LONG-TERM BEHAVIOUR OF NUCLEAR GLASS USED FOR THE CONDITIONING OF HIGH ACTIVITY WASTE

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1. INTRODUCTION : WHY VITRIFY NUCLEAR WASTE?

The conditioning of high activity nuclear waste is aimed at turning waste from the liquid to the solid state, reducing the volume to be stored and, then, disposed of and getting a material which complies with the safety requirements peculiar to storage and disposal.
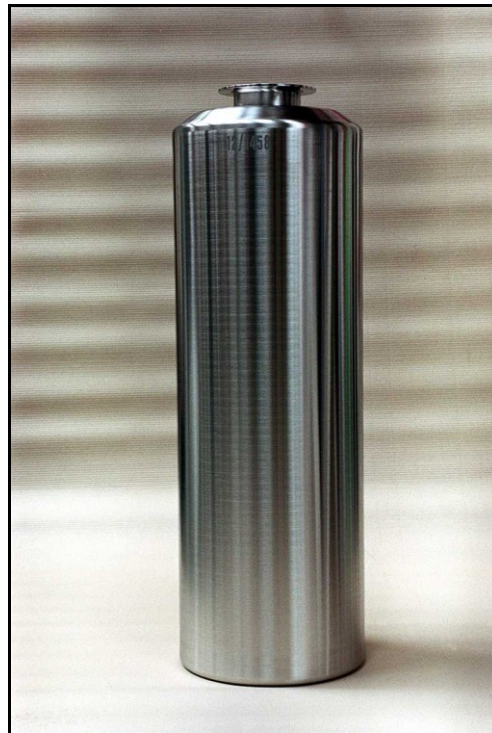

Figure 1. Vitrified waste package (CSD-V)

Glass was selected by the world's community as the confinement material for solutions of fission products, due to the flexibility of its disordered structure that enables glass to confine many chemical elements. It must be emphasized that vitrification is not a mere embedding, but an atomic-scale confinement, since radionuclides are intimately incorporated in glass structure.

Glass is an interesting material for the confinement of radionuclides, because it is endowed with satisfactory properties of thermal stability, chemical durability, quasi insolubility in water and resistance to self-irradiation. The nuclear waste conditioned under the form of glass packages are intended to be disposed of in underground repositories. The design of the repository uses the multibarrier concept to prevent the release of radionuclides long enough for the radioactive decay to take place. Some of the radionuclides contained in the waste have a radioactive half life as long as a million years, it is thus on this timescale that the barriers must play their role. The first confinement barrier is the glass matrix itself. Of course, a direct proof of the durability of glass over a million-year timescale is inaccessible to laboratory experiments, so the task of the researchers is to make sure that the long-term alteration mechanisms of glass are well understood and mastered.

2. REQUIREMENTS FOR THE "NUCLEAR" GLASS MATERIAL

- Glass must be able to incorporate the various elements from the fission product solution to be vitrified (15% in mass)
- Glass must be homogeneous
- Crystallization must be avoided
- Elaboration must be easy (radioactive ambiance): the melting temperature must not be too high to limit volatility, the viscosity must be small to allow glass pouring, the melted glass must not too corrosive for the crucible
- Large chunks of glass must solidify without too much fracturing
- Glass must withstand irradiation and alteration by water.

3. GENERALITIES ABOUT THE PHYSICO-CHEMISTRY OF GLASS

Glass is solid like a crystal, and disordered at the atomic scale, like a liquid. Upon cooling below the melting point, most liquids crystallize, but glass has a continuously increasing viscosity (this viscosity is higher than 10^{13} Poise below the glass transition temperature, T_g = 520°C for borosilicated glass). It is thermodynamically metastable, and could recrystallize, yet this process can be very slow, and we know geological glass which is 100 million years old.

The cohesion of the oxide glass skeleton is ensured by the iono-covalent chemical bonds which are formed by the glass network formers (Si, B, Al) in combination with oxygen atoms. One oxygen atom bound with two network formers is said to be "bridging", whereas one oxygen atom bound with a single network former is said to be "non-bridging". These bonds are oriented and take part in the formation of tetrahedra SiO_4, BO_4, AlO_4, and of triangles BO_3. Silicium tetrahedra and Boron triangles are connected by one oxygen summit. These elementary structures form chains and rings of different sizes, thus contributing to the solidity of the edifice (Figure. 2). These covalent bonds coexist with bonds with a more ionic character, formed between the alkaline or alkaline-earth metals (Na, Ca) and the oxygen atoms.

The Na and Ca elements may play two distinctive roles within the glass network. They may either behave as charge-compensators near a locally negative-charged BO_4- or AlO_4 type group, or they may behave as "modifying" elements, forming a X—O—Na or X—O—Ca bond (with X being a network former). The progressive addition of network modifiers to silica SiO_2 leads to network de-polymerisation by the formation of non-bridging oxygen atoms. Modifying elements contribute to reduce the melting temperature and viscosity, and increase molten glass reactivity, which makes its fabrication easier. Their presence also makes the glass structure flexible, and permits the incorporation of radionuclides in the glass structure.
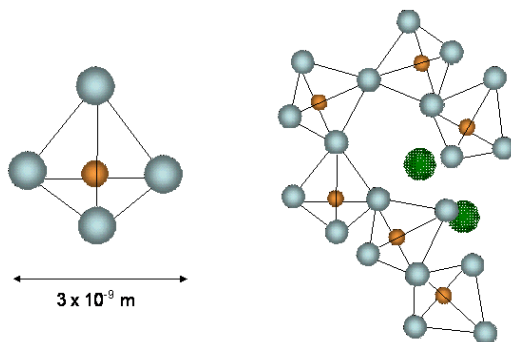

