Joint EM-NE-International Study of Glass Behavior over Geologic Time Scales – 12303

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ABSTRACT

Vitrification has been chosen as the best demonstrated available technology for waste immobilization worldwide. To date, the contributions of physical and chemical processes controlling the long-term glass dissolution rate in geologic disposal remain uncertain, leading to a lack of international consensus on a rate law for glass corrosion. Existing rate laws have overcome uncertainty through conservatism, but a thorough mechanistic understanding of waste form durability in geologic environments would improve public and regulator confidence. If it is possible to take credit for the true durability of the waste form in repository system evaluations, then it is possible to design the repository with less conservatism with concomitant cost savings. To gain a fundamental understanding of the dissolution rate law, six nations have joined together to formulate a joint plan for collaborative research into the mechanisms controlling the long-term corrosion of glass. This report highlights the technical program plan behind the US portion of this effort, with an emphasis on the current understanding (and limitations) of several mechanistic theories for glass corrosion. Some recent results are presented to provide an example of the ongoing research.

INTRODUCTION

This report is a brief summary of the recently completed Technical Program Plan for the International Technical Evaluation of Alteration Mechanisms (I-TEAM);[1] a document which delineates the need for an improved mechanistic understanding of glass corrosion processes, identifies key information gaps or uncertainties that limit modeling the long-term behavior of glass waste forms, and describes the current and planned efforts to fill those gaps and develop a mechanistically-based glass degradation model to fulfill the U.S. objective of safe, technically defensible long-term disposal of nuclear waste. The plan describes the U.S. efforts in this area, but is part of an international collaboration to gain consensus on the mechanism(s) controlling glass dissolution at long times.

The disposition of radioactive waste is a major concern in any discussion of nuclear reactor operation, whether the cleanup of legacy wastes from heavy metals separations, used nuclear fuel (UNF) from power generation, or the options presented in a UNF recycling program. The U.S. Environmental Protection Agency has declared vitrification the best demonstrated available technology for high-level radioactive waste (HLW) stabilization.[2] When immobilized in glass, the radioactive elements become chemically bonded into the glassy matrix resulting in a durable waste form. Silicate glasses, in particular borosilicate glasses, are known to exhibit excellent aqueous durability. Many different elements can be incorporated into borosilicate glasses.

Hence, borosilicate glasses can be specifically formulated to accommodate wastes of different compositions. In addition, technologies are well established for processing borosilicate glasses. For these reasons, borosilicate glasses have become the favored waste form for the immobilization of HLW and are used in almost all reprocessing nations.[*]

One of the primary objectives of radioactive waste immobilization is to control the release of radionuclides into the biosphere over long periods resulting in minimum doses to affected individuals. Because demonstrating this objective is difficult—the calculations must cover many thousands of years—any qualified waste form has been studied extensively. This is certainly the case for borosilicate glasses, with several review papers detailing the extensive research in pure water and potential repository solutions.[3-7] The difficulties begin with the nature of the performance of such a durable product. It is well known that many glasses are extremely durable, with manmade glasses intact after thousands of years in aqueous environments and natural obsidians lasting for millions of years.[8-12] With verification that the release of radionuclides will be controlled over these long times, laboratory time scales are nearly irrelevant; small errors in short-term measurements lead to unacceptably large error ranges when data collected in the laboratory are simply extrapolated to geologic time-scales. 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 some reasonable margin of safety below that required in the applicable regulations.

With the widespread use and study of borosilicate glasses worldwide, several models have been devised to calculate the release over time and under repository relevant conditions, each linked to a portion of the degradation process as currently understood. The two principal models are based on (1) the chemical reactions for glass dissolution and (2) the transport of components through a surface layer controlling the glass degradation rate and radionuclide release. Although each approach successfully models the existing laboratory data, the long-term predictions of models based on the two mechanisms (i.e., for long times inaccessible to direct experiments) differ significantly.

The recent findings of the National Research Council's Committee on Waste Forms Technology and Performance, who stated "Many of the current models that are being used in the United States to model waste form behavior in disposal systems are based on *ad hoc* simplifications specific to the proposed repository at Yucca Mountain." By updating the existing long-term glass corrosion models to better reflect the durability of vitrified HLW, a significant opportunity exists to lower the cost of any geologic repository through less reliance on engineered barrier systems and better utilization of storage volume, both for legacy waste and that from power generation. Again, the Committee agreed, stating "Additional R&D on waste form–near-field interactions and reactive transport would likely improve quantitative modeling capabilities for estimating long-term waste form performance in different disposal environments. Having such an improved modeling capability could allow DOE-EM to take credit for waste form performance in future disposal system performance assessments."[13]

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[*] The prime exception is the use of alumino-phosphate HLW glass in the Russian Federation.

Other countries have also recognized this opportunity to improve the technical basis of glass degradation models and have wholeheartedly embraced the recent collaborative approach to glass corrosion research. Much of this is driven by the licensing of new geologic repositories and/or the development of UNF recycling programs. Since the goal of all these nations— international consensus on dissolution mechanisms and, thus, the development of a more defensible glass waste form rate law—is similar, it is recognized that coordinated research can shorten the timeline for generating the technical basis for a consensus model and achieve the goals of all members.

The critical question in long-term glass performance

The critical question that must be answered to develop a defensible, consensus rate law is:

What is the rate-limiting mechanism for radionuclide release from a glass waste form?

