.6)10^{-14}$	
La	$2.3 \cdot 10^{-13}$	$(1.8 \pm 0.1)10^{-13}$	$1.7 \cdot 10^{-13}$

Table 3: Diffusion Coefficients ($m^2 s^{-1}$)

Typically, in a leaching test, standard deviations of about 10% are considered normal. Secondly, the original clay has an initial content of the various elements which can vary substantially from point to point. This variation, particularly at 50°C where the diffusion of the elements is slower, can affect the derivation of the diffusion coefficient: this is why it has not been possible to calculate the diffusion coefficient of

strontium.   Finally, although the system was carefully tested for leaks, some drying-out of the clay occurred during the tests which resulted in a moderate decrease in the corresponding diffusion coefficient.

The diffusion coefficients obtained with the two glasses I117 and SON 68 were very similar.   This seems quite reasonable in view of the small differences in composition between them.   The effect of changing the temperature from 50°C to 75°C was small and was often less than the uncertainties in the results.

Experimental data on diffusion of single elements can be found in the literature.   In particular, it is interesting to compare our results with those obtained by P N Henrion et al (10) on Boom clay and by B Torstenfelt (16) on compacted bentonite, both studies being conducted at room temperature.

For caesium, the diffusion coefficient given by (10) is lower by an order of magnitude.   Even taking into account that in our tests the temperature is higher, the difference seems too large.   It is possible that in clay caesium is desorbed due to adsorption competition, so that our results show an apparently higher diffusivity.   For uranium, the data given in reference (16) correspond to those obtained in this work with clay charged with iron.   Torstenfelt underlines the complexity of diffusion for substances like uranium in which more than a single chemical species is involved.   Taking into account the difference in tortuosity between the two media, our results appear to fall between the values reported in (10) and (16).

3.   Repositories in Granite

The effect of environmental materials on leaching of transuranium nuclides was measured at Marcoule by placing an Np-237 - or Pu-doped SON 68 glass pellet in a teflon container in contact with a solution and 2 grams of environmental material (1g for bentonite).   Seven media were tested: 3 clays + Volvic water (smectite 4a, illite 7, bentonite 6 or clarsol FB2), 1 clay + clayey water (Boom clay from Belgium), 1 granite + Volvic water, 1 sand + Volvic water and 1 salt + brine (bresse salt from France).

The specific activities of the doped glasses were: Np-237: 2.2×10^5 $Bq.g^{-1}$, Pu-239: $2.7 \times 10^7 Bq.g^{-1}$ and Am-241(Pu-238): $1.3 \times 10^7 Bq.g^{-1}$.   The experiments were carried out in duplicate for 3, 6, 9 and 12 month durations at 90±2°C.   The glass sample surface area to volume of leachant ratio (SA/V) was $50m^{-1}$ and the geological material mass to glass sample surface area ratio (A/SA) was $1.4kg.m^{-2}$ (0.7 for bentonite).

Examination of the normalised boron mass losses (NL(B)) of glass samples shows that glass alteration varied according to the environmental materials.   After one year, the glass alteration was 15 times greater in Boom clay than in bentonite.   Alteration was slight in the presence of sand or granite but considerable with smectite and illite.   These differences are due to the capacity of moist clay, when placed in rich solutions, of consuming elements from solution notably silicon.   As a result of glass dissolution in the water, the silicon enrichment of the medium exceeds the clay equilibrium value (18) and the clay tends to reform in equilibrium with the new conditions.   In this way, clay consumes silicon and prevents or delays a rise to high silicon concentrations in solution and thereby maintains high glass corrosion rates.   Bentonite clarsol FB2 is already at equilibrium with a much higher silicon enrichment: glass dissolution cannot have the same effect, and the clay does not consume silicon.

