



# Long-term alteration mechanisms in water for SON68 radioactive borosilicate glass

T. Advocat<sup>a,\*</sup>, P. Jollivet<sup>a</sup>, J.L. Crovisier<sup>b</sup>, M. del Nero<sup>c</sup>

<sup>a</sup> CEADIECI-Marcoule, BP 171, 30207 Bagnols-sur-Cèze cedex, France

<sup>b</sup> CNRS/ICGS, 1 rue Blessig, 67084 Strasbourg, France

<sup>c</sup> In2P3-Ires, 23 rue du Loess, 67084 Strasbourg, France

## Abstract

Experimental results obtained with high-level radioactive glass specimens typically containing  $10^9$  to  $10^{10}$  Bq  $g^{-1}$  of  $\beta\gamma$ -emitters confirm the behavior observed on simulated non-radioactive glass. Most of the current knowledge of the alteration mechanisms of nuclear glass in water and the kinetic laws of glass alteration developed to model their long-term behavior is based on studies of inactive material. No difference was found between the initial alteration rates measured on active and inactive glass specimens, nor in the long-term alteration rates at advanced stages of reaction progress (typically three or four orders of magnitude lower than the initial rates). At high reaction progress under conditions with very low solution renewal, however, the time necessary for the highly radioactive specimens to reach the low final rate is longer than for the non-radioactive glass. This behavior would suggest that the alteration films are slightly less protective under high  $\beta\gamma$  dose rates ( $>100$  rad  $h^{-1}$ ). The alteration layer has strong retention capacities for the actinides. The key processes, and the corresponding retention models, are highlighted. © 2001 Elsevier Science B.V. All rights reserved.

## 1. Introduction

Radiation effects in HLW glass could potentially impact their long-term properties (see for example the reviewing works of Lutze and Ewing [1] and Weber et al. [2]). On one hand, atomic displacements, ionization/electronic excitations, transmutations by  $\beta$ -decay of the most abundant fission products ( $^{137}\text{Cs}$  and  $^{90}\text{Sr}$ ) and gas production occur. On the other hand, radiolytic processes in aqueous solution are generated by the  $\alpha$ - and  $\beta\gamma$ -radiation fields. The aim of the present work is not to address the radiation effects on the microstructural properties of the glass, but to specifically deal with the chemical durability of highly active SON68 type glasses when radiolytic phenomena in the leachate occur.

Leaching experiments were conducted in initial pure water with borosilicate glass coupons of nominal  $\alpha\beta\gamma$

activity of approx.  $10^{10}$  Bq  $g^{-1}$  for the following purposes:

- To confirm over a relatively wide temperature range (90–150°C) that the initial glass alteration rate  $r_0$  is not affected by  $\beta\gamma$  irradiation at high dose rates ( $>2$  Gy  $h^{-1}$ ).
- To assess the evolution of the alteration rate with the reaction progress by means of a long-term (8-year) experiment and two experiments with flowing leaching solutions, primarily designed to evaluate the relative importance of the alteration gel and the chemical composition of the leaching solution on the diminishing alteration rate.
- To identify the retention processes of the long-lived radionuclide (Np, Pu and Am) in the alteration layers that grow at the glass/solution interface, by specific actinide sorption tests on actual glass alteration layers.

### 1.1. Characterization of the active glass

Three types of highly active glasses were considered in our studies:

\* Corresponding author. Tel.: +33-4 66 79 63 89; fax: +33-4 66 79 77 39.

E-mail address: thierry.advocat@cea.fr (T. Advocat).

- Laboratory active SON68 type glass (called A119) was prepared in 1986 by melting at 1150°C a glass frit with a real highly active ( $\alpha\beta\gamma$ ) fission product, in the research facilities of CEA. The chemical and radiochemical compositions are reported in Table 1.
- Two glass samples were taken, respectively in 1989 and 1994 during a routine pour in, respectively, the R7 and T7 vitrification units at the La Hague UP2-3 reprocessing plants [3,4]. The composition of T7 glass is reported in Table 2.
- $\alpha$ -doped SON68 glasses, respectively doped with 0.85 wt% of  $\text{NpO}_2$ ,  $\text{PuO}_2$  and  $\text{Am}_2\text{O}_3$ , were prepared by melting at 1150°C in the 1980s [5]. Their compositions are reported in Table 3. These glasses contain the main long-term radiotoxicity, which may be reached with the real active glasses after the decay of short-lived radionuclides ( $t > 1000$  years).