The answer to this question is the source of the lack of consensus among worldwide glass corrosion experts. It was the subject of four international workshops on glass corrosion: Seattle, WA – September 2009, Corning, NY – May 2010, Manchester, UK – January 2011, and Savannah, GA – May 2011. These workshops brought together representatives from France, Japan, Belgium, the United Kingdom, Germany, and the United States who are experts in areas relevant to glass dissolution to establish the current state of understanding, discuss the varied theories on dissolution mechanisms, and develop a comprehensive research plan. Although many different areas of scientific uncertainty were discussed, they can be generally grouped into three mechanistic categories:

- Dissolution reaction control
- Control by transport to/from the reacting surface
- Ion-exchange reaction control

One of these mechanisms (or a combination of them) will limit the rate of radionuclide release at any given time. Each is separately discussed below. Although likely operating through one (or more) of the above three mechanisms, the precipitation of crystalline phases has been shown to alter the dynamics of glass dissolution to such an extent that it warrants treatment as a separate topic.

Dissolution reaction control

An intuitive potential mechanism for dissolution control is the energetic drive towards the breakup of the glass network into its solution components. The development of dissolution models controlled largely by solution affinity have been based on the application of an affinity-control transition-state-theory (TST) surface reaction mechanism to aluminosilicate minerals developed by Aagaard and Helgeson.[14] The TST rate equation is given as:

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where k_o = initial rate constant E_a = apparent activation energy
                  R = gas constant Q = concentration of rate-limiting species in solution

T = absolute temperature K_{eq} = pseudo-equilibrium constant for glass
r_∞ = residual rate η = order of reaction with respect to [H$^+$]

A modified TST model applied to borosilicate glasses by Grambow[15-17] includes explicit terms for the effects of temperature, solution pH, and chemical affinity. Because the dissolution rate was found to depend most strongly on the solution concentration of orthosilicic acid, H_4SiO_4, the glass was modeled as amorphous silica and the reaction affinity was defined to include only the hydrolysis of the last silicon-oxygen-silicon bond from a hydrated silica tetrahedra: $\equiv$Si-O-Si(OH)$_3$+ H_2O $\rightarrow\equiv$Si-OH + H_4SiO_4). The reaction affinity is represented as the difference between the existing and equilibrium activities (concentrations) of orthosilicic acid with respect to amorphous SiO_2. As the glass dissolves, the orthosilicic acid concentration (Q) increases and approaches the saturation concentration of H_4SiO_4 in solution with respect to amorphous silica, which is given by the value of K_{eq}. The glass dissolution rate decreases as the orthosilicic acid concentration increases. The residual rate term is an *ad hoc* adjustment factor that accounts for the experimental observation that the dissolution rate never becomes zero. This is because glass is a thermodynamically unstable phase that cannot equilibrate with the solution. Other reactions, such as ion exchange and water diffusion, can continue when the value of Q/K_{eq} is very close to unity such that glass continues to dissolve, albeit at a very low rate.

The total system performance assessment (TSPA)[18] developed for the proposed Yucca Mountain Facility (YMF) geologic repository was based on the TST rate equation, but necessarily used a stochastic model[19] to calculate the degradation rate of HLW glass. To bound the potential effect of alteration phase formation on the glass degradation rate during long-term disposal, the YMF model imposed maximum and minimum rates that were both higher than r_∞. The equation for the maximum rate was simplified to:

$$rate = k \cdot 10^{\eta \cdot pH} \cdot \exp\left(\frac{-E_a}{RT}\right) \qquad (2)$$

where the following values were used for various repository conditions: [19, 20]

Symbol	Definition	Unit	Acid Value (pH<7)	Basic Value (pH≥7)
k	intrinsic rate constant	g/(m^2·d)	8410	28.2
η	pH exponent	unitless	-0.49	+0.49
E_a	apparent activation energy	kJ/mol	31	69

This model was intended to bound the highest potential source term for radionuclide release under modeled environmental conditions and, thus, is conservative by design. For the YMF, the vast majority of the radionuclide inventory was to be present not in glass, but in spent nuclear fuel (SNF). While the number of HLW glass canisters (i.e. co-disposal packages) was to be roughly 10 percent of the total, the radionuclide inventory from HLW glass would have been less than 5% of the total. Because of the large radionuclide inventory in SNF, especially those radionuclides determined to be primary dose contributors, and the relatively poor durability of the SNF in the wet, oxidizing environment, the radionuclide release from SNF dwarfed even the conservative predictions of release from the glass for most scenarios evaluated. Thus, the

glass portion of the scheduled inventory was only a minor factor in modeling the release of radionuclides of concern. For the recently terminated licensing application and the conditions outlined therein, the existing model works well and is suitably valid. Due to the termination of the YMF, however, new repositories need to be developed for HLW disposition. The bounding model developed for YM TSPA may not be adequate for future disposal systems in which radionuclides released due to HLW glass degradation *would* be a principle factor in dose calculations.

Although most models that utilize a reaction control component operate with the assumption that orthosilicic acid is the sole rate-controlling species, other studies suggest that the system may be more complex.[21-25]   Even assuming the simplest case, the variability of parameters with composition, temperature, and solution chemistry demonstrates the intricacy of the problem.

Diffusion control

Many studies have challenged the dominance of reaction control in favor of a mechanism involving protective layer formation on the surface of the glass.[26, 27] The work of Gin and co-workers[26] specifically challenged the application of the kinetic laws derived by Aagaard and Helgeson[14] to describe dissolution of aluminosilicate and borosilicate glasses. Specifically, these authors showed the difficulty in determining the activities of the reactants participating in the limiting step attributed to affinity control. They argued that TST, representing an elementary reaction near equilibrium, was not easily applied to glass dissolution. They further pointed out difficulties encountered by Grambow[16] in applying the Aagaard-Helgeson law to dissolution of nuclear borosilicate glasses. The authors suggested that slow diffusion of species through a hydrated gel layer or precipitation of secondary minerals were likely more important in the prediction of long-term dissolution rates in nearly-static repository relevant environments.

