# Degradation of Simulated HLW Glass and International Simple Glass immersed partially in water– 16474

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## ABSTRACT

Water degradation of glass waste forms destined for geological disposal has been studied in a variety of conditions including of bulk glass immersed completely in static or dynamic water. During the course of repository life, the canisters may be only partially immersed in the initial stages of contact with water. Under these conditions glass degradation occurs on the glass immersed in water and on the glass above water by vapor condensation. In this work degradation of International Simple Glass (ISG) and Simulated High Level Waste Glass (HSG) is examined by immersing partially in distilled water during the course of test. Under static experimental conditions at 90$^{\circ}$C, the condensation of vapor on the ISG glass surface formed Ca-rich precipitates and pits after degrading for 1 and 3 weeks respectively. Whereas HSG precipitated Ca-rich phases predominantly after 1 week and no pits were found on the surface. When compared, HSG was found to change surface chemistry faster than ISG.

## INTRODUCTION

Vitrified nuclear waste disposed of in geological repositories will be protected with a multilayer barrier system. These barriers, during the course of time, will corrode and may eventually leak water into the canisters. In such an event, water will come in contact with glass and activate its corrosion. Glass corrosion was classified by Hench and Clark [1] into 5 types, based on the corrosion medium pH and the gel layer formation mechanisms. With increase in pH, glass corrosion mechanisms and surface gel layer formation vary. Decades of nuclear glass degradation research had helped to derive a sequence of degradation mechanisms that could occur under ideal experimental conditions (i.e., glass is completely immersed in water and is defect free, pristine bulk material). Nuclear glass dissolution can occur in four stages 1. Hydrolysis, 2. Protective layer and solution saturation, 3. Water diffusion and secondary phase precipitation, and 4. Large precipitation of silicate minerals [2]. The time scale of each stage is not defined and is dependent on factors such as temperature, pH, composition, and renewed rate of the solution (ground water) in contact with glass. Most previous studies have been dedicated to understanding surface degradation mechanisms of glass [2, 3] under ideal conditions and very few considered additional physical and chemical influences that can affect the length of

each stage [4, 5, 6]. In reality, at the initial stages canisters may be only partially immersed in water. The effect of partial immersion in water and vapor condensation could change the surface chemical composition and influence the degradation behavior of glass when completely immersed. This effect is not reported in the literature as far as the authors are aware, hence in this paper we discuss the influence of water condensation on International Simple Glass (ISG) and Simulated High Level

Glass (HSG).

## METHODS

The experimental procedure shown in Figure 1 was tested on ISG (provided by James Marra (Savannah River National Laboratory, USA)) and HSG (provided by CIAE, Beijing, China) – compositions obtained by Zhang et al [7] are given in Table 1. The ISG and HSG samples were subject to aqueous corrosion in static conditions at 90$^{\circ}$C in deionised water for one weeks at pH 7. The ISG and HSG were cut into samples of (L × B × H) ~20 mm × 5mm × 2mm size using a diamond blade. These samples were grounded using SiC papers up to 4000 i.e., 2.5μm finish.

| Oxide (wt%) | HSG | ISG |
|---|---|---|
| $SiO_2$ | 50.232 | 60.2 |
| $B_2O_3$ | 18.48 | 16.0 |
| $Na_2O$ | 11.0064 | 12.6 |
| $Li_2O$ | 1.932 | - |
| $Al_2O_3$ | 2.94 | 3.8 |
| $CaO$ | 4.536 | 5.7 |
| $MgO$ | 0.84 | - |
| $SrO$ | 0.0368 | - |
| $Y_2O_3$ | 0.016 | - |
| $MoO_3$ | 0.1941 | - |
| $MnO_2$ | 0.016 | - |
| $Cs_2O$ | 0.1152 | - |
| $BaO$ | 0.0208 | - |
| $Nd_2O_3$ | 1.9728 | - |
| $Fe_2O_3$ | 3.144 | - |
| $NiO$ | 0.5728 | - |
| $K_2O$ | 0.0912 | - |
| $P_2O_5$ | 0.0688 | - |
| $SO_3$ | 0.6448 | - |
| $TiO_2$ | 0.84 | - |
| $Cr_2O_3$ | 0.296 | - |
| $ZrO_2$ | - | 1.7 |
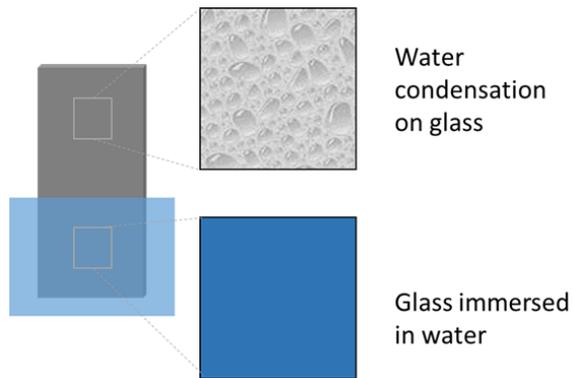