In order to compare the chemical durability of the radioactive glass coupons with the non-radioactive (simulated) one, similar surface finishes were imposed (as cast and as cut).

Table 1

Nominal chemical (in oxide wt%) and radiochemical (in  $10^6$  Bq/g<sub>glass</sub>) compositions for A119 laboratory made  $\alpha\beta\gamma$  active glass

SiO <sub>2</sub>	45.46	CdO	0.03	Nd <sub>2</sub> O <sub>3</sub>	1.58	La <sub>2</sub> O <sub>3</sub>	0.90	Y <sub>2</sub> O <sub>3</sub>	0.20
B <sub>2</sub> O <sub>3</sub>	14.09	SnO <sub>2</sub>	0.02	UO <sub>2</sub>	0.52	Ce <sub>2</sub> O <sub>3</sub>	0.92	P <sub>2</sub> O <sub>5</sub>	0.31
Na <sub>2</sub> O	9.84	Sb <sub>2</sub> O <sub>3</sub>	0.01	ThO <sub>2</sub>	0.12	Pr <sub>2</sub> O <sub>3</sub>	0.44	ZrO <sub>2</sub>	2.64
Al <sub>2</sub> O <sub>3</sub>	4.90	TeO <sub>2</sub>	0.23	PuO <sub>2</sub>	0.20	Cr <sub>2</sub> O <sub>3</sub>	0.50	MoO <sub>3</sub>	1.69
Li <sub>2</sub> O	1.98	Cs <sub>2</sub> O	1.42	AmO <sub>2</sub>	0.01	PdO	0.33	MnO <sub>2</sub>	0.72
CaO	4.05	BaO	0.60	NiO	0.41	Ag <sub>2</sub> O	0.03	Total	100.00
ZnO	2.50	Fe <sub>2</sub> O <sub>3</sub>	2.90	Rh <sub>2</sub> O <sub>3</sub>	0.12	SrO	0.33		
Radiochemical analysis ( $10^6$ Bq/g) on April 16, 1985									
Co <sup>60</sup>	Ru <sup>106</sup> + Rh <sup>106</sup>	Sb <sup>125</sup>	Cs <sup>134</sup>	Cs <sup>137</sup>	Ce <sup>144</sup>	Sr <sup>90</sup> + Y <sup>90</sup>	Pu <sup>241</sup>	Total $\beta$	
0.171	5.39	8.79	19.6	575	36.7	829	306	1781	
Am <sup>241</sup>	Pu <sup>239+240</sup>	Pu <sup>238</sup> + Am <sup>241</sup>	Cm <sup>244</sup>	Pu <sup>238</sup>	Total $\alpha$				
21.0	4.17	318	0.834	297	323				

Table 2

Chemical (in oxide wt%) and radiochemical (in Bq/g<sub>glass</sub>) compositions for industrial T7  $\alpha\beta\gamma$  fully active glass (from [4])

Oxides	Analysis results		Plant operation data (COGEMA)
	wt%	95% c.i.	wt%
SiO <sub>2</sub>	46.34	0.87	47.23
B <sub>2</sub> O <sub>3</sub>	14.52	1.01	14.89
Na <sub>2</sub> O <sub>3</sub>	10.66	0.98	10.57
Al <sub>2</sub> O <sub>3</sub>	4.80	0.06	4.39
CaO	4.04	0.05	4.08
Fe <sub>2</sub> O <sub>3</sub>	0.74	0.03	0.65
Cr <sub>2</sub> O <sub>3</sub>	0.13	0.01	0.05
NiO	0.23	0.02	0.07
MoO <sub>3</sub>	1.40	0.04	1.37
La <sub>2</sub> O <sub>3</sub>	0.47	0.01	0.53
Nd <sub>2</sub> O <sub>3</sub>	1.55	0.07	1.61
SrO	0.28	0.01	0.31
UO <sub>2</sub>	0.11	0.05	0.12
Pd	0.45	0.01	0.44
Radionuclide	Bq g <sup>-1</sup>	95% c.i.	Bq g <sup>-1</sup>
<sup>137</sup> Cs <sup>a</sup>	$1.06 \times 10^{10}$	$6.5 \times 10^8$	$1.21 \times 10^{10}$
<sup>134</sup> Cs <sup>a</sup>	$1.72 \times 10^9$	$9.5 \times 10^7$	$1.77 \times 10^9$
<sup>90</sup> Sr <sup>a</sup>	$6.83 \times 10^9$	$4.5 \times 10^8$	$7.53 \times 10^9$
<sup>239-242</sup> Pu <sup>b</sup>	$1.78 \times 10^5$	$1.91 \times 10^4$	$1.54 \times 10^5$
<sup>244</sup> Cm <sup>b</sup>	$2.38 \times 10^8$	$1.32 \times 10^7$	$2.81 \times 10^8$

<sup>a</sup> Results indicated for date of vitrification: January 18, 1994.

