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DURABLE GLASS FOR THOUSANDS OF YEARS

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ABSTRACT

The durability of natural glasses on geological time scales and ancient glasses for thousands of years is well documented. The necessity to predict the durability of high level nuclear waste (HLW) glasses on extended time scales has led to various thermodynamic and kinetic approaches. Advances in the measurement of medium range order (MRO) in glasses has led to the understanding that the molecular structure of a glass, and thus the glass composition, controls the glass durability by establishing the distribution of ion exchange sites, hydrolysis sites, and the access of water to those sites. During the early stages of glass dissolution, a “gel” layer resembling a membrane forms through which ions exchange between the glass and the leachant. The hydrated gel layer exhibits acid/base properties which are manifested as the pH dependence of the thickness and nature of the gel layer. The gel layer ages into clay or zeolite minerals by Ostwald ripening. Zeolite mineral assemblages (higher pH and Al³⁺ rich glasses) may cause the dissolution rate to increase which is undesirable for long-term performance of glass in the environment. Thermodynamic and structural approaches to the prediction of glass durability are compared versus Ostwald ripening.

I. INTRODUCTION

The durability of natural glasses (e.g., obsidians, tektites, moldavites, and Libyan Desert glass) for millions of years and ancient glasses (e.g., Egyptian, Islamic, and medieval window glass) for thousands of years are well documented in the geological and archeological literature. The need to predict the durability of high level nuclear waste (HLW) glass on such extended time scales has led to decades of research in the United States and Europe into ways of predicting HLW glass durability from kinetics and/or thermodynamics. Processing of HLW into borosilicate glass began in the United States in 1996 in Aiken, SC (the Defense Waste Processing Facility, DWPF) and in West Valley, NY (the West Valley Demonstration Project, WVDP) shortly thereafter [1,2,3,4,5,6]. Additional Joule heated waste glass melters are currently being constructed in Richland, WA [2,4,5,6] at the Hanford Waste Treatment Plant (WTP). Vitrification of HLW wastes in the United Kingdom [7] and France [8,9] has been ongoing for >25 years and vitrification facilities are nearing operation in Germany [10]. All HLW glasses that have been fabricated are in temporary storage at the waste form producers facilities awaiting geological disposal.

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During ultimate geological disposal, the intrusion of groundwater into, and passage through, a repository is the most likely mechanism by which radionuclides may be removed from the HLW glass once the canister degrades (~1000 years). Thus radionuclides may be carried to the biosphere unless the glasses are stable in the presence of water over geological time scales. The most important requirement for HLW glass acceptance for disposal is the chemical durability, expressed as a glass dissolution rate. For the production of durable nuclear waste glasses, it is desirable for glasses to be highly insoluble in the long-term to minimize release to the environment. Models to predict glass dissolution from glass composition and known mechanisms are, therefore, desirable.

Currently, in the US, only 1-5 volume% of the HLW glass within a given canister crystallizes during cooling allowing glass durability to be predicted from the remaining ≥95% amorphous component with accuracy. However, many countries are allowing increased crystallization in the HLW canisters and/or investigating melting technologies that allow partially crystallized glasses to be poured in order to accommodate higher amounts of HLW waste in a glassy matrix. These glassy wastes are known as Glass Composite Material's (GCM's). [4,5,6] It is important that the presence of the crystals does not degrade the overall durability performance of the waste glass form in the context of the durability assumptions discussed in Section II.1.

Prediction of the glass dissolution rate is also of importance for glasses used in building applications, in biological applications (bio-glass), and in the dissolution of fiberglass in lung fluid (as a preventative methodology against asbestosis and silicosis).[11] For the production of biosoluble fiberglass, it is desirable for glasses to be highly soluble in the short-term to eliminate health hazards and in this case, a way to predict glass dissolution from glass composition for these applications is also desirable.

