

ITEAM – An International Mechanistic Approach to Modeling Glass Behavior over Geologic Time Scales – 15527

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ABSTRACT

Vitrification is a common worldwide solution for radioactive waste immobilization. Although the excellent chemical durability of glass has been demonstrated in ancient man-made and natural analogues, the lack of an international consensus on a glass corrosion rate law limits the application of glass in high-level waste repository performance models. The contributions of physical and chemical processes controlling the long-term glass dissolution rate in geologic disposal remain uncertain resulting in this non-consensus. A thorough mechanistic understanding of waste form durability in geologic environments would improve public and regulator confidence. In addition, this understanding could lead to cost savings if it becomes possible to take credit for the true durability of the waste form itself in system evaluations rather than requiring expensive engineered barrier systems. To this end, five nations (US, UK, France, Japan, and Belgium) have joined together to formulate a joint plan for collaborative research into the mechanisms controlling the long-term corrosion of glass.

Over the last five years, the coordinated research performed by these countries has produced a new level of understanding about the glass corrosion mechanisms, specifically as they apply to glasses similar in composition to the French R7T7 glass. Some recent results are presented as they relate to several mechanisms that are thought to control glass alteration at long time periods. It is important to understand the effects of each particular mechanism on the overall radionuclide release and the relative importance of each process model to the performance assessment calculation. In addition, a new series of experiments calls out potential sources of error due to the use of irregular shapes (such as crushed glass powder) in dissolution experiments.

INTRODUCTION

One of the primary objectives of radioactive waste immobilization is to prevent the dispersion of radionuclides during storage and handling operations and minimize their release from engineered geological disposal systems into the biosphere over the regulated period. Demonstrating this objective is difficult, which explains the extensive research performed to date on aluminoborosilicate waste glasses.¹⁻⁵¹ One key difficulty lies with the durability of the product itself. Small errors in short-term measurements lead to completely unacceptable error ranges when data collected in the laboratory are simply extrapolated to the geologic time-scales relevant to high-level waste (HLW) repository lifespans. Thus, the behaviors observed at laboratory time scales and conditions are relevant only to increase our mechanistic understanding and are not necessarily true indicators of long-term durability. It is imperative, therefore, that robust models based on a scientific and mechanistic understanding of the processes responsible for glass degradation and radionuclide release be used to calculate the long-term behavior of a glass waste form and its ability to control the release of radionuclides to the ground water at or below levels required to meet the applicable regulations. Experimental and modeling work conducted under a jointly funded campaign (DOE-EM, DOE-NE, and international partners) has led to new insights

regarding processes occurring at the interface of glass and surface alteration layers, within the layers, and when secondary phases precipitate. These are resulting in continual significant improvements in the suite of analytical algorithms used to model long-term glass corrosion.

Although it is important for the models to be scientifically sound and sufficiently complex, the input into performance assessment (PA) models must be relatively simple. The complexity of repository environments requires that the glass corrosion calculations be simple functions of tracked changes in the local conditions. The logic followed in developing waste form degradation models for these uses, summarized in Figure 1, follows the general method put forward in ASTM C 1174-07.[6] The objective is to provide radionuclide source term values throughout the service life of the disposal system for use in PA calculations. The diamond shape in the background schematically represents the level of scientific detail that must be used at each point in the process and illustrates the importance of having a robust connection to models with strong scientific bases throughout the process. Commensurately, the data needs for each step follow the same trend, showing the wide range of data that must be generated to provide the scientific basis and technical understanding underlying the individual and coupled process models and justifying the simplifications required for integration into a larger PA model. The bottom half of the diamond emphasizes the consolidation of the detailed process models into a concise degradation model that captures the impacts of important process(es) affecting radionuclide release in a semi-empirical analytical model that is appropriate for incorporation into the larger PA model to provide source term calculations. Although the detailed mechanistic understanding of processes contributing to glass degradation is not fully implemented in the degradation model, that understanding provides confidence that the values calculated by simplified empirical models represent the rate controlling processes.

