Long-term behavior of vitrified waste: morphology and protective properties of the gel formed during glass alteration

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Knowledge and understanding of the long term behavior under various environmental conditions of glasses dedicated to the containment of high-toxicity waste are required to design facilities for long term storage and to demonstrate their safety.
In France, borosilicate glasses were adopted as the containment matrix for long-life nuclear waste. Numerous studies were carried out on glass alteration mechanisms in a geological repository environment and especially on the alteration film developed at the glass/solution interface. This film mainly consists of an amorphous, hydrated and porous mixed oxide gel resulting from the re-condensation of cross-linking species (Si, Al, Zr...). It creates a diffusion barrier with respect to reactive species and also retains the long-live radioactive elements. The models predicting the long-term glass behavior take into account the protective properties of the gel layer. As a consequence, a better characterization of the protective properties of the gels is required to enhance the robustness of these models. Innovative characterizations by X-ray reflectometry have been recently developed. They provide important information about the complex morphological evolution of the alteration layers of both nuclear reference glass and simplified glasses.
Key words: nuclear glass, alteration, gel, protective properties, morphology.

1. INTRODUCTION

In France, vitrification is adopted to stabilize the fission product solutions coming from the spent nuclear fuel refining. Borosilicate glasses and particularly the French R7T7 glass [1] has been chosen as a containment matrix. In a geological repository approach, natural barriers limiting radioactive species diffusion in biosphere will be in contact with glass packages. A key step in demonstrating the safety of a high-level radioactive waste repository is to determine the long-term behavior of nuclear glass packages in geological conditions, particularly the alteration by aqueous solutions.

In contact with water, SON68 glass (R7T7-type inactive glass) is subjected to leaching and develops an alteration layer. This film consists in an amorphous, porous and hydrated material formed by recondensing crosslinking species (Si, Al, Ca...). This gel tends to retain long-lived radioactive species contained in the glass [2] and leads to a decrease of the alteration rate about four orders of magnitude compared with the initial dissolution rate [3]. The safety period in a high-level radioactive waste repository is 10.000 years. To demonstrate this safety period it is necessary to have some predictive models. These models integrate the protective properties of the gel [4]. In order to enhance the robustness of these models, the protective properties of the gel were studied. The investigation presented in this paper assesses the relation that exists between protective properties of gels from SON68 glass and simplified glasses and their

morphology. In the first part, the gel morphologies are analyzed by X-ray reflectometry and the results are correlated with data obtained from other characterization techniques. In the second part, the gel protective properties are investigated and are discussed.

2. EXPERIMENT

2.1 SAMPLE PREPARATION

The main glass used is the SON68 glass, a R7T7-type nuclear glass [1], whose composition is detailed in Table I. Two simplified glasses (glasses 1 and 2) [5], based on the same primary components with the same molar ratio as the SON68 glass are also studied. The preparation of monoliths and powders and the alteration protocol have been previously described in [7].

Table I : Glass compositions of studied glasses (w %).

Oxides	SON68	Glass 1	Glass 2
SiO_2	45.5	58.07	59.8
Al_2O_3	4.9	6.27	
B_2O_3	14.0	17.92	18.5
Na_2O	9.9	12.59	13.0
CaO	4.0	5.15	5.3
ZrO_2	2.7		3.5
Ce_2O_3	0.9		
LiO_2	2.0		
Other	16.1		

In a first of set experiments, glass monoliths were

altered in ultrapure water for a surface area over solution volume ratio of 80 cm^{-1}, 90°C during 62 days. Monoliths were placed within glass powder in order to ensure the same alteration rate for the monolith and for the powder by avoiding local concentration effects. Monoliths and powders were taken from the reactor, dried in laboratory atmosphere and analyzed.

The second set of experiments was divided in two steps: a first alteration followed by a second alteration after renewal of solution. The first alteration experiments are detailed in Table II.

Table II : First alteration conditions for the different tests at 90°C and pH = 9.

Tests	S/V (m^{-1})	T (°C)	Time (days)
SON68 glass ref	5000	90	0
SON68 glass PP1	5000	50	21
SON68 glass PP2	5000	90	189
Glass 1 ref	8000	90	0
Glass 1 PP1	8000	50	63
Glass 1 PP2	8000	90	175
Glass 2 ref	8000	90	0
Glass 2 PP1	8000	50	20
Glass 2 PP2	8000	90	100

After removing the leachate from the reactor, altered glass powders were rinsed three times. Then the solution at pH=9 (corresponding to the equilibrium pH of the leachate) was added at 90°C with the same S/V ratio. Subsequently solution samples were ultrafiltered to 10,000 Daltons and diluted in an equivalent volume of 1N HNO$_3$ to be analyzed.

