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LEACHING OF ACTINIDES FROM NUCLEAR WASTE GLASS: FRENCH EXPERIENCE

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ABSTRACT

Results are presented for a large number of aqueous leach tests on glass specimens doped with ^{237}Np , ^{238}Pu , ^{239}Pu , ^{241}Am or ^{244}Cm . The effects of the leaching mode (static or dynamic), temperature and environmental materials are discussed. The amount of actinides contained in the alteration film is characterized by the retention factor $RF = NL(B)/NL(\text{act})$. The neptunium retention factor ranged from 1 to 10 depending on the test conditions; for plutonium and americium, the retention factor varied from 6 to 1300.

In general, the retention factor increased with the temperature. The very important influence of the environmental materials shows that there is competition for actinide retention between the alteration film and the surrounding materials, but in every case the amount of α activity released into solution is very low.

INTRODUCTION

Most of the plutonium and uranium in spent fuel is recovered during reprocessing and can be recycled. A small fraction (about 0.5%) remains in fission product solutions together with some minor actinides (Np, Am and Cm), and these solutions can be vitrified in borosilicate glass. Although the actinides (not including uranium) are only about 0.3 wt% of the glass composition, they constitute the principal long-term radiation hazard. Figure 1 shows the activity concentration versus time of a typical LWR glass: after 300 years, most of the activity is attributable to three actinides (Np, Pu and Am) and to ^{99}Tc . This activity decreases slowly, and some 50 000 years are necessary before the activity concentration drops to the level of the richest natural ores. The safety of a repository will depend on the kinetics of toxic element release from the glass and on the retention or retardant capability of the natural or engineered barriers. This paper reviews the current state of knowledge concerning the kinetics of actinide release from glass subjected to aqueous leaching.

GLASS MATRIX CORROSION KINETICS

Before an actinide enters any leaching solution, the glass must be altered: the diffusion coefficients for heavy elements in the glass such as the rare earths and actinides are extremely low, typically less than $5 \times 10^{-18} \text{ cm}^2\text{s}^{-1}$ at temperatures up to 390°C [1]. The actinide release kinetics therefore never exceed the glass matrix alteration kinetics. The latter were recently reviewed in another paper [2] and may be described by a first-order relation in which r is the corrosion rate, r_0 the pH- and temperature-dependent forward rate of glass dissolution, $a_{\text{H}_4\text{SiO}_4}$ the silicic acid activity in the leaching solution, and $a_{\text{H}_4\text{SiO}_4}^*$ the silicic acid activity at saturation. Typical r_0 values for the French "R7T7" nuclear glass are $0.01 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ at 21°C and $1 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ at 90°C .

$$r = r_0 \left(1 - \frac{a_{\text{H}_4\text{SiO}_4}}{a_{\text{H}_4\text{SiO}_4}^*} \right)$$

DESCRIPTION OF THE α -DOPED GLASS SAMPLES

A large number of actinide-doped glass samples were prepared by the *Commissariat à l'Énergie Atomique* to investigate the leaching kinetics of the major actinides, the effects of radiolysis and α irradiation damage. The glass samples used for the leaching experiments described in this paper are shown in Table I with their actinide oxide concentration and specific activity values. The preparation of doped R7T7 glass samples has been described in