<sup>b</sup> Results indicated for date of analysis: November 20, 1995.

Table 3  
Chemical composition (in oxide wt%) of the  $\alpha$ -doped SON68 glasses

Oxide	wt%	Oxide	wt%
SiO <sub>2</sub>	45.48	MnO <sub>2</sub>	0.72
B <sub>2</sub> O <sub>3</sub>	14.02	CoO	0.12
Na <sub>2</sub> O	9.86	Cs <sub>2</sub> O	1.42
Al <sub>2</sub> O <sub>3</sub>	4.91	BaO	0.60
CaO	4.04	Y <sub>2</sub> O <sub>3</sub>	0.20
Li <sub>2</sub> O	1.98	Ag <sub>2</sub> O	0.03
Fe <sub>2</sub> O <sub>3</sub>	2.91	CdO	0.03
NiO	0.74	SnO <sub>2</sub>	0.02
Cr <sub>2</sub> O <sub>3</sub>	0.51	Sb <sub>2</sub> O <sub>3</sub>	0.01
ZnO	2.50	TeO <sub>2</sub>	0.23
P <sub>2</sub> O <sub>5</sub>	0.28	La <sub>2</sub> O <sub>3</sub>	0.90
SrO	0.33	Ce <sub>2</sub> O <sub>3</sub>	0.93
ZrO <sub>2</sub>	2.65	Nd <sub>2</sub> O <sub>3</sub>	1.59
MoO <sub>3</sub>	1.70	Pr <sub>2</sub> O <sub>3</sub>	0.44
	99.15 wt%		
UO <sub>2</sub> 0.52	NpO <sub>2</sub> 0.85	PuO <sub>2</sub> 0.85	
ThO <sub>2</sub> 0.33			
100 wt%	100 wt%	100 wt%	
Non-radioactive R7T7 glass	<sup>237</sup> Np-doped R7T7 glass	<sup>239</sup> Pu-doped R7T7 glass	

1.2. Temperature-dependence of initial alteration rate

The initial alteration rate  $r_0$  of fully active R7 and T7 glass specimens was measured at 90°C, 100°C and 150°C in 316L stainless steel reactors, in continuously deionized flowing water as well as in static mode with initially pure water at a low SA/V ratio (surface over volume ratio < 0.1 cm<sup>-1</sup>) for periods of maximum 21 days. The initial rates varied in a linear manner with the reciprocal of the temperature according to the well-known Arrhenius relation (Fig. 1). The activation energy associated

with the initial dissolution reaction was about 60 kJ mol<sup>-1</sup> for the radioactive glass, which is similar as for non-radioactive simulant glasses [8] and on natural basaltic (aluminosilicate) glasses [9].

1.3. Alteration rates at high reaction progress in glass-water systems

The alteration of a sodium borosilicate nuclear glass such as SON68 glass proceeds, under nearly static conditions, for a time at the initial rate  $r_0$ , diminishing gradually over time by up to 3 or 4 orders of magnitude [10]. Two major processes are currently postulated to explain the drop of the dissolution rate with the reaction progress: (1) saturation effects, (2) the development of a passivating alteration layer between the glass surface and the leachate.

In order to confirm this behavior with glass of nominal radioactivity (approx. 10<sup>9</sup> Bq g<sup>-1</sup>), leaching experiments were performed at 90°C and at an S/V ratio equal to 0.4 cm<sup>-1</sup> (Fig. 2).

