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Experimental alteration of R7T7 nuclear model glass in solutions with different salinities (90° C, 1 bar): implications for the selection of geological repositories

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In order to simulate the leaching of nuclear wastes in repositories percolated by solutions of variable salinity, leaching tests of R7T7 glass in solutions with different NaCl contents (0, 23.7, 140.8, 233.8 and 285 g kg^{-1}) have been performed at 90° C and 1 bar (10^5 Pa) using static procedure. Combining the data of the solution analysis and the results obtained on the solids by X-ray photoelectron spectroscopy and electron microscopy, the comparison of the efficiency of the different leachants indicated that the alteration was maximum in pure water and in 23.7 g (NaCl) kg^{-1} solution. In deionized water, uranium- and rare-earth elements simulating the actinides were found quite immobile: they have not been detected in solution but are present in the alteration layer as evidenced by energy-dispersive X-ray spectroscopy. On the other hand, in the 23.7 g (NaCl) kg^{-1} solution, high amounts of uranium, cerium and neodymium have been detected in solution and did not accumulate in the solid phases. In the highest salinity brines, the bulk reactivity of the glass decreased. In all leachants, the alteration layer was structured in two parts: hydrated glass and flakes. The flakes were mainly nickel- and zinc-bearing aluminosilicate phases. When crystallized, the flakes were identified as berthierine.

1. Introduction

The disposal of high-activity radionuclide wastes in a geological repository involves different successive barriers (metallic waste container, buffer and backfill materials and finally the massive host-rock) to prevent any spreading of these elements during several thousand years. Firstly, the confining of radionuclides in a solid matrix is supposed to ensure a good packaging of these dangerous pollutants. Synthetic phaneritic rocks or artificial clays have been suggested as this first packaging, but artificial borosilicate glasses appear more convenient because of their practical use [1]. However, the storage glasses have to be poorly reactive with any natural solution which may come in contact with them. Alteration and subsequent dispersion of radionuclides may occur from hydration–dissolution processes by underground waters of variable salinities [2]. In this regard, extreme conditions correspond to pure water and to strong brines equilibrated with evaporite salts.

The aim of this paper is to evaluate the role of the salinity of the leachant in the dissolution mechanism of a model non-radioactive glass, from a set of experiments performed in solutions with variable NaCl content (from pure water to saturated brines with respect to halite). R7T7 glass has been selected by several authorities (Commissariat à l'énergie atomique, Marcoule, France) for modelling different aspects of nuclear waste disposal. A comprehensive study of the alteration of R7T7 glass by pure water was published earlier [3–6] but very little information about the behaviour of this glass in saline solutions was available prior to the present study.

2. Experimental procedure

R7T7 glass is made from a borosilicate flux and amounts of different metals identical to (or stimulating by their chemical properties) the main radioactive elements, especially the actinides (Table I).

Experiments were performed at 90° C, 1 bar (10^5 Pa) under static conditions in 60 ml Teflon beakers. The solutions were neither stirred nor renewed. Only diffusion and the convection currents have to be taken into account for the homogenization of the solutions. For each run, one different glass chip was used with SA/V ratio about 0.5 cm^{-1} (SA = area of the sample, V = solution volume). This low value [7] was chosen to ensure a "water-dominated system" and, accordingly, to maximize the development of an alteration layer at the glass surface. Five different solutions

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TABLE I R7T7 glass composition

Oxide	wt %	Oxide	wt %
SiO_2	45.48	MoO_3	1.70
Al_2O_3	4.91	MnO_2	0.72
B_2O_3	14.02	CoO_3	0.12
Na_2O	9.86	Ag_2O	0.03
CaO	4.04	CdO	0.03
ZnO	2.50	SnO_2	0.02
LiO_2	1.98	Sb_2O_3	0.01
Fe_2O_3	2.91	TeO_2	0.23
P_2O_5	0.28	BaO	0.60
MgO	–	La_2O_3	0.90
NiO	0.74	Ce_2O_3	0.93
Cr_2O_3	0.51	Pr_2O_3	0.44
ZrO_2	2.65	Nd_2O_3	1.59
Cs_2O	1.42	UO_2	0.52
SrO	0.33	ThO_2	0.33
Y_2O_3	0.20		

were used: deionized water, $23.7\,g\,kg^{-1}$, $140.8\,g\,kg^{-1}$, $233.8\,g\,kg^{-1}$ and a brine saturated with respect to NaCl ($285\,g\,kg^{-1}$ at 90° C).

The length of the runs spanned from 1 h to 28 days (1 h, 4 h, 1, 3, 7, 14 and 28 days).

After each run, the pH of the leachants was determined at 90 and 20° C with a Beckman 3500 pH meter. The solutions were analysed by inductively coupled plasma (ICP) spectroscopy (Jobin–Yvon ICP spectrometer). After dilution, the following elements were detected: lithium, boron, sodium, aluminium, silicon, calcium, iron, zinc, molybdenum, cerium, neodymium and uranium.