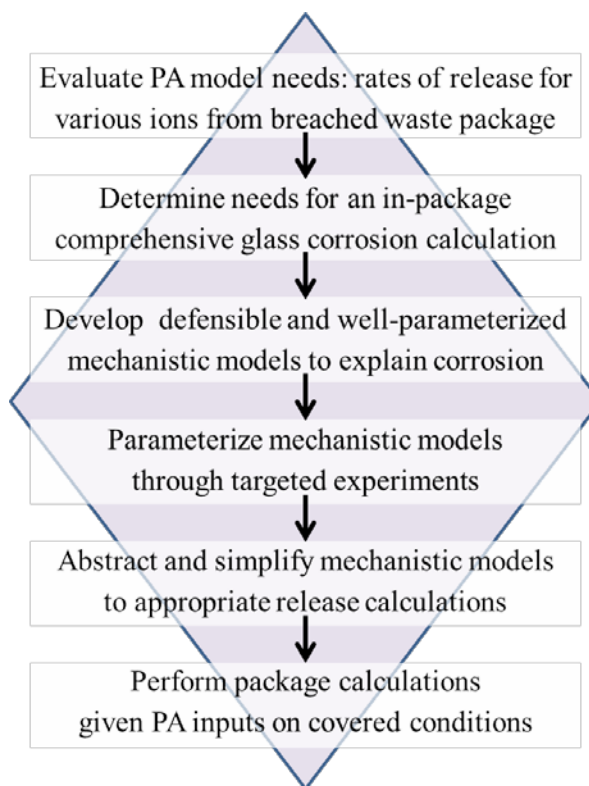


Figure 1. Logic flow diagram for development of HLW glass degradation model.

The goal of these efforts is to produce a thorough mechanistic understanding of waste form durability in geologic environments so as to improve public and regulator confidence in waste disposal. In addition, decreasing the model conservatism currently necessary due to incomplete understandings would allow credit to be taken for the true durability of the waste form itself in system evaluations. As mentioned before, this is an international goal, with six nations joining together in joint research and evaluation to reach this improved understanding.

EXPERIMENTAL FINDINGS

Over the last five years, a large amount of research has dramatically changed our understanding of the mechanisms behind glass corrosion. This effort has been too large to summarize here, so a short summary of a few important new findings is presented.

Monte Carlo

One important advance was a series of studies to determine the role that transport through the amorphous gel region might play in both the solution concentration at the dissolving glass and the evolution of the gel itself. Monte Carlo (MC) models have shown success in modeling processes at this scale. To this end, a systematic study was undertaken to examine the effects of diffusion on the structure and dynamics of the altered layer formed from sodium borosilicate glasses. Three different models were used for the diffusion of dissolved Si species in altered layers developed from a range of borosilicate glasses. Both the diffusion parameters and glass composition were evaluated systematically. The simplest model, termed “M1”, assumed no difference between the concentration of dissolved species at any point in the altered layer and the concentration in the bulk aqueous solution. Only modestly more complex, model “M2” used a simple linear distribution of dissolved Si species in the altered layer between the source at the dissolving glass and the relatively dilute bulk solution. The third model, “M3”, used solutions of Fick’s 2nd law at each MC step to calculate the Si concentration profile through the alteration layer.

While the studied glasses lack the aluminum ions that add durability to most waste glasses, the results obtained with the three models compare well with experimental data of similar glasses. The more simple transport models “M1” and “M2” seemed to match best with data for fast-dissolving borosilicate glasses with low ZrO₂ content. The more important takeaway for the more complex and slow dissolving waste glasses can be seen in the difference between the alteration profiles predicted using the linear “M2” models and those using the Fickian “M3” models. The profiles were very different, with those where Fick’s 2nd law was explicitly solved producing concentration profiles in the altered layer that were not linear, changed significantly with time, and a concentration gradient that lowered with respect to the bulk aqueous solution as corrosion progressed. The difference shows that it is important to explicitly account for the transport of ions through the altered layer, at least with the most complex coupled mechanistic models. As was said earlier, simplified calculations that reproduce the main features of the explicit model will be needed, but results such as these will be instrumental in developing those calculations.

