DU COMBUSTIBLE NUCLÉAIRE AUX DÉCHETS : RECHERCHES ACTUELLES
FROM NUCLEAR FUELS TO WASTE: CURRENT RESEARCH

Estimating the lifetime of R7T7 glass in various media

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Note presented by **Édouard Brézin.**

Abstract   Fission product containment glasses were the first matrices for which long-term behavior studies were undertaken. A substantial body of results has been obtained over the last twenty years, international scientific cooperation programs have been developed, and a strict methodology has progressively been defined to predict the behavior of these materials on a time scale of several tens of thousands of years. The excellent self-irradiation resistance of the French 'R7T7' glass has been demonstrated. Models of aqueous alteration under optimized but realistic geological disposal conditions suggest a glass package lifetime of several million years. ***To cite this article: É.Y. Vernaz, C. R. Physique 3 (2002) 813–825.***
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HLW glass / irradiation / leaching / long-term behavior / lifetime / disposal

Estimation de la durée de vie du verre R7T7 dans différents milieux

Résumé   Les verres de confinement des produits de fission sont les premières matrices pour lesquelles des études approfondies de comportement à long terme ont été entreprises. Un très grand nombre de résultats a été obtenu au cours des vingt dernières années, des collaborations internationales se sont développées et une méthodologie rigoureuse à été définie en vue de prédire le comportement du verre sur des périodes de plusieurs dizaines de milliers d'années. L'excellente résistance à l'auto-irradiation du verre dit « R7T7 » a été démontrée. La modélisation de l'altération par l'eau dans des conditions de stockage géologique optimisées mais réalistes, permet d'estimer la durée de vie d'un colis de verre à plusieurs millions d'années. ***Pour citer cet article : É.Y. Vernaz, C. R. Physique 3 (2002) 813–825.***
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verres de confinement / irradiation / lixiviation / comportement à long terme / durée de vie / stockage

1. Introduction

Fission products account for only 3 to 4% of the total spent fuel mass, but contain over 99% of the activity produced in the reactor. The fission product (FP) solutions generated by reprocessing are stored in stainless steel tanks with cooling and stirring systems. While this type of storage, requiring close surveillance, is acceptable for a few decades, it would be inconceivable over a time scale measured in hundreds or thousands of years. The major Western countries became concerned about the future of their nuclear waste in the

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1950s, and work on the solidification of fission product solutions was undertaken at Oak Ridge in the USA, Harwell in the Great Britain, Chalk River in Canada, and Saclay in France.

The CEA's first initiatives in 1957 were to fabricate mica-phlogopite crystals $M_2Mg_6(AlSi_3)_2O_{20}F_4$ (where M represents an alkali or alkaline-earth metal) [1]. This idea was quickly abandoned, however, because it proved impossible to incorporate all the elements in the FP solutions into a few specific minerals. During several tests, a glass heel was observed that was often more durable than the crystals themselves. At that time, the Canadians had already obtained a containment glass from natural aluminosilicates impregnated with fission product solutions and melted at 1350 °C.

A new application for glass (Fig. 1) was born: waste containment. Or rather, the concept of a containment glass was born: from the concept to the construction of an industrial facility, the path was long to optimize glass compositions for each type of FP solution [2] and to develop vitrification processes suitable for use in a highly radioactive environment [3]. This pioneering work led to the startup in 1969 of *Piver*, the first industrial-scale pilot unit (designated a historic landmark by the American Nuclear Society in 1989), followed by the vitrification facilities at Marcoule in 1978 (AVM) [4] and La Hague in 1989 (R7) and 1992 (T7).

Although converting a highly dispersible liquid into a stable, inert solid wasteform was in itself a major advance in the safety of high-level nuclear waste disposal, the CEA also began investigating the long-term behavior of the resulting glass. Glass specimens doped with ^{244}Cm were fabricated in the late 1970s to study the effects of irradiation damage, and highly active glass specimens were leached in the *Vulcain* cell at Marcoule [5].

In response to the task of predicting the behavior of the glass over periods of several thousand years – a new challenge for chemists or materials engineers – a scientific methodology was gradually developed and perfected [6]. The objective was not so much to devise a complex long-term behavior experiment as to investigate separately each of the basic mechanisms that could affect the glass containment properties, to evaluate their kinetics, and to develop models incorporating the kinetic evolution of the phenomena that have a significant effect over the time scale considered. A vast research program was undertaken jointly with the leading French and international specialists in a broad range of fields including physics, chemistry, materials, geology, geochemistry, and computer modeling.

After twenty years of work, and based on the extensive knowledge acquired in the process, this paper examines the issue of the best estimates that can now be made of the lifetime of the French 'R7T7' glass packages. Following a brief review of our knowledge of dry glass evolution, and the state of our current

Figure 1. Pouring a glass melt in an industrial facility.

understanding of the aqueous alteration mechanisms of R7T7 glass, the results of modeling work and the estimated lifetime of glass under various disposal conditions are discussed.