Surface data of the altered samples were acquired by X-ray photoelectron spectroscopy (XPS) using an AEI ES 200 apparatus, following the method published earlier [2, 8]. To complete this chemical analysis of the surface of solids, the altered samples were studied by SEM and TEM with a Jeol 100 CX electron microscope. Ultramicrotomic sections were prepared following the procedure described by Eberhart and Triki [9] recently applied to the study by TEM of the alteration layers developed on glasses [10–13]. The ultrathin sections were then studied

(a) for their structure and opacity to electrons,

(b) for their composition using an energy dispersive X-ray spectroscopy (EDS) analyser,

(c) for their crystallinity, investigated by electron microdiffraction.

3. Results

3.1. Data from the solutions

3.1.1. pH

The values of pH after reaction are given in Table II. For all leachants, the pH very quickly rose at the beginning of the interaction. Furthermore, in H_2O, $23.7\,g$ (NaCl) kg^{-1} solution and $140.8\,g$ (NaCl) kg^{-1} solution, the values reached a plateau after 3 days, respectively equal to 8.85, 8.70 and 8.20. One can notice that the plateau value is regularly decreasing with respect to the increasing salinity. On the other hand, in the strongest brines the pH was not stabilized at a constant value and was found slightly decreasing with time.

3.1.2. Leached elements

Concentrations determined by ICP were converted to cumulative lixiviation rates (*CLR*) using the relation [4]

$$CLR = \left(\frac{C_i V}{W_i}\right)\left(\frac{W_0}{SA}\right)$$

where CLR is expressed in $g\,cm^{-2}$, C_i is the concentration of the element i in the glass ($10^{-4}\,g\,cm^{-3}$), V the solution volume (cm^{-3}), W_i the weight of the element i in the initial sample (g), W_0 the initial weight (g) and SA the sample area (cm^2).

The results obtained in pure water and in the $23.7\,g$ (NaCl) kg^{-1} solution are displayed in Figs 1 and 2. From a general comparison of the curves, one may notice the following results:

(a) Lithium, boron, aluminium and silicon are leached in both media; in pure water, a plateau value is rapidly reached, which is not the case in the saline solution.

TABLE II pH of the leachant after reaction at 90 and 20° C

Length of run	Temperature (° C)	Leachant				
		Deionized water	$23.8\,g$ (NaCl) kg^{-1}	$140.8\,g$ (NaCl) kg^{-1}	$233.8\,g$ (NaCl) kg^{-1}	Saturated NaCl brine
Initial	90	4.71	4.55	4.40	6.20	6.99
	20	5.16	4.62	4.54	7.05	7.47
1 h	90	7.98	7.61	n.d.*	n.d.	7.90
	20	7.32	7.04	n.d.	n.d.	8.03
4 h	90	8.79	8.11	n.d.	n.d.	7.88
	20	8.20	8.42	n.d.	n.d.	8.03
1 day	90	8.88	8.30	8.12	7.88	7.94
	20	9.07	8.78	8.70	8.64	8.64
3 days	90	8.83	8.66	8.17	8.12	7.98
	20	9.30	9.21	8.74	8.38	8.44
7 days	90	8.84	8.68	8.21	7.80	7.85
	20	9.25	9.20	7.96	8.33	8.17
14 days	90	8.97	8.66	8.22	8.18	7.96
	20	9.26	9.13	8.60	8.37	8.43
28 days	90	8.83	8.74	8.19	7.83	7.53
	20	9.35	9.36	8.61	8.27	7.95

*Not determined.

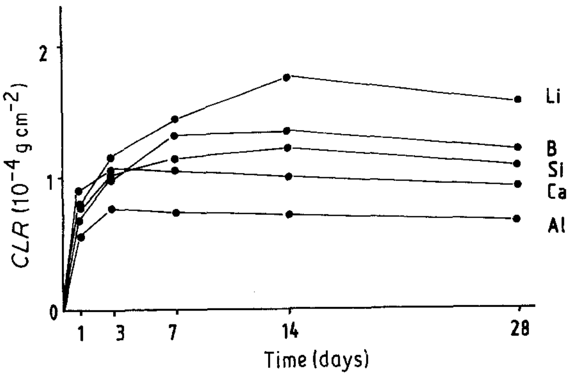


Figure 1 Cumulative lixiviation range of leached elements in deionized water.

(b) Zinc, iron and zirconium have never been detected and accordingly remain accumulated in the surface layer (see XPS data below).

(c) Cerium, neodymium and uranium have not been detected in pure water but are significantly present (especially uranium) in the saline solution.

For the other brines, dilutions were required before ICP analysis because of high NaCl concentrations. Consequently, most of the elements remained either undetected or in very low concentration and the accuracy of the method is then doubtful.