Future MC model work will consider the mechanisms that lead to the formation of a thick gel atop a dense Si-rich layer, as is observed for several nuclear waste glasses, particularly for glasses (and gels) containing aluminum. The glass corrosion team is proving to be an excellent collaboration in this regard, as a NEUP-funded university team is working on developing accurate glass structures using molecular dynamics simulations that will provide improved starting points for the MC models. Another team is using ab initio calculations to develop bond strengths for a number of key species at the glass surface,[7] which is expected to enable the extension of the number of oxide components considered without the need for parameterization from experimental data. The combined effort should mean that MC models for much more complex glass/gel systems will be available soon.

Interdiffusion

Upon initial contact with water, hydrogen-containing species (H_2O , H_3O^+ , OH^-) diffuse into the pristine glass, leading to the formation of a hydrated glass layer. This can occur through two mechanisms: solid-state diffusion of molecular water and ion exchange interdiffusion. The transport of molecular water in glasses has been studied extensively,[8-10] and can be assumed to be a more or less constant very low value. Additionally, molecular water can do little except cause a slightly more open structure, as any ions “dissolved” in the locality of water that arrived via solid-state diffusion would not be able to similarly diffuse through the matrix into solution. Ion exchange and interdiffusion, however, are less well understood and may present a large impact for certain glasses.

In the simplest terms, ion exchange between a glass and a fluid is the replacement of charged ions between the two media. Once ion exchange occurs at the glass/fluid interface, the ion that was initially in the fluid continues to diffuse farther into the glass and replace ions initially present in the glass. Upon replacement by the inward-diffusing ions, the ions initially present in the glass diffuse towards the glass surface and are eventually released into the fluid. This interdiffusion process of continuously exchanging ions creates anti-correlated concentration profiles of the inward- and outward-diffusing ions and the shapes of the profiles are dependent on the diffusion coefficients of the diffusing species.

Ion exchange occurs readily during the aqueous corrosion of glass where either H^+ or H_3O^+ from solution is continuously exchanged with cations from the glass. The reaction has the potential to drive the release of exchangeable radionuclides from the glass waste form without destruction of the silicate network. Because it occurs independently of the dissolution mechanism, it is not accounted for in the affinity-based dissolution model. The mechanism, which has been observed experimentally for decades,[11-13] can be described simply by the exchange of a network modifying cation in the glass, M^+ , with a charged water species (given here as a proton through the hydronium ion is also a possibility), with the following reaction:



This reaction serves to raise the pH of the solution which, in turn, promotes hydrolysis reactions due to the rate of network dissolution increasing at high pH.

Historically, ion exchange mechanisms have not received the level of attention that dissolution mechanisms have received by the glass corrosion community. However, alkali release rates greater than those accounted for through matrix dissolution have been shown to persist after a 1.5 years in pressurized unsaturated flow (PUF) test [14] and in a 24-year lysimeter test,[15] demonstrating the importance of the ion exchange mechanism in long-term disposal conditions. However, it is important to note that ion exchange occurs in parallel with network hydrolysis. Ion exchange is most predominant in high-alkali glasses (attributed to an increase in non-bridging oxygen pairs with increased alkali in the glass), at low temperature (due to the lower activation energy of the diffusive process compared with network hydrolysis), acidic to near-neutral pH (because more H^+ is available for exchange), and in solution near saturation with respect to $\text{SiO}_{2(\text{am})}$ (where the hydrolysis reaction is suppressed and other mechanisms can

dominate).[16-19] This final point is of particular importance in regards to repository conditions where near-saturation conditions are expected to persist for long time periods.

