Degradation of partially immersed glass: A new perspective

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ABSTRACT

The International Simple Glass (ISG) is a six-component borosilicate glass which was developed as a reference for international collaborative studies on high level nuclear waste encapsulation. Its corrosion behaviour is typically examined when it is immersed in a leaching solution, or when it is exposed to water vapour. In this study, an alternative situation is considered in which the glass is only partially immersed for 7 weeks at a temperature of 90 °C. In this case, half of the glass sample is directly in the solution itself, and the other half is in contact with a water film formed by condensation of water vapour that evaporated from the solution. This results in a different degradation behaviour compared to standard tests in which the material is fully immersed. In particular, whilst in standard tests the system reaches a steady state with a very low alteration rate thanks to the formation of a protective gel layer, in partially-immersed tests this steady state could not be reached because of the continuous alteration from the condensate water film. The constant input of ions from the emerged part of the sample caused a supersaturation of the solution, which resulted in early precipitation of secondary crystalline phases. This setup mimics storage conditions once small amounts of water have entered a glass waste form containing canister. It offers a more realistic outlook of corrosion mechanisms happening in such situations than standard fully-immersed corrosion tests.

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1. Introduction

Borosilicate and phosphate glasses are hosts for High Level and Intermediate Level nuclear Wastes (HLW, ILW) [1–3]; the preferred option for such waste forms being disposal in geological repositories. In addition, glass waste forms are also considered as alternatives to bitumen and cement for storage of Low/Intermediate Waste (LILW) in near-surface facilities [4,5]. In both cases, water ingress over time can degrade these glass waste forms and potentially transport radionuclides into the biosphere.

In contact with water or water vapour, nuclear glass undergoes degradation by ion exchange, hydration of the glass network, re-condensation, precipitation and secondary phase formation [6,7]. Glass durability depends on its ability to resist activation of one or more of these mechanisms when in contact with water [8]. Glass degradation in the initial stages occurs by ion exchange until it achieves a steady-state equilibrium due to gel layer formation and solution saturation which limits corrosion [9]. Glass waste forms may eventually fail because of rapid degradation activated by secondary phase formation and growth [10]. Current testing in which glass degradation is measured under standard test conditions (i.e., complete immersion of polished pristine glass in distilled water in a defined glass surface to water volume ratio at a set temperature), does not represent a realistic scenario for glass degradation and only indicates possible degradation mechanisms in specific conditions. Other experiments focus on degradation by water vapour [11,12], which, although complementary to liquid phase leaching tests, still paint an incomplete picture of the typical conditions that wasteforms are likely to be subjected to. In reality, water likely enters the repository slowly, first as water vapour, then as small volumes of liquid water [13]. Soon, after the canisters steel protective layers leak, the moisture/vapour starts to condense on the glass as a thin water film of ~0.01 μm. This water layer swiftly gets saturated with alkali ions from the glass which precipitate as secondary phases modifying the glass surface even before water covers the whole canister [14,15]. Even minor changes in the experimental conditions such as temperature or pH can modify gel layer stability and rate of glass degradation [16–18]. Precipitates on glass surfaces then increase the rate of degradation in water [11,19]. Such secondary phases can also contain or release radionuclides which may then be transported, sometimes in colloids [20–22]. For
example, simulated borosilicate HLW glass degradation experiments of relevance to Yucca mountain disposal reported Pu-enriched colloids in isolated and non-equilibrium aqueous solution [23]. Similarly, Pu-containing colloids were found 1.3 km away from their source in a study at the Nevada test site [24]. In the long run, the solution in contact with the glass is likely to precipitate secondary phases and colloids in the solution or on the glass surface. Such precipitation decreases ions concentrations in solution, which increases the likelihood of glass degradation [25].

Water may come in contact with glass in a variety of scenarios, such as:

1. Rapid immersion;
2. Slow and gradual immersion of the glass-containing steel canisters by water, where canisters are partially immersed for most of the time; and
3. Cyclic immersion and drying of the canisters.