3×10^{-9} m

Figure. 2: Glass structure: a silica tetrahedron (left), and a chain of tetrahedra with lattice modificators (right)

4. GLASS COMPOSITION

The glass composition generally chosen for the conditioning of the fission product solutions from the reprocessing of LWR spent fuel is a borosilicated glass, because of several interesting properties:
- Its lower temperature of elaboration compared to silica;
- Its very low tendency to crystallisation;
- Its very good resistance to water alteration;
- In addition, boron helps digest the calcinate during glass elaboration and lowers the equilibrium pH after leaching.

The good performance of nuclear borosilicate (a temperature melting not too high and a good chemical durability) comes from the right balance between boron and the intermediate elements (Al, Fe, Zr…) on one side and the alkali elements on the other side, allowing a high polymerisation rate as most of alkali are found as charge compensators rather than forming non bridging oxygen links.

Typical French "R7T7" glass incorporates up to 18.5% (mass) of fission product oxides and 0.9% of actinide oxides (Table 1).

Chemical composition range of R7T7 glasses produced in the AREVA - La Hague plant workshops			
Oxides	Specified interval for the industry (wt%)		Average composition of industrial glasses (wt%)
	min	max	
SiO_2	42.4	51.7	45.6
B_2O_3	12.4	16.5	14.1
Al_2O_3	3.6	6.6	4.7
Na_2O	8.1	11.0	9.9
CaO	3.5	4.8	4.0
Fe_2O_3		< 4.5	1.1
NiO		< 0.5	0.1
Cr_2O_3		< 0.6	0.1
P_2O_5		< 1.0	0.2
Li_2O	1.6	2.4	2.0
ZnO	2.2	2.8	2.5
Oxides (PF + Zr + actinides) Fines suspension	7.5	18.5	17.0
Actinide oxides			0.6
$SiO_2+B_2O_3+Al_2O_3$	> 60		64.4

Table 1: Typical composition of borosilicated glass for the conditioning of high activity waste

5. THE VITRIFIED WASTE PACKAGE

The « R7T7 » waste package (Figure. 1) is given here as an example of vitrified waste package. The envelope is 5mm thick stainless steel and contains 150 liters of glass (diameter 40 cm, height 1.3 m). Composition contains 12-18% (in weight) of fission products. Each package is made of two castings, 200 kg each. 13 000 CSDV glass canisters have been produced as of Sept. 2007 in La Hague, confining a total radioactivity of 2.10^8 TBq beta-gamma.

1 glass package (400 kg) corresponds to the treatment of 1.3 tons of spent fuel. It contains 95 to 99% of the radioactivity of the spent fuel. Radioactivity of this glass package is 5800 Ci ($2.1\ 10^{14}$ Bq) alpha; 400 000 Ci ($1.5\ 10^{16}$ Bq) bêta gamma; Dose is 500 Gy/h (contact). One ton of glass corresponds roughly to one TWhe of energy produced.

The heat power dissipated by a glass package due to the radioactivity (processing of UOX fuel) is 2.5 kW (after conditioning), 1 kW (ten years later) and 0.4 kW (50 years later). This power must be evacuated in the glass package storage facilities. The size of the package has been chosen such that, with a convective air cooling, T stays lower than 500°C at the center of the package, (ie below the glass transition temperature).

6. LONG-TERM BEHAVIOUR OF GLASS

Glass alteration by water, self-irradiation and fracturation must be studied because these phenomena may cause the release and migration of radionuclides from the glass matrix.
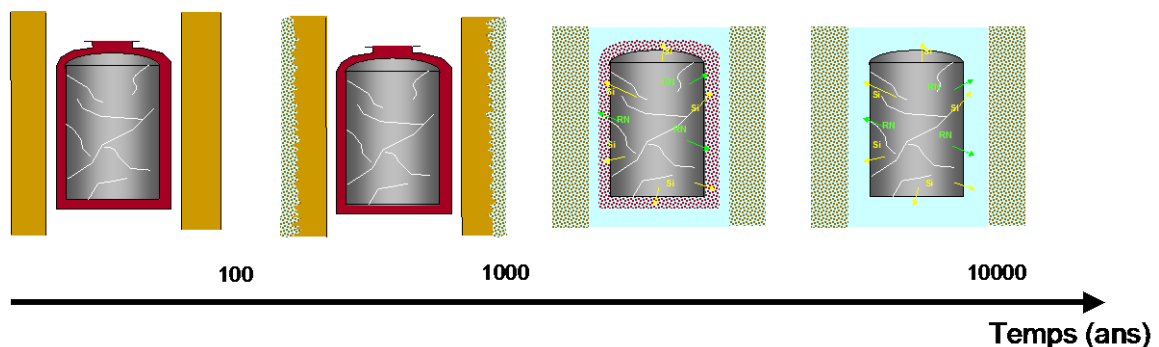

Figure. 3: The sequence of alteration of a vitrified waste package.

In the case of a deep geological disposal for vitrified waste packages, underground water will come into contact with glass sooner or later, after corroding the containers and overcontainers. Glass matrix alteration by water is the chief factor likely to lead to the radionuclide release into the natural environment.

