A borosilicate glass hydration at low temperature

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ABSTRACT

Vapor phase hydration studies of the inactive simulated French nuclear waste glass SON68 were conducted at temperatures ranging from 35 to 125°C and various relative humidities (RH). The purpose of this work was to understand the behaviour and to determine the alteration kinetics of SON68 glass under a non-saturated environment. Fourier Transform Infra-Red spectroscopy (FTIR) technique was used to follow the glass hydration kinetics. The glass hydration increased with increasing temperature and relative humidity. In addition to a hydrated glass layer calcite, powellite and apatite were identified.

Keywords: Borosilicate glass, vapor hydration, alteration, secondary phases.
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INTRODUCTION

In France, high-level nuclear waste glasses poured in stainless steel canisters are expected to be encapsulated in carbon steel container for deep geological disposed. After closure of the disposal site the phenomenon of nuclear glass hydration under unsaturated conditions is likely to occur after the breakdown of the container. Indeed, the massive production of hydrogen following the corrosion in anoxic conditions of the container will probably prevent a rapid filling of the container with the site water. Therefore, unsaturated conditions may persist for thousands of years. The glass should be partially altered with water vapor before being totally submerged by groundwater. Several studies have been conducted in order to understand the hydration mechanisms of nuclear glasses [1-5] and their natural analogues such as obsidian [6-9].

In contact with the glass, the water vapor diffuses and reacts via a hydrolysis and ion exchange mechanism. Consequently, an alteration layer grows on the glass surface. The hydration layer thickness and the nature of surface precipitates depend mainly on the temperature and the relative humidity [10,11] but also on pH [12]. The main secondary phases formed during glasses hydration at low temperatures (<175 °C) are: analcime, weeksite, tobermorite, powellite, apatite and calcite.

The present work was carried out to study the behavior of the inactive SON68 waste glass under unsaturated regime. Many experiments have been conducted at high temperatures but very few hydration experiments have been conducted at low temperatures. In fact, 35°C is the temperature of the argillaceous Callovo-Oxfordian formation where the active R7T7 waste glass is expected to be stored [13], and it is unknown if the glass behaves in the same manner at low temperature. The glass was also hydrated at 90 and 125°C. RH values range between 92 and 99.9% [2].
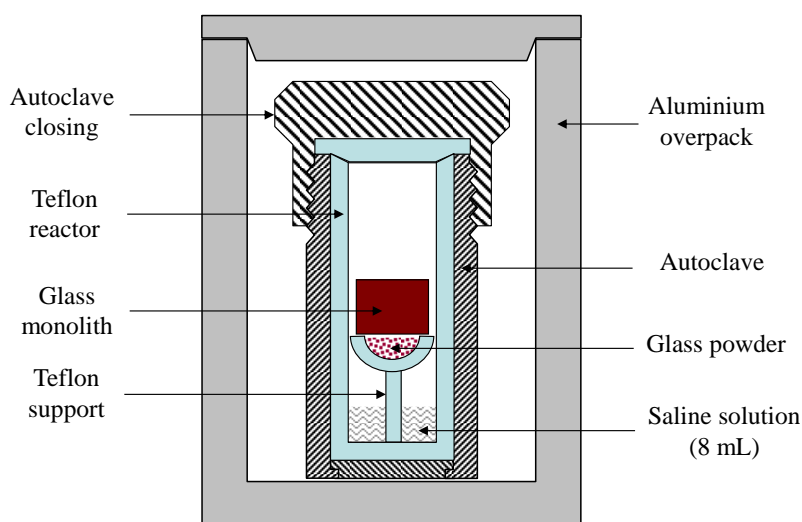
EXPERIMENTAL SECTION

The SON68 glass composition is indicated in Table 1. Thin glass monoliths ($1 \times 1 \times 0.1$ cm) were cut from a glass block and polished to 1 µm, the glass fragments were grinded and sieved. The glass powder (ϕ<32 µm) and monoliths were then carefully cleaned in ethanol during 1h using the ultrasonic cleaner. Samples were hydrated in a

stainless steel autoclave with a Teflon liner (40mL) placed in a 2 cm thick aluminium container (Fig. 1) in order to homogenise the temperature within the autoclave and to prevent the vapor condensation on the glass samples during heating and cooling processes. 8 mL of liquid solution (water + NaCl) was used to ensure a constant RH by varying the NaCl concentration [14]. Thus, saline solutions of 2.23; 1.03; 0.6 and 0.04 mol_{NaCl}/kg_{H2O} were used to obtain 92; 95; 98 and 99.9 % of RH, respectively. All experiments with the operational conditions are summarized in table 2. Samplings were conducted in different time intervals (7−30 days). After each sampling the autoclaves were removed from the oven and left to cool down at room temperature for 6 hours. Glass monoliths were weighted and analyzed by FTIR. The saline solutions were weighted and changed after pH measurements.