**Figure 1: Schematic of ISG Corrosion test setups.**

Only half of the sample was immersed in water while the other half was left in air in the container. This configuration is expected to condense water on the glass surface above water and to clearly distinguish boundary between water-filled glass and water condensed glass. JSM6400 SEM was used to obtain Back Scattered Electron (BSE) images and EDX maps. ImageJ software was used to quantify precipitates found on BSE

images. Olympus BX51 Optical microscope was used to capture meniscus region at the glass water boundary.

**DISCUSSION**
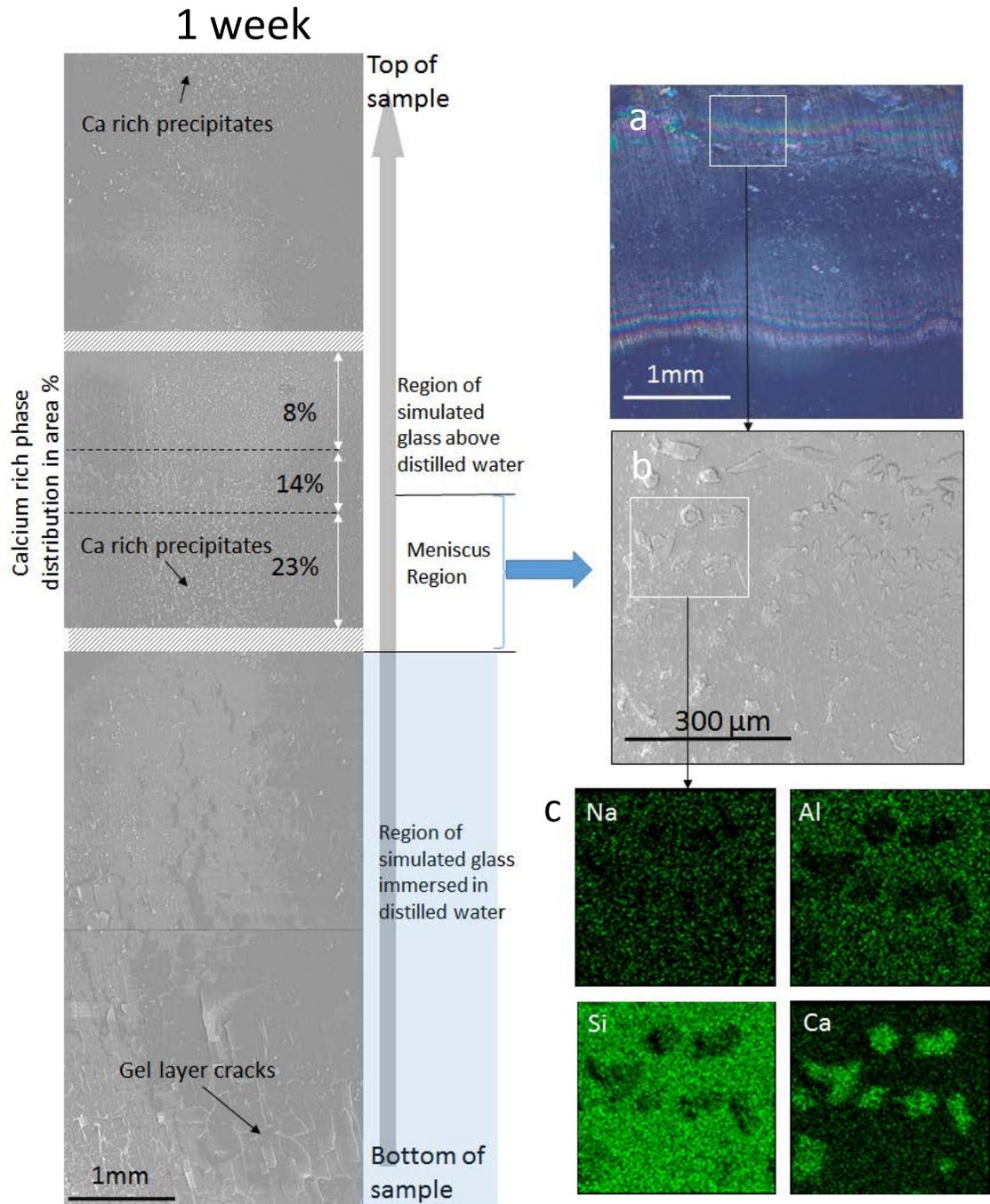


**Figure 2**. BSE images of HSG degraded in distilled water for 1 week at 90°C is shown. At bottom cracks of dry gel layer formed on HSG are observed followed by a region rich in precipitates in meniscus region. The values 23%, 14% and 8% represents the area covered by these precipitates in the highlighted zones. On top region, the HSG surface also show the growth of precipitates (3-5%) due to vapor condensation. Towards right meniscus region of HSG is shown. a. meniscus area captured by optical microscope. b. magnified BSE image of meniscus rich in precipitates. c. EDX map of precipitates shown in b.

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Figure 2 shows back scattered images of HSG which were degraded in distilled water for 1 week at 90$^o$C. The HSG developed a thick gel layer (comparative discussion) at the bottom of immersed region (see Figure 2a). A gel layer formed in this region but cracked after drying because of water evaporation. The size and density of cracks decreased from bottom to glass/water