Isotope	Medium	alteration layer %	Solution				Material	
			Ultrafiltered solution <1.8nm		Filtered solution <0.45µm %	Parent solution %		
			activity in Bq.l⁻¹	%			activity in E6 Bq.kg⁻¹	%
Np-237	Sand	82	8700	11	11	11	0.08	7
	Granite	80	10500	8	8	8	0.2	12
	Bentonite	73	3800	7.5	9	11	0.25	16
	Smectite	55	16800	3.5	3.5	3.5	2.9	40.6
	Illite	64	25900	4	4	4.5	3.1	31.5
	Boom Clay	24	430000	47	47	51	3.3	25
	Bidistilled water		<0.025µm		<0.08µm			
		84	5800	16	16	16		0
Pu-239	Sand	96	1370	0.03	0.07	0.5	4.3	3.5
	Granite	93	1000	0.01	0.19	0.9	8.4	6
	Bentonite	93	250	<0.01	0.06	0.5	18.2	6
	Smectite	99	500	<0.01	<0.01	<0.01	9.6	0.9
	Illite	97	1470	<0.01	0.02	0.05	35.5	2.9
	Boom Clay	96	21000	0.02	0.04	0.25	67.5	3.7
	Bidistilled water***		<0.025µm		<0.08µm			
		98	6570	0.15	0.3	0.5		1.5**
Am-241/ Pu-238	Sand	98	430	0.01	0.02	0.12	1.1	1.85
	Granite	97	310	<0.01	0.05	0.4	2	2.5
	Bentonite	95	190	<0.01	0.05	0.4	5.4	4.5
	Smectite	99	370	<0.01	<0.01	<0.01	5.5	1
	Illite	98	370	<0.01	0.01	0.03	9.2	1.8
	Boom Clay	94	10250	0.015	0.06	0.22	45	5
	Bidistilled water*		<0.025µm		<0.08µm			
		99.7	2440	<0.01	0.015	0.5		0.02**

TABLE 4: PARTITION OF THE ACTIVITY OF THE ACTINIDES FROM THE ALTERATION OF DOPED COUPONS OF GLASS AFTER 12 MONTHS IN DIFFERENT ENVIRONMENTS. *COUPON OF GLASS DOPED WITH Am-241 ONLY; 10⁹ Bq.g⁻¹. **ON THE CONTAINER WALLS. *** AFTER 273 DAYS.

Table 4 shows the partition of the actinides liberated by leaching the glass for 12 months in the presence of environmental materials. This partition is between the gel or altered layer, the solution and the environmental materials. Two filtrations of the solution were carried out to show the percentages of the activity which was present as colloids or on colloidal particles and which was really in solution. Results are given for the parent solution and for those filtered through 0.45μm and 1.8nm filters.

It can be seen from Table 4 that the proportion of Np retained in the alteration layer varies considerably with the medium to which the glass is exposed. Thus in the presence of sand about 82% of the Np remains in the alteration layer whilst in the presence of Boom clay, only 24% is retained there. In double-distilled water, for the same V/SA ratio, 84% of the activity remained in the layer (20).

In the presence of Boom clay, about 50% of the Np was in true solution, ie after a 1.8nm filtration. This dissolution is probably favoured on the one hand by the non-reducing conditions of the experiment (the solubility of the actinides is generally increased in oxidising conditions (21, 22)) and on the other hand by the presence of organic materials and of anions in solution allowing the formation of complexes which favour the dissolution of the actinides (22). The clay solution used in this experiment is rich in SO_4^{--}, Cl^-, F^- and HCO_3^-. For the other media, it is clear that the presence of the environmental materials offers the possibility of increased absorption of the neptunium taken into solution and this is especially true for the clays which have the tendency to produce a suspension of colloidal particles. Because of the affinity that Np has for these materials, activity can be transferred from the gel layer to the environmental material via the solution. Thus about 41% of the activity of the Np released by the alteration of the glass specimen was found in the smectite used.

The partition values for Pu-239 are also given in Table 4. It can be shown that if the environmental materials make any differences, almost all of the activity arising from the corrosion of the glass remains in the alteration layer. This proportion is however a little smaller in the presence of the environmental materials (an average of 96%.) than in double distilled water (98.7%). Furthermore, most of the leached activity is retained in the environmental materials. The fraction of the activity in solution after 1.8nm filtration is below 0.03% of that in the environment. However, it should be noted that for sand, 0.03% represents 1370 Bq.l^{-1} in solution whereas for Boom clay, 0.02% represents 21000 Bq.l^{-1} because of the higher corrosion rate of the glass in this medium. Here again, the high concentration can be explained by the large amounts of complexing agents in the clay solution.