2. Glass package evolution in dry media: current state of knowledge

In *dry media*, the main scientific issues related to the long-term behavior of glass packages are the following:
(1) Is there a risk of glass crystallization and, if so, how can crystallization affect the glass structure and long-term behavior?
(2) Are the glass properties and structure modified by irradiation damage and, if so, to what extent, and with what consequences on its long-term behavior?
(3) Can the degree of glass fracturing evolve over time and, if so, what are the consequences on the reactive surface area and on structural modifications?
(4) Can the dry glass evolution affect the canister integrity (swelling stresses, gas release)?

2.1. Crystallization

Crystallization studies of R7T7 glass have allowed us to quantify the crystalline phases that appear in the material after heat treatment by determining the overall glass crystallization temperature range (lower crystallization temperature, liquidus temperature, occurrence temperature range for each phase) and by determining the crystallized fractions using microscopic analysis methods. The heat treatment scenario producing maximum devitrification results in only 2–3% crystallization, and demonstrates the excellent thermal stability of the material.

The long-term devitrification risk of R7T7 glass has also been investigated [7,8]. This comprehensive study of the mechanisms leading to glass crystallization assessed the thermodynamic and kinetic contributions, and demonstrated that the glass remains fully vitreous in the thermal scenario postulated for the industrial glass package. Under isothermal conditions at temperatures below the glass transition temperature (about 502 °C), several million years are required to reach the maximum theoretical crystallized fraction (4.2%).

R7T7 glass is therefore thermally stable under interim storage or ultimate disposal conditions.

2.2. Self-irradiation effects

The effect of α decay has been investigated in actinide-doped glass. R7T7-type glass specimens doped with 0.5 and 1.5% ^{244}Cm fabricated in collaboration with the Institute for Transuranium Elements (Karlsruhe) sustained doses of up to 5×10^{18} α-emissions per gram of glass, simulating aging of over 10 000 years [9]. These studies have provided reassuring results at macroscopic scale:
- minor volume variation, not exceeding 0.6%);
- no significant change in the aqueous leaching resistance;
- advantageous evolution of the glass mechanical properties (the glass hardness diminishes while the fracture toughness increases: the glass becomes less brittle after self-irradiation).

These changes tend to level off at doses of 2×10^{18} $\alpha \cdot g^{-1}$. This saturation phenomenon suggests that an equilibrium may be reached between defect creation and healing in the glass (Fig. 2).

A second approach is based on atomistic modeling. Molecular dynamics simulations in particular can describe the ballistic effects due to deceleration of the recoil nuclei emitted in the course of α decay. Recent studies of simplified composition representative of the basic R7T7 glass matrix have shown that this type of glass is capable of restoring its structure following the passage of a recoil nucleus, and thus explain the equilibrium between defect creation and healing observed experimentally [10].

Accelerated aging tests have been performed mainly by external irradiation techniques to assess the effects of $\beta\gamma$ radiation. These methods induce disturbances, however, and the results are difficult to interpret. For the French reference glass, although $\beta\gamma$ radiation appears to induce a few structural changes
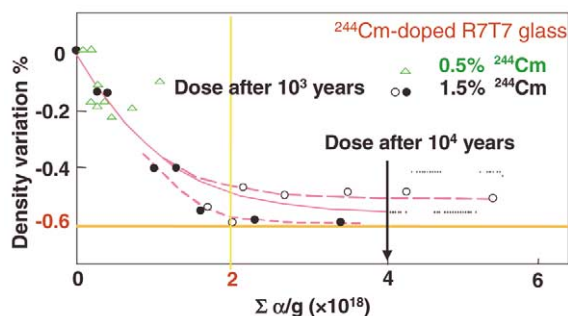
Figure 2. Density variation versus integrated α dose.

measurable by fine spectroscopic analysis (EPR, Raman) [11], they apparently have no measurable effect on the macroscopic properties (volume variation, alterability, etc.) even at cumulative doses simulating the total irradiation that will be sustained by the glass over its entire lifetime. Moreover, highly radioactive R7 and T7 glass samples from La Hague have the same initial dissolution rate as the simulated inactive glasses.

Self-irradiation therefore has no detrimental effect on the long-term behavior of nuclear glass.

2.3. Package fracturing and integrity

The initial fracture ratio of the glass package has been determined [12] to lie between 10 (an optimistic value that does not take the smallest particles into account) and 60 (a penalizing value obtained by destructive analysis of a package). An 'effective fracture ratio' has been defined as the ratio between the quantity of glass alteration tracer elements released from a fractured block retained inside a perforated basket, and the quantity released from a monolithic block. The value obtained for R7T7 glass is about 5, and shows that very fine cracks (probably not through-cracks) have virtually no effect on the initial alteration. Tomographic measurements of the fracture surface area indicated the same order of magnitude [13]; tomography is therefore suitable for quantifying fractures large enough (0.1 mm) to contribute to the initial dissolution rate.