The normalized mass losses of tracer elements such as B, Na and Cs reflect the gradually diminishing alteration rate for the laboratory active glass specimen A119, which decreased by about three orders of magnitude after several years. The final alteration rate at 90°C was calculated between 400 and 2300 days. It is equal to about 8 × 10<sup>-3</sup> g m<sup>-2</sup> d<sup>-1</sup>. This value is comparable to the rate determined for non-radioactive glass samples [10]. Moreover, the same steady-state dissolved silica concentrations in solution were measured

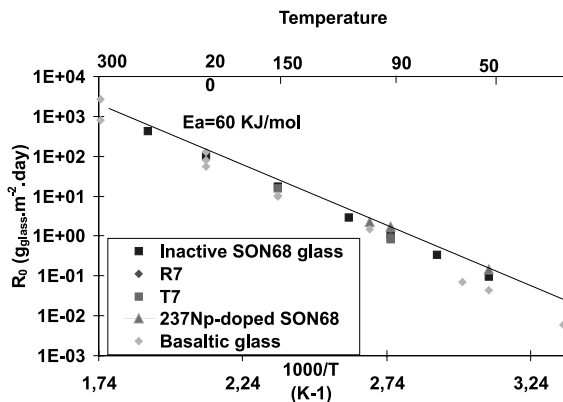


Fig. 1. Initial alteration rate of R7/T7 glasses at nominal activity compared with non-radioactive simulant SON68 type glass (from [8]) and synthetic tholeitic basaltic glass (data from [9]).

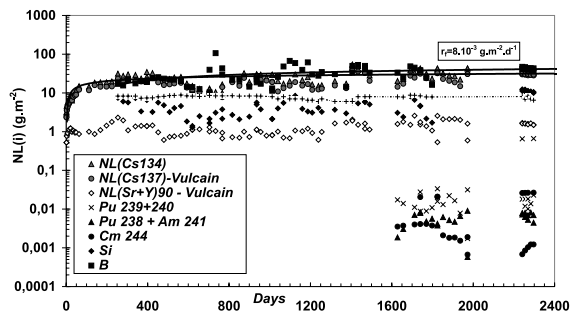


Fig. 2. Normalized elemental mass losses versus time for A119 active laboratory SON68 glass altered at 90°C ( $SA/V = 0.4 \text{ cm}^{-1}$ ; static mode for 1 year, followed by dynamic conditions with a renewal rate of  $2 \times 10^{-4} \text{ d}^{-1}$ ).

with active and inactive glass specimens ( $\log C^*(\text{H}_4\text{SiO}_4) = -2.8$ ). Nevertheless, the inactive and active glasses exhibit significantly different behaviors. The time necessary for the highly radioactive specimens to reach the low final rate is longer than for the inactive glass, and the total glass mass dissolved before the rate drops by three orders of magnitude is about 5 times higher (Fig. 3). Two hypotheses may be postulated:

- The alteration gel that forms on the surface of the radioactive glass appears to be less protective than the gel found on inactive specimens. Such a hypothesis assumes that the protective effect would be related to the microstructure of the gel, i.e., the connectivity of the porous media. The radiation field could modify the connectivity of the silicate-gel layer, and thus enhanced the diffusion of the aqueous species through it. Some arguments are discussed below.
- The mean value for the pH of the leachates with the highly active glass is lower by about 1 unit (7.5 for A119 glass against 8.5 for inactive glasses). Radiolysis phenomena of the aqueous solutions by  $\alpha$  and  $\beta\gamma$

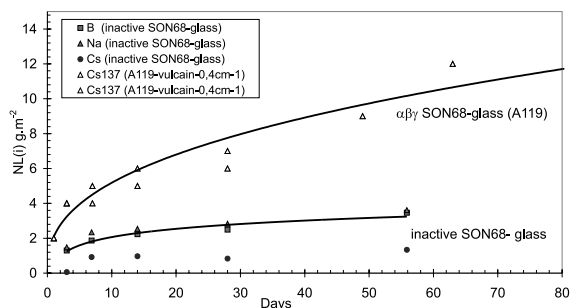


Fig. 3. Normalized mass losses for the highly active A119 glass and the inactive SON68 glass at 90°C and  $SA/V = 0.4 \text{ cm}^{-1}$ , under static conditions (short period of time).

radiation fields are producing nitric acid [11,12]. The protons would then react with the sound glass, by an interdiffusion process with the alkalis ( $\text{Na}^+$ ,  $\text{Cs}^+$ ,  $\text{Li}^+$ ). This mechanism is pH-dependent, and is notably enhanced under acid conditions. In comparison with the basic media, where hydrolysis of the silicate-network is the major corrosion process, under a  $\beta\gamma$  radiation field, the two key mechanisms would happen at the same time. They result in a slightly larger altered depth of the glass.