Table. 1. Chemical composition in weight of the SON68 nuclear glass.

Oxide	% (weight)	Oxide	% (weight)
SiO_2	45.85	NiO	0.43
B_2O_3	14.14	P_2O_5	0.29
Na_2O	10.22	BaO	0.62
Al_2O_3	5.00	Y_2O_3	0.20
CaO	4.07	La_2O_3	0.93
Fe_2O_3	3.03	Nd_2O_3	0.97
ZrO_2	2.75	Pr_2O_3	0.46
ZnO	2.53	Ag_2O	0.03
Li_2O	1.99	CdO	0.03
MoO_3	1.78	SnO_2	0.02
Cs_2O	1.12	TeO_2	0.23
Cr_2O_3	0.53	Others	0.39
SrO	0.35		

Fig.1. The SON68 glass hydration experimental setup

To follow the glass hydration over time, FTIR spectroscopy was used according to protocols developed by [5,10,12,15]. Spectra were obtained with an 8400 Shimadzu between 4000 and 2500 cm^{-1}, and then deconvoluted with five Gaussian using Origin 8.0 software (OriginLab).

Hydrated glass powder and monoliths were analyzed using a scanning electron microscope (SEM) (JSM 5800 LV, 15 kV) coupled with energy-dispersive X-ray spectroscopy (EDX). The samples were coated with a thin carbon layer in order to get a better resolution of the K-lines for lighter glass components (Si, Al and Ca). The final compositions of analyzed areas were calculated assuming oxide stoichiometry and normalization to 100%.

The micro-Raman spectroscopy was used to identify glass corrosion products. Measurements were performed at room temperature using a T64000 Tobin-Yvon/LABRAM spectrometer equipped with a 600 lines/mm diffraction grating. The instrument is equipped with an Olympus microscope (× 100 objectives) and $Ar^+–Kr^+$ laser (514 nm exciting line). The power of illumination was about 5 mW at the sample in order to prevent any deterioration of the material. Single spectra were obtained in the 100–2200 cm^{-1} range with an integration time of 600s.

<div align="center">**Table.2. Summary of each experiment with the operational conditions**</div>

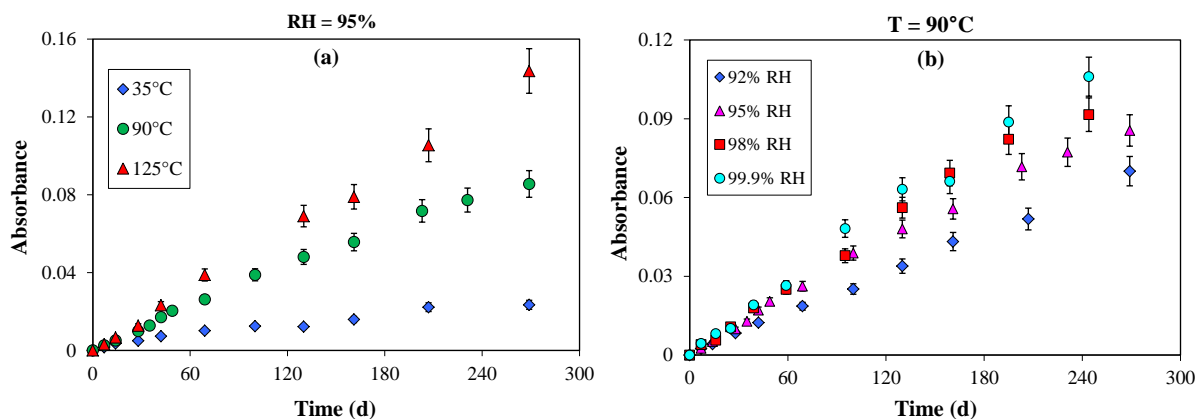| Test	Temperature (°C)	Relative humidity (%)	Days
1	35	95	269
2	90	92	269
3	90	95	269
4	90	98	244
5	90	99.9	244
6	125	95	269