boundary, indicating a gradient over gel layer thickness under water. The exact reasons for this behavior are unknown but probably related to the way the gel layer is formed. Few studies consider gel layer formation on glass as a hydrolysis process [8] while few consider a precipitation mechanism. Also some suggest gel layer formation is both hydrolysis and precipitation mechanism [**Error! Bookmark not defined.**]. In the case of hydrolysis, the gel layer should form uniformly on HSG because of the homogeneous composition of glass, and if gel layer formation is a precipitation mechanism, gravity may play a role [9] especially in the experimental configuration discussed in this paper. The gradient over gel layer thickness in this study suggests that the precipitation mechanisms is active, whether in combination with hydrolysis is not clear.

Because of glass surface tension and the static experimental condition a concave layer of water (a meniscus) is formed over glass at water/glass boundary. The meniscus region on HSG (see figure 2a) gave fringes of colorful bands under optical microscope, indicating differences in gel layer thickness at the boundary. The meniscus region developed precipitates (see Figure 2b) of calcium rich phases (see figure 2c). These phases are quantified using ImageJ software and the values are displayed in Figure 2. The calcium rich precipitates at meniscus region covered areas of ~23%, boundary of meniscus and glass ~14% and glass above meniscus ~8%. On an average the whole HSG surface above meniscus region was found to develop 3-5% ca-rich phases. The surface of HSG did not develop pits due to vapor condensation and evaporation.