This behavior was confirmed by the other alteration experiments with R7 and T7 radioactive glass specimens containing appreciably greater quantities of fission products, with a specific  $\beta\gamma$  activity of  $10^{10} \text{ Bq g}^{-1}$ .

All these experiments on active glasses were also modeled using the LIXIVER kinetic code [13], which couples the first-order rate law in which dissolved silica plays a major role [14], with Fick's second law. The orthosilicic acid is considered to diffuse through the alteration layer, as a consequence of a chemical gradient between the interface of the sound glass with the leached layer and the bulk solution. The calculations (Fig. 4) were able to account for the experimental results with an apparent silicon diffusion coefficient in the gel about two orders of magnitude larger for the radioactive glass than determined for the non-radioactive glass. From the experimental observations and the calculation hypotheses, it appears that the alteration gels on highly radioactive  $\beta\gamma$  glass coupons are slightly less protective. The role of radiolysis of the water and the aqueous species in the hydrated gel by  $\beta\gamma$ -emitters is clearly highlighted. It is important to note that this process, which results in a slight but transient loss of glass durability, has not been observed on glass coupons doped exclusively with  $\alpha$ -emitters [5]. After 1000 years, the  $\beta\gamma$  dose rate of fission product containment glass (Table 4) should be low enough that its effect on the textural properties of the gel becomes nil.

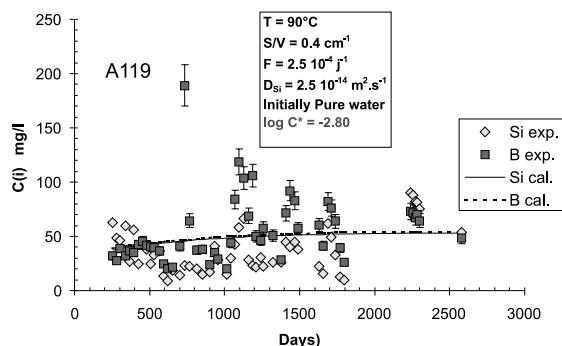


Fig. 4. Calculated (with the LIXIVER code) and experimental Si and B concentrations released in solution during active A119-glass alteration at 90°C.

Table 4  
Calculated dose rates as a function of time at the contact of an industrial R7/T7 glass canister

Time after vitrification	Distance/surface (cm)	$D_\gamma$ (Gy/h)	$D_{\text{neutron}}$ (Gy/h)	$D_{\text{total}}$ (Gy/h)
$T = 30$	0	8.72E + 02	1.39E - 03	8.72E + 02
	5	3.26E + 02	3.33E - 03	3.26E + 02
$T = 100$	0	1.70E + 02	5.85E - 04	1.70E + 02
	5	6.36E + 01	1.40E - 03	6.36E + 01
$T = 500$	0	6.89E - 02	3.26E - 04	6.92E - 02
	5	1.85E - 02	7.78E - 04	1.93E - 02
$T = 1000$	0	4.81E - 02	1.29E - 04	4.82E - 02
	5	1.21E - 02	3.09E - 04	1.24E - 02
$T = 3000$	0	4.24E - 02	2.42E - 05	4.24E - 02
	5	1.17E - 02	5.79E - 05	1.18E - 02
$T = 10\ 000$	0	3.49E - 02	1.19E - 05	3.49E - 02
	5	1.06E - 02	2.85E - 05	1.06E - 02
$T = 50\ 000$	0	2.26E - 02	2.50E - 06	2.26E - 02
	5	7.85E - 03	5.98E - 06	7.86E - 03
$T = 100\ 000$	0	9.35E - 03	1.23E - 06	9.36E - 03
	5	3.09E - 03	2.93E - 06	3.09E - 03

1.4. Actinide behavior and retention properties of the alteration gel

The alteration silicate-gel, developed on top of SON68 glass altered in aqueous solutions, exhibits a high retention capacity for the actinides [5,6].  $\text{UO}_2$ ,  $\text{ThO}_2$ , REE- $\text{O}_2$ , are enriched up to 5–10% in weight in the gel layer, for less than 1% in mass in the bulk glass [5,7]. Three major retention processes are involved (Fig. 5):

- precipitation,
- sorption,
- and coprecipitation.