3. Results and discussion

3.1. Glass hydration kinetics

Fig. 2 shows an example of the evolution of a typical FTIR spectrum with time for a sample hydrated at 90°C and 99.9 RH for 244 days. Other experiments show similar spectral evolution. A Gaussian deconvolution of the five peaks was performed for each spectrum in order to distinguish the molecular water from the silanol group (SiOH). The different bands and their contributions are detailed in [12]. The glass hydration was determined by following the evolution of the absorption band at 3595 cm^{-1} which corresponds to the vibration of SiOH group.
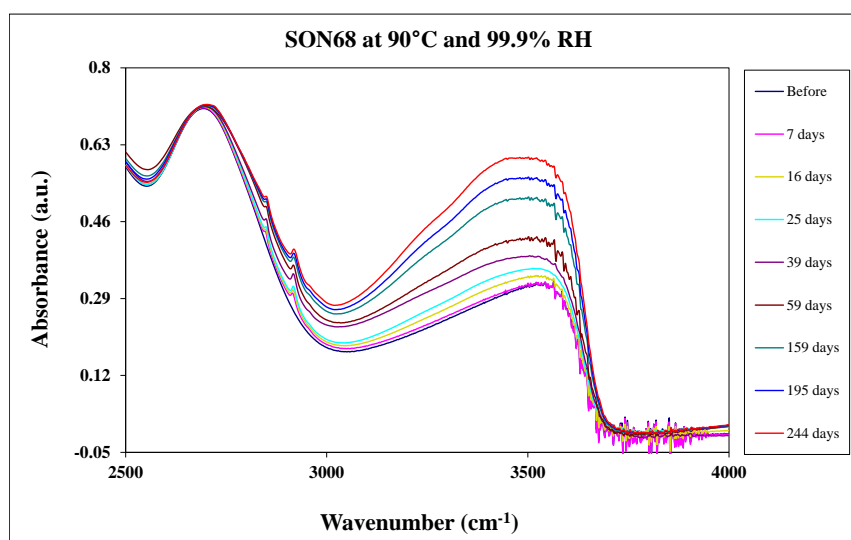
Fig.2. Evolution of FTIR spectrum with time for a glass sample hydrated at 90°C and 99.9% relative humidity

Fig.3. The absorbance evolution of the SiOH peak at 3595 cm^{-1} as a function of time and temperature for SON68 glass hydrated with relative humidity of 95%. Errors are under 8%

3.1.1. Effect of temperature and relative humidity on the glass hydration

The absorbance evolution of the SiOH peak at 3595 cm^{-1} as a function of time at different temperatures for SON68 glass hydrated with relative humidity of 95% is shown in Fig. 3(a). The absorbance values were normalized using the SiOH absorbance at time zero (i.e. from a FTIR spectrum obtained on the pristine glass). It is seen that the glass hydration which depends on the water diffusion in the glass [5] increased with increasing temperatures. Fig. 3(b)

shows the absorbance evolution of the SiOH peak at 3595 cm^{-1} as a function of time at 90°C and different relative humidity values. The glass hydration seems to be linear with time, it increases with relative humidity and also with time. This is due to the increase of the number of water monolayers on the glass surface.

3.2. Analysis of hydrated glass by SEM/EDX and Raman spectroscopy
SEM observations of hydrated samples show the formation of honey-comb like structure, similar to smectite, which morphology depends on the temperature and relative humidity. Fig. 4 illustrates an example of glass monoliths hydrated under 95% RH at 35 °C (a) and 90 °C (b) to 269 days. Different crystals are also formed on the surface, their abundance and chemical composition vary depending on the temperature. X-ray diffraction performed on glass samples altered at varying temperatures reveals an important amount of amorphous materials with the absence of diffraction peaks. EDX spectra show an enrichment of the surface in Ca at all temperatures. In addition, P and Mo peaks are identified at 90°C (Fig. 4b) and 125°C, suggesting the presence of molybdate and phosphate. Raman spectroscopy analyses confirm the presence of calcite, powellite and apatite for samples hydrated at 90 and 125°C. For samples hydrated at 35°C, only calcite was identified. These phases were identified during vapor alteration of SON68 glass [10,11]. They were also identified during leaching experiments of SON68 glass in dynamic mode and under silica rich conditions for the same temperatures values [16].

