

GLASS PACKAGES GUARANTEED FOR MILLIONS OF YEARS

Whichever solution(s) is/are finally adopted for long term management of minor actinides and fission products, the issue of the long term behavior of vitrified waste has come up since the early days, as this is how these particular categories of waste are currently being conditioned in France and could be disposed of in the future in deep geological formations. Scientists are basing their demonstration on the study of three main effects: heat, self-irradiation and deterioration by water, the latter being unavoidable in the very long term, irrespective of the disposal scenario. They have developed specific, then general models that incorporate physical and chemical mechanisms described with increasing precision, and can guarantee lifetimes of over a million years for this type of conditioning in optimized conditions.



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Long-term behavior (LTB) studies of glass packages containing **fission products** were undertaken at CEA/Valrhô-Marcoule over twenty years ago to answer the following questions: Are the intrinsic properties of glass (vitreous state, chemical durability, mechanical properties, etc.) likely to alter in the long term, for instance through the effect of heat or **self-irradiation**? Glass-**package** alteration by water is unavoidable over the very long term; can its kinetics be mathematically **modeled**, in relation to the different geological **disposal**

scenarios and, if so, how accurately? (see *Predicting the long-term behavior of waste packages*).

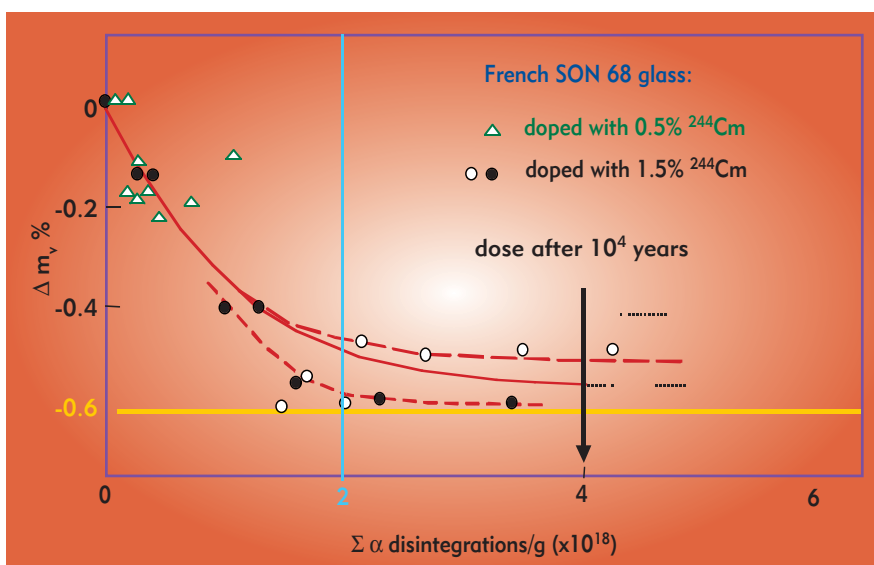
Thorough methodology

It takes roughly 10,000 years for the **activity** level of a glass package containing fission products produced by **reprocessing pressurized-water reactor fuel** to revert to the level of the initial natural ore. Merely extrapolating from laboratory results will not suffice to make incontrovertible calcu-

The **Atalante** laboratory high-level waste ("DHA") shielded line at Marcoule, where actinide-doped glass packages are fabricated to carry out "speeded-up" studies of the effects of self-irradiation. The inset shows a ^{238}Pu -doped glass package manufactured in the Vulcain laboratory in 1975.



Figure 1. Density of R7T7-type glass doped with curium-244 versus the integrated dose.



lations in the light of this type of timescale. LTB predictions will therefore be based on understanding the basic alteration mechanisms and modeling their kinetics. Furthermore, the LTB of a material is not an inherent datum but is subject to considerable environment impact. It will only be possible to determine LTB for specified scenarios. A meticulous scientific approach has thus been drawn up and is codified in an international standard⁽¹⁾.

Millennia simulated in the space of a few years

The main sources of radiation in nuclear glass originate from **alpha** (α) disintegrations emanating from **actinides** (americium, curium, plutonium, etc.), **beta** (β) disintegrations emanating from fission products (cesium-137, strontium-90, etc.), and **gamma** (γ) transitions that accompany β and α disintegrations. The main sources of atom displacements are α disintegrations, characterized by the creation of a **recoil nucleus** and the emission of an α -particle (4–6 MeV⁽²⁾), which at the end of its path generates a helium atom. Recoil nuclei in particular deposit a lot of energy (~ 0.1 MeV) over a short distance (~ 30 nm⁽³⁾), leading to cascading dis-

placements that break many chemical bonds, hence this type of disintegration is the main cause of long-term potential damage.