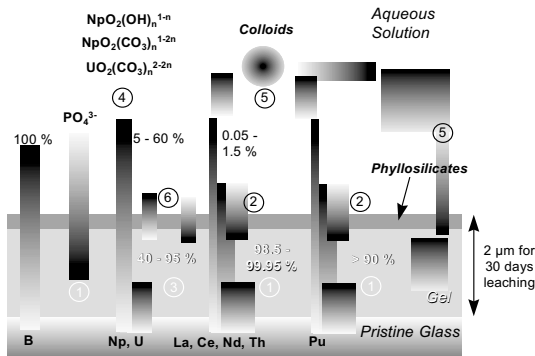


Fig. 5. Principal mechanisms involved in controlling the mobility of the REE and actinides during leaching of SON68 glass under simulated geological disposal conditions (from [7]): (1) coprecipitation; (2) chemisorption; (3) precipitation of oxide/hydroxide phases; (4) complexation; (5) colloid transport; (6) ion exchange.

1.4.1. Precipitation of single actinide phases

The first process was carefully examined by several authors (see for example [7,15–17]). Menard et al. [7] have notably conducted leach tests at 90°C under oxic conditions with  $\alpha$ -doped SON68 glasses in Si-enriched fluids and in the presence of various ligands (carbonates, sulfates and chlorides). More than 98% of the lanthanides, Th and Pu, and over 90% of the U and Np released during glass dissolution remain confined in the secondary alteration products (Fig. 5). One important conclusion from this work is that precipitation of oxides or hydroxides of the actinides (U, Th, Pu, Np, Am) does not account for the concentrations measured in the glass leaching solutions. Control of solubility by such simple phases would imply values about two orders of magnitude higher for most of them. Safety assessment models for the long-term behavior of glass canisters, including

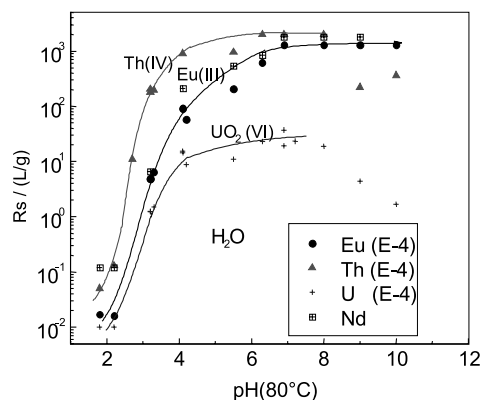


Fig. 6. Retention factors  $R_s$  of Eu, Th and U on GPWAK-glass alteration products in water at 80°C (from [16,18]).

such solubility controls, are from this point of view probably too much conservative.

#### 1.4.2. Sorption of actinides

The chemisorption process was studied experimentally [16–19]. Sorption studies were performed by Kienzler et al. [17] and Lucksheiter et al. [18] on alteration products from the borosilicate glass GP-WAK1 over a period of 10 days at 80°C and  $SA/V = 1000 \text{ m}^{-1}$ , under aerobic conditions. The results obtained clearly indicate that sorption processes contribute to the retention of Th and U, at pH values ranging from 4 to 8 (Fig. 6).

A first modeling approach of actinide sorption on real SON68 glass alteration products (gel-like material) was given by Del Nero et al. [19]. During the experimental phase reported by these authors, the surface charge of the alteration gel of SON68 glass was determined at 25°C ( $\text{pH}_{\text{zero point of charge}} = 7.7$ ). The corresponding specific surface area was equal to  $67 \text{ m}^2 \text{ g}^{-1}$ ; Specific sorption experiments with  $\text{Np}(V)$  diluted in aqueous solutions were then performed at imposed pH values for durations not exceeding 7 days. The test results (Fig. 7) were best reproduced using a non-electrostatic surface complexation model (NEM), based notably on the two following relations:

1.  $\text{Np}(V)_{\text{solution}} \ll C_{\text{gel surface site}}$
2.  $\text{SOH} + \text{NpO}_2^+ \leftrightarrow \text{SONpO}_2 + \text{H}^+$ .

$[\text{SO}^-]$  is a surface site of the gel layer, which becomes  $[\text{SOH}]$  after proton adsorption, and  $[\text{SONpO}_2]$  after Np adsorption. The optimized set of values (Fig. 7) for the Np sorption constants on the gel surface sites ( $K_{\text{Np}}^{\text{NEM}} = [\text{SONpO}_2][\text{H}^+]/[\text{SOH}][\text{NpO}_2^+]$ ) is, respectively,  $-3.7$  (for  $\text{Np} = 0.1 \mu\text{M}$  in the solution) and  $-4.52$  (for  $\text{Np} = 10 \mu\text{M}$  in the solution).