6. 1 Long-term behaviour of glass in contact with water

When the underground water reaches the glass package after the loss of the tightness of the envelopes, a slow dissolution of the components of the glass then occurs (Figure. 3), with release in the rock porewater of the glass radioactive content. The dissolution rate depends on the glass composition and on its degree of fragmentation, which determines the reactive surface area between glass and water. Other parameters also come into play, e.g. temperature and ion content of the water. These parameters determine the dissolution -precipitation phenomena in the vicinity of the glass.

6.1.1 Phenomenology of glass alteration by water :
When a silicated glass is exposed to water, after a quick period of alkali and water interdifusion, one observes the dissolution of silica in water. The initial kinetics of this dissolution is quite rapid at high temperature (typically a few $g.m^{-2}.d^{-1}$ at 100°C, pH 7, ie 1 µm/day, and 1 nm/day at 20°C), but a significant slowdown occurs after some time if the water renewal is slow.

One also observes the formation of an amorphous layer of hydrated silica (Figure. 4). Its thickness depends on the experimental conditions, and especially on the modalities of the water circulation around the glass sample. One also often observes the precipitation of newly formed crystals (phyllosilicates) onto the outer surface of the hydrated layer.

If the water flow is slow enough, the mass flow of dissolved silica is independent of the glass surface area, and is simply proportional to the water flow and to the solubility limit of amorphous silica (60 mg/L at pH 8 and 90°C). This dissolved silica comes probably from the dissolution of the hydrated layer itself.

The release rate of tracers contained in the glass (eg Li, B) is initially high, and decreases slowly with time (Figure. 5). However, this tracer release never goes to zero for very long times, even in the absence of water renewal and in water already saturated with silica. The residual alteration rate becomes a constant which can be as low a 10^4 times smaller than the initial alteration rate. This rate depends on the pH of the water, and on the glass composition.

Isotopic tracer experiments suggest that the hydrated layer forms at the internal interface (between the layer and the pristine glass) by transformation of oxide glass into an hydrated oxide layer.
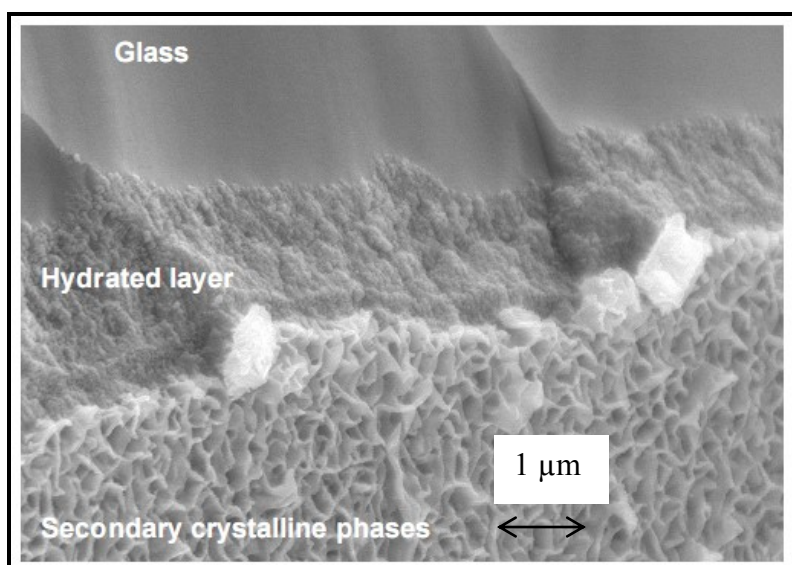