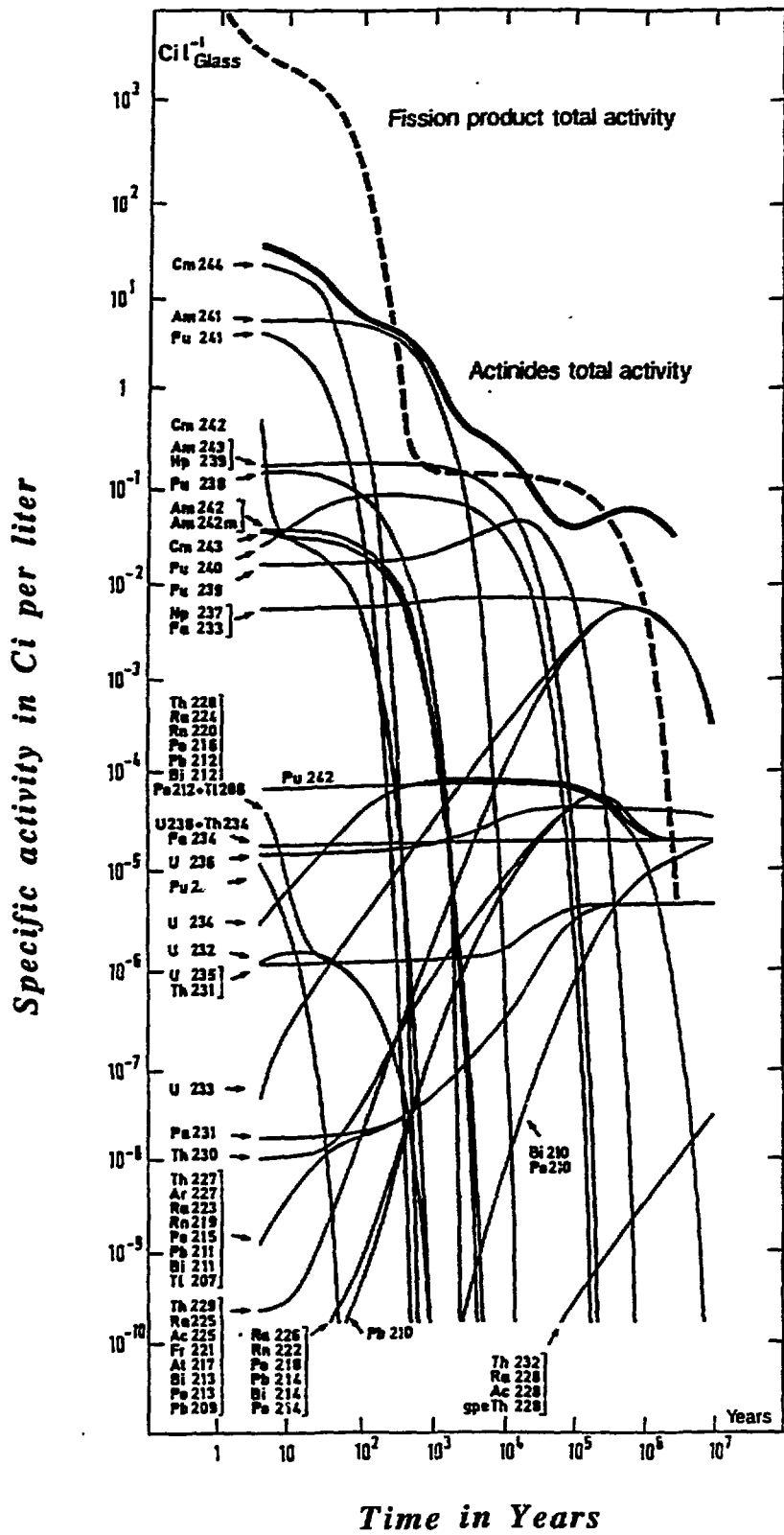


Figure 1. Typical LWR Glass Specific Activity versus Time

detail [3] and the exact composition of the earlier glass formulations SON 58, SON 61 and SAN 55 was published in another paper [4].

DYNAMIC LEACHING EXPERIMENTS IN PURE WATER

Room-Temperature Leaching

Experiments were conducted with R7T7 glass doped with ^{237}Np , ^{239}Pu and ^{241}Am . The specimens, measuring $25 \times 25 \times 3$ mm, were tested as cut, after ultrasonic cleaning. The glass coupons were leached for 70 days at room temperature with daily water renewal, and the specific activity of the leachate was measured daily by α spectrometry.

The daily actinide leach rate became relatively constant after a few days, and the following mean values were measured:

$$\text{LR}(\text{Np})_{25^\circ\text{C}} = 6 \times 10^{-3} \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$$

$$\text{LR}(\text{Pu})_{25^\circ\text{C}} = 6 \times 10^{-3} \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$$

$$\text{LR}(\text{Am})_{25^\circ\text{C}} = 3 \times 10^{-3} \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$$

The mass leach rate was about $\text{LR}(\text{mass})_{25^\circ\text{C}} = 12 \times 10^{-3} \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ for all the tests.

The actinide retention factor RF in the alteration film is defined as the ratio between the normalized boron mass loss and the normalized actinide mass loss. Assuming the approximation $\text{NL}(\text{B}) \approx \text{NL}(\text{mass})$, the actinide retention factor under dynamic leaching conditions at room temperature was about 2 for Np and Pu, and about 4 for Am.

Effect of Water Renewal Rate

Figure 2 shows the daily cesium and plutonium leach rates from a 1680 g block of R7T7 glass containing 500 Ci β and 27 Ci α , leached for 76 days at room temperature in the *Vulcan* cell. The leaching solution was renewed daily except for three short periods indicated by horizontal arrows on the chart. The leach rates dropped quickly for all the elements, probably as a result of the formation of an ion exchange zone at the glass surface. With an initial corrosion rate of $10^{-2} \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ at room temperature, the hydration front advanced only 36 Å per day; it is not unexpected that a few days were required to obtain a corrosion front measuring a few hundred angstroms. After about a month, the leach rates were relatively constant and virtually identical for Cs and Pu: $\text{LR}(\text{Cs})_{25^\circ\text{C}} \approx \text{LR}(\text{Pu})_{25^\circ\text{C}} \approx 2 \times 10^{-3} \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$. As long as the water was renewed daily, plutonium was leached at nearly the same rate as a mobile element such as cesium. Conversely, when the water renewal was interrupted, the plutonium leach rate dropped significantly while the cesium leach rate was unaffected.

Figure 3 indicates the measured Pu leach rate for SON 58 glass as doped with ^{238}Pu . In this experiment, the water was renewed daily except during weekends and holidays (the periods without renewal are indicated on the figure by three contiguous dots connected by a dotted line). The activity leached from the glass after 3 or 5

Table I. Actinide-Doped Glass Characteristics

Glass Reference	Actinide Content	Specific Activity
R7T7 ^{237}Np	0.85% NpO_2	226 kBq·g ⁻¹
R7T7 ^{239}Pu	0.85% PuO_2	38 MBq·g ⁻¹
R7T7 ^{238}Pu	0.85% PuO_2	1.3 GBq·g ⁻¹
R7T7 ^{241}Am	0.85% AmO_2	1.1 GBq·g ⁻¹
SON 58 30 20	2.8% PuO_2	2.6 GBq·g ⁻¹
SON 61 30 14	2.8% AmO_2	3.0 GBq·g ⁻¹
SAN 55 20 20	1.3% CmO_2	18 GBq·g ⁻¹

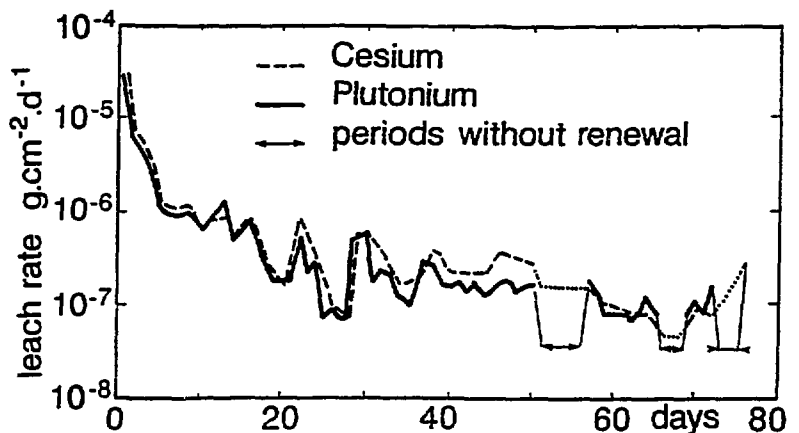


Figure 2. Dynamic Leaching of R7T7 Glass (ref A110) at Room Temperature

days without renewal was not much greater than the activity leached in 24 hours and the daily Pu leach rate dropped to an extent proportional to the duration of the nonrenewal period. The same phenomenon was observed for Am-doped SON 61 glass and for Cm-doped SAN 55 glass.