The effect of alpha disintegrations was first investigated by making *actinide-doped glass packages*. Doping glass with curium-244 obtains **integrated doses** in the space of a few years equivalent to what genuine nuclear glass would have received after several millennia, that is of the order of $4\text{--}5 \times 10^{18}$ α disintegrations per gram (α/g) for the French **R7T7** reference glass after 10,000 years.

The macroscopic findings of this work on the effects of *self-irradiation* are reassuring. The first lesson is that volume variation is low and levels off at a value of 0.6% above an integrated dose of around 2×10^{18} α/g (figure 1); the second is that no significant modification in aqueous-corrosion resistance is observed. Lastly, not only is the glass not embrittled by the integrated dose, but quite to the contrary, its mechanical properties improve (reduced fragility and increased fracture toughness). The measurement of this phenomenon again levels out at a dose of 2×10^{18} α/g . These saturation phenomena suggest that an equilibrium is probably reached between fault creation and recovery.

Quasi-instantaneous reconstruction of the structure under α irradiation

A second approach focuses on atomistic modeling. In particular, **molecular dynamics** can provide insight into the ballistic effects induced by the deceleration of recoil nuclei (RN) emitted at the end of α decay. Recent studies conducted on simplified glasses representative of the basic matrix of R7T7 glass (SiO_2 , B_2O_3 , Al_2O_3 , Na_2O , ZrO_2) demonstrated the remarkable capacity of this type of glass to restore its structure following the passage of a recoil nucleus.

Computers can be used to study the phenomenology of these atomic displacements, even if current computation tools impose restriction on the energy of the nuclei to avoid going outside a “cell” of 500,000 modeled atoms. Research into displacement cascades, for example, enables us to assess the number of atoms displaced by more than 1 angstrom following the collision of a uranium nucleus of given energy with the vitreous network (figure 2).

Studying the degree of depolymerization⁽⁴⁾ undergone by the vitreous lattice characterized by the difference between the number of broken and restored bonds (figure 3) shows that the vitreous structure effectively goes through a depolymerization peak immediately after the recoil nucleus has passed. It then reconstructs itself almost totally a few picoseconds (10^{-12} s)

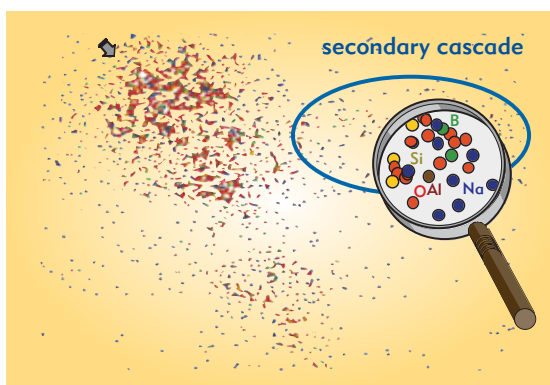


Figure 2. Molecular dynamics simulation of atom displacement cascades, showing the atoms displaced by more than one angstrom induced by a 4-keV uranium recoil nucleus in the basic R7T7 glass matrix.

(1) European standard ENV 12 920 defines the methodology for determining the leaching behavior of waste in specified conditions.
(2) Megaelectronvolt (1 MeV = 10^6 eV).
(3) Nanometer (1 nm = 10^{-9} m).
(4) Gradual break up of a chain of similar molecules or “monomers”.

later because of the α disintegration-induced thermal wave. It is interesting to note that lattice reconstruction is aided by the presence of sodium atoms, which are less tightly bonded to the lattice and probably assist in the reorganization of the displaced entities needed for the glass to repolymerize. This type of approach thus complements the experiments and aids in interpreting at microscopic level the macroscopic findings obtained on doped glass packages.

Alterability unchanged by β and γ radiation

In the case of β and γ radiation, aging simulations have been conducted mainly by means of external irradiation (electron beams, γ radiation). These techniques engender disturbing effects that make it hard to interpret the results. Using precision spectroscopy this type of radiation has been seen to produce some visible structural modifications on simple glass packages. However, no variation in any of the macroscopic properties such as volume or alterability has been measured on nuclear glass irradiated with β and γ rays.

A better understanding of chemical alterability

Major progress has been made in understanding the alteration mechanisms of complex glasses. The impetus for this has come from the research required to predict the long-term behavior of nuclear waste glass. In France much effort has gone into understanding and modeling the aqueous alteration mechanisms of both R7T7 glass and simplified model glasses, in relation to the many parameters that prevail in the **storage** or disposal environments: temperature,



Sampling leachate on Soxhlet-type equipment to assess the concentrations of elements leached from a "nuclear waste" glass package.