Figure. 4: Scanning electron microscope view of a borosilicated glass sample altered at 150°C for 4 months in pure water. One can distinguish from top to bottom: the unaltered glass, the hydrated layer and the secondary phases which precipitated from the solution.
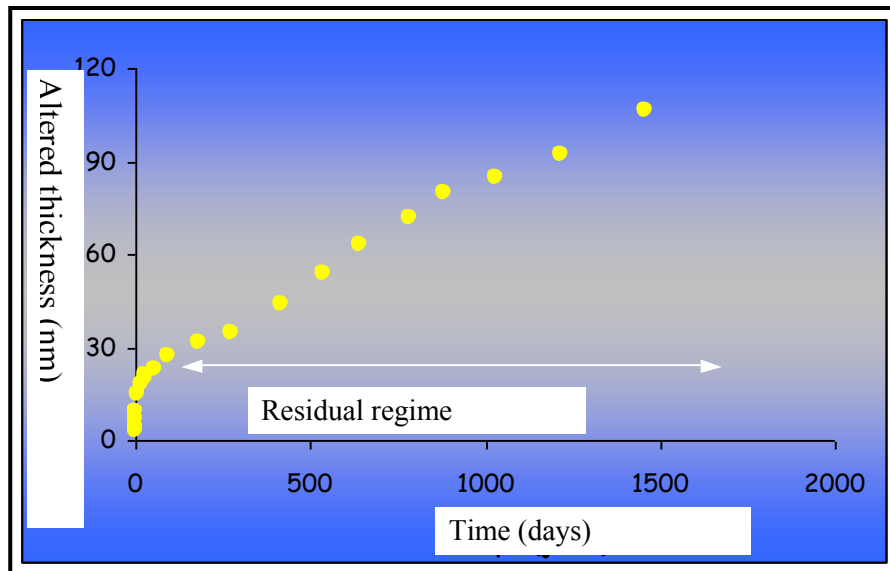
Figure. 5: Kinetics of glass alteration by water. Evolution of the thickness of R7 T7 altered glass at 90 °C. In the conditions of the experiment (large glass surface area, small quantity of water, the residual regime (where the alteration rate is constant) is rapidly reached. Note the order of magnitude of the residual alteration rate: 0.03 μm/year, or 3 cm in 1 million years at 90°C. After Gin et coll. (2003)
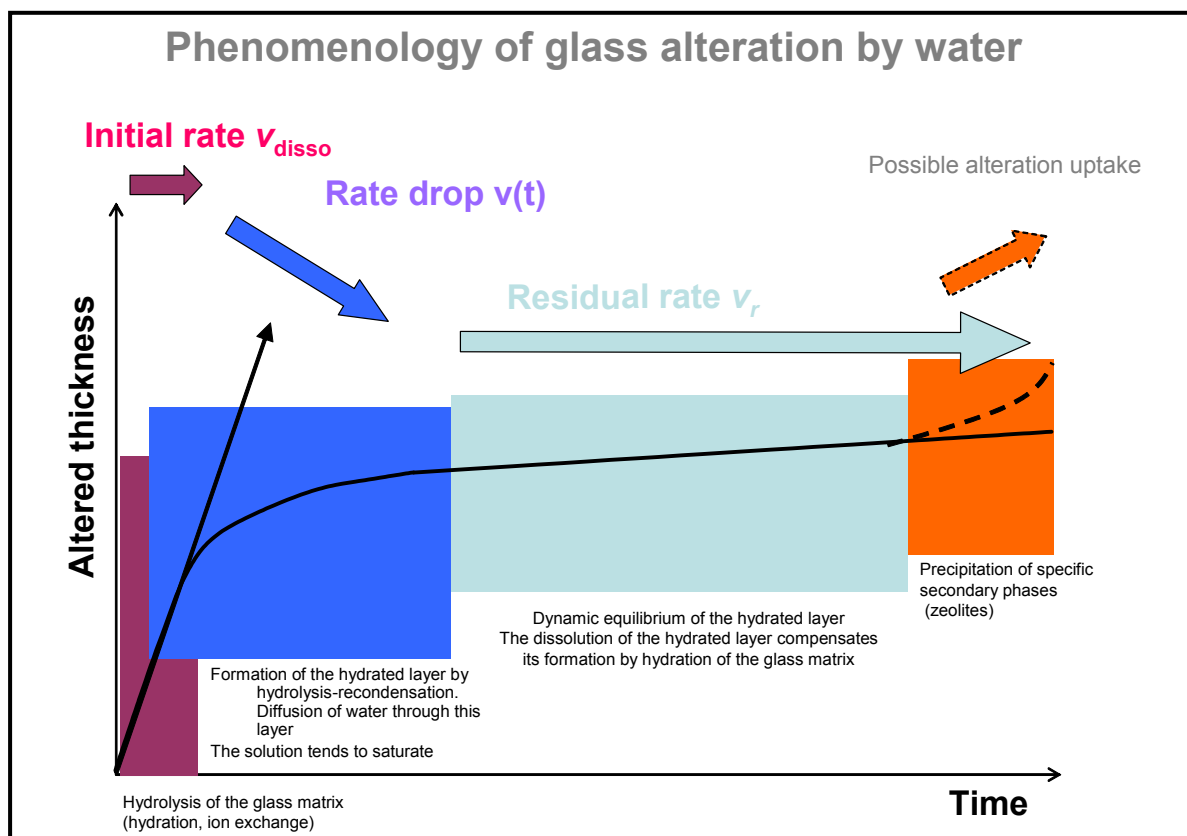

Figure. 6: Phenomenology of glass alteration by water

In the alteration regimes of borosilicated glasses, one can distinguish (Figure. 6):

The initial rate, limited by the hydrolysis of the silicated lattice; The rate drop, associated to the formation of a dense and passivating layer within the hydrated layer. This zone builds up by ion exchange reactions, hydrolysis reactions, and *in situ* recondensation of a fraction of the hydrolyzed silica. At the same time, this layer gets dissolved on its external interface, as long as the solution does not become saturated; This layer acts as a diffusive barrier for water, and for the hydrolyzed species from glass.

The residual rate regime corresponds to a dynamic equilibrium between formation (at the internal interface) and dissolution (at the external interface) of the hydrated layer. When this dynamic equilibrium is reached, the hydrated layer thickness becomes constant, as well as the glass alteration rate. Water renewal and precipitation of secondary phases like phyllosilicates can withdraw silica from the solution. By acting as silica sinks, these two mechanisms are the motors by which the glass alteration goes on in this "residual" regime.

A possible alteration uptake can eventually occur in special cases, when the composition of the porewater surrounding the glass permits the precipitation of zeolitic secondary phases. Conditions for this to occur are met only in very basic waters which are not likely met in geological media, except possibly in the vicinity of concrete artefacts (*Vernaz, 2002*).