The results suggest that with frequent solution renewal, the actinides are leached at room temperature at the same rate as the other glass elements. If the renewal is interrupted, however, the activity in solution quickly reaches a virtually steady-state value, and the apparent leach rate drops with the renewal rate.

This implies that the actinide release kinetics are controlled by the solubility of an actinide compound at the glass surface. It is difficult to measure such a solubility limit, however, since much of the activity is found in undissolved form in solution, as we shall see later. The pH in all these tests was about 8.5, and the water was at equilibrium with the atmospheric CO₂.

Temperature Effect

The actinide leach rates measured with daily leachate renewal at 25, 50 and 70°C for ²³⁸Pu-doped SON 58 glass, ²⁴¹Am-doped SON 61 glass and ²⁴⁴Cm-doped SAN 55 glass specimens are compared in Figure 4. The daily Pu and Am leach rates did not increase significantly with the temperature, and the curium leach rate dropped sharply.

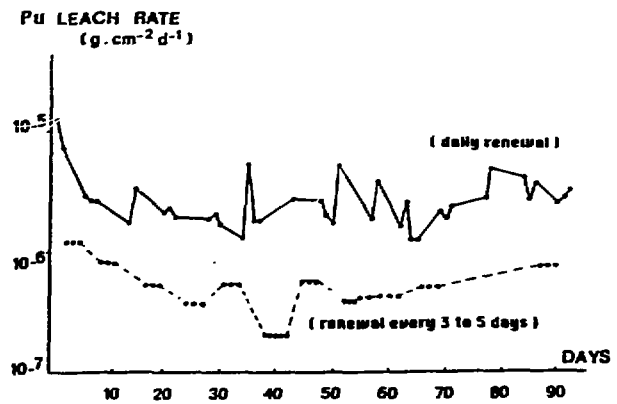


Figure 3. Results of Dynamic Leach Tests at Room Temperature of SON 58 Glass Doped with ²³⁸Pu: Effect of Water Renewal Interval

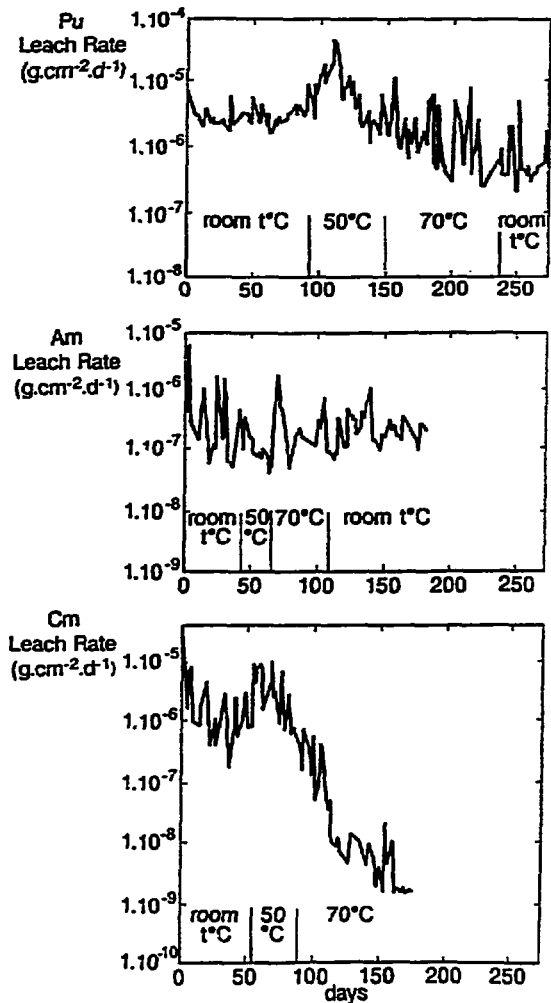


Figure 4. Results of Dynamic Leach Tests at 25, 50 and 70°C: ²³⁸Pu-Doped SON 58 Glass, ²⁴¹Am-Doped SON 61 Glass and ²⁴⁴Cm-Doped SAN 55 Glass

Soxhlet Mode Leach Tests

Alpha-doped R7T7 glass specimens were leached at 100°C in a Soxhlet device with continuously flowing water. At the end of the 28-day leaching period the leachates were acidified with 14N nitric acid before analysis (ICP, α and γ spectrometry, etc.). The daily leach rates were as follows:

$$\begin{aligned} \text{LR(Np)}_{100^\circ\text{C}} &= 0.6 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1} \\ \text{LR(Pu)}_{100^\circ\text{C}} &= 0.005 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1} \\ \text{LR(Am)}_{100^\circ\text{C}} &= 0.003 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1} \\ \text{LR(B)}_{100^\circ\text{C}} &= 2 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1} \end{aligned}$$

The actinide retention factors $\text{RF} = \text{LR(B)}/\text{LR(act)}$ were then 3.7 for neptunium, 412 for plutonium and 469 for americium. Thus, even under Soxhlet conditions in which the solubility limits were never reached (except perhaps in an interface layer around the glass) the actinides remained mostly trapped in the gel layer with a relatively low retention factor for neptunium and high values for plutonium and americium. This significant difference compared with room-temperature dynamic leaching may be explained by the higher Pu and Am retention factors in the gel at higher temperatures, and by the much greater thickness of the alteration film under Soxhlet conditions. For these samples the gel layer was about 20 μm thick. Electron microprobe analysis confirmed the high actinide enrichment of this layer.

STATIC LEACHING AT 50°C AND 90°C

Static leach tests were conducted on R7T7 glass doped with 0.85% actinide oxides at 90°C in double-distilled water for up to one year with an SA/V ratio of 50 m^{-1} . The experimental protocol has been described elsewhere [5]. All experiments were performed in duplicate. The results are shown in terms of pH, activity, concentration, normalized mass losses and retention factors in Tables II and III. The results marked "tot" in the tables refer to the total activity or concentration in solution; those marked "filt" refer to the activity or concentration after filtration across a 250 Å filter.