However, due to the formation of various alteration layers in the presence of water, it is difficult to conclusively deconvolute the mechanisms of ion exchange from other processes occurring simultaneously during corrosion. In a recent study,[20] an inert non-aqueous solution was used as an alkali source material to isolate ion exchange and study the solid-state diffusion of lithium. Specifically, the experiments involved contacting simulated nuclear waste glass coupons, the 6-oxide CJ-6 and the 26-oxide SON68, with a non-aqueous solution of $^6\text{LiCl}$ dissolved in dimethyl sulfoxide at 90 °C for various time periods. The depth profiles of major elements in the glass coupons were measured using time-of-flight secondary ion mass spectrometry (ToF-SIMS). Lithium interdiffusion coefficients, D_{Li} , were then calculated based on the measured depth profiles. The results indicate that the penetration of ^6Li is faster in the simplified CJ-6 ($D_{6Li} \approx 4.0\text{-}8.0 \times 10^{-21} \text{ m}^2/\text{s}$) compared to the more complex SON68 ($D_{6Li} \approx 2.0\text{-}4.0 \times 10^{-21} \text{ m}^2/\text{s}$). These values are roughly an order of magnitude greater than measured water diffusion in glasses at similar temperatures. Additionally, sodium ions present in the glass were observed to participate in ion exchange reactions; however, different diffusion coefficients were necessary to fit the diffusion profiles of the two alkali ions.

The experiments that determined the above formalism[20] did not address the key species in ion exchange: hydrogen. The more complex experiments needed to do that evaluation, enabled by this preliminary research, are scheduled for completion in FY 2015. Additionally, the exchange shown in Equation (2) likely occurs at the interface of the glass and solution, which is likely an altered interphase region (described in the next section). At whatever location it occurs, this reaction is potentially the rate-limiting step in ion exchange release rather than the diffusion of ions mentioned above. Again, the experiments this past year were specifically designed to eliminate this effect from consideration to isolate the diffusion portion of this coupled mechanism. With the diffusion portion understood, modeled, and parameterized, we will then be able to examine coupled processes and, by accounting for the diffusion portion, be able to quantify the impact of the localized exchange reaction.

“Passivating Reactive Interphase”

The key feature to much of the uncertainty with the mechanistic models of long-term dissolution is the interfacial region that separates the glass from the gel. Although the concept of such a layer has been around for decades,[18, 21, 22] we use here a term for this interfacial region that was coined by Frugier et al. in a relatively recent paper: the “Passivating Reactive Interphase” or PRI.[23] Since the PRI is the solid phase contacting the pore solution, it is the phase upon which all the mechanisms operate (possibly excepting precipitation). As was already mentioned, it is believed that the actual exchange of ions that is tracked with the ion exchange mechanism (Equation 1) occurs at the solution-solid interface. Once the ions are exchanged, they proceed to migrate through the glass per the model described in the previous section. The interfacial exchange, however, is the source term for those models. The dissolution reaction is even more directly impacted by the PRI. In essence, the dissolution that is occurring is of the PRI rather than the glass. This is accounted for in the model used for dissolution through the K_g term in affinity-based rate equations. In the model development literature, it is acknowledged that the glass itself is not the solid phase that is driving the affinity model. Instead, a pseudo-equilibrium constant is used for

the dissolving solid phase, as mentioned earlier, with properties generally intermediate between quartz and amorphous silica,[24] typically of the same order as silica-rich phases such as chalcedony.

The complication, however, arises from the use of a constant material to represent the PRI. The PRI is not a static entity and its evolution over time is the source of much of the existing uncertainty. Detailed knowledge of the composition, evolution, and sensitivity to the solution composition of the interfacial region is required to incorporate its effects into the mechanistic models and the glass corrosion calculation. This is important because changes in the structure and composition of surface alteration layers will not be tracked in disposal system performance assessments. Studying interfacial alteration layers is challenging because they are very thin and, more importantly, are buried beneath the growing gel and crystalline alteration products. Additionally, by nature the layers are dynamic and sensitive to changes in solution chemistry, thus it is difficult to “freeze” any given structure for solid-state characterization. Multi-year isotope swap experiments have provided a detailed view of the interfacial region where glass corrosion is occurring and new insights to the structures in this area. In those experiments, atom-probe tomography (APT) data demonstrated the presence of two reaction areas: a very sharp interface locating the depth to which boron was released and another interface closer to the solution that defines where silica from solution has begun to be incorporated into the alteration layer through condensation reactions. The region between these two features may indicate the leached and restructured area is thought to represent the PRI. The physical dimension of this region matches the predictions put forward by CEA scientists who assume the region represents a transport barrier with a specific diffusion coefficient.[25, 26] Tests have shown that the efficiency of PRI in limiting glass corrosion is related to the solution composition[27] and this was postulated to be a result of transport limitation, although the actual species being limited has come into question.[28]