The model for HLW glass degradation that arose from these observations (termed GRAAL, or "Glass Reactivity with Allowance for the Alteration Layer") attributes the residual dissolution rate to the diffusion-controlled release of silica.[28-32] Through observations that the range of saturation concentration values are measured under different test conditions (primarily tests conducted at different surface area-to-volume ratios, or *S/V*) and that the value of *K* in the affinity term is not an intrinsic value of a glass, it was argued that that results of tests conducted with the nuclear waste glass R7T7 are better described with a diffusion-based model: "For most glasses, the dissolution rate is not controlled primarily by the chemical affinity of the hydrolysis reaction, but rather by the transport properties of the reacting species through the gel layer, which evolve significantly during glass leaching…"[32] The analytical expression for the degradation rate is essentially identical to that proposed for including a transport term with the reaction affinity model.[33] That equation can be written with the same terms as Equation (1), with separate terms for hydration reaction and diffusion:

$$R_{hydration} \quad = \quad k_0 \left[H^+ \right] \exp \left[\frac{-Ea}{RT} \right] \left(1 - \frac{a_{PRI}}{a_{PRI}^*} \right) \tag{3}$$

$$R_{diffusion} = \rho \left\{ \left(\frac{D_o \left[OH^- \right]^{\eta'} \exp\left(\frac{-E_a}{RT} \right)}{\pi \, t} \right) \right\}^{1/2} \qquad (4)$$

The *passivating reactive interphase* [*PRI* in Equation (4)] refers to the assumed rate-limiting diffusion barrier on the surface of the glass. The terms a_{PRI} and a^*_{PRI} refer to an effective activity product for the PRI (modeled as a single phase) at any solution composition and at Si-saturation, respectively. The density of the unreacted glass is given by ρ and D_o is a constant representing a common reactive diffusion coefficient for all ions through the PRI.

Much research has been conducted over the past 12 years to identify the alteration layer that provides the diffusion barrier. Although it is often referred to as a gel, the PRI is understood to be a generic term for the layer acting as a rate-limiting barrier to further dissolution from all other alteration products. The actual location and structure of the PRI is not known. Theories for this layer include: a dense area of the porous gel[27] formed by dissolution and reprecipitation, a capping crystalline layer on the outer gel surface, or the hydrated residual glass that is partially depleted of alkali metals and boron.[28, 34, 35] Even more theories have been put forward on which compound is rate limited by transport through the PRI. Choices include water, related water compounds (H^+, H_3O^+, OH^-, etc.), orthosilicic acid, aluminum compounds, magnesium, alkali, and boron. More data is needed at high resolution to conclusively determine the transport properties of these species and whether they have the potential to limit radionuclide release at long times.

Ion-exchange release mechanisms

The third mechanism with a potential to drive the release of radionuclides from a glass waste form involves the transport of mobile ions through and out of a glass monolith without requiring the destruction of the silicate network. This mechanism is similar to the two previously discussed mechanisms, having elements of diffusion control (access of solution to and reactants from the ion exchange site) and reaction control (the ion exchange process itself). The discussions above, however, focused on the dissolution of the silicate network. Ion exchange provides a mechanism for the release of mobile radionuclides without requiring that the network be disrupted. Indeed, Ojovan et al. stated that "Ion exchange is the principal radionuclide release mechanism for conditions when glass network hydrolysis is suppressed, such as in silica-saturated solutions when ion exchange may persist over geological time scales."[36] Specifically, ion exchange refers to the replacement of mobile ions in glass with equivalently charged species from solution (such as Na^+ with H^+ or H_3O^+). Many studies have investigated this mechanism, finding evidence that ion exchange could potentially dominate the dissolution behavior.[36-45] It is important to note that ion exchange occurs simultaneously with network hydrolysis (parallel reaction), and the dominant mechanism depends on the environmental conditions. In general, conditions of low temperature, circum-neutral pH, and high dissolved Si concentrations favor the dominance of ion exchange reactions. The other

important factor that governs the ion exchange reaction is the glass composition. For example, chemical compositions of glass that are alkali-rich (e.g., molar Na > Al +B) are susceptible to ion exchange and this mechanism may prevent these glasses from attaining the very low "residual rates" that other glasses experience.

It is also possible that ion exchange or similar mechanisms affect the release of other elements besides network modifying alkalis. The network former, boron, has a different geochemical behavior compared to other network formers, such as aluminum and silicon, because boron compounds are very water soluble. In a recent paper, Valle et al. reported element profiles in reaction rims that developed on the surface of SON68 exposed to aqueous solution.[45] The sodium profile showed a sigmoidal decrease in concentration from the pristine glass to the reaction layer, corroborating the findings of previous investigators. They defined a narrow (~2□m) zone (termed the inter-diffusion zone) that, theoretically, corresponds to an area in which sodium is leached from the glass. Interestingly, the boron profile was identical to that for sodium and could be interpreted to indicate boron diffusion. In addition, radionuclides of interest often either are released concurrent to alkali ions, are co-located with them in the glass structure, or both. If true, ion exchange reactions for a number of elements may be important general corrosion mechanisms