3.2. Data from the solids

3.2.1. Weight loss

The weight loss of the glass sample was determined after rinsing and drying. The data were then converted to "equivalent thickness of dissolved glass" (*ET*) using the following relation:

$$ET = 10^4\, W/d\, SA$$

where ET is expressed in μm, W = weight loss (g), d = density ($2.75\,\mathrm{g\,cm^{-3}}$) and SA = sample area (cm^2).

The results are given in Table III. Most of the equivalent thickness of the dissolved glass scatters in the range 0.1 to 1.1 μm [14]. Some of the data seemed to us as artefacts probably due to the peeling of a part of the alteration layer (see SEM results). Such doubtful data are expressed in brackets.

In all leachants, an increasing ET with time is noticed. The increase is found greater in pure water and the 23.7 g (NaCl) kg^{-1} solution than in the highest saline solutions. This fact suggests a lower reactivity of the bulk glass in the latest leachants. This is probably due to either solution saturation or diffusion limiting processes [15].

3.2.2. XPS data

All the samples were analysed by XPS (spectra recorded in the range 1000 to 1250 eV). In Fig. 3 we report a first set of spectra which illustrates the evolution of the surface composition with time, for one leaching condition (23.7 g (NaCl) kg^{-1}). For each detected element, it is possible to give qualitative comparisons. Firstly, variations are noticed between the reference glass and the surface of the glass altered during 1 h with a significant decrease of the intensity of the B(1s) peak and an

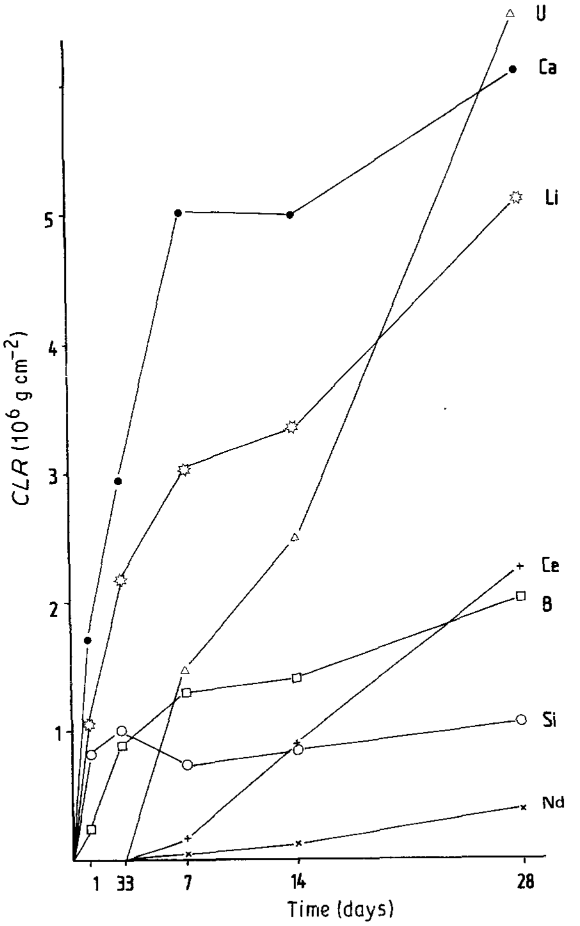


Figure 2 Cumulative lixiviation rates of leached elements in 23.7 g (NaCl) kg^{-1} solution.

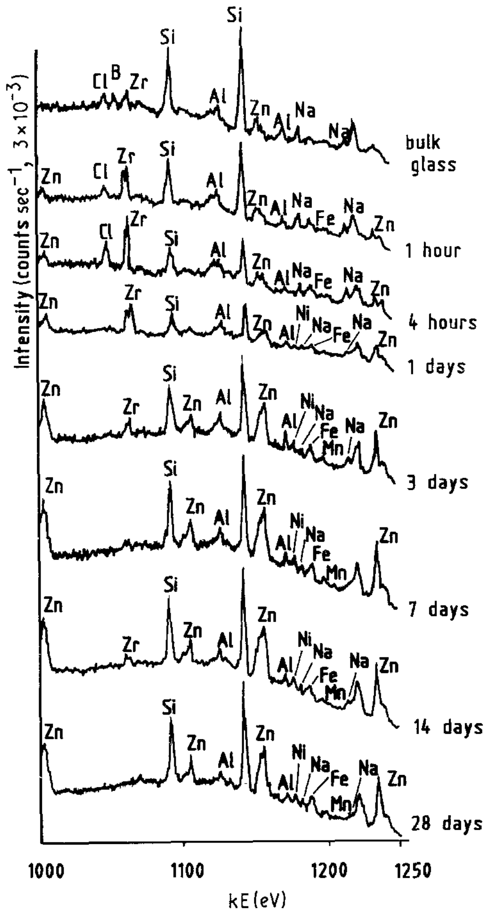


Figure 3 XPS spectra. Evolution of the surface composition of the glass chips with time for lixiviation in 23.7 g (NaCl) kg^{-1} solution.