(1) Thermodynamic Models Based on Glass Composition

While kinetic models such as diffusion-controlled models [12,13] and solubility-controlled models [14] describe the leaching behavior of a given glass, they cannot predict which of a given group of glass compositions would be most or least durable. Several thermodynamic models have been successfully used to predict the durability of borosilicate nuclear waste glasses, the durability of medieval window glasses, and the biosolubility of fiberglass compositions in lung fluids. These thermodynamic models are modifications of the seminal work by Newton and Paul. [15,16,17]

The chemical thermodynamic approach developed by Newton and Paul between 1977 and 1982 attempted to compare the thermodynamic stability of glass component reactants in solution to the product species predicted by known solubility (pH vs. concentration) relationships. This method predicted the relative durability of glasses from their chemical composition. Newton and Paul assumed that the glass/water reactions could be described in terms of the summation of the thermodynamic free energies for the hydration reactions of individual silicate and oxide components in a glass. This thermodynamic parameter, the free energy of hydration, was then found to correlate linearly to the logarithm of the loss of thickness of the gel layer (in

mm/century). A series of poorly durable medieval glasses, Roman window glass, modern container glass, Pyrex laboratory ware, and natural flint glass.[17]

The thermodynamic approach of Newton and Paul [15,16,17] assumed that glass is a mechanical mixture of silicate and oxide components. In particular, the cation hydration equations assumed certain silicate structural components, e.g., $MgSiO_3$. In general the silicate species chosen were those shown to be additive by Huggins and Sun [18].[†] Newton and Paul were unsuccessful in applying their approach to borosilicate glasses and to glasses with varying REDuction/OXidation (REDOX) states, e.g., the transition metal oxides and some radionuclides. Although they attempted to use solubility (pH vs. concentration) diagrams to predict hydration products, they did not consider any pH dependency of the glass dissolution.

Between 1981 and 1992, Jantzen and Plodinec [19,20,21,22,23,24,25] expanded Newton and Pauls' approach in order to quantify the relative durabilities of a wide range of man-made, geological, and nuclear waste glasses. Terms were added for transition metal oxides, radioactive species, and to represent borosilicate glasses. This model became known as the Free Energy of Hydration (FEH) model based on the well-known Linear Thermodynamic Energy Relationship (LFER).[26] The FEH model provided a historical context for the durability of nuclear waste glasses on the time frame of thousands to millions of years. Nuclear waste glasses were predicted to be more durable than ancient and medieval glasses that had survived in the environment for thousands of years (10^3 - 10^4 years) and less durable than geological glasses that had lasted millions of years (10^6 - 10^7).

(2) Thermodynamic Models Based on Glass Composition and Dissolution Mechanisms

Advances in the understanding of the dissolution mechanisms of borosilicate glasses proposed for nuclear waste solidification were extensively studied in the 1980's-1990's [27,28,29,30,31, 32,33,34,35] and such mechanisms are still being studied.[36,37,38,39] At least four operative mechanisms have been shown to control the overall glass durability. These four mechanisms are ion exchange, matrix dissolution, accelerated matrix dissolution, and surface layer formation (possibly of a protective or passivating nature). These mechanisms were incorporated into the hydration equations of the FEH and a revised model known as the Thermodynamic Hydration Energy Reaction Model (THERMO™) was developed.[40,41] THERMO™ attempts to mechanistically express the tendency of a glass to hydrate based on the known dissolution mechanisms of ion exchange and surface layer formation shown in Figure 1. Glass components are chosen based on Coulomb force calculations and/or the degree of covalency of oxide species. Gel hydroxide components are chosen based on Coulomb force calculations, experimental results from elemental depth profiling, and known Eh-pH stability diagrams. The mechanisms expressed in THERMO™ apply to either short-term or long-term durability. However, for application to long-term durability, the aging of the gel layer into mineral phases from co-precipitated gels is not considered in THERMO™ because mineral surface layers that form in

[†] Huggins and Sun demonstrated that the energy for $CaO \bullet SiO_2$ was approximately the sum of the energy values for CaO and SiO_2 and that the energy for $2CaO \bullet SiO_2$ was approximately the sum of the energy values of $2CaO$ and SiO_2 .

nature during weathering are known to form from co-precipitated gels that subsequently age into altered mineral phases (see Section IV.2). THERMO™ can be considered a tool for formulating durable glasses for HLW wastes that attempts to incorporate a mechanistic understanding of glass dissolution.