Crystalline alteration phase precipitation effects

The dissolution rates of many borosilicate glasses have been seen to increase coincidentally with the precipitation of certain crystalline phases in the gel layer. Zeolite structures such as analcime, hershelite, and phillipsite appear to be associated with the largest resumption in alteration,[46-51] while the precipitation of other phases, such as various smectite clays, has little discernible effect on the glass dissolution rate. In addition, the change in dissolution rate is not universal for various glass compositions, even with the precipitation of the same phases. The dissolution rates of some glasses increase by orders of magnitude upon precipitation of certain phases, while the rates of other glasses increase only slightly or simply stop decreasing. The mechanism by which the precipitation of alteration phases affect the glass dissolution rate, and even whether that is the cause, is not understood. There are theories put forward in the frameworks of the affinity-based models [52, 53] as well as the diffusion-control models,[50, 54, 55] but they are only rudimentarily included in the formal models. The effect of the precipitation of rate-affecting phases on the magnitude of the increase in the glass dissolution rate cannot currently be calculated. This adds a high degree of uncertainty to the predicted releases of radionuclides from waste glasses to the environment and to the performance of a repository system.

Results from recent tests on a glass formulated for potential reprocessing waste streams and termed "AFCI-glass" effectively illustrate the importance of these effects.[56] The glass was developed to be a durable waste form for high concentrations of alkali, alkaline earth, lanthanide, and transition metal fission products. The glass exhibited low release an extended version of the product consistency test (PCT) for nearly 100 days and was accepted as a tentative potential composition for this waste stream. For nearly 100 days, results from a high S/V static corrosion tests showed that the AFCI glass reacted slower than the SON68 glass. After approximately 182 days, however, the dissolution abruptly became more rapid. By 300 days, dramatic increases in the releases of B, Na, and Li occurred while the Si concentration in

solution increased at a lower, but still rapid, rate. Based on XRD evidence from the 450-day reacted specimens showing the presence of zeolites, the higher releases are thought to be coincident with the precipitation of zeolitic nuclei, although this has not been directly confirmed. This phenomenon has been observed previously as well. Van Iseghem et al. and Barkatt et al. also observed large excursions in dissolution rate in borosilicate glasses, potentially tied to high Al levels in the glass and the crystalline phases forming in the altered layers.[57, 58] Even SON68, which did not exhibit the same behavior as the AFCI glasses in the recent study, has been shown to suddenly begin to alter at a relatively fast rate when kept in a high pH (>11) solution.[50] This was attributed again to the precipitation of certain zeolite phases. Upon an artificial reduction in pH, the zeolites redissolved and the glass dissolution again slowed to the residual rate.

In any case, much of this effect is likely due to the composition of the precipitate and its precipitation kinetics. The desire to accelerate lab testing can produce conditions that are unlikely in a repository environment. High temperatures, high ionic strength, and high amounts of available surface area for nucleation can provide conditions for unrealistic nucleation and growth of alteration phases. It appears that zeolites possess fast formation kinetics in these conditions that would be suppressed in a more moderate environment.[59, 60] The relatively harmless phyllosilicates may be favorable from an energy standpoint, but could take a long time to crystallize. Only in non-accelerated (and more realistic) slow dissolution conditions would the fast crystallization of zeolites be inhibited and the phyllosilicate evolution favored. Obviously, a more complete understanding of precipitation kinetics as well as the variation in thermodynamic driving forces with changes in conditions is critical to the prediction of these phenomena.

METHODOLOGY

The technical program plan[1] developed to produce a more robust understanding of the relative importance of the above mechanisms was based on ASTM Standard Practice C1174, "*Prediction of the Long-Term Behavior of Materials, Including Waste Forms, Used in Engineered Barrier Systems (EBS) for Geological Disposal of High-Level Radioactive Waste.*"[61] It focuses heavily on the initial portion of this process, with the goal of providing a strong foundation for the eventual model(s). The waste form of interest is borosilicate glass and the modeling objective is prediction of the release rates of radionuclides that are incorporated into the glass. The mechanisms discussed above each hold the potential to limit the rate of this release. The key objectives of this research program are to (1) determine which of these process(es) controls the glass degradation rate during waste disposal and (2) provide the technical basis for a predictive model based on the appropriate process or processes, if they are coupled.

With such a multifaceted problem, the division of labor between vested and capable partners is critical to mission success. After outlining the several specific areas of need, a series of tasks have been designed to provide results that can be used to fill these critical knowledge gaps. Emphasis is placed on the division of resources to avoid duplication while encouraging frequent communication between the participants to leverage the combined strengths and experience of the group. Beyond the U.S., these activities are part of a coordinated and collaborative international effort with partners in France, Japan, the U.K., Belgium, Germany, and Italy. The use of commonly synthesized baseline materials and constant peer review has helped maintain confidence in the data of every member state.

International meetings and scientist exchanges are leading to commonly-developed interpretations of the data and collaborative theories on the relative importance of the various mechanisms at specific times of corrosion. Though the needs of these countries vary, the end goal is common: the generation of a consensus understanding of the mechanisms governing glass dissolution in different geological environments, leading to a robust and defensible model for calculating long term radionuclide releases under potential disposal conditions.