2.2 Characterization

Concentrations in solution were determined by plasma Atomic Emission Spectroscopy (AES) for Si, B, Na, Li, Al, Ca. The precision is roughly 5% when the concentrations are above the detection limit (0.05 mg.L^{-1}). Then the altered glass thickness Ee(B) is calculated from boron (glass alteration tracer) and the density of the altered glass ρ_{SA} from all the element concentrations [7]. The mass of altered film per surface area unit m$_{SA}$ (mg.m^{-2}) is defined by the following expression (1):

$$m_{SA} = \rho_{SA} \times Ee(B) \quad (1)$$

Density ρ_R and thickness e$_R$ of alteration film on monoliths were obtained from X-ray reflectivity measurements (XRR). The critical angle is related to the electron density of the layer and of its substrate [6]. XRR measurements on dried samples were obtained with a Brucker D5000 diffractometer equipped with a special reflectivity stage and a graphite monochromator in the reflected beam. Cu-L$_{3,2}$ ($\lambda = 0.15051$ nm and 0.15433 nm) radiation and standard θ-2θ scan were used for the data collections. Reflectivity curves are generally presented as the logarithmic evolution of the intensity received by the detector as a function of the incident angle θ. Details concerning XRR application on alteration films are available in [7]. All XRR-related calculations were performed with the program IMD 4.1 [8]. This program was used to adjust the experimental reflectivity curves to models in terms of density, thickness and roughness of a few layers. The method used to adjust parameters is described in [9].

Nitrogen measurements on altered glass powder were carried out using a conventional volumetric apparatus Micromeritics ASAP 2010. Classical characteristics related to the porosity of the sample were obtained from isotherms such as pore volume, specific surface area determined by BET method and average pore size by the BJH model using the adsorption branch of the isotherm curve [10].

Ultramicrotome cross-sections of altered glass 2 powder were prepared according to the technique described by Ehret et al [11] and observed using a Transmission Electron Microscope (TEM) Philips CM 120.

3. RESULTS AND DISCUSSION

3.1 Alteration mechanisms and gel morphology

The alteration of SON68 glass in non-renewed system involves several parallel mechanisms resulting in different successive alteration film morphologies. These morphologies were investigated by XRR on altered glass monoliths in order to find the density and the thickness by simulations of reflectivity data [9]. Additional nitrogen adsorptions on altered glass powder were performed for analyzing the open porosity [9]. The evolution of the altered thickness for the SON68 glass is shown in Fig. I. Several steps were evidenced for the alteration.

The first step (1) is an interdiffusion process. This process is an ionic exchange between modifier cations from glass and protons from solution. The alteration layer consists in a de-alkalinized glass with a density gradient. The second step (2) is the hydrolysis of the silicate network at an initial rate. The alteration layer corresponding to this step is essentially constituted of an amorphous, hydrated and homogenous gel. The third step (3) is characterized by a drop in the alteration rate by several orders of magnitude compared with the initial rate. This decrease in the rate is assigned to an increase of the gel density leading to the formation of a complex density gradient [6]. At high reaction progress (4) a residual quasi-constant alteration rate is observed [12]. At this alteration step, the gel exhibits a dense zone within the gel, located between the glass and a porous layer (Fig. 2). Nitrogen adsorption results have shown an increase in the pore size, in the pore volume and in the specific surface area showing a gel alteration process.
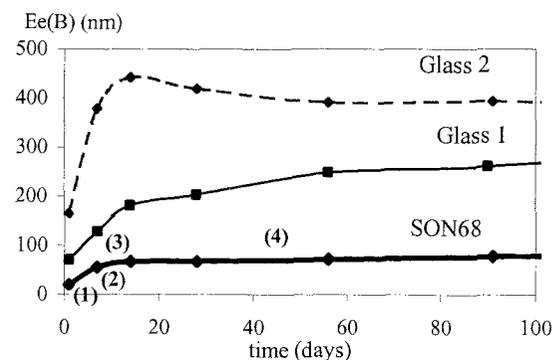
Fig. I: Altered glass thickness a function of time for the SON68 glass, Glass 1 and Glass 2 altered at S/V = 80

cm^{-1}, 90°C and pH=9. The different steps of alteration are indicated for the SON68 glass.