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pH, ratio of glass surface area to water volume, groundwater type and flow rate, environmental materials, etc. These studies are carried out in partnership with a large number of French and European laboratories and are at the crossroads of many disciplines (materials science, physics, chemistry, geochemistry, mathematics, etc.).

Generally when a glass package comes into contact with water, following an initial phase marked by interdiffusion⁽⁵⁾, dissolution of the glass becomes congruent

(5) Preferential release of alkali and alkaline-earth elements in a very thin glass layer.

for the major elements (silicon, boron, aluminum, sodium, etc.). This is the phase in which the glass dissolves at an initial rate r_0 and is characterized by intrinsic matrix stability. It represents the maximum **hydrolysis** rate in pure water. The r_0 value is essentially tied to the composition of the glass, temperature (activation energy of around 70 kJ/mole) and pH (minimum at neutral pH).

In static leaching conditions or with the very low renewal rates typical of deep disposal, this phase is quickly followed by an intermediate phase during which the concentrations in solution increase at a slower

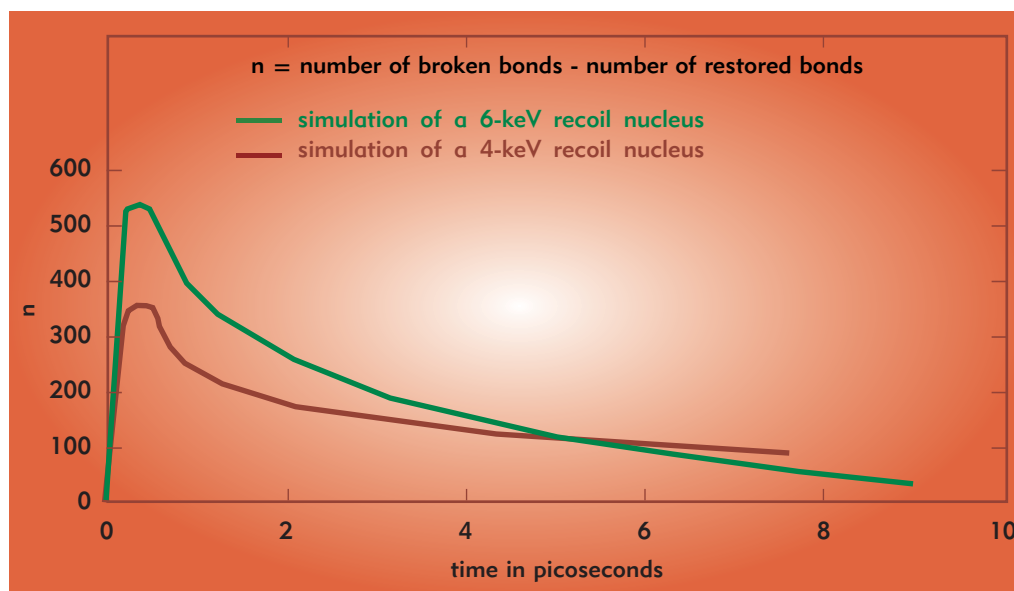


Figure 3. Evolution over time of the degree of depolymerization of the vitreous lattice in a glass, characterized by the difference between the number of broken and restored bonds following the passage of a recoil nucleus.

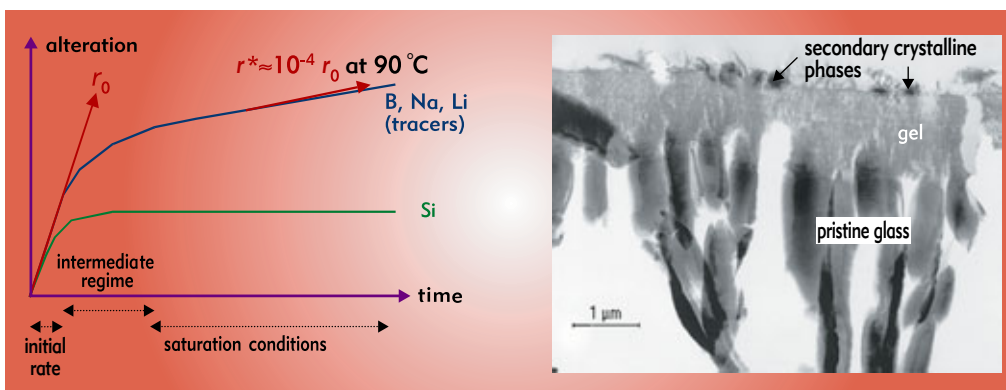


Figure 4. Typical evolution of the alteration kinetics of R7T7 type nuclear waste glass package in a static system at 90 °C. The concentrations are measured in solution for the “tracer” elements not retained in the alteration products. View taken with a transmission electron microscope showing the alteration film formed on the glass.

rate. Then, depending on the surface area/volume ratio, virtually steady-state conditions (“saturation” conditions) are eventually reached-particularly for silicon; the glass alteration rate drops by several orders of magnitude compared with the initial rate r_0 . Scores of **leaching** tests have been conducted at the typical temperature of 90 °C; it is generally accepted in the international community that glass packages in a disposal site will be below this temperature when the water arrives (figure 4).