TASKS AND RESULTS

The tasks currently being investigated through this program are:
- Determination of the effects of temperature, pH, and silicon saturation level on the dissolution of glass per a reaction-control model – Lead: Jonathan Icenhower (LBNL)
- First-principles modeling of glass-water interactions – Lead: Peter Zapol (ANL)
- Development of molecular dynamics models of bulk glass, glass surfaces, and surface gels – Lead: Louise Criscenti (SNL)
- Tracking the diffusion profiles of key elements through a mature set of corrosion layers using isotopic tags – Lead: Joe Ryan (PNNL)
- Testing theories of diffusion control mechanisms through solution exchange experiments – Lead: Bill Ebert (ANL)
- Modeling the behaviors of solutions and surfaces in constricted pore spaces and the potential impact on diffusion through a corrosion layer – Lead: Ian Bourg (LBNL)
- Investigation of the active reaction sites within an evolving corrosion layer – Lead: Carlo Pantano (The Pennsylvania State University through a NEUP grant)
- In-situ characterization of corrosion layer formation – Lead: David Shuh (LBNL)
- A study of ion exchange mechanisms – Lead: Jim Neeway (PNNL)
- Examination of medium-range structural order in glasses and its effect on ion exchange and dissolution surface area – Lead: Joe Ryan (PNNL)
- Studying the effects of glass structure and composition on the formation of alteration phases – Lead: Eric Pierce (ORNL)
- Geochemical model prediction of alteration phase precipitation – Lead: Denis Strachan (PNNL)
- Advanced characterization of ancient glasses and long-term laboratory samples – Lead: Joe Ryan (PNNL)
- Static dissolution tests to provide modeling input and target specific effects (such as alteration phase formation) – Leads: Bill Ebert (ANL) and Jim Marra (SRNL)
- The development of a kinetic micro-continuum (KμC) model, enabling the combination and modeling of several mechanisms simultaneously and the integration of the model with far transport codes – Lead: Carl Steefel (LBNL)
- Utilizing inverse modeling techniques to parameterize existing models using multiple data sets, also obtaining the sensitivity of those parameters – Lead: Rick Williford (PNNL)

A summary of the excellent progress being made in all of these tasks is beyond the scope of this paper. One set of recent results, however, is presented as a sample of the type of collaborative effort common throughout this program. In the mid-1980's, the Commissariat à l'Énergie Atomique (CEA) lab in Marcoule, France began a study to follow the effects of semi-

static granitic groundwater at 90 °C on SON68, the designation applied to the glass composition designed to simulate the glass produced in the R7 and T7 plants at La Hague.[29] This test was recently terminated after a duration of 25.75 years.[62] The alteration layers formed on the glass during the test were extensively characterized, producing detailed compositional profiles and analytical electron microscopy results.[63] The compositional profiles were somewhat limited, however, due to the necessarily targeted nature of the nanoscale secondary ion mass spectroscopy (nanoSIMS) technique. As part of this collaboration, a sample of this corroded glass was loaned to scientists at PNNL to attempt the use of a new characterization tool, atom probe tomography (APT), to obtain a much more detailed compositional and structural profile of key areas of the reacted glass surface region. The area of particular interest is the interface between the pristine (unaltered) glass and a hydrated layer of glass depleted of most mobile ions, theorized to be the PRI – the major barrier to the transport of reactants and/or products to or from the pristine glass.[32] A detailed understanding of the chemistry and structure of this layer after a long exposure time would help determine the mechanisms of its formation and evolution.

Atom-probe tomography[64-66] is an experimental microstructural analysis technique that combines field ion microscopy with time-of-flight mass spectrometry. The experimental setup is displayed schematically in Figure 1. A sharp, needle-shaped specimen with an end diameter less than 100 nm is placed in ultrahigh vacuum (< 10^{-10} Torr) and cooled to cryogenic temperatures (< 80 K). The specimen, often referred to as a "tip", is subjected to a large positive DC voltage (several kV relative to ground), lowering the energy barrier for field ionization of individual atoms. Individual atoms are ideally evaporated from the surface of the tip and identified by mass-charge ratio one-by-one, atomic plane-by-plane, allowing for a 3-D reconstruction to be made of the tip.[67, 68] In brief, the x and y position of a detected ion are determined directly from the X and Y position measured on the position-sensitive detector using a simple point- projection reconstruction algorithm. The z position is then increased incrementally
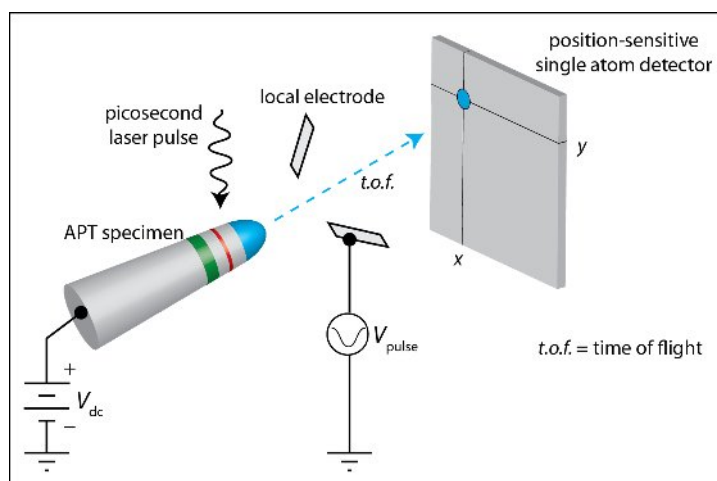

Figure 1:   A schematic of the primary components of the APT system

based on the volume of ions detected, accounting for appropriate estimations of tip radius and detector efficiency, providing the third-dimension of the reconstruction. The time-of-flight mass spectrum and 3D position information are used to generate a 3D elemental map with single-

atom sensitivity, near-atomic resolution in depth, and sub-nm lateral resolution. Traditional, voltage-pulsed APT has been used for the last ~30 years but has been limited to the study of conductive, metallic specimens. The introduction of laser-pulsed APT systems over the last 5 years[69] has opened to door to APT examinations of semiconducting[70, 71] and insulating materials systems, including bulk[72, 73] and thin-film oxides[74-76]. Simultaneous advancements in APT sample preparation using dual-beam scanning electron (SEM)/ focused-ion beam microscopes (FIBs)[77-79] have made possible the site-specific APT specimens from virtually any material.