A preliminary analysis suggests that fracturing, which is related to the stresses that accumulate as the package cools, should not be subject to major changes in time. Although stress corrosion is possible in the presence of water in the most heavily stressed (i.e., the largest) blocks, the stresses are relieved by propagation of the cracks. Propagation ceases as soon as the K_1 stress intensity factor at the tip of the crack becomes lower than the static fatigue limit K_{1SCC} [14].

Analysis of natural analogs such as hyaloclastite (highly fractured basaltic glass) [15] also suggests that over the very long term the finest cracks are probably sealed by secondary alteration products resulting in significant induration of the glass block.

Preliminary calculations of the internal pressure generated by helium release show there is no risk of overpressure that could damage the canister integrity.

3. Aqueous alteration kinetics of nuclear glass

3.1. Principal glass alteration mechanisms

When glass is exposed to water, three mechanisms occur simultaneously, but with very different kinetics (Fig. 3):

- Water first diffuses into the pristine glass (hydration), then H_3O^+ ions are exchanged with alkali metals in the glass (*interdiffusion*) leading to release of these elements at a higher rate within a very thin layer of the glass. This phenomenon, which evolves with the square root of t with diffusion coefficients characteristic of the solid material (typically 10^{-18} to 10^{-25} $m^2 \cdot s^{-1}$ for temperatures below 100 °C) is significant during the initial instants, but quickly becomes negligible.

Figure 3. Principal glass alteration mechanisms.
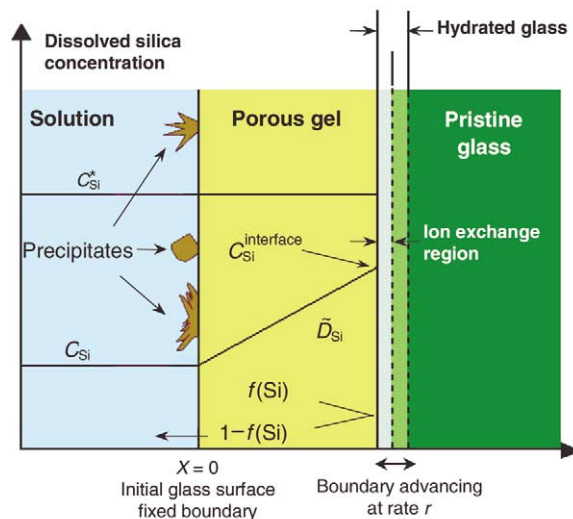
- *Hydrolysis* of oxygen-metal bonds in the network-forming oxides (typically $SiO_2 + 2H_2O \rightarrow H_4SiO_4$) leads to quasi-congruent dissolution of the glass (stoichiometric release of the all major elements: Si, B, Al, Ca, Na, etc.). As long as the leachate remains dilute and a surface layer has not yet formed sufficiently to slow down the alteration process, the glass dissolves at a constant 'initial dissolution rate' (r_0), i.e., the maximum hydrolysis rate in pure water. This rate is characteristic of the intrinsic stability of the matrix, and depends mainly on the glass composition, the temperature (the activation energy is about $70 \text{ kJ} \cdot \text{mol}^{-1}$) and the pH (minimum at neutral pH).
- *In situ recondensation* of a fraction of the hydrolyzed elements (Si, Al, Zr, Ca, REE, Fe, etc.) leads to the formation of an amorphous alteration film or 'gel' [16]. In the case of nuclear glasses, basalts or complex industrial glasses containing a sufficient quantity of silica, rare earth elements, zirconium or iron, the gel volume is comparable to the hydrated glass volume: alteration may be regarded as a constant-volume process.

The fraction of recondensed species, which depends on local equilibria at the pristine glass/gel interface, varies widely with the concentration of species in solution, the glass-surface-area-to-solution-volume (S/V) ratio, and the overall kinetics of the exchanges occurring at the interface. Generally, although the alteration remains a constant-volume phenomenon, the proportion of recondensed species increases substantially as the concentrations rise in solution, as the S/V ratio increases, or as the rate at which the leached species are removed from the interface diminishes: the gel becomes increasingly dense and compact [17]. The gel formed by recondensation of a fraction of the hydrolyzed silica and various elements from the glass (Al, Zr, Ca, REE (Rare Earth Elements), etc.) constitutes a diffusion barrier for the reactive species [18] and retains some of the radionuclides (mainly the heavy metals and actinides) by sorption and coprecipitation.

Finally, as the alteration solution becomes increasingly concentrated in glass alteration products and depending on the environmental conditions, various secondary phases may reach their solubility limit and precipitate at the gel/solution interface. Unlike the gel that develops from the initial interface into the pristine glass, the precipitates grow outward from the interface [19] (Fig. 4).