These scenarios are relevant to both HLW or ILW waste forms in deep geological storage as well as LILW waste forms in near-surface repositories. Considering them brings into question the relevance of current glass degradation knowledge gained from direct immersion experiments. Other studies have already shown the limitations of extrapolating results from immersion tests to vapour tests [11,26]. In this paper, another approach is undertaken in which the glass sample is only partially immersed in water during the experiment, in contrast with the more standard setups in which the sample is either completely imimerged in water, or only in contact with water vapour. In this partial immersion test methodology, only half of the glass is immersed and the other half is exposed to water vapour (see Fig. 1). These experiments, by reproducing more closely the conditions in which water comes into contact with glassy waste forms, both in geological and near-surface repositories, give new insight into likely glass degradation mechanisms and also highlight the importance taking into account partial immersion in long-term degradation of waste-glass containing canisters.

2. Experimental

The International Simple Glass (ISG) used in this study—provided by James Marra, Savannah River National Laboratory, USA—is a six-component borosilicate glass which was developed as a reference for international collaborative studies on high level nuclear waste encapsulation. Its composition in mol% is SiO2 - 60.2, B2O3 - 16.0, Na2O - 12.6, Al2O3 - 3.8, CaO - 5.7, ZrO2 - 1.7. The block of ISG was sliced and cut into slabs of about 2.0 × 1.0 × 0.2 cm using a diamond saw blade. The surfaces of these samples were ground in sequence down to 4000 grit SiC paper (2.5 µm surface roughness) and cleaned with ethanol. Distilled water with a measured pH of 7.3 at room temperature was used to degrade ISG. The surface area of glass S to distilled water volume V ratio of ~15 m⁻¹ was measured at the start of each experiment. In the partial immersion experimental setup, the bottom half of the ISG slab is in distilled water, with the remaining surface exposed to the environment inside a Teflon container held at 90 °C. During the experiment, the water in the container evaporates and condenses over the glass surface exposed to vapour. Because the glass is nearly vertically placed at an angle of ~10°, water condensing on the glass is expected to drip along the surface into the water in the bottom half of the container. The condensation and dripping of water is a continuous process over the course of the experiment. Surface modifications during this time would change the surface roughness and the surface tension of the glass when compared to pristine glass, with the material potentially developing hydrophobicity or hydrophilicity. These modifications are expected to define the rate of dripping of condensed water on the surface of ISG. However, the rate of water dripping could not be measured in this system because of experimental setup limitations.

In this paper, standard test refers to a test methodology in which the glass is completely immersed in the water for the total test period. The parameters of the standard test are the same as those of the partially immersed test, hence the results of both are comparable and discussed. Degradation tests were conducted using the experimental setup as shown in Fig. 1, with test times ranging from 2 h to 7 weeks. The degraded glass after the test was dried in air and observed using backscattered electron (BSE) imaging in an SEM (Jeol JSM-6400). The features developed on the glass surface were analysed using energy dispersive X-ray (EDX) spectroscopy point scan and mapping. Solutions from containers were measured for leachate concentrations using inductively coupled plasma-mass spectrometry ICP-OES (iCap 6000 Series, Thermo Scientific). The data from partially immersed samples was normalised to standard experiments according to the ASTM standard for static leaching of monolithic waste forms for disposal of radioactive waste (C1220 – 10). The gel layer and the secondary precipitates formed on the glass surface were peeled off using carbon tape to expose the degraded ISG. Throughout the experiment, the pH was measured from solution samples brought to room temperature, using a Thermo Scientific Orion 3-star bench-top pH meter.

3. Results and discussion

3.1. International simple glass degradation under water and vapour

The results of partial immersion of ISG for 1 and 3 weeks have been reported elsewhere [27]. In this previous works, a gel layer was observed on the region of ISG degraded under water. The section of ISG exposed to vapour precipitated complex Ca-rich secondary phases after only 3 weeks, while both 1 and 3 week samples developed etch pits.