The concentrations obtained with a smectite backfill are not dissimilar to those obtained by Boult et al (24) using the CEC Repository System Simulation Test. The latter obtained 2500, 220 and 130 Bq.l^{-1} for Np, Pu and Am compared to 17000, 500 and 370 in the present work.

Studies carried out on the physico-chemical form of Pu-239 in the leachate (23) showed that it was found mainly in the form of particles larger than 0.45μm with a strong tendency to sorb on the vessel walls. Plutonium is released from glass into double-distilled water either in ionic form or as Pu(OH)$_4$ monomers which quickly flocculate.

The behaviour of the couple Pu-238/Am-241 (Table 4) is similar to that of Pu-239. The proporion of these actinides retained in the altered layer

is a little larger and the amount in the ultrafiltered solution is somewhat lower. In double-distilled water, the amount in the leached layer of a coupon of glass, doped with Am-241 at a specific activity of 10^9 Bq.g^{-1}, was 99.7% and 0.2% was fixed on the container walls (20).

Three tests were conducted using mockups designed to take account of the parameters imposed by storage in a granite environment. TAV experiments (1) were prepared to simulate the model as closely as possible. The experimental system comprises two identical teflon-lined stainless steel containers mounted in series: a leaching vessel and a conditioning vessel in which the leaching agent reached equilibrium with the environmental materials. The leaching vessel contains a cylindrical R7T7 glass block placed at the centre of the medium including pieces of granite simulating the host rock, steel or metals simulating the glass canister and sand containing 5wt% smectite 4a to simulate the nearfield engineered barrier.

Three experiments were run for 2 years at 90°C using the Np-237 and Pu-239 glasses prepared for the experiments described above and an Am-241 doped glass with an activity of 1.0×10^9 Bq.g^{-1}. The SA/V ratio was 70m^{-1} (60m^{-1} for the Am-doped glass) and the A/SA ratio was 2.4kg.m^{-2} (2.6 for the Am-doped glass). The leachant was Volvic mineral water.

Results show that only slight activity was found in solution (<0.02% of the total): most of the activity was retained by the smectite. On the experimental scale (ie 2 years at 90°C) the activity was quickly fixed and did not diffuse significantly in the leaching vessel. About 75% of the Np activity, 90% of the Am activity and 99% of the Pu activity were confined to within one centimeter from the surface of the glass block.

The actinide retention in the glass alteration layer were roughly the following: 50% for the Np activity, 98-99% for the Pu and 87% for the Am activity. The lower value for the retention of americium compared to those measured either in double-distilled water or in the tests described above was eventually explained by the nearness of the environmental materials to the surface of the glass and thus a greater sorption of the actinide by the clay.

At Harwell, (24) samples of glass were made up containing a full inactive simulant of the high-level-waste. These were doped with isotopes of Tc, Np, Pu and Am and after crushing (to speed up the approach to equilibrium) were mixed with possible components of a repository in granite and loaded into capsules. The loading was carried out in an argon 5% hydrogen filled glovebox to enable the reducing conditions that will occur in a repository to be established. The sealed capsules were held in an oven for periods of up to a year before they were opened and the water overlying the solids sampled and analysed. A weighed coupon of glass was included in some of the capsules to enable the weight-loss leach rate to be measured. Most of the experiments were on the MW glass composition which is used in the vitrification plant at Sellafield but some experiments used SON 68 so that intercomparisons with other work could be made. The two compositions are very similar (24).

In the majority of the experiments, the dopant concentrations in the glass were Tc-99: 2 MBq.g^{-1}, Np-237: 0.1MBq.g^{-1}, Pu-238: 0.37MBq.g^{-1} and Am-241 1.8MBq.g^{-1}. The proportions of the repository components in most of the capsules were: glass 1, iron (overpack) 5, backfill 10, water 20.