Based on observations by Guittonneau, Gin et al.[62, 63] of the same sample that was provided by CEA, we were able to identify the primary corrosion layers of the glass: the recrystallized zone, the porous gel layer (~10 μm), a thin (1–2 μm) hydrated layer (HL), and the pristine glass (Figure 2). A small defect acted as a convenient marker for the area of interest – the HL/pristine glass interface. Using FIB lift-out techniques, a ~25 × 2 μm^2 rectangular bar was sampled from this interface, from which 8 individual APT specimens ("tips") were produced.
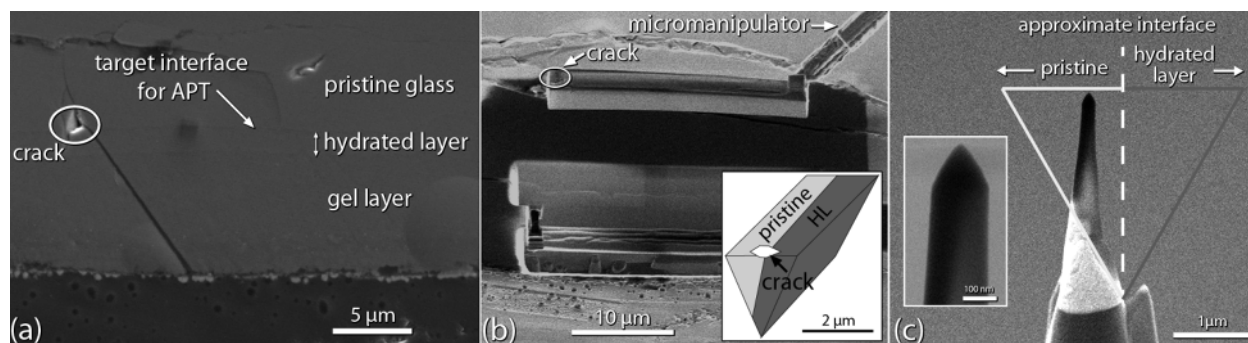

Figure 2: Secondary electron SEM images of the (a) targeted corrosion layers, (b) lift-out of the region
used to prepare 8 APT specimens, and (c) a finished APT specimen on a Si micropost.

Overall, the experiments were tremendously successful, with nearly all samples producing 2 million to105 million atom reconstructions. A 100+ million count run is impressive even for more commonly characterized conductive samples and is one of the largest data sets ever collected on a glass specimen. In addition to the large amount of data, the compositional profile of the HL was captured in several runs. Three specimens exhibited striking elemental concentration gradients, with one run (R31_01223) showing the direct transition from pristine glass to hydrated glass. Information on the runs is given in Table I.

Table I: Summary of APT run results.

Reference	Location	# Ions (x10^6)
R31_010 41	hydrated layer, Na/Li gradient	14
R31_011 98	hydrated layer, no gradients	11.4
R31_011 99	pristine glass	5
R31_012 22	hydrated layer, Na/Li/K gradients	18
R31_012 23	hydrated layer, B/Al/Na/Li/K gradients	104
R31_012 24	hydrated layer, no gradients	4.4
R31_013 11	pristine glass	2.9