THERMO™ predicts the primary glass dissolution products: aqueous species and co-precipitated hydroxides. Repository reaction path modeling [42] using geochemical codes has been unsuccessful in predicting the long-term glass dissolution reactions that form clay or zeolite reaction species on the glass surface directly from glass composition. Successful repository reaction path modeling [43] of long-term glass dissolution has had to rely on the experimental determination of the primary glass reaction products, e.g., hydroxides, to accurately predict how these products age to form clay reaction species, as found on natural glasses in natural environments. Since THERMO™ predicts the reaction species, including those of the gel layer, and their relative molar concentrations, THERMO™ may be able to provide needed input to the geochemical long-term glass durability reaction path modeling approaches. [40,41]

Similar to the Newton and Pual approach, THERMO™ has been used to model the relative durability of natural analog glasses, medieval window glasses, and waste glasses. The response of THERMO™ has been correlated to different types of glass surface layers that are a function of the strong base [SB] minus weak acid [WA] equilibria set up in the leachate by the competition between the ion exchange reactions which liberate SB and the surface layer formation reactions that consume SB [25]. The THERMO™ model is currently being used to predict the relative durability of HLW glasses made in the DWPF vitrification facility at the Savannah River Site to determine if the HLW glasses being made today are as durable as those made since startup in 1996 years ago. Over 11,000,000 lbs. of HLW glass have been poured since startup. In 2008, THERMO™ was used successfully to predict the relative durability of a HLW glass buried in soil at the Savannah River Site for ~25 years compared to other glass formulations vitrified in DWPF.[39]

(3) Improved Thermodynamic Models Based on Glass Composition and a Crystalline Reference State (c.r.s)

THERMO™, like its predecessor FEH, is based on oxide and silicate anionic structural groups in glass. Conradt [44,45,46] improved the FEH free energy of hydration, ΔG_{hyd} , approach by demonstrating how the crystalline reference state (c.r.s.) of a glassy material could be calculated. For simple binary, ternary, and known quaternary systems, Conradt determined the c.r.s. phases from existing phase diagrams.[44,45] For multi-component systems Conradt applied the geochemical approach known as the Cross-Iddings-Pirsson-Washington (C.I.P.W.) calculation.[47] This approach calculates the normative mineral contents of igneous (glassy) rocks from their overall composition. The sequence of the crystallization and the phases used in the C.I.P.W. are based on the known crystallization mechanisms and crystallization sequences observed in the field for these molten rocks. Conradt used the constitutional phases in the MgO-CaO-SiO₂-Al₂O₃ system to predict the durability of fiberglass. He used the phases in the Na₂O-B₂O₃-Fe₂O₃-SiO₂ system to predict the durability of the HLW glass known as PNL 76-68 produced from the Hanford bulk waste composition.[44] For both systems, the quaternary end

members accounted for >87% of the glass composition and the c.r.s. for the glass, $\Delta G_{(gl)}^f$, was determined to be in agreement with calorimetric heats of formation. Conradt went on to show that the c.r.s. phases were related to the medium range order (MRO)^f in glasses [45] and that the inclusion of the $\Delta G_{(gl)}^f$ term in the ΔG_{hyd} calculation improved the accuracy of the FEH/THERMO™ models. In addition, Conradt has used the C.I.P.W. and the c.r.s. approach to predict melt rate (i.e. the theoretical heat demand of the batch-to-melt conversion) that was later confirmed with calorimetric measurements [48].

(3) Kinetic Models Based on Dissolution Mechanisms and Rates

Kinetic modeling of the chemical durability of glass, e.g., glass-solution interactions, has paralleled the modeling of mineral-solution durability in that the mathematical treatments have systematized the effects of pH, temperature, saturation state, ionic strength, and inhibition on the overall dissolution rate by developing models that treat each effect individually [49]. The kinetic effects of saturation state as a function of pH, temperature, and ionic strength have primarily been handled by the application of Transition State Theory (TST) and the free energy dependence of irreversible dissolution reactions [50,51] as indicated in Equation 1.