The experimental and calculated results indicate that the sorption process contributes to the retention of some radionuclides, although the fraction of Np retained by sorption has not been quantified with respect to the

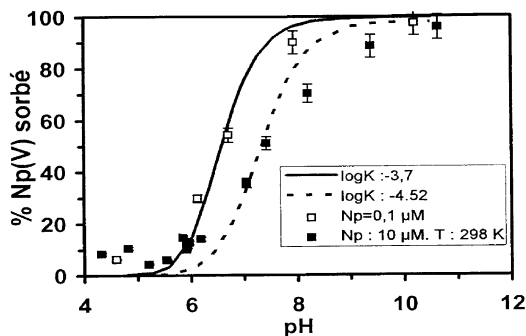


Fig. 7. Sorption curve for  $\text{NP}(V)$  as a function of pH at 25°C on SON68 glass alteration products (from [19]).

fraction retained by coprecipitation with silica during the gel formation. In fact, additional sorption tests, particularly in reducing media, must be carried out to identify the nature of the sorption process, and confirm the validity of the surface complexation model. Moreover, the occurrence of only a single type of sorption site on the real alteration layers needs to be demonstrated on a larger range of redox values.

#### 1.4.3. Coprecipitation of actinides

Retention of radionuclides by coprecipitation with the major chemical elements of the system (e.g., Si, Al and Ca) was neither yet investigated nor modeled. Up to now, geochemical modeling of glass alteration has been developed to quantify the sequence of secondary phase formation [15,17,20–23]. Such an approach emphasizes the most probable sequences of secondary phase formation, and their impact on solution chemistry and dissolution kinetics of the glass. For the actinides, mainly oxide and hydroxide phases are considered in the data banks of the geochemical codes. The corresponding thermodynamic data were carefully measured, and critical reviews were published [24,25]. Nevertheless, as already stated before, the real gel-like alteration products are silicate-based gel-like material, where such single actinide oxides/hydroxides are not encountered. This first-generation modeling is, therefore, too conservative. It can be improved, by considering non-stoichiometric and non-ideal phases, which may be a better approximation of the real secondary products [26]. The goal is then to describe the capacity of gel-like materials to retain and immobilize minor elements, as a microscopic mixture with silicates. In order to achieve this, we attempted to model the alteration layer as a complex solid-solution of hydroxides or oxides of radionuclides and silicated-phases.

The preliminary modeling results, obtained with the *KINDIS* geochemical code, are reported in Figs. 8–10. In the first case (Fig. 8), glass dissolution was calculated and stoichiometric secondary phases (oxides, hydroxides and carbonates) were considered. This is the conventional option, widely used up to now to model the secondary phase formation, without any solid-solution to simulate the gel. A second calculation was then conducted (Fig. 9) and the gel layer has been considered as a solid-solution of the following end-members, with well-documented solubility products: amorphous  $\text{SiO}_2$ ,  $\text{ThO}_2$ ,  $\text{ZrO}(\text{OH})_2$ ,  $\text{LaPO}_4$ ,  $\text{CePO}_4$ ,  $\text{NdPO}_4$ ,  $\text{AmPO}_4$ ,  $\text{UO}_2$ ,  $\text{NpO}_2$ ,  $\text{PuO}_2$ . The predicted sequence of secondary phases indicates that the gel, i.e., a solid-solution, forms and remains stable as a function of the increasing reaction progress (expressed in gram of glass dissolved per liter of solution). Other stoichiometric phases, notably silicates, are also predicted (clays, etc.). The main result of this calculation is reported in Fig. 10. The chemical composition of the gel changes as a function of the

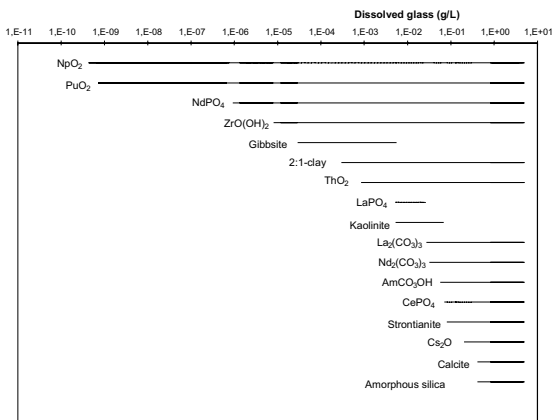


Fig. 8. Sequence of formation of secondary phases calculated with the KINDIS geochemical code during SON68 glass dissolution in water at 25°C and SA/V = 0.5 cm<sup>-1</sup> (no solid-solution).