Three APT reconstructions in the hydrated layer exhibited clear composition gradients in B, Li, Na, K and H associated with the corrosion front at the hydrated layer / pristine glass interface. Three-dimensional APT reconstructions (atom maps) that highlight these elemental gradients are depicted in Figure 3. The image sequence in panels (a)–(c) is believed to be in order of increasing distance from the pristine glass / hydrated layer interface. The reconstruction in panel (a) (R31_01223) begins in mostly pristine glass consisting of high concentrations of Na, Li and B. At approximately $z = 20$–40 nm a clear interface is present around which the glass composition shifts dramatically to very low Na, Li and B concentrations and higher concentrations of K. The evaporation behavior also appears to change at approximately $z = 120$ nm. Closer to the pristine glass, the evaporation was observed to be smooth and uniform, even within the region depleted of Na, Li and B. At depths $z > 120$ nm the evaporation is less uniform, with localized regions of higher/lower atomic density apparent. This likely indicates a microstructural change, likely nanoporosity, which occurs at a distinctly different location than the elemental gradient.
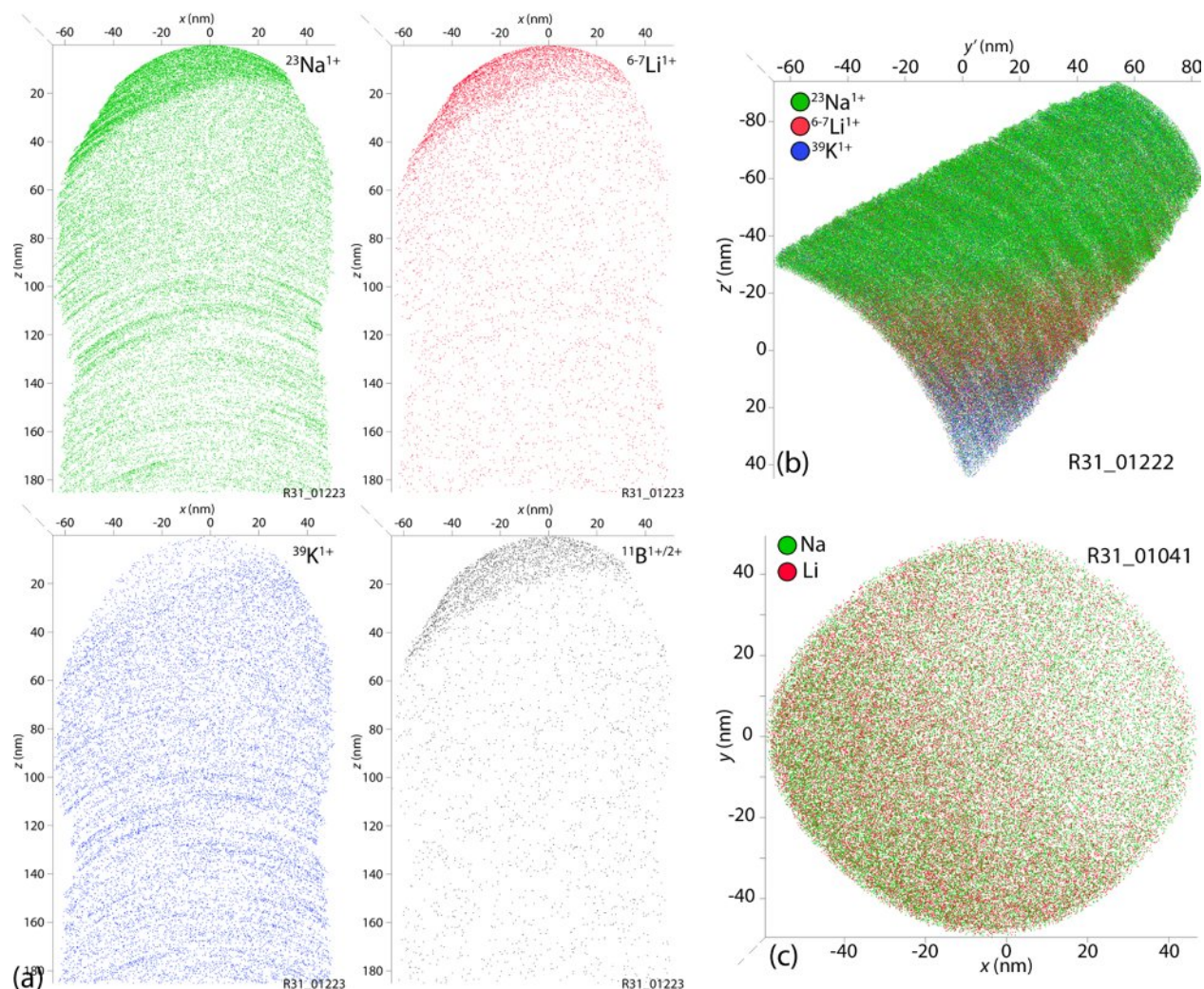
Figure 3:   Representative cross-section views of APT reconstructions of the HL near the HL/pristine interface from (a) R31_01223 (10 nm image depth), (b) R31_01222 (20 nm image depth) and (c) R31_01041 (60 nm image depth). The panel sequence (a)-(c) is believed to be in sequence of greater distance from the interface.

A very different elemental gradient is apparent in R31_01222, depicted in Figure 3(b). The evaporation throughout this reconstruction was non-uniform, suggesting it is well within the nanoporous hydrated layer. Strong elemental gradients are apparent for Na (green), Li (red) and K (blue), which appear to be lamellar in nature. Note that Na, Li and K are present in appreciable amounts throughout the reconstruction, in contrast to the sharp gradients exhibited in Figure 3(a). Finally, a very subtle concentration gradient was also seen in R31_01041, which is exhibited in Figure 3(c). The visually apparent concentrations of Na (green) and Li (red) decrease from the lower-left to the upper-right of the image. In contrast to the previous two reconstructions, there was no apparent K gradient present in this sample.

The elemental concentrations were quantified by use of a cylindrical sampling volume positioned normal to the visually apparent interfaces depicted in Figure 3. The resulting 1-D concentration profiles are exhibited in Figure 4. The concentration profiles from R31_01223