Equation 1

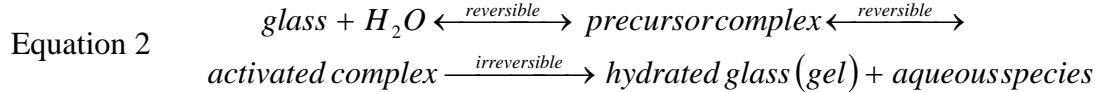


These TST and irreversible dissolution reactions are those currently being used to predict HLW waste glass dissolution for the geological repository in the United States [52].

The original kinetic treatment of mineral dissolution using the TST theory (developed by Aagard and Helgeson [50] in 1982) was followed (in 1984) by a rigorous demonstration that mineral dissolution was controlled by surface activated complex reactions, e.g., the dissolution rate is controlled by reactions at the solid/aqueous solution interface by activated complexes.[53] This “surface reaction hypothesis” was the only mechanism that was deemed consistent with the TST theory and the irreversible thermodynamics used to derive the rate equations for the hydrolysis of minerals.

In 1988 Wieland, Wehrli, and Stumm [54] developed an activated complex theory for the dissolution of minerals to bridge the gap between thermodynamic information (surface coordination and lattice or site energy) and kinetic information. This approach is consistent with the more recent approaches of Lasaga in 1995 [55]. The dissolution rate is considered proportional to the free energy of conversion of the activated surface complex which is considered the rate determining irreversible step governing dissolution. This energy is, therefore, related to the activation energy of the rate-determining step in the dissolution [54,56], and only the last step in the dissolution process is considered irreversible (see Equation 2)

^f In glasses short range order (SRO) has a radius of influence ~1.6-3 Å around a central atom or first nearest neighboring atoms, i.e. polyhedra such as tetrahedral and octahedral structural units while medium-range order has a radius of influence ~3-6 Å which encompasses second- and third-nearest neighbor environments around a central atom. Sometimes the MRO in glasses form highly ordered regions, referred to as clusters or quasicrystals that have atomic arrangements that approach those of crystals (see references 71 and 72).



The role of activated complexes has been integrated into the TST theory in 2001[57] and applied to glass dissolution as well as mineral dissolution. This approach was previously used to describe the inhibition of dissolution [58] for aluminosilicates. In the recent treatment of the role of activated complexes on chemical durability, the rate-limiting step is considered to be the destruction of the slowest breaking metal-oxygen bonds, e.g., those that are essential for maintaining the mineral or glass structure. For dissolution of feldspars (alkali aluminosilicates), the rate limiting step was found to be partial liberation of a metal by the removal of adjacent metals through previously equilibrated exchange reactions, e.g., an Al^{3+} is exchanged for 3H^+ (3 protons) on the surface of the mineral or glass that leads to the formation of three partially liberated Si atoms [56, 58]. The three partially liberated Si atoms that form due to the leaching of an Al^{3+} are then partially detached forming the slow-exchanging metal oxide precursor complex that is rate controlling. The activated complex has the same stoichiometry as the precursor complex but the activated complex has more energy and represents some fraction of the precursor complex available for dissolution. The overall dissolution rate is, therefore, proportional to the quantity of the precursor complexes on the glass (or mineral) surface.

The Al/proton exchange has also been shown to be the step that forms the precursor activated complex in basalt glass [59] regardless of whether dissolution is in acidic or basic solutions. The basalt glass dissolution is described as the rapid removal of univalent and divalent cations from the near surface followed by the Al^{3+} and 3H^+ exchange. The breaking of the Al-O bonds does not destroy the glass framework, but it partially liberates the silica tetrahedral chains as in the crystalline feldspar dissolution mechanism [56]. The detachment of this partially liberated silica that is the rate determining step, e.g., partially detached silica dissolves more readily than attached tetrahedral silica. The basalt glass dissolution, is therefore, proportional to the concentration of partially detached framework tetrahedral Si near the surface, which is linked through the law of mass action to the concentration of Al in the glass via the Al/proton exchange reaction and to the aqueous aluminum activity in the leachate.