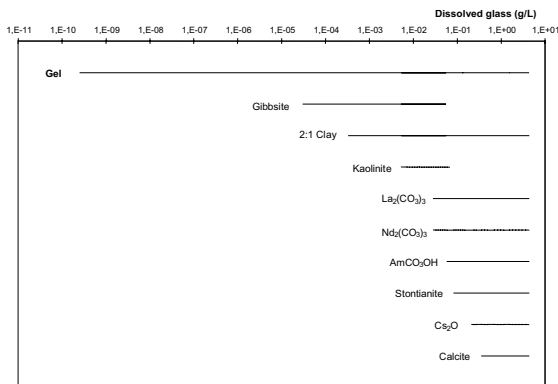


Fig. 9. Sequence of formation of secondary phases calculated with the KINDIS geochemical code during SON68 glass dissolution in water at 25°C and SA/V = 0.5 cm<sup>-1</sup> (with solid-solution).

reaction progress. In highly diluted solution (first stages of the calculations), the gel would contain only two end-members: the less soluble compounds NpO<sub>2</sub> and PuO<sub>2</sub>. The major result is that the gel gradually incorporates other components, and finally amorphous silica. The gel is then progressively enriched in silica, which becomes the main component. Moreover, other silicates form at the same time, like clay minerals (Fig. 9).

Such a ‘chemical’ trend clearly fits with the experimental observations on SON68 glasses (see for example [7,27–29]). The alteration layers are progressively enriched in silica. Other calculations could be conducted, notably by varying the combination of the pure end-members, to evaluate the sensitivity on the complex

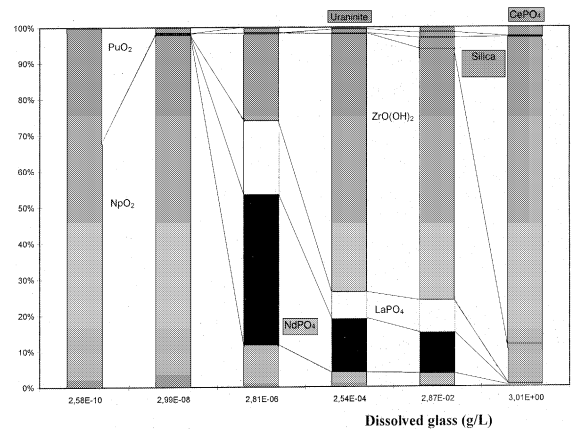


Fig. 10. Evolution of the composition of the gel (in wt% of the end-members) as a function of the increasing mass of dissolved glass, as simulated in Fig. 9.

chemistry, and the long-term thermodynamic stability of the gel layer.

### 1.5. Conclusions-future works

In contact with aqueous solutions, highly active SON68 borosilicate glass samples have the same initial behavior as the inactive glass. The  $\alpha\beta\gamma$ -radiation field does not modify the initial dissolution rates  $r_{(0)}$ . For higher reaction progress, the diminution of the dissolution rate for the highly radioactive glass by three orders of magnitude is not as quick as with non-radioactive glass. The  $\beta\gamma$  radiolysis effects could temporary modify the microstructure of the alteration gel layer, and its protective efficiency, as long as short-lived fission products such as Cs and Sr decay. Such hypothesis has been tested with the LIXIVER code [13]. The occurrence of that radiolysis phenomenon is limited in time under geological disposal conditions;  $\beta\gamma$  radiation field would have strongly decreased after 1000 years, which is the minimum time required for water to saturate the engineering barrier and eventually interact with the glass canister. Another hypothesis assumes that the acidification of the leachates by  $\beta\gamma$  radiolysis could enhance the resumption of ionic exchange in the glass between alkalis and the protons.

The gel layer formation has a strong impact on the radionuclide mobility, after glass alteration. Preliminary experimental approach demonstrates that sorption and coprecipitation reactions would occur at the same time. One major progress is to model coprecipitation of radionuclides with the major constituent element of the gel, such as silica. The geochemical code KINDIS has been implemented to model the complex chemical composition of the alteration gel, considering a solid-solution of oxide and hydroxide compounds.

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