The four mechanisms at play during the alteration of glass by water are (Figure. 7):

- The building of a hydrated layer by hydration of the pristine glass at the interface between this pristine glass and the hydrated layer;
- The destruction of this hydrated layer by dissolution at its external interface
- The diffusive transport of water through the hydrated layer
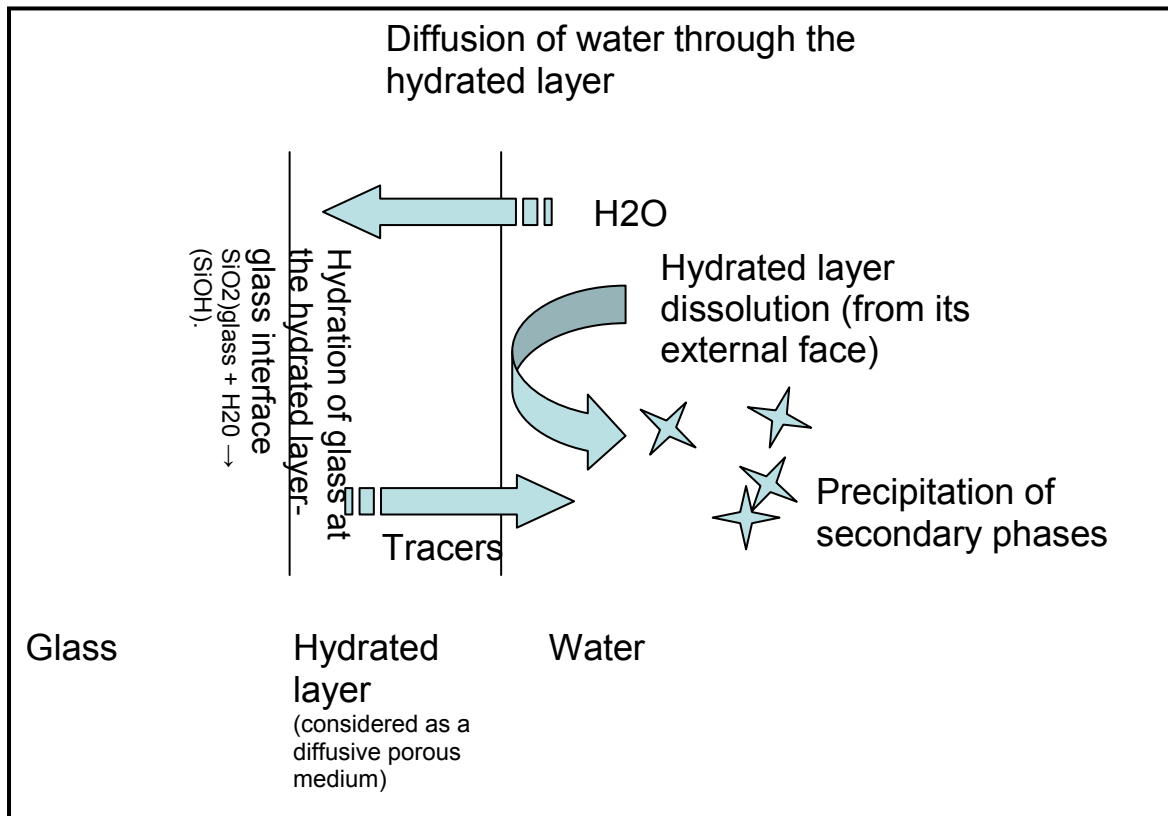- The precipitation of secondary phases in the water surrounding the glass.

Figure. 7: Mechanism of glass alteration by water

6.1.2 Towards a model of glass alteration : We describe in the following a typical model of glass alteration. The GRAAL model incorporates the known phenomenology in a form as simple as possible (*Frugier et al., 2008 ; Frugier et al., 2009*).

Please keep in mind that it is not the only possible model. This is a domain where research is open!

Hypotheses

The hydrated layer is soluble; it is the dissolution of this layer which provides the silica present in the water. Hydrated layer dissolution goes on if water is renewed.

The hydration reaction which transforms the glass (oxide) into a hydrated oxide is initially rapid, but becomes limited by the transport of water through the hydrated layer.

The hydrated layer plays the role of a diffusive barrier for the water which goes from the solution to the reactive glass interface.

The hypotheses listed above can be easily transcribed into equations:

- One equation for the dissolution of the hydrated layer (assuming for example a first order kinetics)
- One equation for the glass hydration (assuming again a first order kinetics)

- One equation for the transport of water through the hydrated layer (assuming a diffusive transport and uniform water concentration gradient across the hydrated layer)
- One equation for the precipitation of secondary phases (assuming a 0th or 1st order kinetics).

In the simple case of a glass sample placed in a recipient where the concentrations can be considered uniform everywhere in the solution, these equations close the system, which can then be readily solved.

In the more complicated case of a glass sample embedded in a porous environment (for instance clay), the concentration in dissolved silica cannot be considered uniform in the porous medium, and one must add another equation for the transport of solute in the medium to close the system.

Such a model reproduces all phases of glass alteration, including the transient ones at the beginning of alteration, and the residual regime, where the hydrated layer reaches a dynamic equilibrium between its building by glass hydration at the internal interface and its dissolution at the external interface.

Parameter values can be extracted from independent experiments. We give here a few orders of magnitude:
- C_{sat} = hydrated layer solubility = 2 Mol.m^{-3}
- D = diffusion constant of water in the hydrated layer = 5. 10^{-21} m^2.s^{-1}
- V_{hydr} = kinetic constant of glass hydration = 10^{-11} m.s^{-1}
- V_{disso} = kinetic constant of hydrated layer dissolution = 10^{-12} m.s^{-1}
- V_{pr} = kinetic constant of secondary phase precipitation = 10^{-15} m.s^{-1}.