3.2. Degradation of region of ISG immersed in distilled water

In the standard, fully-immersed ISG degradation experiments, a uniform gel layer formed on the glass surface with still no secondary precipitation after 7 weeks. The partially immersed ISG degraded for 7 weeks also showed gel layer formation on its immersed part, but Ca precipitates were also found to develop on the gel layer (see Fig. 2). This difference indicates that a change in the glass configuration from the standard technique influences glass degradation. Fig. 2 shows the gel layer and various Ca-rich precipitate morphologies (confirmed by EDX mapping) that formed on different layers of the region of ISG degraded in a partially immersed water for 7 weeks. The regions are numbered from 1 (at the bottom) to 6 (at the top), with the meniscus between regions 4 and 5. In region 1, no precipitates were formed and only the gel
layer was observed. In region 2, both gel layer and precipitates were found. These precipitates were the finest (~20 µm) compared to precipitates in regions 3 (~80 µm) and 4 (~50 µm in length). In region 3, precipitates grew as sheets with the core of the sheets rich in Si and the outer rim rich in Ca. Beneath the precipitates a layer of fine (~10 µm diameter) agglomerates of Ca and Si-rich phases was observed. In region 4, elongated (~40 × 10 µm) Ca-rich precipitates were formed.

Though no previous studies using the partial immersion setup have been reported, such precipitation of Ca-rich phases may arise from electrical charge difference [25] between the glass surface (negative) and solution created by acid-base reactions [28]. The negatively charged glass surface attracts positive ions such as Ca2+ and colloids in the solution [29]. Such ion deposition on the glass surface in region 3 may explain the sheet-like precipitation of Ca and Si, whereas fine (region 2) and elongated (region 4) phase precipitation is because of colloid deposition and growth. In a standardised degradation test of ILW in calcium-saturated solutions, Ca-rich phase precipitation was observed [30], similar to the precipitation of the Ca-rich phase in the partially immersed region of ISG during these tests. These Ca-rich precipitates still formed on the ISG samples, despite the use of only distilled water instead of calcium-saturated solution.

In standard experiments with distilled water as degrading medium with a pH lower than 9, secondary precipitation is not expected to occur early [31], which is what we observed in our standard experiments. As soon as glass reacts with water, the Si and alkali ion concentrations in solution increase gradually and eventually reach saturation. With time, because of super saturation, elements released into the solution re-precipitate onto the hydrated glass surface and container walls as secondary phases. The reaction of glass to form secondary phases is driven by the thermodynamically unstable nature of glass. Water allows the glass to react with alkali ions leached into water and transform into precipitates which are thermodynamically stable [32]. These precipitates can grow or re-dissolve into solution as pH changes, high pH being known to favour precipitation of fine-grained secondary minerals on the glass surface [25,33]. Therefore, the presence of these precipitates on the glass surface indicate that Ca supersaturation or high pH have been attained to cause them. However, no precipitates have been observed close to the bottom of the container, which indicates that these conditions depend on the location on the surface of the sample.

### 3.3. Water vapour induced degradation of ISG

In partial immersion experiments, some of the water from the solution evaporates and condenses on the glass surface that is exposed to air in the closed container. The region of ISG exposed to water vapour for 7 weeks displayed secondary precipitates growth (see Fig. 3). The vapour-hydrated region just above the meniscus is indicated as region 5 and farther above is region 6. The Ca-rich precipitates (confirmed as containing Ca by EDX) formed in region 5 are acicular. Unlike precipitates in regions 2 and 4, the precipitates in region 5 are embedded in the gel layer indicating that growth of the precipitates the gel layer occurred simultaneously. The Ca-rich precipitates that formed in region 6, which grew with a diamond shape, were similarly embedded in the gel layer. Though ISG glass is homogeneous in composition, a change in the state of the degradation medium resulted in different degradation behaviour from region to region. During the early stages of vapour condensation on glass, 50 to 100 monolayers, i.e. a 0.01 µm thick film of water will form. The film thickness can vary with respect to glass composition, temperature, relative humidity and surface roughness [34]. Growth of secondary precipitates and gel layer can also enhance either hydrophobicity or hydrophilicity of the glass surface over time, which in turn influence the water film thickness. In repository conditions, nuclear waste-containing can be inhomogeneous in composition or heterogeneous (e.g. containing remnant crystals, glass composition striations, bubbles and radiogenic heat induced crystals). The change in local glass composition may also change the thickness of the water film as well as the growth mechanism of secondary precipitates.