(4) Advanced Thermodynamic Models Based on Glass Composition and Dissolution Mechanisms

An improvement in the thermodynamic modeling approach has recently been proposed by Jantzen and Pareizs [60] based on MRO structures in glass and activated complexes. The structures are mineral-like clusters (moieties) that represent the c.r.s. and are calculated from the bulk glass composition. Because the thermodynamic information driving the activated complex theory (Equation 2) is derived from surface coordination and lattice or site energies, there is a dependency of the thermodynamics on the MRO structures in glass (Section III.1) and, hence, on the glass composition. The stoichiometry of the mineral clusters is assumed proportional to the stoichiometry of the activated complex by the law of mass action. A discussion of predicting the

MRO from glass composition (NORMCALCTM) and the Activated Complex Theory (ACTTM) is summarized below (Section IV) although more details are provided elsewhere.[60]

II. BASIC CONSTRUCTS

(1) Modeling a Single Source Term

A basic assumption in all glass dissolution models, as well as in all mineral dissolution models, is that the solid being modeled is comprised of a single phase and so the durability response has only one source term. Therefore, phase separated glasses (with two source terms) cannot be modeled in this fashion. The approach to durability prediction for phase separated glasses is often referred to as mixed mechanism modeling, e.g., the separated phase for borosilicate glass is often boron rich and has a poorer durability than the bulk and/or the matrix phase. Having a poorly soluble second phase may be desirable for biosoluble glasses, but not for HLW glasses where the distribution of the radionuclides in the two glassy phases would have to be known for every waste glass fabricated. Additional mixed mechanisms can occur if crystals are present in a glass because crystals create grain boundaries that can (1) selectively undergo accelerated dissolution (Figure 2) while the crystals themselves may have a different dissolution response [61] or (2) have compositions not representative of the bulk glass.[62]

To ensure that HLW glasses are homogeneous, a minimum Al₂O₃ limit is applied. The effect of insufficient Al₂O₃ was first reported by French researchers [63] who determined that many glass durability models were non-linear, e.g., glasses had release rates far in excess of those predicted by most models, in regions corresponding to low Al₂O₃ and in excess of 15 wt% B₂O₃ and independently by Jantzen, et.al [40,41,64]. Homogeneous glass formulations, or formulations with only 1-2 wt% crystals, are targeted for HLW in the US. Crystals such as iron spinels have little impact on glass durability as they are themselves very durable and cause minimal grain boundary dissolution since the spinels and the glass are both isotropic [61,65]. However, for other phases such as nepheline, acmite, and lithium silicates which are less durable than iron spinels and not isotropic, the impact on glass durability from the crystal and the grain boundary can be pronounced. This is especially true if the crystal sequesters radionuclides as this gives a secondary source term for radionuclide release. Therefore, durability testing must be performed to confirm that any crystallization that might occur during canister cooling or during GCM formation has minimal impact. [66,67,68,69] This ensures that the last 3 terms in Equation 3 approximate zero and that the dissolution models do not represent mixed mechanisms.

Equation 3

$$\sum \text{Durability} = \underbrace{\text{durability}_{(\text{homogeneous})}}_{\text{1st term}} + \underbrace{\text{durability}_{(\text{amorphous phase separation})}}_{\text{2nd term}} + \underbrace{\text{durability}_{(\text{crystallization})}}_{\text{3rd term}} + \underbrace{\text{durability}_{(\text{accelerated grain boundary})}}_{\text{4th term}}$$

(2) Representing the Maximum Radionuclide Release

Since the geological repository is most interested in the maximum radionuclide release, the most important elements to be analyzed for in a durability test are the leachate species that represent the maximum dissolution of the glassy waste form. For example, elements that are not sequestered in precipitates that participate in surface alteration reactions, and are also not solubility limited are good indicators of waste form durability. In the case of a multi-phase glass ceramic waste form it may be important to analyze for elements from each significant phase present. Extensive testing of any glass or glass ceramic waste form must be performed in order to determine what these elements are as specified in the durability test procedure ASTM C1285 also known as the Product Consistency Test (PCT). [70]