The glass matrix alteration is characterized by the normalized boron mass loss NL(B). After one year of alteration at 50°C or 90°C, NL(B) was relatively similar for all the tests except the ^{238}Pu - and ^{241}Am -doped specimens leached at 50°C, for which the glass was considerably less altered. This difference appears to be directly related to the leachate pH, which was acidic for both tests [6]. A radiolysis phenomenon involving either the water or the small teflon holder supporting the glass coupon clearly occurred with the specimens containing the highest α activity. The radiolysis effect on the pH was less pronounced at 90°C, probably because of the higher initial glass dissolution kinetics.

The uranium concentrations in solution after leaching for one year were on the same order of magnitude at 50°C and 90°C (about 100-200 ppb). The uranium retention factor was slightly higher at 90°C ($\text{RF} \approx 9$) than at 50°C ($\text{RF} \approx 6$).

The neptunium concentrations after 1 year were lower at 90°C than at 50°C, as reflected by a sharp increase in the Np retention factor between 50°C ($\text{RF} \approx 3$) and 90°C ($\text{RF} \approx 10$). The concentrations did not change after ultrafiltration, indicating that the leached neptunium was not present in colloid or particle form.

The plutonium concentrations after one year were similar at 50°C and 90°C, and dropped by about one order of magnitude after ultrafiltration, indicating that after one year about 90% of the leached plutonium is found in colloid or particle form. The Pu retention factor was about 50 for ^{239}Pu -doped glass and about 24 for ^{238}Pu -doped glass; the difference could be related to the more acid pH of the leachate with ^{238}Pu -doped glass, notably at 50°C.

The americium concentrations were lower at 90°C than at 50°C after one year, and dropped by about two orders of magnitude after ultrafiltration: about 99% of the leached americium was found in particle form after one year. The Am retention factor was much higher at 90°C ($\text{RF} \approx 600$) than at 50°C ($\text{RF} \approx 23$); this major difference can probably be attributed to two phenomena (the RF increases with the temperature and diminishes with the pH) although it is not possible to determine the relative importance of each phenomenon.

Table II. Static Leach Test Results at 50°C (SA/V = 50 m⁻¹)

Natural U	pH (25°C)			C(U) tot (ppb)		NL(U) (10 ⁻² g·m ⁻²)	NL(B) (10 ⁻² g·m ⁻²)	RF
1	7.9			20				
3	8.4			20		9.7	42	4
7	8.4			20		9.5	60	6
14	8.2			20		9.7	74	8
28	8.6			25		11.9	92	8
56	8.4			52		25.9	102	4
91	8.1			66		31.9	103	3
182	8.6			100		47.6	219	5
273	9.4			100		47.6	264	6
364	9.5			185		83.8	848	10
237Np	pH (25°C)	A(Np) tot (kBq)	A(Np) filt (kBq)	C(Np) tot (ppb)	C(Np) filt (ppb)	NL(Np) (10 ⁻² g·m ⁻²)	NL(B) (10 ⁻² g·m ⁻²)	RF
1	7.8	22		28		8	15	2
3	7.5	67		85		21	28	1
7	8.4	89		113		29	39	1
14	7.9	155		198		51	86	2
28	8.5	189		241		62	111	2
56	8.8	211		269		73	133	2
91	9			421		109	179	2
182	9	477	411	609	524	119	376	3
273	9.4	1032	1010	1317	1289	339	910	3
364	9.4	888	910	1133	1161	283	1148	4
239Pu	pH (25°C)	A(Pu) tot (kBq)	A(Pu) filt (kBq)	C(Pu) tot (ppb)	C(Pu) filt (ppb)	NL(Pu) (10 ⁻² g·m ⁻²)	NL(B) (10 ⁻² g·m ⁻²)	RF
1	6.3	1.89		13		4.4	16	4
3	7.7	2.78		19		5.9	28	5
7	8	2.44		17		5	47	9
14	8.3	1.89		13		4.4	72	16
28	7.7	5.66		40		10.4	65	6
56	8.2	5.55		39		11.3	115	10
91	7.8					5.8	147	25
182	9.2	7.88	0.39	55	2.7	14.6	319	22
273	9.1	3.66	0.67	26	4.7	9.2	713	78
364	8.6	11.54	0.36	81	2.5	17.9	977	55
238Pu	pH (25°C)	A(Pu) tot (kBq)	A(Pu) filt (kBq)	C(Pu) tot (ppb)	C(Pu) filt (ppb)	NL(Pu) (10 ⁻² g·m ⁻²)	NL(B) (10 ⁻² g·m ⁻²)	RF
1	8.7	78		15		4.2	22	5
3		404		78		20.5	114	6
7	7.5	145		23		8	37	5
14	6.2	205		40		11	44	4
28	7.2					14	74	5
56	5.9	205		40		12	114	10
91	5.5	174		34		8	112	14
182	5.9	311		60		16	112	7
273	5.4	300	222	58	43	17	112	7
364	5.8	322	21	62	4	12	287	24
241Am	pH (25°C)	A(Am) tot (kBq)	A(Am) filt (kBq)	C(Am) tot (ppb)	C(Am) filt (ppb)	NL(Am) (10 ⁻² g·m ⁻²)	NL(B) (10 ⁻² g·m ⁻²)	RF
1	4.8	16		4		1.0	31	31
3	5.9	13		3		0.9	37	41
7	6.6	14		3		1.0	50	50
14	5.4	13		3		0.8	66	83
28	5.1	22		5		1.5	67	45
56	4.3	47		11		3.4	78	23
91	6	42		10		3.4	92	27
182	5.7	44	1.4	11	0.3	3.5	148	42
273		137	1.1	33	0.3	9.7	191	20
364	5.7	123	11.1	30	2.7	8.3	193	23

Table III. Static Leach Test Results at 90°C (SAV = 50 m⁻¹)