In a previous study of ISG vapour hydration tests performed at 175 °C at different humidity levels [12], slight enrichment in Si (72.98 wt%) and loss of Na (8.59 wt%) in the hydrated glass layer were recorded when compared to the pristine glass (Si: 69.20 wt% and Na: 12.95 wt%). The corrosion products on the ISG surface were
mostly amorphous with some crystalline phases such as analcime (sodium aluminium silicate, NaAlSi2O6), tobermorite (calcium silicate hydrate, Ca5Si6O16), and calcite (CaCO3). In a similar study on vitrified simulated ILW (borosilicate CSD-B glass) at 90°C, vapour hydration resulted in the growth of a gel layer depleted in Na and Ca and precipitation of crystalline phases such as calcite [35] and apatite on the glass surface, with degradation rates similar to SON68 [36]. In the current partial immersion tests, the crystalline phases formed on ISG were not analysed beyond the EDX scans shown in Figs. 2 and 3, but are expected to have similar phases as reported in Refs. [12] and [36] discussed above.

The humidity in partially immersed experiments was not measured, because they were performed in a closed container with no access to control this parameter. However, the vapour degradation of glass is expected to increase with humidity in the environment [12,13]. Condensate vapour reacts with the glass surface to form a gel layer and precipitate the saturated phases (mostly Ca- or Na-rich) [35]. If a film of water condenses on the glass surface, the alkali metal ions diffuse from the glass and saturate the adjacent water film. The pH then increases above 9 in the saturated film. At high pH the glass silica network and the reaction products are deposited on the glass surface, resulting in formation of a double hydration layer, one penetrating into the glass and the other forming minerals on the glass surface [26]. These effects are commonly observed in vertically stacked glass sheets in humid atmosphere, causing irreversible damage to the glass surface within days at room temperature [14]. A similar mechanism could degrade the ISG exposed to vapour in the current work because of its near-vertical configuration during the total experiment.

Depth composition profiling of vapour hydrated ISG is not considered in this paper, but is expected to show a thinner corrosion layer compared to a liquid hydrated glass because of its effectively larger S/V ratio due to the thinness of the water film in contact with the glass [11]. Because of this, the solution quickly reaches saturation, which reduces the depth of corrosion. In water hydration in equivalent conditions, a thick (~30 μm) gel layer forms causing greater mass loss whereas in vapour hydration the gel layer is thinner (~4 μm) [11,37]. On vapour-hydrated glass, that gel layer may not be significantly depleted in alkali when compared to a liquid water hydrated glass. With lower humidity conditions during vapour hydration, the leached alkalis quickly saturate in the water film and develop into secondary precipitates, thus inhibiting further ion diffusion from the pristine glass to the surface layer [11]. Although the rate of precipitation is rapid, the rate of hydration of glass in a vapour environment is lower than the corresponding rate in liquid water hydration [26]. A basic vapour hydration mechanism sequence was derived which could apply to vapour hydrated regions of ISG [38]: water adsorption, absorption and diffusion, dealkalization, network hydrolysis, crystallization of, or precipitation in, the highly hydrolysed outer portions of the layer, and precipitation of secondary phases onto the glass surface.

3.4. Precipitation of Ca-Si rich phases at the bottom of container

After degrading partially immersed ISG for 7 weeks in distilled water, a transparent thick sludge (multiple gel layers of ~1–10 μm) was found deposited at the bottom of the test container. From visual inspection, the thickness of sludge was not uniform. Instead, it was thicker near the ISG and thinner farther from the sample. Some of the sludge was removed from the bottom of the container using carbon tape and analysed in the SEM, revealing it to be rich in Ca and Si.