TABLE III Weight loss of the glass sample and equivalent thickness of dissolved glass

Time	Weight loss (mg)					Equivalent thickness (μm)				
	Deionized water	23.7 g (NaCl) kg^{-1}	140.8 g (NaCl) kg^{-1}	233.8 g (NaCl) kg^{-1}	Saturated NaCl brine	Deionized water	23.7 g (NaCl) kg^{-1}	140.8 g (NaCl) kg^{-1}	233.8 g (NaCl) kg^{-1}	Saturated NaCl brine
1 h	0.2	0.0	n.d.*	n.d.	0.0	0.05	–	n.d.	n.d.	–
4 h	0.6	0.3	n.d.	n.d.	0.5	0.15	0.07	n.d.	n.d.	0.12
1 day	1.5	0.2	0.3	0.4	0.9	0.36	0.05	0.07	0.10	0.22
3 days	1.9	2.0	1.9	0.3	1.3	0.46	0.49	0.46	(0.07)	0.30
7 days	2.1	2.3	1.8	0.1	0.4	0.51	0.56	0.44	(0.03)	(0.10)
14 days	2.5	2.7	1.7	1.0	0.9	0.61	0.66	0.40	0.24	0.22
28 days	1.1	4.5	1.2	1.6	0.2	(0.24)	1.10	(0.29)	0.39	(0.05)

*Not determined.

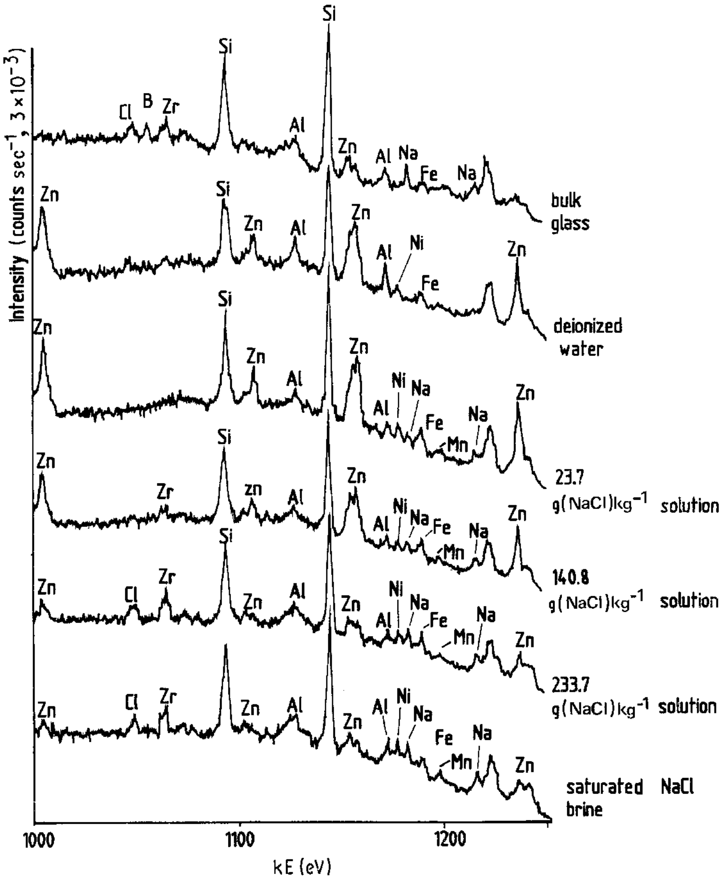
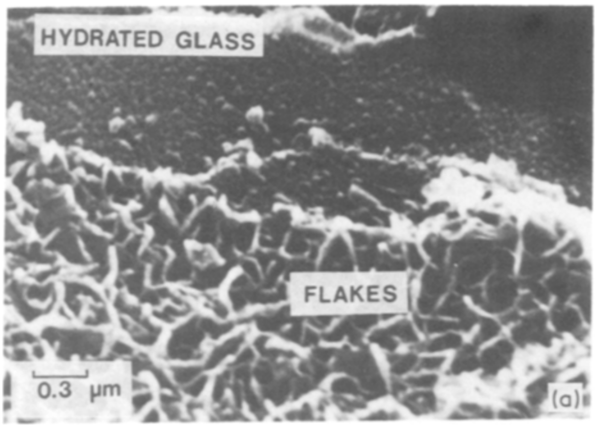


Figure 4 XPS spectra. Evolution of the surface composition of the glass chips altered during 28 days in solution with different salinities.

increase of the intensity of the Zr(3d) one. The main evolution occurred after 3 days: one can see an important increase of the intensity of the Zn(2p) and Ni(3p) peaks, correlated with a decrease of the intensity of the Zr(3d) peak. These variations suggest a change in the chemical composition of the surface phases with time, with a zirconium-dominated phase at the beginning of the interaction and a zinc-bearing aluminosilicate layer developing later. Similar data have been acquired for the other leachants [14]. Fig. 4 illustrates a second set of spectra related to the salinity of the solutions (length of runs: 28 days). The most striking result is the regular decrease of the zinc content from pure water to saturated brine; moreover, in this last medium, the bulk surface composition is similar to the unaltered reference glass (except for the leaching of boron and limited nickel accumulation), suggesting a limited interaction of the R7T7 glass with strong brines.