3.2. Phenomenology

Under static leaching conditions or with the very low solution renewal rates characteristic of a geological repository, the initial linear dissolution phase is quickly followed by an intermediate phase during which the
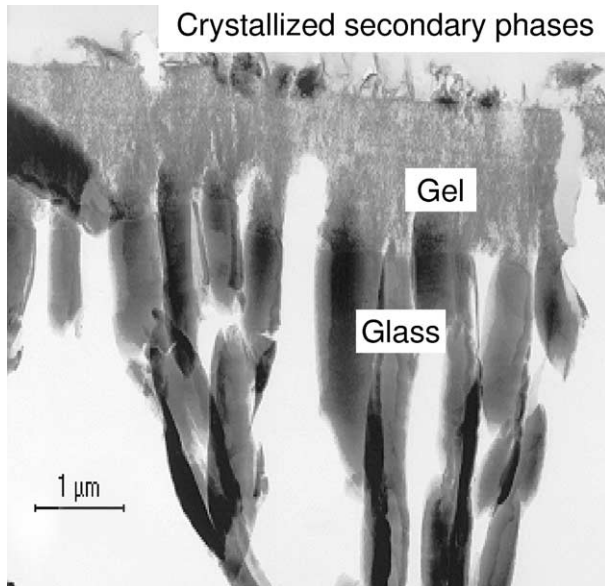
Figure 4. Transmission electron micrograph of the alteration film.
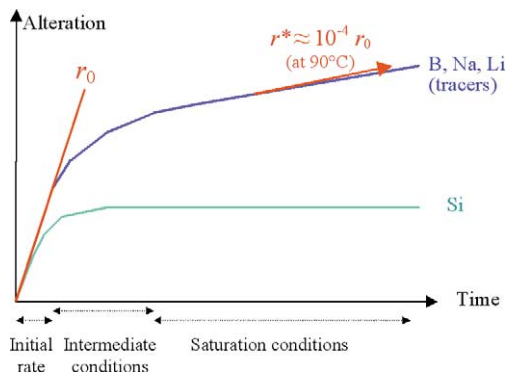

Figure 5. Glass alteration kinetics versus time for an R7T7-type glass in a static system at 90 °C.

concentrations in solution rise more slowly. After a time that depends on the S/V ratio, the system reaches a virtually steady-state Si concentration ('saturation conditions') at which the glass alteration rate drops by several orders of magnitude below the initial rate r_0. Fig. 5 shows the typical evolution of the measured concentrations in solution for Si and for the 'tracer elements' B, Na and Li (which are not retained in the alteration products, and are thus characteristic of the degree of glass alteration) during a static experiment at 90 °C.

3.3. The thermodynamic hypothesis

The drop in the glass alteration rate under saturation conditions was long assumed to correspond to a thermodynamic equilibrium between the solution and the glass/gel interface. Most of the long-term behavior models developed between 1985 and 1995 were thus based on a chemical affinity function derived from the general law proposed by Aagaard and Helgeson [20]:

$$r = k^+ \cdot \exp\left(-\frac{E_a}{RT}\right) \prod_i a_i^{n_i} \left[1 - \left(\frac{Q}{K}\right)^\sigma\right], \tag{1}$$

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where r is the dissolution rate, k^+ the forward rate constant ($g \cdot m^{-2} \cdot s^{-1}$), E_a the activation energy ($J \cdot mol^{-1}$), a_i the activity of ith aqueous species, n_i the corresponding stoichiometric coefficient, Q the ion activity product of the rate-controlling reaction, K the equilibrium constant of this reaction, and σ the net reaction order. A simplified expression of this law is:

$$r = r_0 \left[1 - \left(\frac{Q}{K} \right)^{\sigma} \right], \tag{2}$$

where r_0 is the initial dissolution rate (depending mainly on the glass composition, the temperature and the pH) and $1 - (Q/K)^{\sigma}$ is an affinity term characterizing the decreasing solution aggressiveness with respect to the glass as it becomes increasingly concentrated in dissolved elements and as the ion activity product Q of the reactive species approaches the material solubility product K.

This kinetic law was adapted by Grambow [21], who postulated that hydrolysis of the silica in the glass is the rate-limiting step:

$$r = r_0 \left(1 - \frac{C_{Si(solution)}}{C^*_{Si(saturation)}} \right). \tag{3}$$

The simple expression is the well-known 'first-order law' ($\sigma = 1$) in which only silica from the glass is assumed to limit the dissolution reaction. This type of law assumes that an intrinsic saturation constant C^* exists for SiO_2 (assumed to represent the glass) and that it depends only on the glass composition, temperature and pH.

For nuclear waste glasses, if allowance is made for silica diffusion and sorption in the gel layer, this type of model can satisfactorily account for a single data set. If different data sets are compared, however, they cannot be fitted with the same solubility parameter (C^* or K, depending on the model). Clearly, the value of C^* is not intrinsic to a given glass composition, but depends on how the equilibrium conditions were obtained. This demonstrates that this parameter, the value of which depends on the way in which it was reached, is not a thermodynamic property of the material [22]. Moreover, experiments at high flow rates with saturated leachates have shown that the affinity term could account for a rate drop by a factor of 5 at the most, but in no case by four orders of magnitude as observed with R7T7 glass [23].