The morphologies of sludge regions varied but the most common are shown in Fig. 4. Fig. 4a is a digital photograph of the bottom of the experiment container showing sludge while Fig. 4b shows agglomerated spheroids rich in Ca and Si, forming a thin ~2 μm layer deposited on the container bottom. Fig. 4c shows interlinked oblate spheroids while Fig. 4d shows nodular agglomerates. This sludge was thicker near the partially immersed glass but was otherwise distributed throughout the container. Sludge could arise from colloid growth in the solution, followed by deposition on the bottom of the container under gravity, or on to
the surface of the glass due to surface tension.

Colloids formed from nuclear waste form corrosion are found to be rich in silica minerals [39]. These colloids nucleate in solution or form by spallation of reacted glass. A sudden burst of colloid precipitation can occur in solution if flocculating agents are present [39]. Colloid nucleation and growth in solution is sensitive to concentration, pH and temperature. These parameters can influence the colloids zeta potential which can in turn influence their size, shape and stability. At pH ≤ 6, colloids have been reported to have different charge regimes which can limit their size. At pH 1 to 6, because of the weak electrostatic repulsions between the colloid particles (Van der Waals forces), colloids grow and form chain-like structures. At intermediate pH (>6), the negative charge on the surfaces of the colloidal particles dominates and induces electrostatic repulsion, which results in fine particles dispersed in the solution. Colloidal silica particles form a stable sol and the particles grow by Ostwald ripening. As the pH increases to 9, the colloids become less negatively charged and weakly repel each other which results in their growth. The colloids charge and size influence their stability, transport properties, and interactions with the glass surface [40]. When colloids become too large to stabilise in the solution, they settle due to gravity [20]. At pH 10, spontaneous colloid nucleation and growth occurs in solution. At this pH the precipitated solids do not show significant morphological differences [41]. The change in Ca:Si ratio in solution was found to change the morphology of silicate particles from microbeads-like particles to slightly spherical or massive particles, which consist of agglomerates of many fine (∼10 × 20 μm) platy crystallites.

Formation of colloids in aqueous media takes place at conditions in which saturation exceeds a critical limit. These supersaturated concentrations under certain pH and temperature conditions and in the presence of certain impurity ions such as NaOH [42] trigger nucleation of Ca-Si-H colloids. Colloids can nucleate on the glass surface and container walls as well as in the solution [25] and may be adsorbed on to the glass surface when their zeta potential is opposite to the zeta potential of the glass surface or when they have the same charge but different potential [43]. This is the likely formation mechanism for the Ca-rich phases deposited on the ISG in the region immersed in water shown on Fig. 2.

In parallel with immersion experiments, ISG glass was degraded at pH 10 in distilled water (results not shown). The leachate of these samples contained agglomerates of particles which could be the result of spallation of a reacted glass surface layer. At higher pH, the silicate network structure on the glass surface broke down and as a result the glass tended to dissolve. Such weakened bonds on the reacted surface layer, because of gravity, could be drawn into the solution under the slightest stresses, even those created by dripping water. The elements present on the hydrated ISG glass surface and in the particles are similar, hence it can be said that the colloids are activated by the spallation of the glass surface [44]. How mechanically stable the reacted glass surface is at different pH, temperature and stress conditions is unknown.

3.5. Surface chemical composition change of ISG in water and vapour regions

In partial immersion experiments, the regions of ISG exposed to liquid water and water vapour for 7 weeks degraded differently as discussed earlier. To analyse the change in chemical composition of the two degraded areas of ISG, EDX point scans were performed on regions 1 to 6 (see Fig. 5). The regions of glass degraded in water are to the left of Fig. 5 (labelled 1–4) and the areas exposed to water vapour is to the right of Fig. 5 (labelled 5–6).