(Figure 4(b)) depict a very sharp element interface. The interfacial widths of the B, Na, Al and H profiles are all on the order of 2 nm. Lithium appears to exhibit a significantly broader interfacial width, on the order of 10 nm. Note that the concentrations reached on both the hydrated and pristine sides of the interface are very close to those measured by bulk analysis (Figure 4(a)).
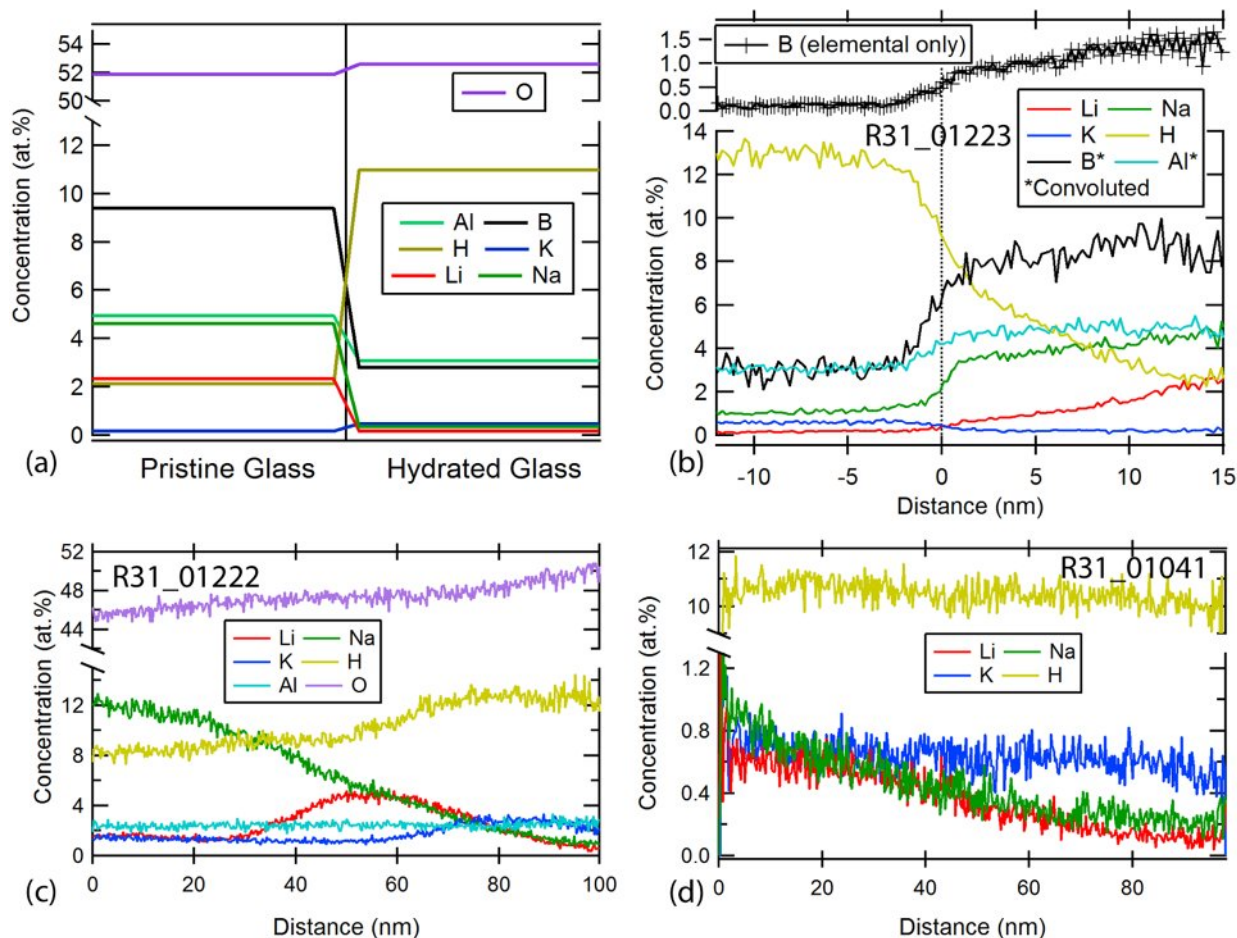

Figure 4: (a) Nominal bulk elemental concentrations measured by APT for the hydrated and pristine glasses plotted as a pseudo-concentration profile. (b)–(d) 1-D concentration profiles measured by APT across elemental concentration gradients within the hydrated layer.

   The 1-D concentration profile across the lamellar structure of R31_01222 (Figure 4(c)) depicts several interesting features. The Na concentration reaches a maximum of ~12 at%, which is approximately 2.5 times that measured within the pristine glass. Lithium is concentrated to approximately 6 at% as the Na concentration decreases and the K concentration increases. Again the measured Li concentration is approximately 2.5 times that in the pristine glass. Note, however, that the glass is clearly hydrated as evidenced by the high H concentration. It is again interesting that the O and H concentrations are substantially smaller than observed elsewhere in the hydrated glass. There was no measureable amount of B within this region, or any concentration gradient in Al.

Lastly, the 1-D concentration profile from R31_01041 (Figure 4(d)) depicts a long-range, low-concentration gradient in Na and Li, neither of which rises above 1 at%. No concentration gradient is evident for H, K, B, or O or any other element within this region. A similar long-range, low-concentration gradient was also apparent in R31_01223 (not shown) far from the sharp elemental interface (z > 150 nm in Figure 3(a)).

SUMMARY

Atom probe tomography has been used to provide a high-resolution analysis of elemental concentration gradients present at the hydrated glass / pristine glass interface in SON68 after 25.75 years of corrosion in a simulated granitic groundwater at 90 °C. The most valuable result of these initial studies is the success of the technique. Characterization by APT had never been previously demonstrated for glass corrosion layers. The resolution of APT is a powerful addition to the tools with which we can investigate the mechanisms dominating glass corrosion.

Some other key results of this study include the observation that the elemental interfacial width between the hydrated glass and pristine glass appears to be much sharper (~2 nm for B, Na and Al) than had been previously measured using nanoSIMS (~240 nm). It is not clear whether the APT analysis and nanoSIMS characterizations were possibly performed on topographically unique regions, or whether nanoSIMS overestimated the elemental width. However, the APT data seems very convincing that the elemental width *can* be much sharper than was previously thought. This result calls into question some of the assumptions made for the diffusion-control models of glass dissolution, since such a sharp profile would not match the diffusion coefficients used to date. Other results, such as the observation of apparently layered concentration profiles, show that gel evolution is not as simple as is currently assumed in nearly every model.

This task is a good example of the collaborative nature of the I-TEAM effort. Based on experimental needs and differences in expertise, scientists from DOE and CEA worked together to change the level of understanding in the field. These types of interactions are nearly ubiquitous among the tasks in the technical program plan.   With the excellence of the team in place and the willingness of the participants to work together for a common understanding, the stated goal of consensus on the mechanistic basis for radionuclide release from glass is well within reach.

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