Natural U	pH (25°C)			C(U) tot (ppb)		NL(U) (10 ⁻² g·m ⁻²)	NL(B) (10 ⁻² g·m ⁻²)	RF
1						9	17	
3				62		29	265	9
7				64		30	301	10
14				76		36	329	9
28	9.3			66		31	343	11
56				96		45	367	8
91				126		57	386	7
182	9.3			100		47	459	10
273				134		63	550	9
364	9.7			161		75	689	9
237Np	pH (25°C)	A(Np) tot (kBq)	A(Np) filt (kBq)	C(Np) tot (ppb)	C(Np) filt (ppb)	NL(Np) (10 ⁻² g·m ⁻²)	NL(B) (10 ⁻² g·m ⁻²)	RF
1	9.1	111		142		38	173	5
3	9.1	122		156		39	261	7
7	9.1	144		184		47	305	6
14	9.1	155		198		53	360	7
28	9.1	178		227		59	404	7
56	9.2	189		241		63	422	7
91	9.3	255		326		78	447	6
182	9.2	144	139	184	175	41	477	12
273	9.5	301	276	425	439	97	677	7
364	9.4	224	218	368	368	64	624	10
239Pu	pH (25°C)	A(Pu) tot (kBq)	A(Pu) filt (kBq)	C(Pu) tot (ppb)	C(Pu) filt (ppb)	NL(Pu) (10 ⁻² g·m ⁻²)	NL(B) (10 ⁻² g·m ⁻²)	RF
1	9.2	0.8		6		1.5	153	102
3	9.3	1.1		8		2.2	229	104
7	9.4	1.6		11		3.3	272	82
14	9.4	1.3		9		2.8	280	100
28	9.3	1.8		12		3.8	323	85
56	9.1	2.6		18		4.2	341	81
91	8.8	4.2		30		8.9	352	40
182	9.5	5.0	0.9	35	6.2	8.7	470	54
273	9	4.3	0.3	30	1.9	9.3	443	48
364	8.6	5.1	1.2	36	8.3	10.4	468	45
238Pu	pH (25°C)	A(Pu) tot (kBq)	A(Pu) filt (kBq)	C(Pu) tot (ppb)	C(Pu) filt (ppb)	NL(Pu) (10 ⁻² g·m ⁻²)	NL(B) (10 ⁻² g·m ⁻²)	RF
1	5.5	63		12		3.5	129	37
3	9	64		12		3.5	220	63
7	9	104		20		5.7	253	44
14	8.8	91		18		5	298	60
28	8.6			30		8.9	344	39
56	8.2	222		43		12.3	417	34
91	8.1	255		49		13.5	434	32
182	8.6	622		120		38.1	974	26
273	8.4	744	19	143	4	37.5	960	26
364		844	125	163	24	39.9	975	24
241Am	pH (25°C)	A(Am) tot (kBq)	A(Am) filt (kBq)	C(Am) tot (ppb)	C(Am) filt (ppb)	NL(Am) (10 ⁻² g·m ⁻²)	NL(B) (10 ⁻² g·m ⁻²)	RF
1	8.8	3.3		0.8		0.2	157	785
3	8.87	3.6		0.9		0.2	224	1120
7	8.8	3.1		0.8		0.2	273	1365
14	8.2	5.4		1.3		0.4	325	813
28	7.9	5.0		1.2		0.3	330	1100
56	7.7	9.8		2.4		0.7	373	533
91	8.4	5.6		1.3		0.3	401	1337
182	8.5	44.4	0.6	10.8	0.13	2.7	964	357
273	8.3	58.8	0.3	14.3	0.08	3.9	944	242
364		30.0	0.6	7.3	0.13	1.6	962	601

Table IV. Influence of Environmental Materials on Neptunium and Plutonium Leach Rates at 90°C (SA/V = 50 m⁻¹)

Np-Doped Glass

Recovered ²³⁷Np Activity

Time (months)	Sand		Granite		Smectite		Bentonite		Illite		Boom Clay		Salt	
	total filtered		total filtered		total filtered		total filtered		total filtered		total filtered		total filtered	
	Bq	Bq	Bq	Bq	Bq	Bq	Bq	Bq	Bq	Bq	Bq	Bq	Bq	Bq
3	1050	820	1300	1049	3100	705	300	127	4300	1204	6600	1288	1200	794
6	400	255	500	255	5100	277	450	172	7300	800	14500	2853	2000	988
9	350	272	650	167	6400	538	500	189	8400	1195	21000	11710	2100	1443
12	400	264	700	316	6400	506	400	117	7000	777	21000	12848	3400	1770

Normalized Mass Loss for Np and B in g·m⁻²

Time (months)	Sand		Granite		Smectite		Bentonite		Illite		Boom Clay		Salt	
	NL(Np)	NL(B)	NL(Np)	NL(B)	NL(Np)	NL(B)	NL(Np)	NL(B)	NL(Np)	NL(B)	NL(Np)	NL(B)	NL(Np)	NL(B)
	3	3.4	10.3	4.3	11.2	10.2	56.1	1.1	3.1	13.8	32.5	21.0	42.3	3.8
6	1.2	7.6	1.6	11.2	15.1	37.4	1.4	4.7	21.6	54.7	48.5	96.8	6.3	19.4
9	1.2	9.3	2.0	10.6	20.0	40.2	1.6	5.4	26.3	62.2	65.8	96.5	6.7	16.6
12	1.3	7.6	2.1	10.5	20.2	45.8	1.3	4.9	22.1	61.8	65.3	85.9	10.5	32.9

pH and Np Retention Factors

Time (months)	Sand		Granite		Smectite		Bentonite		Illite		Boom Clay		Salt	
	pH	RF	pH	RF	pH	RF	pH	RF	pH	RF	pH	RF	pH	RF
	3	8.6	3	9.0	3	8.7	6	9.5	3	8.6	2	8.0	2	7.1
6	8.5	6	9.0	7	8.5	2	9.6	3	8.7	3	8.1	2	7.0	3
9	9.4	8	9.4	5	8.9	2	9.8	3	8.8	2	8.5	1	7.0	2
12	9.5	6	9.4	5	8.9	2	9.8	4	9.0	3	8.7	1	7.0	3