Shape

Due to the exceptional durability and slow dissolution rates of glass waste forms, individual mechanisms of glass dissolution must be analyzed using accelerated laboratory tests, often involving high surface area powders. One key parameter that is not sufficiently taken into account with these tests is the effect of evolving particle shape on the dissolution rate. If particles with the same sieve sizes but different shapes exhibit different dissolution behavior, shape may impose a significant time-dependent effect on the accelerated tests. Macroscopic experiments conducted using two highly soluble amorphous glasses (sugar glass and an alkali borate glass) confirmed the presence of a geometric effect on particle dissolution rate. Using this data, a simple computational technique was developed to quantify corrosion behavior as a function of particle geometry. The observed impact has led to the investigation of different techniques for test acceleration that mitigate the effect.

In order to observe changes in bulk glass particle shape within a reasonable time period, a very soluble alkali borate glass (65:14:21% B₂O₃:Na₂O:K₂O, by mass) was developed for use. The sample shapes were produced using molds and then refined by grinding and polishing into quantifiable shapes of interest. Dissolution was carried out in dilute semi-static conditions. The glass samples were immersed in an agitated large tank of deionized water in trays with plastic dividers and a polymer screen on the bottom to allow for even dissolution on all sides. Although no flow in or out of the tank took place during dissolution, the amount and motion of the water kept the concentration of dissolved glass low

around the sample. After the desired time, the samples were taken out of the water, dried, and their geometries measured and imaged.

All regularly shaped glass geometries (spheres, cubes, rectangles and rhombuses, etc.) largely retained their shape during the entire dissolution process. There was no evidence that sharp corners rounded during the process, as is commonly assumed. Conversely, rounded exterior corners tended to become sharp during dissolution. This is illustrated in Figure 2(top), where the initially rounded edges of the coffin-shaped sample sharpened with time, with the radius of the corner approaching zero after 15 hours. In Figure 2(bottom), the U-shaped sample was initially prepared with two sharp (90°) interior corners. The original sample image was not available since the size of this sample was too large to fit under the microscope. The three images shown were taken after 20, 40, and 60 hours in water, clearly showing the rounding at the corners. Interestingly, this effect is also notable in Figure 2(top) with minor defects on the glass surface etching into deep pits within the 15 hour experiment. This pit etching is the same process by which the internal corners rounded in the U-shaped specimen.

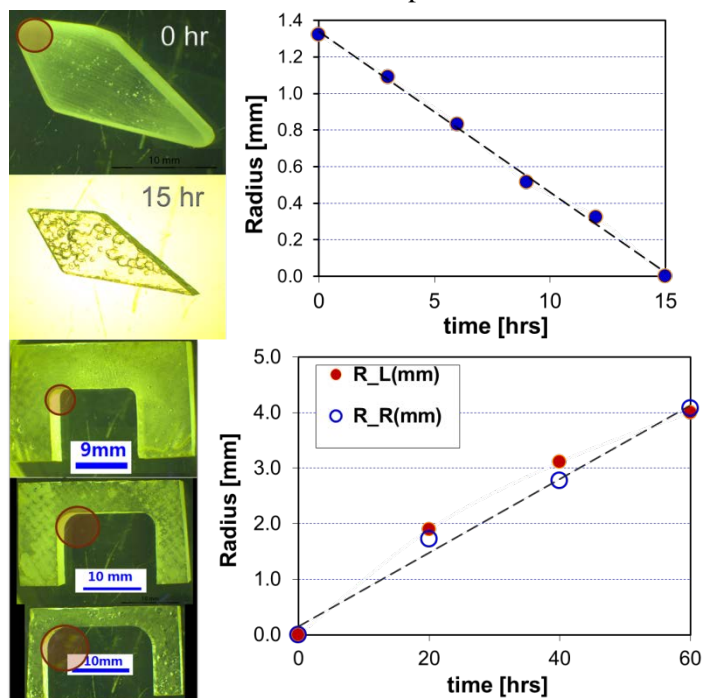


Figure 2. Rapid dissolution experiments showing the evolution of shapes with rounded external corners (top) and those with sharp internal corners (bottom).