BSE images of region 1 of the degraded ISG surface show no secondary precipitation; only a gel layer was observed to grow. The absence of secondary precipitation is also confirmed by the
uniform Si composition in the EDX point scans shown in Fig. 5a for region 1. Uniformity in composition is indicative of homogeneity in solution ion concentrations and pH. Therefore, region 1 can be considered as a baseline for gel layer composition and so will be compared to other regions in the following discussion. Region 2 of the degraded ISG shows a dark region in BSE images with a sharp boundary between regions 1 and 2. At high magnification the dark region was found to be comprised of clusters of 20 \( \mu m \) Ca-rich precipitates shown in Fig. 2. EDX point scans of this region confirm that this region is enriched in Ca. The mechanism for formation of such a sharp boundary of Ca precipitates is hypothesised to arise from a change in gel layer surface charge because of the presence of the impurity ions arising from Na (in this case) in the glass and or change in the localised pH of solution. Colloids grow in size when the local pH is favourable, indicating the importance of localised solution inhomogeneity in glass degradation. The transition to region 3 is marked by an increase in Si concentration. This is the area where precipitates with sheet-like morphology are found (see Fig. 2 label 3). The Si concentration in this region is higher than in region 1 and 2, whilst Ca concentration dropped below that of region 1. If the change in morphology of the Si + Ca rich precipitates in region 3 is related to the colloid precipitation mechanism discussed in Section 3.4, then the solution pH near the gel surface is likely to be different from that near regions 1 and 2. The pH in this region must have favoured colloid precipitation on to the gel layer and growth as sheets with Ca ions re-depositing only at the corner of the sheets (see Fig. 2 label 3). The start of region 4 until the meniscus, which is the end of region 4, shows a gradual decrease in Si concentration and a gradual increase in Ca concentration reveals. At the meniscus, although no secondary precipitation was observed, the concentration of Si is slightly lower and the Ca concentration slightly higher than in region 1. Regions 5 and 6 in Fig. 5 are the regions of ISG degraded in water vapour. In these areas, Ca-rich precipitates surrounded by a gel layer are observed. In these regions, the point scan values tend to vary but overall the concentrations of Si and Ca are similar to those found in region 1.

In standard degradation studies, ionic concentrations and the solution pH are considered homogeneous. However, this is not necessarily the case in partial immersion tests, where there is a constant influx of ions from the emerged part of the specimen, brought to the solution by the dripping condensate. This could cause local changes in both pH and composition in the solution. The fact that the surface structures shown in Fig. 5 are different from one region to the next shows that the water degrading the glass is inhomogeneous at least near the surface of the glass and at different levels from the bottom of the sample to the meniscus.

3.6. Degraded ISG surface

The gel layer and the secondary precipitates formed on the glass surface were peeled off using carbon tape to expose the degraded glass. The gel layer formed on the vapour-hydrated surface was weakly bonded to the glass surface and was peeled off easily. In contrast, the gel layer on the immersed part of the sample showed
resistance to peeling which indicates strong adhesion. Although no adhesion strength measurements were performed in this study nor to our knowledge have any been reported in the literature, the gel layer mechanical stabilities appear different under different hydration and hence repository conditions.

The ISG surface after removal of the gel layer (Fig. 6) showed aligned but individual and connected pits. Pits in both regions are similar in size and morphology: either circular with radii of ~10 μm, or elongated perpendicularly to the meniscus with lengths up to 100 μm. Such pit growth has been speculated to arise from pH change in the solution trapped at the interface between the gel layer and the hydrated layer of glass [43,45]. Local increase in pH enhances Si dissolution compared to the overall glass surface, which is why pit growth occurs. Glass degradation progresses as a uniform moving front with local pitting. Pitting in glass was found to be enhanced with stress either induced on solidification or polishing, phase separation, and surface roughening [43]. The rounded nature of the pit tips in ISG suggests that stress arising from them does not play a role in crack formation [46]. The influence of polishing defects may be significant in the initial stages of degradation but their influence in the later stages will be limited once pits tend to form a rounded front. The presence of a Ca-rich surface degradation layer was found to favour localised pitting [47]. Pitting causes the surface area of the glass exposed to the leach solution to increase with time and this will affect any kinetic modelling of system [45].