The molar concentrations found after 6-12 months and after filtering through a 25000 molecular weight cut off membrane (= 1.8nm) are given in Table 5. They are compared with the Limiting Concentration for each isotope: this is the concentration which, if present in drinking water,

Backfill	Variant	pH	Molar concentrations			
			$Tc/10^{-8}$	$Np/10^{-10}$	$Pu/10^{-14}$	$Am/10^{-13}$
OPC(1)/PFA(3)		12	1	6	40	20
OPC(1)BFS(3)		12	2	5	50	20
OPC(1)/ Limestone(6)		11.5	200	10	30	20
OPC(1)/PFA(10)		10.7	3	2	0.5	2
	Oxidising (Fe)	10.8	2	5	0.5	2
	Oxidising (Fe_2O_3)	10.4	8000	15	0.5	2
	90°C	9.6	3	13	0.5	2
	SON 68	10.9	3	6	0.5	2
	Ti/SS	10.7	200	6	0.5	2
	Humic acid	10.7	3	15	0.5	1
Boom Clay		7.7	6	1200	40	15
Bentonite		8.0	3	70	60	40
Limiting Concentrations			7	2	230	0.5
Inventory in capsule			1.5×10^5	9×10^6	2×10^7	3×10^7

Table 5: Molar Concentrations found in capsule experiments

Standard conditions: 60°C, reducing conditions, MW glass, Fe backfill.
OPC = Ordinary Portland Cement.   BFS = Blast Furnace Slag.
PFA = Pulverised Fuel Ash.   SS = Stainless Steel.

Isotope	Doped glass	Fully-active glass		Limiting Concentration (d)
		Magnox	THORP	
Tc-99 (/10⁻⁸)	1.2 (a) 8000 (b)	<500	15 (c)	6.7
Cs-137 (/10⁻⁷)		3.4	2.0	0.000003
Np-237 (/10⁻¹⁰)	1.7	40	60	2.1
Pu-239/40(/10⁻¹²)	0.06(40)(e)	500	10	2.3
Am-241 (/10⁻¹²)	0.2	6	0.3	0.047
Cm-244 (/10⁻¹⁵)		4	0.8	3.6
Conditions: pH Eh(mV)	10.7/10.8 -390/-570	10.0 +20	10.4 +155	

(a) Reducing (b) Oxidising
(c) After 1 month (d) For an annual dose of 1mSv
(e) The value in brackets is that found where the glass had a comparable Pu concentration to the fully active glass.

TABLE 6
Molar concentrations after 6 months at 60°C (0.45um filter)

Water	Time (months)	Tc-99 Filter pH	Eh (mV)	Tc-99 0.45 µm (/10⁻⁸M)	25000 MWCO	Actinides pH	Eh (mV)	Np-237 0.45 µm (/10⁻¹⁰M)	25000 MWCO	Pu-239/240 0.45 µm (/10⁻¹²M)	25000 MWCO	Am-241 0.45 µm (/10⁻¹²M)	25000 MWCO
Volvic	1	11.7	-500	3	2.5	11.6	-550	8	4	13	10	5	7
	3	11.6	-550	2	2	11.4	-550	15	24	24	23	3	8
	6	10.7	-250	2	2	10.7	-170	2	3	100	18	6	2
(24)	6	8.4	+20	1600	1500	8.2	(+150)	5000	5000	300	170	55	40
Sea	1	9.3	-400	2	2	9.4	-400	1.7	1.2	20	20	7	6
	3	9.8	-130	2	1.5	10.1	-150	0.4	0.2	250	5	40	2
	6	10.3	-480	0.4	0.4	10.2	-470	0.1	0.1	35	14	3	2
(24)	6	7.5	N/A	80	70	7.5	N/A	350	360	55	50	37	8
Limiting Concentration				6.7x10⁻⁸M				2.1x10⁻¹⁰M		2.3x10⁻¹²M		0.47x10⁻¹²M	

TABLE 7
Molar concentrations in the supernatant water
in the RSST containers at 90°C

would result in an annual dose of 1mSv to someone drinking 2 litres per day. The inventory of the active isotopes in the capsules was 5-7 orders of magnitude greater than most of the concentrations observed.