3.4. The kinetic hypothesis

The apparent solubility C^* determined from the dissolved silicon concentration at equilibrium therefore does not express the inherent solubility of the glass, but rather an equilibrium between the quantity of silica hydrolyzed from the glass and gel and the quantity of silica condensed in the gel. This is a dynamic – and not a thermodynamic – equilibrium that depends on the conditions under which the equilibrium was reached (S/V ratio, silica removal kinetics, etc.) and not only on the concentrations in solution. Research work in recent years has clearly demonstrated the highly protective properties of the gel obtained under 'saturation conditions' [23–25]. Although the gel initially formed in dilute media is only slightly protective because of its porosity, as alteration progresses the proportion of recondensed Si, Al, Ca, and other elements increases and the porosity diminishes (in terms both of volume percentage and pore size). The apparent silicon diffusion coefficient in the gel gradually evolves from values typical of liquids in porous media (10^{-11} $m^2 \cdot s^{-1}$) to values typical of diffusion in solids ($\leqslant 10^{-18}$ $m^2 \cdot s^{-1}$) [19].

3.5. Initial alteration rate and alteration rate under saturation conditions

The initial R7T7 glass dissolution rate at 90 °C at neutral pH is about 0.5 $\mu m \cdot d^{-1}$ (about 0.01 $\mu m \cdot d^{-1}$ at 50 °C). Under 'saturation conditions', i.e., when the site is saturated with water and is loaded with glass alteration products, the rate drops to less than 0.1 $nm \cdot d^{-1}$ at 90 °C (0.02 $nm \cdot d^{-1}$ at 50 °C, or less than 10 μm per thousand years).

The explanation for the very low residual rates observed under saturation conditions is still a subject of research. Some authors consider it to be related to water diffusion and to interdiffusion, which becomes observable as the hydrolysis rate tends toward zero; in this case it would continue to evolve as a function of $\sqrt{t}$ and would become totally negligible over the long term. For others, the persistence of gel dissolution at a very low rate is related to the slow growth of phyllosilicates; in this case, the rate would remain linear until the system eventually became sealed.

In either event, these rates are so low that they would have only a very minor effect on repository safety. The important issue is to guarantee that the rates remain at these low values, and there is no resumption of corrosion over the long term. This point has been extensively investigated, and is highly dependent on the glass composition [26]. No resumption of alteration has been observed with R7T7 glass, in which the Si/Al ratio is much higher than that of zeolite precipitates. An experiment at high pH was performed to demonstrate that alteration will not resume even over the very long term. At pH 11.5 the formation of zeolites resulted in a significant increase in alteration after a few months due to a reduction in the protective properties of the gel. When the pH was reduced to 9.5 the zeolites were gradually redissolved, the gel again became highly protective, and alteration ceased [27]. No resumption of alteration will occur with this glass as long as the pH is maintained between 7 and 10.

4. Predictive modeling

4.1. The PREDIVER code

The PREDIVER code [28] describes the alteration of one or more glass packages in a geological repository vault. The glass alteration rate is given by the '$r(t)$' model [29] based on the following major hypotheses:

- The alteration rate is described by a first-order law with respect to the silicon concentration C_{int} at the glass/gel interface, to which is added a final rate r_{fin} reflecting the current uncertainty on the residual rate under saturation conditions;
- The silicon retention factor f_{Si} in the gel is described empirically by an exponential law: $f_{Si} = 1 - e^{-\alpha^{C(R,t)}}$;
- The gel formed by glass alteration constitutes a silicon diffusion barrier modeled as a steady-state condition (corresponding to a linear silicon gradient in the thickness of the gel in one-dimensional Cartesian geometry);
- Glass alteration is considered as a constant-volume process in which the gel thickness is equal to the altered glass thickness.

In cylindrical geometry, these hypotheses yield the following expression for the alteration rate:

$$r(t) = \frac{dx}{dt} = r_0\left(1 - \frac{C_{int}(t)}{C^*}\right) + r_{fin} = r_0\left(\frac{1 - C(R,t)/C^*}{(1 + r_0 C_{slb}(t)/(D_g C^*))}(x(t) - R)\ln(1 - x(t)/R)\right) + r_{fin}, \quad (4)$$

where

r_0: initial glass dissolution rate,
r_{fin}: residual glass alteration rate,
$C_{int}(t)$: silicon concentration at pristine glass/gel interface,
$C(R,t)$: silicon concentration in solution,
$C_{slb}(t)$: solubilizable silicon concentration = $(1 - f_{Si}) \cdot C_g$,
C_g: silicon concentration in the glass,
C^*: silicon concentration at apparent saturation,
$x(t)$: altered glass (gel) thickness,
R: glass block radius,
D_g: apparent silicon diffusion coefficient in gel porewater.