These results fit well to a model of shape evolution that simply assumes an even dissolution rate at every surface. To illustrate this concept, consider an interior corner as shown in Figure 3. The boundary edges will move in parallel to their original position as the sample dissolves with time. At the interior corner, however, the material dissolves in such a way that it will have to take the blue arc in order for the dissolution rate normal to the surface to be constant. The rounding at the interior corner expands with respect to a common point, which corresponds to the intersection of the dissolving faces as illustrated in Figure 3. Similarly, the radii of rounded exterior corners, based on the assumption of the geometric model concept, will shrink with respect to a common point (center), finally becoming a sharp corner.

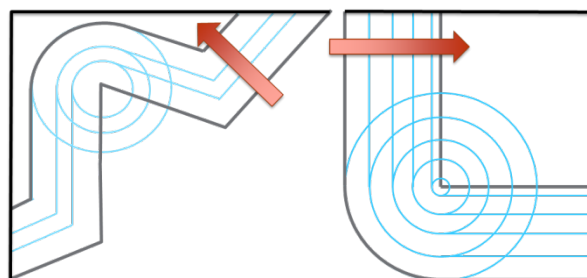


Figure 3. A geometric model to explain the dissolution behavior of glass, showing (at left) the rounding of an interior corner, and (at right) the sharpening of an external corner, all via uniform dissolution.

This behavior was modeled using a series of simple MatLab calculations developed utilizing the concept of pixel erosion to remove the pixels a certain distance from the edges of a simulated particle. The 2D version of this model divided a silhouetted glass particle into pixels, then removed all of the pixels within a certain distance of the periphery during each time step. In the most successful version, each pixel was assigned a value that represents how far it is from the nearest edge. Next, closed contours were drawn at desired distances. Rudimentary functions calculated the area and perimeter for each closed contour. Three dimensional versions of these codes were also developed, founded on the same principles. To estimate the apparent dissolution rate, the volume remaining was calculated at each time step. For both two and three dimensional analyses, many particle shapes produced “observed” dissolution rates quite different from the actual dissolution rate imposed on the systems. In some cases, these differences were strongly dependent on dissolution extent, particularly when gouges or other internal corners were present. The time-dependence lessened when large sample sizes were examined, however, presumably due to the presence of counteracting positive and negative impact shapes. A strong offset was observed even in large sample sizes that was due to the particle sizes being different from the assumed sizes based on the sieves used to isolate a specific particle size range.

The results from these studies and others have brought into question whether there might be an alternative way to perform accelerated tests that does not require the use of oddly shaped particles. Two ideas are being studied. One is the use of topographical characterization to evaluate steps corroded into polished flat glass samples. In this method, a polymer mask is used to shield a portion of the sample from corrosion. Following exposure to a dilute solution, the mask is removed and the step height quantified. Preliminary results show good agreement with solution single pass flow through data when atomic force microscopy is used to characterize the step. Another idea to mitigate the problems inherent in using high surface area powders is the use of glass fibers. With fibers, fines are non-existent, the fiber diameter can be controlled to high accuracy, and the shape/surface are consistent. Fibers can be engineered to have the same surface area as powder materials so the experiments will be just as accelerated as before. A key advantage with both methods is the availability of cross-sectional characterization to better understand the depth of interaction and the composition/structure of alteration phases. Powder cross-sections can often not be used because the original surface is unknown and it is difficult to ensure that the alteration layers are not being viewed at an angle due to the cross-section not cutting perfectly perpendicularly through the heart of a particle.

CONCLUSIONS

Experiments such as these among the international community are increasing the mechanistic understanding of glass corrosion. Each mechanism is being fit to appropriate mathematical constructs and the parameterization of each is improving all the time. This all is designed to fit the goal of accurate calculations capable of being inserted into performance assessment models. A more detailed description of all of these efforts will be present in a government report at the end of the 2015 fiscal year.

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