3.7. ISG leach data from standard and partially immersed experiments

Ion release was measured using ICP-OES for both ISG degraded by a standard complete immersion method and by a partial immersion method. The solution is filtered before taking these measurements. Therefore, this does not account for precipitates, gel layer or colloid deposited either on the glass surface or on the bottom of the container. For each species i, the mass loss per unit of surface area \( L_i \) was calculated from solution concentrations \( C_i \)

\[
L_i = C_i V S
\]

where \( S \) is the total surface area of the glass sample and \( V \) is the volume of solution. The evolution of the weight loss for the different elements over time is shown in Fig. 7a and b for the partial immersion and standard test respectively. These figures can then be used to compare both experimental methods and to develop an understanding of the influence of change in conditions on ISG degradation. The solution pH was measured at the end of each degradation measurement and is also given in Fig. 7.

Current understanding is that the glass surface at first undergoes ion exchange, with network modifiers going to the solution and being replaced by water molecules. This results in reorganisation of the silicate structure which forms a passivation layer, which prevents further alteration. This interpretation is consistent with the behaviour observed in the standard test which shows a decrease in the alteration rate and a stabilisation of the mass loss for all considered species, with almost no variation between 500 and 1200 h. Over the same time frame, pH is stable between 9 and 9.5. The mass loss can be used to calculate an effective thickness for the alteration layer

\[
e_i = \frac{L_i}{\rho_{Si}}
\]

The effective thickness is different for each species, because it is based on solution data that cannot account for the passive layer, colloids or precipitates. To estimate the thickness of the altered layer, we consider the effective thickness calculated for boron. Indeed, as B cannot easily be retained in the alteration products nor crystallize as secondary phases [48], it is expected that most B in the altered layer goes into the solution.

Results from the standard test in Fig. 7b show the typical features expected from such an experiment [31]. As soon as water comes in contact with the glass, mobile ions dissolve congruently [49]. Congruent dissolution is followed by in-situ re-polymerisation of the silicate network. Such re-polymerised Si on the bulk glass acts as a molecular filter with ~1 nm pores, which physically inhibits further ion diffusion into the water [50]. The physical inhibition achieves a steady state equilibrium of glass degradation. The consequence is that after an initial regime with high release of Si and Na, their concentrations stabilise. Boron concentration follows a similar pattern and its initially high release rate drops over the course of the test. Concentrations in solution and normalised mass loss after 1200 h are shown in Table 1. At this point, the effective thickness \( e_B \) is 6.29 μm and the solution has a pH of 9.5.

In the partially immersed test, Ca and Si release was similar as in the standard test, and reached steady state equilibrium. However, whereas Ca and Si concentrations were similar as the standard test, Na and B concentrations were significantly higher, as can be seen in Table 2. Boron concentration, in particular, did not show any sign of saturation even after 1200 h in the partial immersion test, whilst it

![Fig. 6. Degraded surface of ISG forming pits under the gel layer in partially immersed experiment: a. pitted ISG region above meniscus and gel layer below meniscus; b. meniscus region, region pitted below and above meniscus.](image-url)
had started to level off in the standard test. This indicates that ISG continues to degrade longer in the partial immersion than the standard test. The pH values initially rose quickly, but started stabilising within a day. After 1200 h, the pH of the solution was 10.6 in the partial immersion test.

Saturation indices were calculated from the concentration measurements using the PhreeqC software with the LLNL database [51]. They predicted that the solution is still under-saturated in SiO_2 in the case of the standard test, which is consistent with other experimental studies. The apparent saturation observed in our results could actually be a major drop in dissolution rate, somewhat hidden by the short time scale considered here. The calculations indicated that in the partial immersion test, the solution is closer to saturation with respect to SiO_2 and that some Ca-rich phases would precipitate. This is partially consistent with our results, however there is an additional factor to consider. The calculations do not account for any concentration gradient in the solution. In contrast, our observations show significant changes in the composition and morphology of the precipitates on the surface of the glass coupon, which indicates local changes in the solution’s composition. These changes could however not be quantified.

3.8. Degradation mechanism in partially immersed ISG

So far in the partial immersion experiments, various glass degradation mechanisms have been found to act individually and simultaneously:

4. ISG samples immersed in water formed a gel layer and precipitated Ca-rich phases of different morphologies. This observation led to the conclusion that ion concentrations in the solution are inhomogeneous near the glass surface. Differences in ion concentrations also mean there is a localised pH change.