3.2.3. SEM results

In Fig. 5 is displayed the alteration layer after 14 days interaction between the glass and pure water (Fig. 5a),



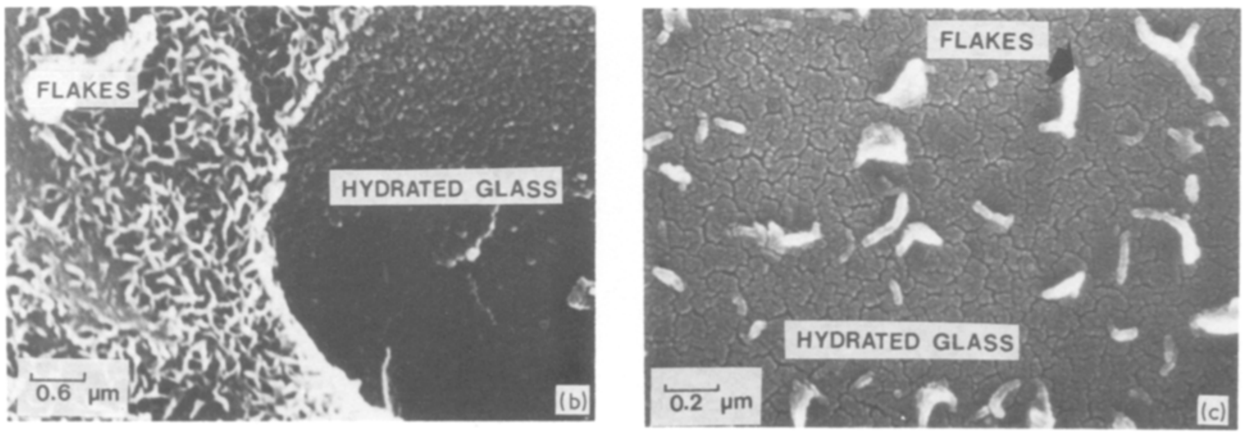
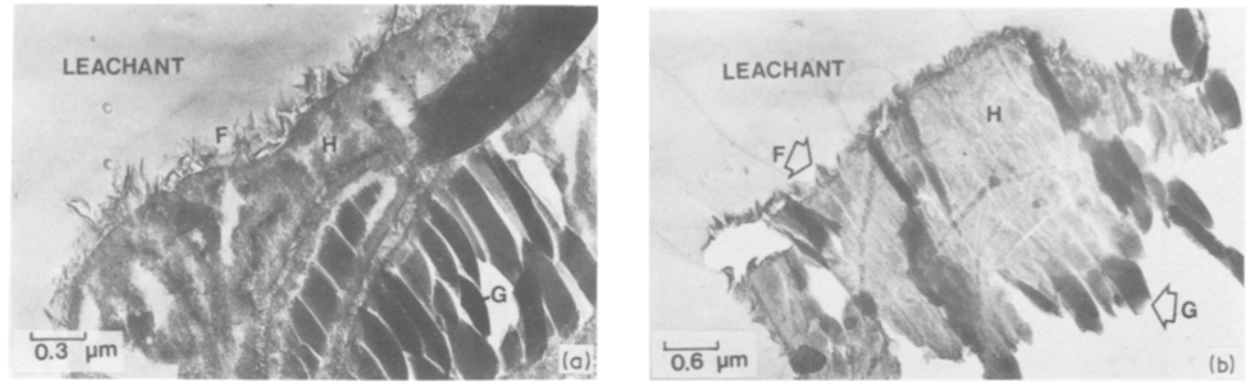


Figure 5 Morphology of the surface sample of the R7T7 glass altered during 14 days, (a) in deionized water, (b) in 23.7 g (NaCl) kg^{-1} solution, and (c) in saturated NaCl brine.



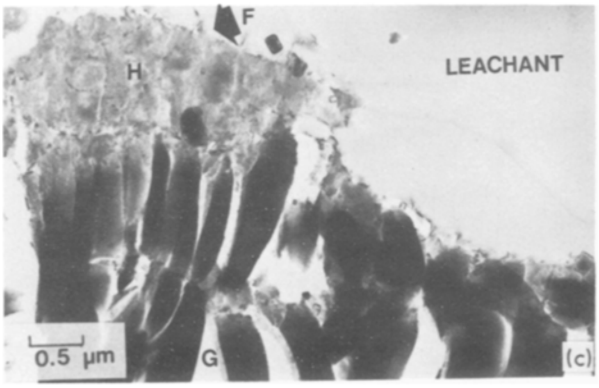


Figure 6 Ultrathin section of the R7T7 glass altered during 28 days (a) in deionized water (b), in 23.7 g (NaCl) kg^{-1} solution, and (c) in saturated NaCl brine. G, glass; H, hydrated glass; F, flakes.