The formation of a dense zone within the gel at high reaction progress is not specific to SON68 alteration layer. However, glasses 1 and 2 have different alteration behaviors (Fig. I). Glass 1 exhibits a continuous decrease in the alteration rate and glass 2 presents an abrupt stop. These different kinetics are related to specific morphologies of the alteration films.

Simulation results from reflectivity curves are presented in Fig.II and in Table III. As for SON68 glass, glasses 1 and 2 show a dense zone within the gel. The roughness obtained from simulation both for SON68 and glass 1 altered samples 1 are in agreement with the mean pore size obtained from nitrogen adsorption (Table IV).
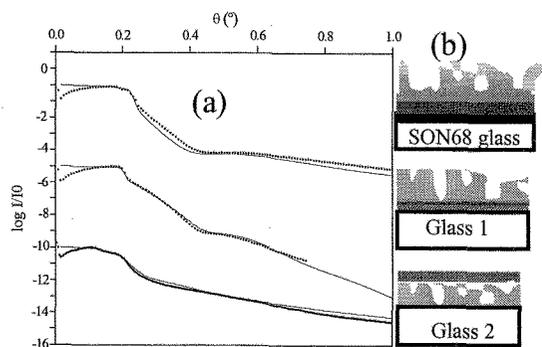
Fig.II: (a) Experimental and simulated reflectivity curves of altered SON68 glass and altered glasses 1 and 2. The curves have been shifted vertically for the sake of clarity. (b) Morphologies of the alteration layers. In this alteration conditions alteration films do not present secondary phases.

Table III: Simulation results from XRR data and altered glass thickness Ee(B) for the SON68 altered glass, altered glasses 1 and 2. The dense layer is in a grey area.

	Tests	SON68	Glass 1	Glass 2
Layer 1	$\sigma_{air/2}$ (nm)	7 ± 0.5	5 ± 0.5	0.5 ± 0.1
Layer 1	e_{R2} (nm)	27 ± 1	180 ± 10	19 ± 1
Layer 1	ρ_{R2} (g.cm^{-3})	1.5 ± 0.1	1.9 ± 0.1	1.3 ± 0.1
Layer 2	$\sigma_{2/1}$ (nm)	2 ± 0.2	2.0 ± 0.1	3 ± 0.2
Layer 2	e_{R1} (nm)	6 ± 0.5	12 ± 0.5	370 ± 30
Layer 2	ρ_{R1} (g.cm^{-3})	2.0 ± 0.1	3.0 ± 0.1	0.8 ± 0.1
Glass	$\sigma_{1/s}$ (nm)	2.2 ± 0.1	2.7 ± 0.1	0.5 ± 0.1
Glass	ρ_S (g.cm^{-3})	2.4 ± 0.1	2.6 ± 0.1	2.0 ± 0.1
	Ee(B) (nm)	71	147	221

Table IV: Nitrogen adsorption results of dried altered glass powder of the test SON68 glass and Glass 1.

Tests	S_{BET} (m^2.g^{-1})	V_P (cm^3.g^{-1})	Mean pore size (nm)
SON68	0.83 ± 0.03	0.0010 ± 0.0005	8
Glass 1	3.44 ± 0.01	0.0040 ± 0.0005	6

For the glass 1, the dense zone is located between a thick gel in contact with water and the glass. At this alteration progress the rate has dropped about three orders of magnitude compared with the initial dissolution rate. This dense zone could contribute to this decrease in the alteration rate.

For glass 2, the alteration curve presents an abrupt stop. The alteration layer is composed of two layers, one rather dense in surface and another less dense underneath. This zone is thick enough to be observed by TEM as shown in Fig. III. The thin surface layer could constitute an alteration-blocking zone. So far, explanation about this different layer location is unknown.
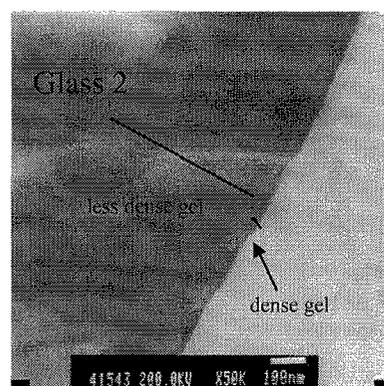
Fig. III: TEM image of the altered layer of glass 2.

All these results show the dependence of gel morphology with glass composition that manages the competition between the diffusion of the species to the solution and their recondensation. The formation of a dense and thin zone, related with a decrease or a stop in the alteration, brings some important informations about the gel protective properties.