The PREDIVER 1 code solves the system for a convective medium (as in the case of slight water flow in a fractured rock [30]) while PREDIVER 3 takes into account silica removal in a diffusive medium (coupling of glass matrix alteration with material balance and transport equations in an engineered barrier in 1D cylindrical geometry [31]). The codes can be used to determine the following:

- estimated quantity of altered glass after a given time period (100, 1000, 10 000 years or more);
- estimated glass package lifetime (50% or 100% alteration) for a given disposal scenario;
- impact of disposal parameters (temperature, flow rate, pH, groundwater composition, silica transport into the backfill, etc.) on the altered glass quantity;
- importance of the major model parameters (r_0, C^*, D_{Si}, etc.) on the altered glass quantity to orient research on new matrices to optimize the parameters truly representative of long-term behavior;
- estimated error on predictions from the uncertainty range for all the parameters and hypotheses.

4.2. Estimating the long-term behavior of R7T7 glass in granitic media

The percentage of altered glass is plotted versus time for different granitic groundwater flow rates in Fig. 6. No residual rate is taken into account here ($r_{fin} = 0$) since the long-term alteration will generally be controlled by the flow rate.

The model parameters were measured for temperatures between 50 °C and 150 °C and for pH values ranging from 7 to 10. At 50 °C and neutral pH the model yields the following results: $r_0 = 0.02 \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$, $D_g \approx 10^{-15} \text{ m}^2 \cdot \text{s}^{-1}$, $f_{Si} = 1 - \exp(-0.1 C_{Si})$, $C^* = 5 \text{ mg} \cdot \text{L}^{-1}$. With a flow rate of $10^{-3} \text{ L} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ (typical of the granitic media studied by ANDRA in the late 1980s) only 0.1% of the glass would be altered after 10 000 years.

Even if the flow rate were multiplied by a thousand (i.e., $1 \text{ L} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$), saturation would be maintained with respect to the gel and the altered fraction after 10 000 years would not exceed 2.5%. The package lifetime – estimated at 52 million years under low-flow conditions ($10^{-3} \text{ L} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$) – would be only moderately shortened to 24 million years at $1 \text{ L} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$, as the gel would remain highly protective at this flow rate.

These figures must be considered in the light of the 10 000 years necessary for the radiotoxic inventory of the glass to drop to the level of the original natural uranium ore.

4.3. Estimating the long-term behavior of R7T7 glass in a clay engineered barrier

In the presence of an engineered barrier, silica would no longer be removed by groundwater flow, but by diffusion and sorption in clay. Two scenarios were considered. In the first, the engineered barrier clay was assumed to be saturated with respect to the silica from the glass, and sorption was assumed negligible.
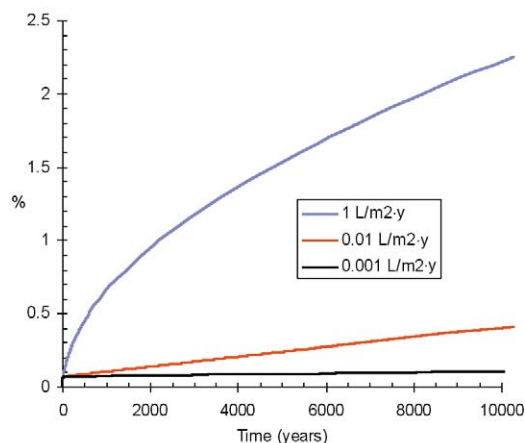

Figure 6. Altered glass percentage versus time for various flow rates in granitic groundwater.

This is the case, for example, with the 'FB6' clay studied by the CEA, which is naturally at equilibrium with an opal phase; it is also valid for any of the other clays studied ('FoCa', Boom, Paris region, southern France, etc.) when preconditioned with a small quantity of amorphous silica or glass frit [32,33]. The model parameters at 50 °C and pH 7.5 again provide an excellent fit in this case: $r_0 = 0.02$ g $\cdot$ m$^{-2} \cdot$ d^{-1}, $D_g \approx 10^{-15}$ m$^2 \cdot$s^{-1}, $f_{Si} = 1 - \exp(-0.1 C_{Si})$, $C^* = 20$ mg$\cdot$L^{-1}. Depending on the residual rate considered ($r_{fin} = 5 \times 10^{-5}$ g $\cdot$ m$^{-2} \cdot$ d^{-1} and a fracture ratio of 1 or 5) the altered glass fraction after 10 000 years ranges from 0.1% to 0.5%.