23.7 g (NaCl) kg^{-1} solution (Fig. 5b) and 285 g (NaCl) kg^{-1} solution (Fig. 5c). Two types of phase may be easily distinguished: flake-like solids and altered glass underneath. This description is quite similar to the morphology observed by Flintoff and Harker [16]. From the SEM photographs, the following general conclusions have been drawn:

1. For a given run duration, the higher the salinity, the lower the covering rate by flake-like solids.
2. After the runs performed in the strongest brines, the morphology of the underlying glass is comparable to that of the unaltered glass.
3. On the contrary, in pure water and in 23.7 g (NaCl) kg^{-1} solution, the underlying glass is very different from the unaltered glass after interaction. It appears as a granular layer, suggesting the precipitation of isometric particles in a leached glassy matrix.

3.2.4. TEM data

Ultrathin sections (about 50 nm thick) were cut perpendicular to the sample surfaces for an investigation by transmission electron microscopy. The general organization of the alteration layer and underlying glass is displayed in Fig. 6. Three distinct zones are clearly observed:

(i) unaltered glass, appearing dark because of its opacity to the electrons (labelled G);

(ii) hydrated glass, progressively grading to the former and easily distinguished due to a lesser opacity to electrons than the former zone. This sub-layer (labelled H) appears locally enriched in rare-earth elements (REE) as evidenced by EDS;

(iii) an outer zone, made of poorly crystallized flake-like solids, as illustrated by the scarcity of electron diffraction patterns (labelled F)

The chemical characterization by EDS of the three ultrathin sections described above is presented in Figs 7, 8 and 9 (NB: sodium was not detectable and copper, from the support grid, was always present):

(i) The unaltered glass (A) is characterized by the presence of aluminium, silicon, calcium, iron and limited zinc.

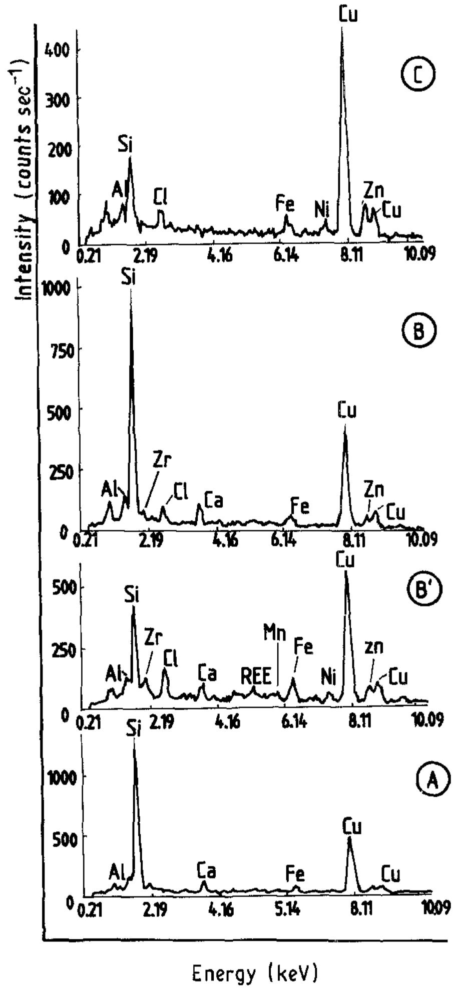


Figure 7 TEM–EDS of ultrathin sections of R7T7 glass corroded in deionized water. 90° C, 28 days. (A) Unaltered glass, (B) clear hydrated glass, (B′) dark hydrated glass, (C) flakes.

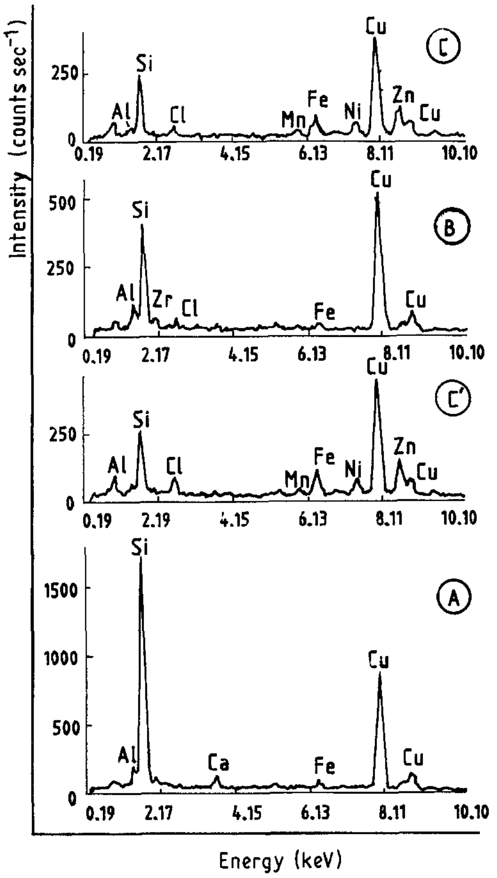


Figure 8 TEM–EDS of ultrathin sections of R7T7 glass corroded in 23.7 g (NaCl) kg^{-1} solution. 90° C, 28 days. (A) Unaltered glass, (B) hydrated glass, (C) flakes, (C′) flakes filling crack.