The molar concentration of Tc primarily depended on whether conditions were oxidising or reducing, throughout the capsule. Even with an air atmosphere in the capsule, if metallic iron was present, there were presumably reducing conditions local to the iron particles which immobilised the Tc. With a Ti "overpack", the Tc concentration in solution was also high, suggesting that an Fe/Tc compound may be significant. The Np concentrations were uniformly low when OPC (Ordinary Portland Cement) was present. The concentrations with a bentonite or Boom clay backfill were 1-2 orders of magnitude higher. The Pu and Am concentrations were also lower with an OPC(1)/PFA(10) backfill (PFA = pulverised fuel ash) than with Boom clay or bentonite, probably due to the high pH due to the cement. The actinide concentrations were not affected by oxidising or reducing conditions or by the presence of humic acid. Filtering through a 25000 MWCO membrane gave similar results to 0.45μm filtration suggesting that little or none of the material is present in colloidal form. This may be attributed to the high pH.

It was thought that the high pH due to the cement might be detrimental to the weight-loss leach rate of the glass, but this was not so, indeed the reverse was the case compared to leach-rates measured in pure water or in the presence of bentonite or clay. At 60°C, the weight-loss leach-rates of MW were, in $\mu g.cm^{-2}.day^{-1}$:

Fe only present:	7
Fe + OPC/PFA:	0.2 ± 0.07
Fe + Bentonite:	27
Fe + Boom clay:	21

The latter result is close to that obtained at Ispra (Section 2 above).

Similar experiments were carried out with fully active glass. These gave somewhat higher concentrations for most isotopes than were found with the doped glass as is shown in Table 6. Reducing conditions were not achieved in the fully active experiments which accounts for the higher values obtained for Tc. The Pu concentrations obtained in the fully active experiment were about one hundred times higher than in the capsule experiments. This was shown to be due to the unrealistically low concentrations of Pu in the doped-glass. When this was increased to a comparable value, comparable concentrations were obtained. The Pu concentration in the fully active glass tested was about a factor of ten higher than is expected in commercial vitrified HLW.

It is possible that the repository will be established beneath the sea-bed or near the shore and thus that the composition of the water entering it may be close to that of sea-water. Accordingly some additional experiments based on the EC Repository System Simulation Test (9) have been carried out. These used OPC(1)/PFA(10) (Ordinary Portland Cement/Pulverised Fuel Ash) as the "backfill" rather than a sand-smectite mixture, with sea-water in one pair of tests and the "standard" Volvic granite water in another. Only the supernatant water from the specimen chamber was analysed, for Tc and the actinides only. The results are given in Table 7. Reducing conditions were achieved in these experiments and the Tc results were much lower than in the original experiments where conditions were more oxidising (24). Similarly, the actinide concentrations were also lower than in the original experiments, very considerably so in the case of neptunium. This is presumably also due

partly to the reducing conditions but more particularly due to the higher pH arising from the presence of the OPC in the backfill. In these experiments, the equilibrium concentrations after filtering through a 25000 molecular weight cut-off membrane were less than the "limiting concentrations" for Tc and Np but higher by factors of about 8 and 5 for Pu and Am respectively.

The weight loss leach-rates, measured on coupons of glass included in the experiments were about a factor of five greater in the sea-water than in the granite water ($8\mu g.cm^{-2}.day^{-1}$ compared to 1.5).

4. Conclusions

(a) The concentrations of the mobile fractions of Cs, Sr, Pu and Am in simulated repository conditions in clay were very low – for Pu and Am they were below the detection limit. The mobile fraction of Pu and Am was less than 0.2% of the total inventory leached, the rest being adsorbed on the clay.

(b) Cs diffused fairly readily through a clay column but U and – by inference – the other actinides remained near the glass/clay interface.

(c) In granite-repository simulations, most of the Np, over 93% of the plutonium and over 95% of the Am remained in the alteration layer on the glass. Only 3 to 11% of the Np and 0.01% of the Pu and Am went into solution.

(d) In repository systems with backfills containing Ordinary Portland Cement (OPC) and under reducing conditions, the amounts of Tc, Np, Pu and Am in solution were respectively 0.2, 1, 20 and 4 times the "Limiting Concentration" which, if present in drinking water, would lead to an annual dose of 1mSv to someone drinking 2 litres of it per day.

(e) The presence of OPC reduced the leach-rate of the glass rather than increasing it, despite the high pH.

(f) Sea-water entering the repository would not have a deleterious effect on the Tc and actinide concentrations.

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