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# Vapor hydration of SON68 glass from 90 °C to 200 °C: A kinetic study and corrosion products investigation

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ABSTRACT

Corrosion of nuclear waste glass in unsaturated conditions is expected to occur upon the closure of the repository galleries during disposal cell saturation in the proposed French disposal site. The objectives of the present work were to determine the alteration kinetics of the SON68 reference in such conditions. Vapor hydration tests were conducted using thin, polished SON68 glass coupons contained in stainless steel autoclaves. Temperatures ranged between 90 °C and 200 °C and the relative humidity (RH) was maintained at 91 ± 1%. Additional experiments at 175 °C and 80, 85, 90 and 95% RH were also conducted to assess the role of RH on the glass corrosion rate. The nature and extent of corrosion have been determined by characterizing the reacted glass surface with scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy dispersive X-ray spectroscopy (EDS). Elemental profiling of the glass hydrated at 90 °C was studied by TOF-SIMS. The chemical composition of the external layer depends on experimental conditions. The hydration rate at 90 °C (TOF-SIMS analysis) is 10× higher than the generally accepted final rate of SON68 in water at 90 °C (~$10^{-4}$ g $m^{-2}$ $d^{-1}$). This may indicate that the glass hydration process cannot be simulated by experiments in aqueous solution with a high *S/V* ratio. Subsequent leaching (corrosion in an aqueous solution) of samples weathered in water vapor showed dissolution rate values higher than those of pristine glass. This result indicates that mobile elements are trapped within the alteration products during the hydration step and it gives insight into mobility variations of the considered elements.

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## 1. Introduction

In France, long-lived radioactive waste from spent nuclear fuel reprocessing is confined in a borosilicate glass matrix. The resulting glass is to be placed in an underground Callovo-Oxfordian claystone formation in the north-eastern Paris Basin for long-term disposal [1]. After closure of the disposal galleries, steel confinement containers will block any access of clay pore waters to the glass thus assuring isolation of the waste for periods of thousands of years. Nevertheless, due to slow corrosion and geostatic pressures, the container will finally breach, allowing for fluids to contact the glass. Void spaces inside and outside of the container will remain open as a result of pressure build-up caused by $H_2$ gas emanating from the corroding stainless steel over-packs under anoxic conditions [2]. This post-closure phase is expected to last for about 10,000 years until $H_2$ production has reduced sufficiently for hydrogen dissolution and diffusion to predominate. Under post-closure conditions, water vapor is expected to alter a portion of the glass package before the claystone host rock is resaturated and liquid water completely infiltrates the container. A situation such as this would lead to the first contact of liquid water with the glass being with a hydrated glass surface.

Several studies have been concerned with water vapor alteration of radioactive waste glass [3,4], simulants [5–9] and natural obsidian analogs [5,10,11]. We are aware of only one test that was not conducted at 100% RH [6]. Water vapor alteration tests have been shown to produce surface weathering which leads to an increased release of glass constituents in leaching tests that initially exceed releases from pristine glass monoliths [12].

During tests in unsaturated conditions, a thin layer of water adsorbs on the glass surface. The thickness of this layer depends on the type of glass, alteration time, and RH. For example an obsidian sample has been shown to have 5–6 water layers at 99% RH and 23 °C while the high-alkali SRL165 glass has been shown to have 30 under the same conditions [13]. The condensed water vapor on the glass surface diffuses or reacts with the glass through ion exchange, hydrolysis, condensation, and the precipitation of secondary alteration

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products. These mechanisms lead to an in situ reorganization where the elements are spatially redistributed based on local thermodynamic constraints. Some of the glass network ions migrate to the glass surface where they are rapidly oversaturated with respect to crystalline alteration products. For this reason, one of the main purposes of the vapor hydration test is to identify potential precipitates from a given glass composition because these secondary minerals are formed at shorter time periods compared to static leaching tests [14,15]. Experiments have also shown that the formed precipitates are similar to those seen by corrosion processes that occur in nature [5].

We also draw attention to the advantages of using a glass monolith in vapor conditions over tests on glass powders in liquid solutions at high glass surface-to-volume-liquid (S/V) ratios. Advantages of using these tests are: (1) an accurate surface area of powder is difficult to obtain, (2) the surface of a glass powder is difficult to analyze after the experiment has ended and (3) a large amount of the altered glass powder must be analyzed to ensure that all precipitates have been observed [9]. For these reasons the vapor hydration test (VHT) method is recognized by the American Society for Testing and Materials (ASTM) for the study of glass and glass ceramic corrosion upon exposure to water vapor at elevated temperatures and 100% RH [16]. The glass surface to volume (S/V) ratios for vapor tests are generally on the order of $10^7$–$10^9$ $m^{-1}$.