Pu-Doped Glass

Recovered ^{239/240}Pu Activity

Time (months)	Sand		Granite		Smectite		Bentonite		Illite		Boom Clay		Salt*	
	total filtered		total filtered		total filtered		total filtered		total filtered		total filtered		total filtered	
	kBq	Bq	kBq	Bq	kBq	Bq	kBq	Bq	kBq	Bq	kBq	Bq	kBq	Bq
3	6.3	30	16.1	26	32.5	11	19.9	3	46.9	22	67.2	1940	17.2	199
6	6.8	178	22.0	32	22.7	11	17.8	6	66	11	112.6	520	35.4	283
9	19.0	31	34.0	21	12.5	11	21.1	5	25.3	22	142.5	932	89.9	279
12	9.1	41	19.8	31	23.3	133	19.6	8	77.3	44	143	633	74.7	1005

(*gross α activity for salt)

Normalized Mass Loss for Pu and B in g·m⁻²

Time (months)	Sand		Granite		Smectite		Bentonite		Illite		Boom Clay		Salt	
	NL(Pu)	NL(B)	NL(Pu)	NL(B)	NL(Pu)	NL(B)	NL(Pu)	NL(B)	NL(Pu)	NL(B)	NL(Pu)	NL(B)	NL(Pu)	NL(B)
	3	0.2	7.7	0.4	5.9	0.8	23.1	0.5	4.9	1.2	56.6	1.7	68.6	0.3
6	0.2	6.6	0.6	7.2	0.6	35.6	0.5	4.9	1.7	56.5	2.9	69.1	0.6	7.9
9	0.5	6.2	0.8	7.5	0.3	37.1	0.5	4.3	0.6	56.5	3.4	87.4	1.6	15.5
12	0.2	6.4	0.5	7.0	0.6	45.8	0.5	7.1	1.9	73.0	3.7	90.6	1.3	23.1

pH and Pu Retention Factors

Time (months)	Sand		Granite		Smectite		Bentonite		Illite		Boom Clay		Salt	
	pH	RF	pH	RF	pH	RF	pH	RF	pH	RF	pH	RF	pH	RF
	3	8.6	48	9.0	14	8.7	28	9.5	10	8.6	47	8.0	40	7.1
6	8.5	39	9.0	13	8.5	61	9.6	11	8.7	33	8.1	24	7.0	13
9	9.4	14	9.4	9	8.9	124	9.8	9	8.8	93	8.5	26	7.0	10
12	9.5	29	9.4	15	8.9	83	9.8	15	9.0	39	8.7	24	7.0	18

STATIC LEACHING IN THE PRESENCE OF ENVIRONMENTAL MATERIALS

Experiments with Small Quantities of Different Materials

These experiments were conducted at 90°C following a procedure similar to the MCC-1 protocol, but with an SA/V ratio of 50 m⁻¹. Two grams of crushed material (1 gram for bentonite) were placed at the bottom of the teflon container. The crushed material consisted of sand, granite, bentonite, smectite, illite, Boom clay or salt, as described in reference [7]. R7T7 glass coupons were doped either with ²³⁷Np or with ²³⁹Pu, and all the tests were duplicated. The results are shown in Table IV.

The total recovered activity from which the normalized actinide mass loss was determined corresponds to the sum of the activity recovered in the leachate, on the environmental materials and on the container walls. The "filtered" activity is the activity in the leachate after ultrafiltration (18 Å). The difference between the total and filtered activities is thus due either to the presence of colloids or to activity fixation by the materials and the container.

The normalized boron mass loss confirms the effect of the environmental materials on the glass alteration rate. As with similar inactive tests [7] moderate alteration was observed in the presence of sand, granite and a highly siliceous bentonite; alteration was severe with smectite, illite and Boom clay, while salt gave intermediate results.

In all the test media, the Np retention factor in the alteration film was less than 10, but was slightly higher in sand and granite than in clay; neptunium retention was virtually nil in the gel layer with Boom clay. The plutonium retention factors varied as follows:

$$RF_{\text{bentonite}} = RF_{\text{salt}} = RF_{\text{granite}} < RF_{\text{sand}} = RF_{\text{illite}} = RF_{\text{Boom clay}} < RF_{\text{smectite}}.$$

These results could not be correlated with the pH.

Tables V and VI show the activity distribution on the environmental materials and in solution, along with the size distribution. The righthand column in each table shows the percentage of activity that was not leached, but remained trapped in the gel layer on the glass surface (this percentage is directly related to the retention factor by the expression $\% = 1 - (1/RF)$).

When R7T7 glass is altered at 90° under the slightly oxidizing conditions of a laboratory atmosphere, a fraction of the neptunium from the altered glass region remains trapped in the surface gel. This fraction was relatively small in Boom clay (24%) but substantial in sand (82%) and in granite (80%). Part of

Table V. Distribution of Np Activity Leached from Np-Doped R7T7 Glass Specimens Altered for 12 Months at 90°C in Various Media

Medium	Solution				Environmental Material		Alteration film
	Ultrafiltered solution (< 18 Å)		Filtered solution (< 0.45 µm)	Parent solution	Specific activity (Bq·g ⁻¹)	%	
	Spec activity (Bq·ml ⁻¹)	%					
Sand	8.8	62	63	63	80	37	82
Granite	10.5	42	2	44	200	56	80
Bentonite	3.9	28	34	39	240	61	73
Smectite	16.9	8	8	8	2900	92	55
Illite	25.9	11	-	12	3000	88	64
Boom Clay	428	62	-	68	2700	32	24
Salt	59	50	50	50	800	50	68
Distilled water	(< 250 Å)	97	98.5	100	0	0	75

Table VI. Distribution of Pu Activity Leached from ²³⁹Pu-Doped R7T7 Glass Specimens Altered for 12 Months at 90°C in Various Media

Medium	Solution				Environmental Material		Alteration film
	Ultrafiltered solution (< 18 Å)		Filtered solution (< 0.45 µm)	Parent solution	Specific activity (kBq·g ⁻¹)	%	
	Spec activity (Bq·ml ⁻¹)	%					
Sand	1.5	0.4	0.9	6	4.3	94	96
Granite	0.9	0.2	2	13	8.4	87	93
Bentonite	0.3	0.04	1.7	6	17.5	94	93
Smectite	0.4	0.05	0.05	0.6	8.9	99.4	99
Illite	1.5	0.06	0.6	1.4	34	98.6	97
Boom Clay	21	0.4	1.0	4.5	57	95.5	96
Salt	33	1.4	22	45	20	55	94
Distilled water	(< 250 Å)	30	50	100	0	0	98

the leached neptunium is fixed on the environmental material. For the test conditions, this fraction ranged from 32% (Boom clay) to 92% (smectite). In each case, the activity remaining in solution was soluble, as it was not removed by filtration or by ultrafiltration.