Due to its tetragonal structural variability, powellite mineral (CaMO$_4$) can accommodate a wide chemical substitutions such us trivalent actinides (Am, Cm) and lanthanides (La, Nd) [17,18]. The benefits of this mineral allowed the formulation of a new calcium and zirconium-enriched alumino-boro-silicate glass matrix. The latter can be able to incorporate 12 wt% of Mo as CaMoO$_4$ [19]. Apatite is a calcium phosphate compound with a chemical formula of Ca$_5$(PO$_4$)$_3$X, where X can be a F$^-$ (fluorapatite), Cl$^-$ (chlorapatite) or an OH$^-$ ion (hydroxyapatite). This phase was also identified during vapor alteration of basalt glass [20], and SON68 glass [10,11]. The orthophosphates ions have the capacity to form aqueous complexes with most the rare earth elements (REE) and the transition metals [21]. The long term alteration of nuclear glass produced abundant nanoparticles of lanthanide and Zr phosphates [22]. The presence in the protective gel layer of elements with high coordination numbers such as Zr and REE enhance the passivating nature of the gel. However, the small amount of phosphates in SON68 is not being able to retain all the REE present in the glass [23]. The calcite CaCO$_3$ precipitate can also incorporate trivalent actinides and lanthanides [17,18]. Only the calcite was observed at 35°C. Glass powders hydrated at temperatures above 90°C are slightly cemented. SEM/EDX and Raman analyses revealed the presence of the same phases observed on the surface of the glass monoliths hydrated into the same autoclave.