Among all of the different tests concerning the alteration of nuclear waste glasses by water vapor only two were concerned with rates of alteration. In one of the tests [9] two types of borosilicate glass monoliths ($Al_2O_3$: 5.77/7.37%; $B_2O_3$: 9.00/11.69%; $Fe_2O_3$: 11.38/12.10%; $Na_2O$: 9.38/8.72%; $SiO_2$: 44.98/43.94%) were sealed in 8 mL autoclaves with 0.25 mL of deionized water and placed in a 200 °C oven. No control of system RH was performed. Total reaction times were up to 40 days. A reaction rate of 2.4 μm per day (6.5 g/m$^2$d) was observed for the first glass sample while a reaction rate of 21 μm per day (56.7 g/m$^2$d) was observed for the second glass sample after an incubation period of five days. The rapid increase of the reaction rate was concluded to occur at the same time as the formation of secondary phases on the surface. These secondary phases were identified as apatite, weeksite, analcime, and a calcium silicate phase. In the work by Gong et al. (1998), conducted in saturated water vapor conditions at 200 °C with the SON68 reference waste glass up to 1021 days, the authors describe the formation of secondary phases as a function of time using cross-sectional analysis by electron microscopy techniques. The secondary phases identified were analcime, gyrolite, tobermorite, apatite, and weeksite. Several different alteration zones were identified which varied in elemental composition. Mo and rare earth elements were trapped in a poorly crystalline layer while transition metals including Fe, Zn, Mn and Cr precipitated on the crystalline external layer. A smectite layer was identified at the pristine glass/reaction layer interface. TEM cross-section studies showed a non-homogeneous alteration layer thickness of 4 μm between the pristine glass and the glass surface after 91 days of hydration. An alteration rate of $\sim 2\times10^{-2}$ μm per day ($5.5\times10^{-2}$ g/m$^2$ d) was measured throughout the entire reaction which is 1.5 orders of magnitude below the forward dissolution rate of SON68 in dilute liquid conditions [17].

In the present work, we aim to further study the alteration of SON68 glass in the presence of water vapor. Instead of working in saturated conditions we have chosen to work in environments below 100% RH to ensure that no water condensation occurs at the glass surface. Tests have been conducted at several temperatures to see how the reaction rate changes as a function of this variable. The effect of RH is also investigated. At the end of each experiment the alteration products were identified. At the end of the hydration test, a representative sample at each RH and temperature was leached in ultrapure water to study the release of common glass dissolution tracers.

## 2. Experimental techniques

The French reference nuclear waste glass SON68 was provided by the French Atomic Energy Commission (CEA) and its composition is listed in Table 1. The SON68 non-active glass is made primarily of the network formers (Si, B, and Al) and network modifiers (Na, Ca, and Li). This particular glass is made up of oxides of the above elements (~81%) and the remaining mass (~19%) is mainly composed of transition and rare earth oxides that represent fission products and minor actinide oxides. The composition is representative of the radioactive R7T7 glass produced at AREVA's La Hague site.

Thin glass monoliths with dimensions of 25 mm × 25 mm × 1 mm were cut, polished to 3 μm and cleaned with acetone in an ultrasound before use. After polishing, the glass specimens were transparent to light.

Experiments were conducted in a stainless steel autoclave (Parr 39 mL) with a Teflon liner. The glass monolith was placed on a Teflon support manufactured in house that fit into the Teflon liner. An 8 mL saline solution was placed below the support. A relatively large liquid volume was used to ensure a constant RH even as the system lost small quantities of water vapor with time. The Teflon liner was placed in an autoclave which was subsequently placed in a 2 cm thick aluminum container to prevent temperature gradients that may cause vapor condensation on the glass sample during the heating and cooling processes. A schematic view of the system can be seen in Fig. 1.

Tests were conducted at 90 °C, 125 °C, 150 °C, 175 °C and 200 °C. The RH of these experiments was maintained at 92% by placing a solution of 13 wt.% NaCl in the autoclave [18]. Tests were also conducted at 175 °C and relative humidities of 80%, 85% and 95% (25, 18, and 6 wt.% NaCl, respectively). Relative humidities in the given range were chosen because they encompass an inflection point in a graph of the number of surface water layers versus RH calculated for an obsidian sample [13]. A list of all the experiments can be seen in Table 2.

After a desired time period (usually 14 days), the autoclave, including the overpack, was removed from the oven and left to cool for 6 h. Once cool, the Teflon liner was weighed to track water mass loss due to diffusion through the lining. Then, the glass monolith was taken and analyzed using Fourier Transform-Infrared (FTIR) spectroscopy. After obtaining the FTIR measurements, the monoliths were placed back onto the sample holder and a fresh saline solution was added. The amount of time that the sample was outside of the oven was accounted for in the kinetics calculations. It was assumed that the monolith did not react with the ambient environment while outside the autoclave.

During the reaction at temperature it was concluded that no water condensed on the monolith because (1) no liquid water was seen in the Teflon support after cooling and (2) no pH change in the liquid solution was measured. A pH change in the solution would have been indicative of a release of components from the glass into solution [9]. The fact that water did not condense on the monolith is in contrast with previous experiments performed at 100% relative humidity

**Table 1**
The French reference SON68 nuclear waste glass composition.

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

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