3.2 Gel protective properties

One way to evaluate the gel protective properties is to renew the leaching solution with pure water at pH=9 in order to observe if an altered glass is more altered than a non-altered glass. Moreover the gel dissolution can be estimated to evaluate its stability.

During the first alteration, altered glass layers with different thickness and density have been formed. Table V shows the characteristics of the altered glass before the renewal of solution.

Table V: Characteristics of the altered glass before the renewal of solution for the different tests calculated form solution analysis data. Ee(B)1: first altered glass thickness.

Tests	Ee(B)1 (nm)	ρ_{SA} (g.cm^{-3})	m_{SA} (mg.m^{-2})
SON68 glass PP1	28	1.67	47
SON68 glass PP2	115	1.72	198
Glass 1 PP1	78	1.38	108
Glass 1 PP2	229	1.57	360
Glass 2 PP1	108	1.42	153
Glass 2 PP2	286	1.54	440

Fifty-six days after the solution renewal, altered glass

thicknesses, silicon concentrations and alteration rates were calculated. The results are presented in Table VI.

Table VI: Solution analysis 56 days after solution renewal (except for the reference-ref tests), altered glass thickness after perturbation $Ee(B)_2$, silicon concentration $C(Si)$ and alteration rate $V(B)$ calculated between 28 and 62 days.

Tests	56 days after solution renewal		
	$Ee(B)_2$ (nm)	$C(Si)$ (mg.l^{-1})	$V(B)_{28<t<56j}$ (g.m^{-2}.j^{-1})
SON68 glass ref	90	88	13.10^{-4}
SON68 glass PP1	55	62.2	4.10^{-4}
SON68 glass PP2	15	36.3	5.10^{-4}
Glass 1 ref	249	145.3	40.10^{-4}
Glass 1 PP1	123	128.3	19.10^{-4}
Glass 1 PP2	40	46.6	13.10^{-4}
Glass 2 ref	290	182.0	0
Glass 2 PP1	232	298.4	0
Glass 2 PP2	119	232.7	0

Considering each test, these results show a decrease in the altered glass thickness $Ee(B)_2$ depending on the altered glass amount m_{SA} formed during the first alteration. For long first alteration time, the gel seems to be more protective. This increase of the protective properties could be attributed to the presence of a dense zone within the gel, particularly for the test SON68 glass PP 1 and PP2 and Glass 1 PP1 and PP2.

The silicon concentration values depend both on the glass composition, and on the altered glass amount m_{SA} formed during the first alteration. If the gel is porous and not dense enough, then the solution renewal can induce the dissolution of the gel leading to a higher silicon concentration than for the reference test. Tests on SON68 glass and Glass 1 PP1 and PP2 show a decrease in the silicon concentration with the first alteration duration. This indicates a better stability of the gel thanks to the first alteration progress. Differences in the morphology could explain this phenomenon. The less dense zone within the gel in contact with water can easily be dissolved after the solution renewal. This dissolution increases with the specific surface area, reflecting the accessible water area, as Table IV shows. The dense zone located underneath the less dense zone, being not directly in contact with water, could still act as a diffusive barrier.

Tests on Glass 2 PP1 and PP2 exhibit a higher silicon concentration than the reference test. In this case the silicon comes both from the glass and the gel. As previously discussed, the alteration film of glass 2 presents an alteration layer constituted of a dense zone within the gel in contact with water. This zone can be dissolved after the renewal of solution leading to an alteration of the less dense gel underneath (Table III). This gel part cannot play the role of a diffusive barrier as well as the dense zone made. This phenomenon could explain higher silicon concentration in solution than for the reference test on glass 2. Meanwhile the dissolution of the gel does not seem to perturb the system because the alteration rate 56 days after perturbation stops. For the other tests, 56 days after perturbation, the glass is altered at a rate close to the residual rate.

From this last experiment, it can be concluded that the protective properties and the stability of the alteration gels can be correlated to their complex morphology. All these characteristics strongly depend on the glass composition and on their alteration conditions.

4. CONCLUSIONS

The coupling of different techniques as XRR, nitrogen adsorption, TEM and solution analyses have assess the different morphologies of the altered glass layers. The relation established between the complex microstructure of the alteration layers and their protective properties should be integrated in the predictive models of the long-term behavior.

The experimental approach applied for the nuclear glasses could be usefully extended to the study of the long-term behavior of other containment matrices like vitrified domestic waste incineration fly-ash [13] and glass-ceramics [14].

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