The absence of diffractions peaks does not allow us to identify crystalline phases. In addition to this, it is difficult to distinguish the nature of precipitates by EDX spectrum because it contains a large number of elements. Micro-Raman spectroscopy, an effective and non-destructive analytical technique, was used in this study in order to identify the various corrosion products observed using electron microscopy. The Raman spectrum of calcite obtained on the surface of sample hydrated at 35°C and 95% RH is shown in Fig. 5(a). This phase was identified on the surface of all samples. Fig. 5(b) illustrates the Raman spectra of apatite and powellite obtained on the surface of sample hydrated at 90°C and 95% RH. The presence of these phases was also confirmed by Raman spectroscopy for the other samples except that hydrated at 35°C where only calcite was identified.
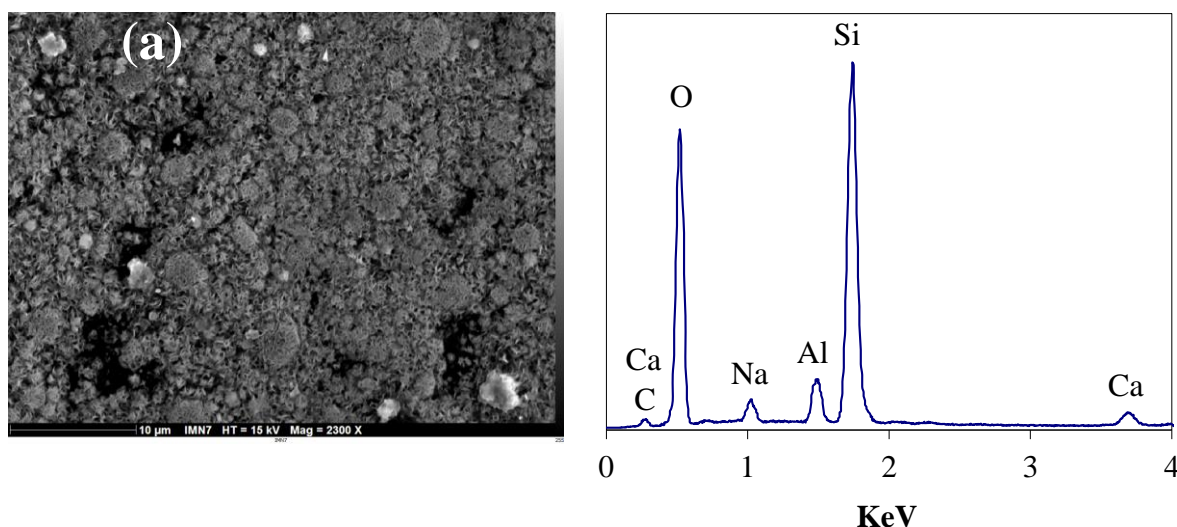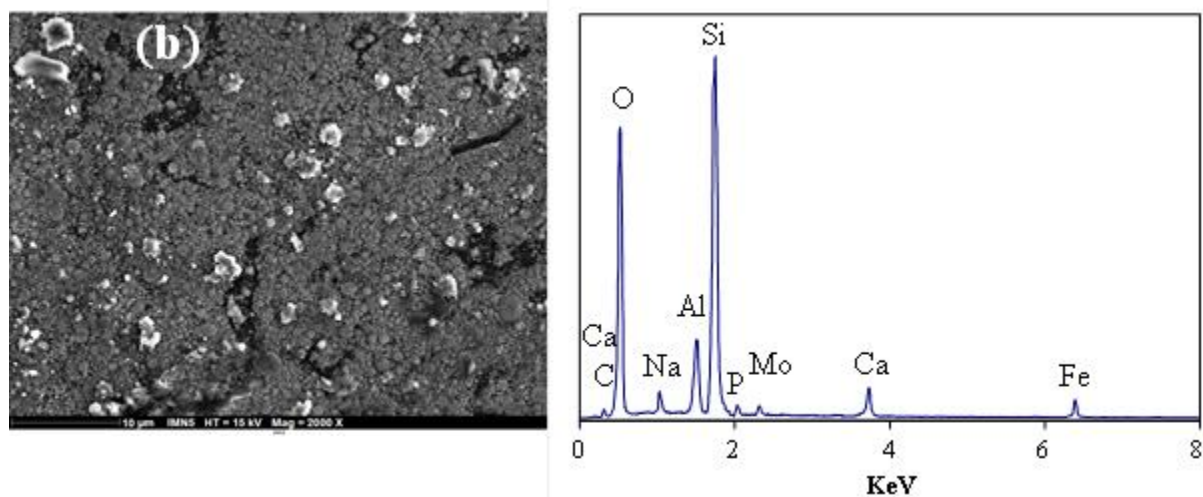
Fig.4. SEM micrographs with the corresponding EDX spectra of the SON68 glass hydrated under 95% RH at 35°C (a) and 90°C (b) to 269 days
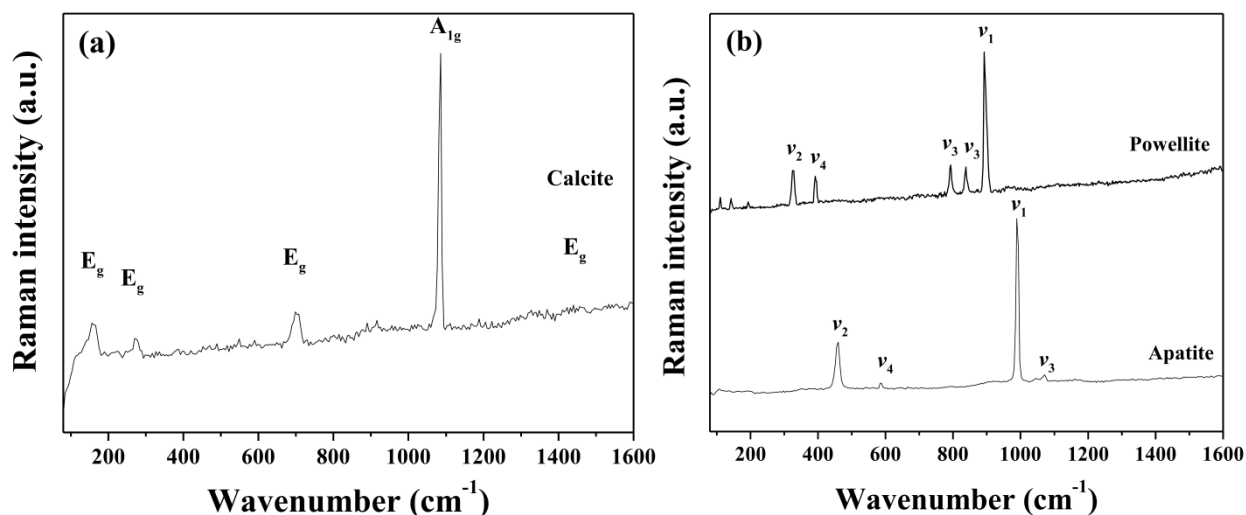

Fig.5. Raman spectra obtained on the surface of the SON68 glass monolith hydrated under 95% RH at 35°C (a) and 90°C (b) to 269 days

CONCLUSION

In this study, the inactive SON68 waste glass was hydrated at different temperatures and under different relative humidity values. The results show the efficiency of FTIR technique in monitoring the glass hydration kinetics. The hydration of the glass increases with temperature and relative humidity. SEM/EDS and Raman spectroscopy revealed the precipitation of secondary phases even at low temperature. The calcite precipitates on the surface of sample hydrated at 35°C. For samples hydrated at temperatures above 90°C, calcite, apatite and powellite were identified.

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