The laboratory experiments on glass alteration are usually performed by putting glass (often in a divided form to increase the glass surface area and thus accelerate the alteration process) in a recipient where water is controlled in temperature, and renewed with a determined flow rate. The concentration in glass constituents and tracers (Si, B) in the water are then measured at the exit of the recipient. The total amount of altered glass can then be deduced from these concentration measurements.

6.1.3 The residual alteration regime of glass : is of special importance for the safety of a glass repository, because the glass will spend most of its time in this regime. The residual alteration regime is reached when the hydrated layer reaches its equilibrium thickness. From that moment on, the layer growth by glass hydration at the hydrated layer-glass interface compensates the hydrated layer dissolution at the hydrated layer-water interface. The residual alteration rate then equals the hydrated layer dissolution rate. This rate depends on the modalities of water renewal in the vicinity of the altering surface. The important parameter which describes this water renewal is the ratio Q/S (water flow rate / glass surface area).

If the water renewal is very fast (case of a piece of glass in a stream of running water), the alteration rate v is limited by the kinetics of dissolution of the hydrated layer, and the residual rate is simply equal to the kinetic constant of this dissolution V_{disso}.
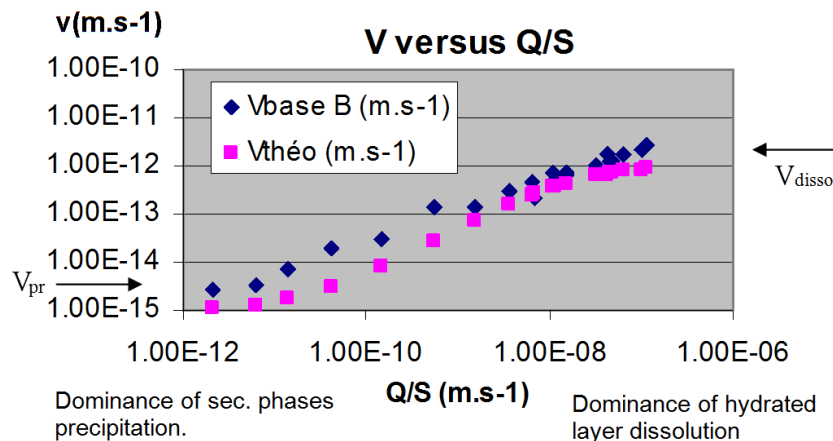

Figure. 8: The residual alteration rate as a function of the water renewal rate.
Comparison between the experimental results and the GRAAL alteration model.

If the water renewal is very slow, the water in the glass vicinity has enough time to become saturated in dissolved silica, and the residual alteration rate depends on the rate of secondary phase precipitation kinetics V_{pr}. It should be noted that precipitation of secondary phases removes silicium from the solution and is equivalent to an effective renewal of the water. The model thus predicts the existence of a residual alteration even in the case of perfectly static water.

This **residual alteration rate of glass depends strongly (3 orders of magnitude) on the glass environment**: surrounding minerals and modalities of water renewal.

Altogether, the model reproduces reasonably well the laboratory experimental data on the residual alteration rate of glass, for various values of the rate of water renewal (Figure. 8).

The GRAAL model incorporates the main features of the phenomenology of glass alteration, but is probably too simple : as suggested by more sophisticated models, the assumption that the transport properties of the hydrated layer are constant is questionable (Figure. 9).
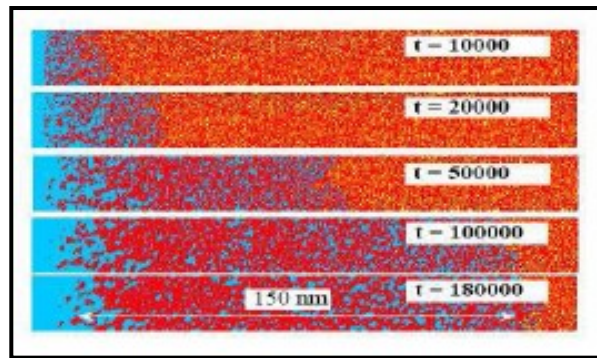
Figure. 9: Simulation of the alteration of glass by Monte-Carlo method. Bond-breaking and bond-forming probabilities are treated as free parameters. Water appears in blue, Si in red, Zr in black and B in black. The porosity of the hydrated layer evolves with time. In soft alteration conditions, this porosity tends to close, thus enhancing the protective properties of this layer. (Cailleteau et al., 2008).

Laboratory experiments are unable to demonstrate the confinement properties of a glass matrix on a million-year timescale. The longest laboratory experiment on glass alteration has lasted for 25 years only. But Nature did the experiment for us with **natural analogues**, both geological and archaeological (*Figure. 10*).