In the second scenario, the clay engineered barrier 25 cm thick was assumed not to be initially saturated with respect to the silica from the gel, and its sorption capacity was characterized by a sorption coefficient, $K_d = 0.03$ m$^3 \cdot$ kg^{-1}. Two sets of operating conditions were then considered: sorbing conditions in which the gel is relatively nonprotective ($D_g = 10^{-11}$ m$^2 \cdot$ s^{-1}, i.e., the same as the silicon diffusion coefficient in the clay) and alteration occurs at a higher rate, followed by a second phase in which the clay eventually becomes saturated and the gel becomes protective ($D_g = 10^{-15}$ m$^2 \cdot$ s^{-1}). In this scenario about 3% of the glass is altered during the first 3000 years, after which the alteration diminishes to the same very low values as above, and resulting in a total package lifetime of some 46×10^6 million years in both cases (Fig. 7). The figure of 3% and the characteristic time of 3000 years depend directly on the K_d value and engineered barrier thickness assumed for the calculation. It may be noted that this two-step (sorbing and nonsorbing) approach is highly penalizing: although it has been demonstrated that the gel is nonprotective during the initial sorption phase [34], as the distances increase between the glass and the clay layers to be saturated, the silica flow at the glass/clay interface will be slowed by diffusion in the clay and the gel will become increasingly protective.

5. Natural analogs: evidence for validation

Extensive experimental work has been performed to acquire evidence that could validate these results. This includes specific artificial aging experiments (with doped glass specimens [9], extreme temperature or pH values [35], high flow rates or other parameters) designed to intensify certain phenomena, integral experiments [36] or in situ experiments [37] to validate coupling phenomena, experiments with high-level industrial waste glasses [38], etc.

Additional evidence has been provided by studies of natural glass analogs altered over periods of several thousand to several million years. Basaltic glasses constitute useful analogs: their silica content is comparable to that of nuclear glasses and their alteration mechanisms are similar [39]. They develop a largely amorphous alteration film known as 'palagonite'.
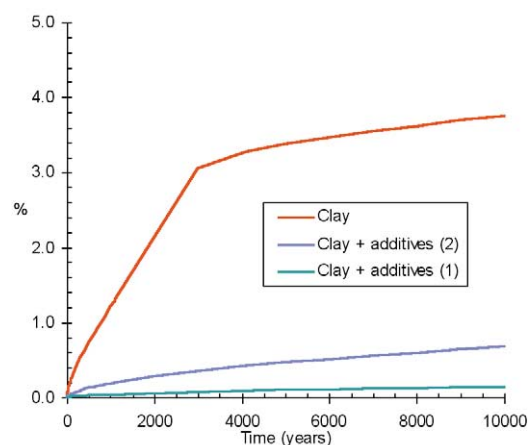

Figure 7. Altered glass percentage versus time in clay media.
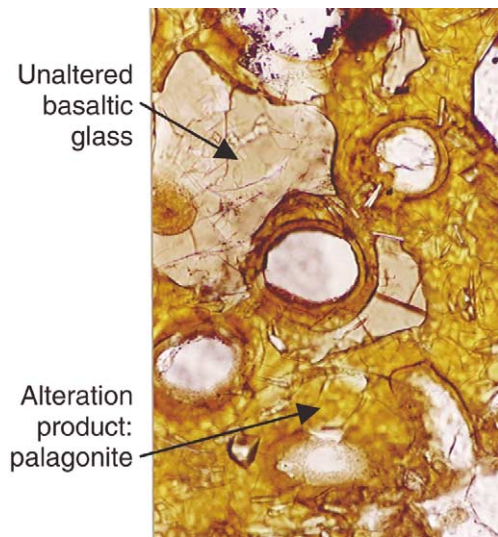
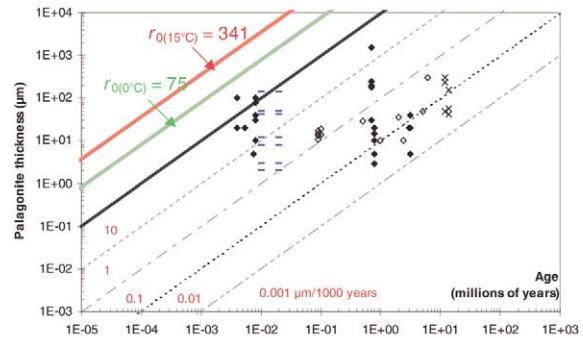**Figure 8.** Optical micrograph of an altered basaltic glass.

Figure 9. Mean alteration rate of basaltic glass altered in a continental environment.

Fig. 8 is an optical micrograph of an altered basaltic glass (hyaloclastite of Aci Castello, Sicily) [40], showing the unaltered pristine glass, the amorphous palagonite, and a few crystalline clay and zeolite phases. As in the case of nuclear glasses, the alteration was virtually a constant-volume process: the mean palagonite thickness thus corresponds to the mean glass thickness altered over 1.4 million years.