Protective gel on the surface of the glass

The drop in the glass-alteration rate has long been interpreted as the sign of a thermodynamic equilibrium between the solution and the glass/gel interface (“affinity” models). These models have been called into question in recent years in favor of diffusional limitation created by the gel, whose protectiveness gradually increases as saturation conditions are reached. This gel produced by recondensation of part of the

hydrolyzed silica and various elements from the glass (aluminum, zirconium, calcium, rare earths, etc.), forms a diffusion barrier for reactive species and traps part of the radionuclides by **sorption** and coprecipitation.

For R7T7 glass, the order of magnitude of the initial rate at 90 °C and neutral pH is 0.5 μm/day. Under “saturation” conditions, i.e. when water has saturated the site and becomes loaded with glass alteration products, it decreases to below 0.1 nm/day ($\approx 20 \mu\text{m}/1,000 \text{ years}$). This is the order of magnitude corresponding to the alteration rates recorded on volcanic glass altered in the natural environment. Under these conditions, which are realistic for a deep geological repository, a residual rate persists for R7T7 glass at a value around 10,000 times lower than the initial rate at 90 °C; the origin of this residual rate is still under investigation.

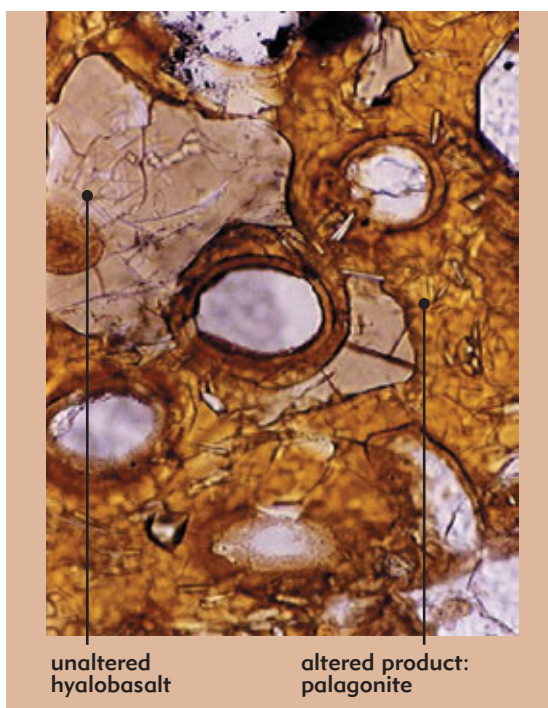
The long-term behavior of glass is thus heavily contingent on the conditions under which the gel forms and in particular on silica removal by the environment. The role

of environmental materials thus predominates in that they will govern the transfers (sorption, diffusion, precipitation). By adding, say, a small quantity of glass frit to an **engineered** clay **barrier**, all the sorption sites can be saturated with silica. This will provide saturation conditions in which the annual fraction of altered glass is of the order of 10^{-7} when the package comes into contact with water. These phenomena will thus have to be incorporated in the “integrated models” that aim to predict long-term behavior for a given scenario.

A guarantee given by two types of model

In recent years great strides have been made toward understanding and modeling the complex mechanism of nuclear glass alteration. Specific models have been developed to account for the more general phenomenological and behavioral models - “operational models” - and to estimate long-term behavior under specified environmental conditions. The latter requires the use of some empirical parameters, but the existing very extensive knowledge base on R7T7 glass alteration makes it possible to qualify the validity of these parameters.

Some divergences within the international scientific community remain as to the interpretation of the slow alteration rates observed in saturation conditions. While they justify continuing high-quality basic research effort on glass alteration mechanisms, they do not necessarily have any major operational impact. Whether the focus is on models based on reaching a glass solubility limit, or models based on the formation of very protective gels, the findings obtained to date for realistic disposal conditions indicate very long glass package lifetimes in excess of a million years.



Hyalobasalt from Salagou (Hérault), 1.4 million years old, viewed through an optical microscope.

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