The study of **glass natural analogues** permits to:
- Validate the long-term model predictions, and confirm the orders of magnitude of the alteration rates;
- Stress the importance of environmental parameters (glass in a clay environment does not alter at the same rate as a glass in seawater, because the clay environment limits the renewal of water around the glass, inhibits the transport of silica, and favors the precipitation of newly formed phases).
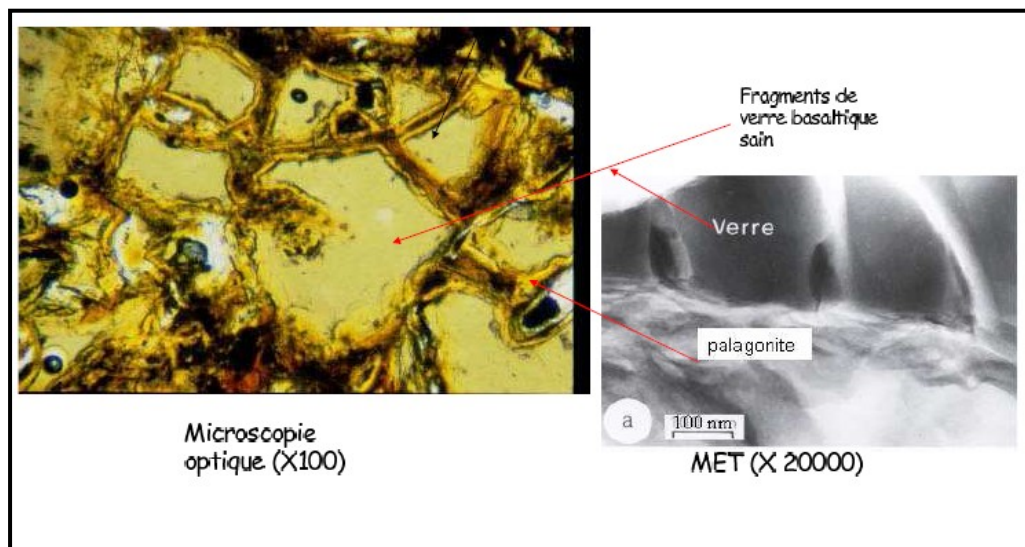

Figure. 10: A natural analogue of glass alteration: Iceland hyaloclastite (basalt, 90 000 years)

Altogether, if one assumes a 10^{-15} m/s for the residual alteration rate, the lifetime of a vitrified waste package is of the order of one million years.

6.2 Long-term behaviour of glass: the effect of self irradiation

During its lifetime, the nuclear glass will undergo self irradiation (Table 2)**:** Alpha disintegrations cause atomic displacement and ionization; It is mainly the recoil nucleus from these alpha disintegrations which cause the atomic displacements. Beta gamma irradiation cause only ionization.

Characteristics of the various radiation sources in nuclear glasses (the number of disintegrations per gram refers to the R7T7 glass used for vitrifying solutions arising from the treatment of PWR spent fuels with a 33GWd/t burnup).						
Radiation sources	Path in the glass	Energy deposited (Gy)		Number of atomic displacements per event	Number of disintegrations per gram of glass over 10^4 years	Number of atomic displacements per gram of glass over 10^4 years
		over 10^4 years	over 10^6 years			
α **disintegration** Helium ion (4 to 6 Mev) Recoil Nucleus (0,1Mev)	~ 20 µm ~ 30 µm	~ 3.10^9 ~ 6.10^7	~ 10^{10} ~ 3.10^8	~ 200 ~ 2,000	~ 3.10^{18}	~ 6.10^{20} ~ 6.10^{21}
β **disintegration**	1 mm	~ 3.10^9	~ 4.10^9	~ 1	7.10^{19}	7.10^{19}
γ **transition**	qqs cm	~ 2.10^9	~ 2.10^9	~ 1	2.10^{19}	~ $2\ 10^{19}$
Reactions (α, n)	1 m	~ 2.10^2	~ 9.10^3	200 à 2,000	3.10^{12}	6.10^{14} à 6.10^{15}
Spontaneous and induced fissions	FP : 10µm neutron: 1m	~ 2.10^4	~ 4.10^4	10^5 200 à 2,000	10^{11} à 10^{12}	10^{16} à 10^{17} 2.10^{13} à 10^{15}

Table 2: Characteristics of the various radiation sources in nuclear glass

During the lifetime of a high activity glass in a repository, one atom out of three will have been displaced once, due to radioactive decays in the glass. One needs to know whether this self irradiation modifies the glass structure and hampers the long-term durability of the glass matrix.

The typical kinetic energy of a recoil nucleus due to alpha decay is 70 keV. Its range in the glass is of the order of 30 nm. The max temperature of the heat wave is about 1200 K, and the typical cooling time is 12 ps. The number of displaced atoms is about 2000. Most broken bonds are restored within a few picoseconds (Figure. 11). Glass is a self repairing material.

For research purposes, one can accelerate irradiation damage in glass by doping the glass with actinides. For example, a glass doped with a few percent ^{244}Cm undergoes the same number of alpha disintegrations in a few years as an industrial glass during its whole life.

A slight modification of the glass density is observed but the little swelling has stabilized at a level below 1% after a cumulative dose of 2.10^{18} alpha disintegrations per gram (Figure. 12). The glass mechanical properties are also modified by irradiation: fracture toughness is increased and then stabilizes at the same cumulative dose.