Fig. 9 shows the reported palagonite thicknesses for a large number of specimens from various continental sites. Dividing the measured thickness by the specimen age yields a mean alteration rate, shown by the diagonal lines in Fig. 9. The specimen history (water flow rates, sealing, etc.) is only partially known; the results do not correspond to a true rate at a given time but rather to a mean rate on a geological time scale. Although the data points are scattered – which is not surprising, considering the diversity of the sample origins – the mean alteration rate never exceeds 20 μm per thousand years. This is much lower than the initial dissolution rate, and is of the same order of magnitude as the final rates observed under saturation conditions. The mean rates are even lower for the oldest specimens, suggesting either complete sealing over the very long term, or the appearance of extremely protective gels.

6. Conclusions

Fission product solutions have been vitrified industrially in France since 1978 with no serious problems. By the end of 2001 nearly all the French backlog of fission product solutions (over $11\,000$ m^3 of solutions with an activity of over 1.5×10^8 TBq) had been vitrified in about $11\,500$ canisters containing some 4000 metric tons of glass.

The complexity of the physicochemical phenomena involved in the alteration of a glass comprising over 30 oxides in a complex geological environment implies that some empirical parameters must be taken into account in the models at the present time. In the case of R7T7 glass, these parameters are well documented, and predictions are now possible with a satisfactory confidence level. The following points have been demonstrated to date for this glass:

- No glass devitrification is expected over the long term;
- Self-irradiation has no detrimental effect on the glass containment performance;

- Under geological disposal conditions, the aqueous alteration kinetics of the glass are very slow, and the quantity of glass altered after 10 000 years will be approximately 0.1% under an optimized disposal scenario.

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Discussion

Question de J. Dercourt

Concerne l'analogue naturel basalte évoqué dans l'exposé : L'analogue présenté affleure et a subi les variations de circulation d'eau et de températures associées aux différentes phases des cycles climatiques ;

qu'en est-il des basaltes inter stratifiés dans des roches peu (ou pas) perméables ? Les basaltes se refroidissent vite après leur émission en surface ou inter stratifiés dans les strates sédentaires : quelles modifications interviennent lorsqu'à contrario la température croit progressivement dans le verre ?

Réponse de É. Y. Vernaz

L'analogue présenté provient du Salagou (Hérault) et à fait l(objet de la thèse d'Isabelle Techer (1999, Univ-Montpellier 2) ; il est échantillonné dans un filon basaltique, mis en place il y a environ 1,4 Ma au sein d'un sédiment argileux daté à 250 Ma, et dont la bordure est vitreuse. L'épaisseur de palagonite formée donne une estimation de la vitesse moyenne d'altération inférieure de plus de 2 ordres de grandeur à la vitesse de dissolution initiale. L'altération s'est donc faite dans les conditions de saturation c'est à dire en quasi absence de circulation des fluides. Ceci est confirmé par l'analyse chimique et isotopique de l'argile qui n'est très peu modifiée au contact du basalte. Dans ces conditions la vitesse d'altération est contrôlée par la vitesse d'évacuation de la silice et dépends peu de la température. On montre donc la très faible vitesse d'altération du basalte dans une argile très peu perméable, même à faible profondeur.

Question de B. Tissot

Compte tenu de l'énergie d'activation de 70 kJ $\cdot$ mole^{-1} que vous avez observée dans la phase initiale d'altération des matrices vitreuses, quelles seront les conséquences de l'accroissement du taux de combustion, et du passage de UO^2 à MOX ?

Réponse de É. Y. Vernaz

En milieu fortement renouvelé, on l'on peut s'attendre à une cinétique pilotée par la vitesse de dissolution initiale, la température est effectivement un paramètre essentiel. On a typiquement une vitesse de dissolution initiale de 0.1 nanomètre par jour à 4 °C tandis qu'elle passe à 0.3 microns par jour à 100 °C. C'est la raison pour laquelle dans une première approche de sûreté basée sur un modèle « Vo » très majorant, l'ANDRA avait imposé que le verre ne verrait pas d'eau à une température supérieure à 50 °C.

Par contre si l'on tient compte de l'atteinte rapide de « conditions de saturations » (modèle « $V(t)$ ») l'effet de variations de température entre l'ambiante et 100 °C est beaucoup plus faible. Ce point étant fait, l'impact de l'accroissement des taux de combustion sur la cinétique d'altération du verre dépend de la politique de traitement et de stockage. Si on maintient une même composition de verre, donc un même taux d'oxydes de produits de fission dans le verre, la puissance thermique du colis sera inchangée ; c'est ce qui est prévu pour les UOX2. On fait alors un peu plus de verre à la tonne de combustible que pour les UOX1 mais la quantité de verre ramenée au TW·h est inchangée. Cette politique n'est pas arrêtée pour les UOX3 et les MOX. Si l'on retenait de faire des colis plus chauds il conviendrait soit d'augmenter le temps de refroidissement en entreposage, soit d'avoir une emprise plus grande du stockage pour ne pas dépasser les températures limites qui seront fixées dans les concepts de stockage ; dans la communauté internationale il est généralement admis que le verre ne doit pas voir l'eau tant qu'il est à plus de 100 °C.