The plutonium fraction retained in the surface gel during this type of test was much greater than for neptunium, ranging from 93% (granite, bentonite) to 99% (smectite). The leached plutonium fraction fixed by the materials was also much larger, between 55% (salt) and 99.4% (smectite). Most of the leached activity that was not fixed on the materials was in particle form, and was removed by filtration. The specific activity of the ultrafiltered (< 18 Å) leachate was very low (approx 1 Bq·ml⁻¹) with most of the tested materials, much lower than in pure water.

Integral Experiments

Other experiments simulating the conditions of a geological repository were carried out using glass blocks doped with ²³⁷Np, ²³⁹Pu and ²⁴¹Am. These "TAV" (*Test d'Altérabilité des Verres* or glass alterability test) experiments, in which mockups containing a glass block surrounded by environmental materials are submitted to alteration at 90°C under a pressure of 10 MPa, have been described in earlier publications [8,9]. In this case, the environmental materials were granite and a mixture of sand and smectite simulating an engineered barrier.

Two types of results are provided by integral experiments:

First, the apparent normalized mass loss is calculated from the activity of leachate samples taken at 2-month intervals using a sampling tube that extends into the test vessel next to the glass block. The values in Table VII were three orders of

magnitude lower for americium than for neptunium. These "apparent" values do not allow for activity fixed on the environmental materials.

Second, the true normalized mass loss is determined at the end of the test from the total activity recovered in the leachate, on the vessel walls and on the environmental materials. The actinide retention factors in the glass alteration film are determined by comparing these results with the normalized boron mass loss. After 22 months at 90°C under integral conditions, the results were as follows:

$$\begin{aligned} \text{NL(B)} &= 100 \text{ g}\cdot\text{m}^{-2} & \text{RF(Np)} &= 2 \\ \text{NL(Np)} &= 50 \text{ g}\cdot\text{m}^{-2} & \text{RF(Pu)} &= 100 \\ \text{NL(Pu)} &= 1 \text{ g}\cdot\text{m}^{-2} & \text{RF(Am)} &= 6 \\ \text{NL(Am)} &= 18 \text{ g}\cdot\text{m}^{-2} & & \end{aligned}$$

The leaching environment thus strongly influences the actinide retention factor, since RF(Pu) was higher than in pure water (Table III), while RF(Am) was two orders of magnitude lower. It should be noted, however, that over 99% of the leached activity was fixed by the environmental materials, and that the activity in solution after 2 years at 90°C was extremely low. Typical values for Np, Pu and Am were 1 Bq·ml⁻¹, corresponding to concentrations of about 40 ppb for Np, 0.2 ppb for Pu and 0.02 ppb for Am.

Experiments in Moist Clay

R7T7 glass samples doped with ²³⁹Pu were subjected to alteration in contact with moist clay as detailed elsewhere [10]. Glass coupons measuring 25 × 25 × 3 mm were altered in smectite grade "4a" at 90°C under a pressure of 10 MPa for periods of 1 to 6 months. On completion of the test, the glass was rinsed to remove the clay gangue. Glass alteration was determined from the specimen mass loss and from the thickness of the alteration film. The

Table VII. Apparent Normalized Actinide Loss (10⁻² g·m⁻²·d⁻¹) for TAV Tests with ²³⁷Np, ²³⁹Pu and ²⁴¹Am

Time (months)	NL(Np)	NL(Pu)	NL(Am)
2	8.2	1.88	0.060
4	10.9	0.86	0.093
6	12.7	1.17	0.006
8	6.3	0.20	0.004
10	14.4	0.43	0.002
12	17.1	0.54	0.003
14	4.3	0.20	0.003
16	4.7	0.16	0.003
18	0.6	0.30	0.006
20	3.9	0.12	0.005
22	5.3	0.02	0.004

normalized Pu mass loss was determined by measuring the $^{239+240}\text{Pu}$ activity in the clay after testing. The α activity leached from the glass was very strongly fixed on the clay; repeated rinsing in 1N HNO_3 did not extract all the activity, and the final measurement was obtained only after alkaline melting and dissolution of the clay.

The principal results are summarized in Table VIII. Although the alteration film was rather thick (about $60\ \mu\text{m}$ after 6 months) the plutonium retention factor in the film was relatively low (5 to 8).

Table VIII. Normalized Plutonium Mass Losses and Plutonium Retention Factors for Glass Altered in Moist Clay at 90°C

Time (months)	NL(m) ($\text{g}\cdot\text{m}^{-2}$)	NL(Pu) ($\text{g}\cdot\text{m}^{-2}$)	RF(Pu)
1	27	5	5
2	39	7	6
3	56	9	6
6	98	13	8

DISCUSSION

Room-temperature dynamic leaching experiments showed that actinides are initially released into solution at the same rate as the other glass matrix elements: dissolution is congruent. However, as corrosion progresses, an amorphous "gel" alteration layer forms on the glass surface and retains most of the actinides.

Depending on the experimental conditions, the neptunium retention factor in the gel [$\text{RF} = \text{NL}(\text{B})/\text{NL}(\text{Np})$] varied from 1 to 10. The Np concentration in the leachate increased with the glass dissolution, and did not appear to be controlled by any solubility limit. The redox conditions were slightly oxidizing in all these experiments, but the retention factor still did not exceed 10 in other tests under reducing conditions [11].