(ii) Clear hydrated glass (B) contains the same elements with extra zirconium.

(iii) Dark hydrated glass (B′) is only present in Fig. 7. Zones enriched in nickel and manganese contain significant amounts of REE (probably lanthanium, cerium, neodymium and praseodymium). On the other hand, zinc, zirconium and iron appear slightly more concentrated than in clear hydrated glass.

(iv) Flake-like solids (C and C′). They are present on the sample surface and as crack fillings, and have the same chemical characterization pattern in both cases. The high zinc and nickel contents and the absence of zirconium and REE distinguish these phases from the hydrated glass. This last result is in good agreement with prior XPS data.

TABLE IV Chemical characterization of the alteration layers and R7T7 glass

Element	Result*		
	Flakes	Hydrated glass	Unaltered glass
Al	x	x	x
Si	xx	x	xxx
Zr	–	xx	x
Ca	–	†	xxx
Mn	x	–	x
Fe	x	x	x
Ni	xxx	–	–
Zn	xx	x	x
REE	–	†	x

*(x) Elements detected by EDS or present in the glass composition; (xx) elements accumulated; (xxx) elements strongly accumulated or in great amount in the glass composition.

†Only deionized water.

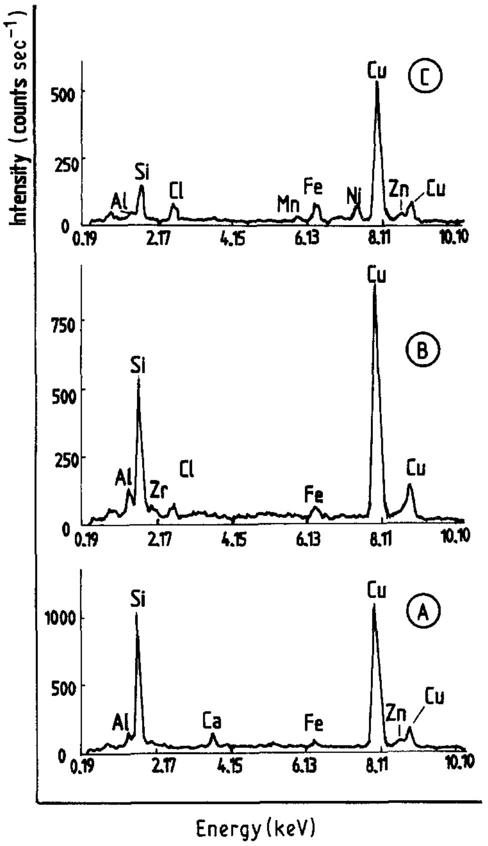


Figure 9 TEM–EDS of ultrathin sections of R7T7 glass corroded in saturated brine. 90° C, 28 days. (A) Unaltered glass, (B) hydrated glass, (C) flakes.

The general features of the ultrathin sections observed by TEM and microanalysis are quite complementary of the results of Lutze *et al.* [17] who described such layers after 3 days' alteration of a glass in deionized water at 165° C.

Table IV presents the qualitative abundance of the elements in different parts of the alteration layer. One may notice that REE were only detected in the hydrated glass (sample leached by deionized water).

The mineralogy of these poorly crystallized solids may be derived from electron diffraction patterns (Table V). The observed values in pure water and 23.7 g (NaCl) kg^{-1} solution are compatible with a zinc–berthierine structure [3, 18]. No patterns were obtained in the 233.8 g (NaCl) kg^{-1} solution. In saturated brine, flakes remain unidentified but their structures clearly differ from that of the berthierine.

The mean thickness of the alteration layers measured on the ultrathin sections is reported in Table VI. Important differences are noticed related to the

TABLE V d_{hkl} values observed from electron diffraction patterns

Leachant	*d* (nm)
Deionized water	0.455, 0.265, 0.152, 0.139
23.7 g (NaCl) kg^{-1}	0.465, 0.265, 0.152, 0.139, 0.132
140.8 g (NaCl) kg^{-1}	No patterns
233.7 g (NaCl) kg^{-1}	No patterns
NaCl-saturated brine	0.282, 0.199, 0.153, 0.128

TABLE VI Mean thickness of the alteration layers (μm)

Leachant	Thickness (μm)	
	Flakes	Hydrated glass
Deionized water	0.2	1.2
23.7 g (NaCl) kg^{-1}	0.2	2.6
140.8 g (NaCl) kg^{-1}	n.d.	n.d.
233.7 g (NaCl) kg^{-1}	0.1	0.4
NaCl-saturated brine	0.1	0.3

salinity of the leachants, with a maximum value for the 23.7 g (NaCl) kg^{-1} solution. From these data, one may notice that the thickness of the flaky layer remained nearly constant whereas the thickness of the hydrated glass was variable.