Molecular dynamics enables one to understand why the glass properties get stabilized beyond a cumulated dose of 2.10^{18} alpha disintegrations per gram: beyond this limit, the number of broken bonds no longer increases, as the bonds broken by the ballistic effects are restored by the heat wave induced by the radioactive decay (Figure. 13). The question as to whether the glass alteration rate can be altered by self irradiation has been investigated. No significant influence of the self irradiation on the glass initial dissolution rate is observed for the fluences encountered in high activity, long life waste.
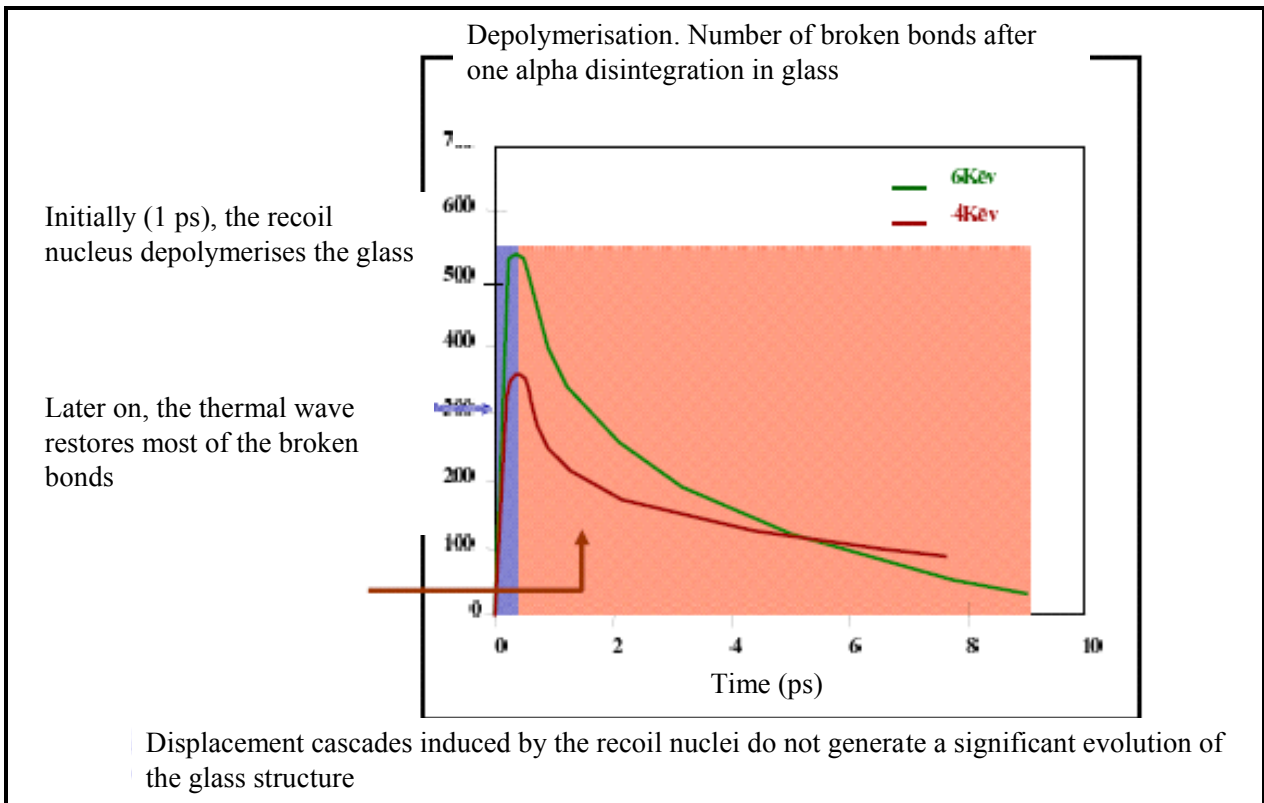
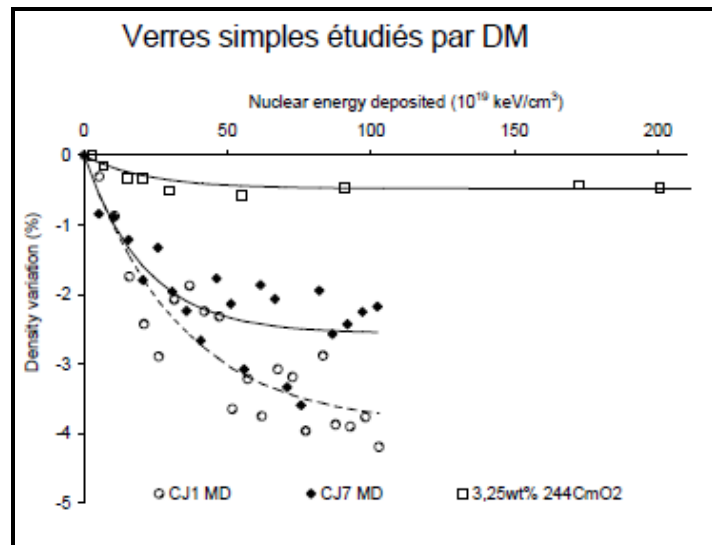*Figure. 11: Structural evolution of glass under irradiation. (Peuget et al., 2006).*

Figure. 12: Evolution of the density of glass under irradiation. (Peuget et al., 2006 ; Bureau, 2008)
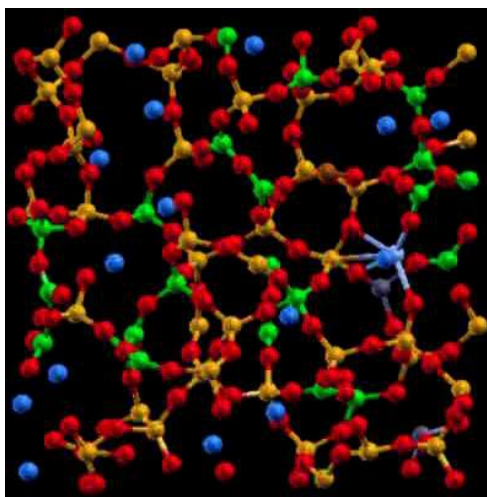
Figure. 13: A simulation of glass under irradiation by molecular dynamics(Delaye 2000).

7. CONCLUSION

Glass: a robust conditioning form for high activity nuclear waste!

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