In a similar experiment, ISG samples were degraded in distilled water for 1 week and 3 weeks respectively (see Figure 3). The ISG degraded for 1 week was found to develop gel layer (see Figure 3a). This gel layer developed cracks upon drying. The size and density of cracks were found to decrease from bottom to glass/water interface indicating a gradient over gel layer thickness under water. The ISG also formed a meniscus region rich in Ca-rich precipitates. The region above the meniscus was not affected by the condensation of water, therefore no morphologies or chemical changes were found. The top region of ISG sample developed pits due to water saturation with leachates.
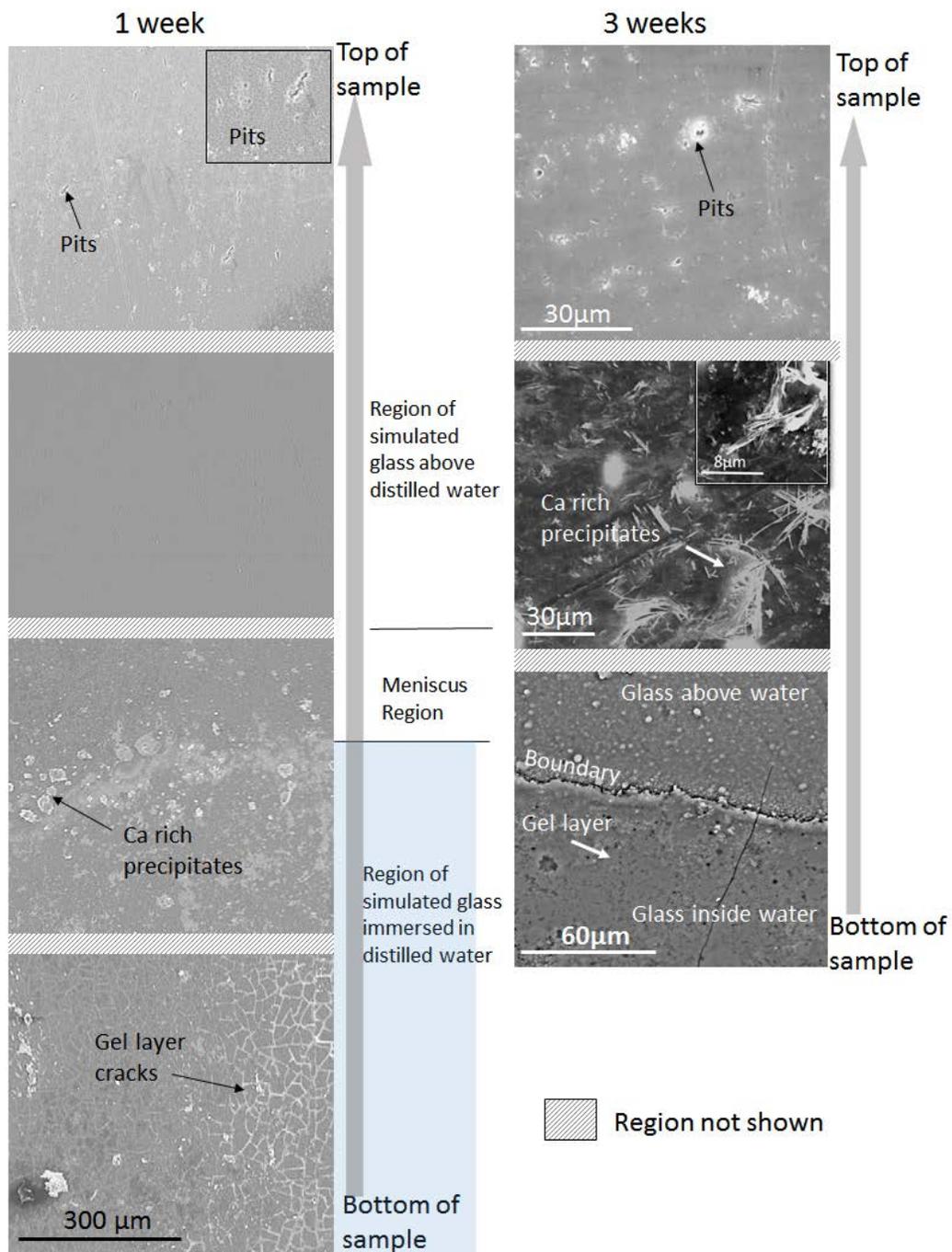
Figure 4. Show ISG glass surface degraded in partially immersed distilled water for 1 week (left) and 3 weeks (right) at 90°C. **1 week:** At the bottom cracks of dry gel layer formed, followed by Ca-rich precipitates and a zone with no surface modifications and a region rich in pits. **3 weeks:** At the bottom a clear boundary between glass degraded in water and glass above water is seen. Followed by Ca-rich precipitates and region highly pitted.

The BSE images of ISG degraded for 3 weeks are shown in Figure 3 (right). This sample clearly distinguish boundary between the area immersed in water and area above water. The ISG surface under water formed a gel layer while the ISG surface above water formed precipitates of Ca-rich phases. Further above ISG water/glass boundary was found to develop complex morphologies of Ca-rich phases because of vapor condensed. Droplets of water on the glass surface saturated with leachates grew calcium silicate rich phases (see Figure 3 - right) (confirmed by EDX) and pits. Similar effects have been found in archaeological glasses where a protective Ca-rich surface layer was found on the surface of glass, this layer hindered inward growth of the dissolution reaction favoring localized pitting. The pitting is caused by water condensation followed by its slow evaporation leading to increased pH [10]. We believe a similar effect is occurring on ISG glass.

Similar 3 weeks experiments on HSG are in progress. We plan to perform degradation studies on ISG and HSG surface which precipitated Ca rich phase.

## CONCLUSIONS

1. A gel layer thickness gradient from bottom to glass/water boundary is found in both ISG and HSG.
2. The 1 week degradation of HSG precipitated Ca-rich phases on the surface above water indicating that water condensation can modify glass surface. HSG showed resistance to pitting where as ISG was found to develop pits.
3. ISG developed Ca-rich precipitates with complex morphologies only after 3 weeks degradation testing.

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