4. Discussion and conclusion

From our results, large differences have been noticed in the behaviour of the R7T7 model glass in pure water and different saline solutions:

1. In water, a steady state is quickly reached. This fact is underlined by a constant value of the pH after reaction, by the concentration of the leached elements (including boron) which grows to a plateau (Fig. 1) and by a constant value of the equivalent thickness deduced from the weight losses (Table III). These conclusions are also supported by the study of the solids. The XPS results indicate a superficial layer whose composition is dominated by silicon, zinc, nickel and aluminium. Ultrathin sections studied by TEM and microanalysis lead to similar conclusions.
2. In 23.7 g (NaCl) kg^{-1} solution, the alteration of the glass did not reach a plateau even at 28 days. The weight loss increased with time; the extent of the leaching was much greater than in deionized water and the XPS data were quite different (zirconium-dominated phase at the beginning of the alteration, a zinc-bearing aluminosilicate layer developing later).
3. In other saline solutions, conclusions are less clear because of the high NaCl concentration preventing any precise analysis of the solutions through ICP and lowering the reactivity of the glass itself. The weight losses also were less and the alteration products remained uncrystallized in this regard. No analcime was evidenced as found at higher temperatures [17].

For the point of view of nuclear waste disposal, our results, obtained from the analyses of the solutions and from the investigation on the solids, lead us to underline the geochemical behaviour of certain elements:

(i) In deionized water, uranium and the REE-simulating artificial actinides are quite immobile, not detected in solutions even after 28 days alteration; REE are present in the alteration layer, as evidenced by EDS, with uranium probably present at concentrations below detection.

(ii) In the 23.7 g (NaCl) kg^{-1} solution, the situation is reversed with high amounts of uranium, cerium and neodymium detected in solution and no accumulation of these elements in the alteration layer.

(iii) In the strongest brines, the reactivity of the glass R7T7 decreases as evidenced by SEM and TEM data. However, due to the great dilution before ICP analysis, no indications about the behaviour of REE are available, but some leaching may occur because these elements did not accumulate in the hydrated glass and the alteration layers.

A chemical explanation of these data rests *a priori* on a decrease of H_2O activity (a_{H_2O}) with increasing salinity. In concentrated solutions, the thickness of the hydration layer at 28 days (0.3 to 0.4 μm) is significantly less than in pure water (1.2 μm). However, the greatest thickness (2.6 μm) is noticed in the 23.7 g (NaCl) kg^{-1} solution, underlining the role of some other parameters than a_{H_2O} to explain the kinetics of glass hydration.

In this respect chloride complexing may be involved [19]. From the XPS data, a roughly inverse correlation is noticed after 28 days between the presence of zinc and the salinity of the solution (Fig. 4). This suggests a significant role of chloride complexing in the partitioning of zinc between the solution and the surface phases. Moreover, chlorine has been identified inside the hydrated glass by EDS. Whatever its exact position (substitution of OH^-, aqueous Cl^- in interstitial solutions) and the transport mechanism (diffusion across the hydrated zone, migration through microcracks, etc.), the complexing of metal in the bulk of the hydration layer appears likely. This process probably favours the leaching of Zn^{2+} as well as Fe^{3+}. On the other hand, a direct influence of the ligand Cl^- on the behaviour of uranium and REE is doubtful, depending on the Cl^- content and the lower stability of the corresponding chloride complexes [20, 21]. The observed leaching of these elements during interaction with the 23.7 g (NaCl) kg^{-1} solution may result from their accumulation in the hydrated glass. Indeed, a phosphate-bearing compound with high amounts of iron and REE is present as a discrete layer [3, 6]. Other kinds of precipitates (oxyhydroxides?) including REE, iron, manganese, nickel and possibly zirconium are disseminated in the hydrated glass, explaining the higher opacity of some zones (Fig. 5). Chlorine could then indirectly help in the solubilization of REE by enhancing the mobility of iron and preventing the formation of REE-rich iron-bearing precipitates. A general picture of glass–brine interactions would require supplementary data about the reactivity with sea water (a magnesium-rich solution) and basinal brines with high amounts of calcium.

As a conclusion, moderately saline solutions have been found to be highly aggressive against the model glass R7T7 and consequently the salinity of percolating fluids must be considered in the selection of a geological site suitable for a nuclear waste repository.

Acknowledgements

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