In the pH range of these experiments (7–10), the retention factors for the other nuclides (Pu, Am and Cm) varied from 6 to 1300. The fraction of these elements retained in the gel increased with the temperature, and was inversely proportional to the leachate renewal frequency. The release kinetics of these elements thus appear to be partly controlled by the solubility of an actinide compound that forms in the interface gel (if it formed in solution, a high retention factor would not be observed for the Soxhlet tests). The solubility of this compound apparently diminishes to some degree with the temperature.

Pu, Am and Cm may continue to be released slowly even after the solubility limit of this compound is reached, as these actinides also form particles or colloids in solution. After 1 year at 90°C in pure water, over 80% of the leached plutonium and 99% of the leached americium were found in particle form.

The environmental materials have a very important role in determining the actinide fraction retained in the alteration film. One of the most surprising results of this research concerns the influence of smectite 4a. As long as the clay is not in direct contact with the glass (e.g. in the test with an SA/V ratio of $50\ \text{m}^{-1}$ where the clay was at the bottom of the vessel, or in the TAV experiments) it has little effect on the plutonium retention factor, which remains high ($\text{RF} = 80$ after 1 year at 90°C , and $\text{RF} = 100$ after 2 years at 90°C in TAV tests). In the moist clay experiments, however, where the smectite was in direct contact with the glass under a pressure of 10 MPa, the Pu retention factor dropped to only 6. It thus appears that the vital process occurs either in the gel layer or in a very narrow region immediately adjacent to the glass. If the clay is present in this zone, there is competition between the gel and the clay for plutonium incorporation.

As a rule, the actual actinide concentrations in solution (i.e. after ultrafiltration) are very low: typical equilibrium concentrations in pure water at 90°C are a few ppb for plutonium and a few tenths of a ppb for americium. These values drop by an order of magnitude for the integral experiments: 0.2 ppb of Pu and 0.02 ppb of Am in solution after 2 years of TAV testing in a granite medium. These very low values may be attributable either to very high sorption factors on the environmental materials, or to very low solubility of the compounds in which the actinides are incorporated in the materials, or to a diminishing solubility of amorphous compounds in time (e.g. the evolution of amorphous $\text{Pu}(\text{OH})_4$ toward crystallized PuO_2) [12].

CONCLUSION

A large number of laboratory leach test experiments on radioactive glass samples have shown that in most repository conditions over 90% of the plutonium and 99% of the americium do not enter the leaching solution, but are contained by the surface gel layer or by other glass alteration products. Conversely, neptunium is only fixed to a slight degree. Moreover, most of the Pu and Am leached from the glass do not remain in solution, but are either fixed on the environmental materials or are present in suspension as particles larger than 0.45 μm .

A major research effort remains necessary to determine the nature and stability of the generally complex phases that immobilize the actinides. A stronger scientific basis appears desirable before these observations can be taken into account in safety analyses.

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REFERENCES

1. H.J. Matzke, "Actinide Diffusion in Waste Glasses", in *Thermodynamics of Nuclear Materials*, vol 1, pp 311-329, IAEA Vienna (1980).
2. E. Vernaz and J.L. Dussossoy, "Current State of Knowledge of Nuclear Waste Glass Corrosion Mechanisms: the Case of R7T7 Glass", accepted for publication in *Applied Geochemistry* (Special Issue: 1991).
3. E. Vernaz, S. Fillet, N. Jacquet-Francillon, "Les actinides dans les verres", *Journal of Less Common Metals*, 121 (1986 London and Bonn), 637-644.
4. E. Vernaz, N. Jacquet-Francillon and R. Bonniaud, "Effets des désintégrations alpha dans les verres", *Echos CEA*, Special Issue (1982), 38-43.
5. S. Fillet, J.L. Noguès, E. Vernaz and N. Jacquet-Francillon, "Leaching of Actinides from the French LWR Reference Glass", Scientific Basis for Nuclear Waste Management IX, *Mat. Res. Soc. Symp. Proc.*, 50, 211-218 (1985).
6. T. Advocat, J.L. Crovisier, E. Vernaz, G. Ehret and H. Charpentier, "Hydrolysis of R7T7 Nuclear Waste Glass in Dilute Media: Mechanisms and Rate as a Function of pH", Scientific Basis for Nuclear Waste Management XIV, *Mat. Res. Soc. Symp. Proc.*, 212 (1991).
7. N. Godon, E. Vernaz, J.H. Thomassin and J.C. Touray, "Effect of Environmental Materials on Aqueous Corrosion of R7T7 Glass", Scientific Basis for Nuclear Waste Management XII, *Mat. Res. Soc. Symp. Proc.*, 127, 97-104 (1989).
8. E. Vernaz and N. Godon, "Key Parameters of Glass Dissolution in Integrated Systems", Scientific Basis for Nuclear Waste Management XIV, *Mat. Res. Soc. Symp. Proc.* 212, 19-30 (1991).
9. J.L. Noguès, E. Vernaz, N. Jacquet-Francillon and S. Pasquini, "Interaction between a Nuclear Glass and Nearfield Materials in Various Rigs Simulating a Geological Disposal", Proceedings of the International Seminar on Radioactive Waste Products, Jülich, Germany, June 10-13, 1985.
10. N. Godon and E. Vernaz, "R7T7 Nuclear Waste Glass Behavior in Moist Clay : Role of the Clay Mass/Glass Surface Area Ratio", Scientific Basis for Nuclear Waste Management XIII, *Mat. Res. Soc. Symp. Proc.*, 176, 319-326 (1990).
11. J.L. Dussossoy, J.L. Chouchan, M. Bouchon and E. Vernaz, *Leaching Sensitivity to Geologic Environmental Parameters*, CCE contract No FI 1W 0027, Final Report, EUR 13603 EN.
12. I. Puigdomenech and J. Bruno, *Plutonium solubilities*, SKB Technical Report No 91-04.