5. The vapour hydrated glass formed a thin ~2 μm water layer because of water condensation which then quickly saturated with leachates and developed Ca-rich precipitates of different morphologies.

6. The colloids formed in the solution because of solution supersaturation precipitated on the gel surface and grew in size. The growth of colloids could also have occurred in the solution, they would then be deposited on the container bottom.

7. Partially immersed ISG degrades more rapidly than ISG immersed completely in water.

Fig. 8 shows schematically the corrosion mechanisms occurring as suggested by the partial immersion experiments of this study.

In the current experimental setup half of the ISG specimen was exposed to water and the other half was exposed to water vapour. The experiments were performed in a closed container to mimic partially filled canisters under repository conditions. Our experiments indicate that soon after vapour condenses on the glass the alkali ions rapidly diffuse into the water film. Water evaporated from the water source then condenses on the glass surface to form a water film, which thickens with continuous water condensation and gains mass. Ion enriched water film drips off the glass surface under gravity, thus transporting leachates into the solution below. The precipitates which then form on the vapour hydrated glass are rich in Ca. The fresh vapour condensates create an affinity for ion diffusion from bulk glass and so unstable Ca phases are also transferred from the water film into the solution below. The area of immersed glass leaches ions into the solution at the initial stages of

![Fig. 7. ICP-OES and pH data normalised to surface area of glass, as a function of time: a. ion release data of partially immersed ISG; b. ion release data of ISG degraded in a standard complete immersion experiment.](image)

![Fig. 8. Schematic of various mechanisms active during ISG degradation in partially immersed experiment.](image)
degradation and then attains a steady state equilibrium within a day. However, the solution still gets enriched with the leachates from the vapour hydrated region of glass because of continuous ion transportation by dripping. Such a mechanism supersaturates the solution and increases the solution pH. Such a supersaturated solution is unstable and forms colloids that precipitate on the glass surface and also grow in solution under the influence of pH. These precipitates have different morphologies under different pH regimes. These mechanisms are responsible for the growth of precipitates in the gel layer and their deposition at the bottom of container.

In the standard experiments the ISG degradation followed the known mechanisms i.e., ion exchange at initial stages followed by steady-state equilibrium and in the long term may probably grow secondary precipitates and finally fail (see Fig. 9a). The initial Type I and Type II stages are identical in both standard and partially immersed tests, until the solution reaches saturation. However, instead of observing a slowdown in the growth of the altered glass layer as in the steady-state step of standard tests, the rate of glass alteration remains high. Due to the continuous rise of ion concentrations in solution and the mechanisms discussed above, secondary phase precipitation and growth is quicker. Continuous glass degradation was measured even at 7 weeks, at which point the system is still expected to be in the steady-state phase in standard fully-immersed tests. Based on the understanding achieved from partial immersion tests, it can be postulated that stages III and IV of standard glass degradation coexist in partially immersed experiments (see Fig. 9b). This raises serious concerns over the extrapolation of long-term durability of nuclear waste glass by considering data only from standard immersion experiments.

4. Conclusions

We have demonstrated the different behaviour of ISG under partially-immersed conditions compared to standard fully-immersed tests. The presence of a thin water film caused by water condensation on the emerged glass surface significantly changes the kinetics of glass alteration. Because of the small volume of this film, it saturates quickly in the early stages of the experiment resulting not only in early precipitation of second phases on the emerged part of the sample, but also in early supersaturation of the solution surrounding the immersed part of the sample, thus increasing the pH in the solution. This causes the formation of colloid and precipitates that would not be observed at this stage in a standard test. This also suppresses the steady-state stage of glass alteration observed in standard tests, which results in an effectively higher alteration rate. This could additionally explain the discrepancy between some of the precipitate observed in long-term field experiments and models that do not take partial immersion into account [52,53].

As partial immersion is more realistic and representative of storage conditions, either in geological or near-surface repositories, this underlines the importance of considering the combined effect of leaching from the solution itself, but also from condensates on emerged surfaces of the glass to predict long-term behaviour of glassy waste forms.

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