Often the maximum normalized release of the radioactive constituents can be compared or bounded by the release of non-radioactive indicator(s) elements that can be more readily and accurately measured. The nonradioactive indicator(s) should be capable of representing radionuclides that are present at concentrations as low as 10^{-8} weight % and/or radionuclides that are difficult to measure. Once the pertinent indicator(s) is/are determined for a given glass waste form, these constituents should be analyzed in the leachate. For example, in high level borosilicate waste glass, Tc⁹⁹, present at $\sim 4.1 \times 10^{-4}$ weight % in the waste form, has been shown to be released at the same maximum normalized concentration as boron, lithium, and sodium. Therefore, for borosilicate glass waste forms, the leachates are routinely analyzed for boron, lithium, and sodium if these elements are present at > 1 mass % in the glass and durability models are often based on the release of these bounding non-radioactive constituents. Additional mechanistic information about high level borosilicate waste glass durability is gained by analyzing for other elements present at > 1 weight % in the glass.

(3) Thermodynamic Models Apply Only to Near Equilibrium Test Responses

Thermodynamic models can be applied to steady state equilibrium [71] and to irreversible equilibrium [71] but not to equilibrium far from steady state. Therefore, thermodynamic models should not be applied to data gathered from durability tests at high flow, e.g., far from steady state, such as the Single Pass Flow Through Test (SPFT) (ASTM 1662) as demonstrated recently in 2008.[72] The equilibrium states related to glass corrosion are well discussed by Conradt [44] who states that “the nature of this equilibrium may be described by a complex solubility product changing with the amount of matter dissolved” and that both geochemical and thermodynamic models depend on a quantitative determination of the equilibrium. Therefore, the durability response from flow through tests, which are far from equilibrium saturation, cannot be modeled thermodynamically, but the durability tests from static tests can.

III. STRUCTURAL CONTROL OF GLASS DISSOLUTION

(1) Role of Medium Range Order (MRO) in Glass Dissolution

Borosilicate waste glasses and melts, like natural silicate glasses and melts, possess short-range order (SRO; radius of influence $\sim 1.6\text{-}3\text{\AA}$) around a central atom, e.g., polyhedra such as tetrahedral and octahedral structural units [73]. Glasses also possess MRO [73] which

encompasses second- and third-neighbor environments around a central atom (radius of influence ~3-6 Å). The more highly ordered regions, referred to as clusters or quasicrystals, often have atomic arrangements that approach those of crystals [73,74].

The existence of MRO in melts and glasses led to a redefinition [75] of the widely accepted Zachariasen-Warren random-network structure model of glass [76,77,78] and its predecessor the crystallite structure model of glass [79]. The “modified crystallite model” of glass structure treats the degree of medium-range order as spatial fluctuations in the glass network [75]. Similarly, Greaves [80] proposed a “modified random network (MRN)” model that involves two interlacing “sublattices.” One sublattice is more highly ordered (network regions) while the other is not (inter-network regions comprised of large concentrations of network modifiers). The MRN model is able to describe the existence of large cation-rich clusters in glass, e.g., clusters of Ca in CaSiO₃ glasses [80] and Na₂MoO₄ in French HLW glasses.[81](Figure 3)

MRO in glasses and melts has been measured for many single component mineral melts and glasses, e.g. SiO₂ glass [73], diopside glass [73], and nepheline glass [82], as well as in complex natural silicate melts [73]. For example, the formation of nuclei (clusters or quasicrystals) of Ni-diopside, (Ca,Mg,Ni)₂Si₄O₁₂, were observed “in-situ” at a temperature of approximately 1100K in a diopside composition glass containing 2 wt% Ni [83]. Thermodynamic data from glasses and melts have been used to establish a hierarchy of the relative stability of aluminum-bearing silicate clusters or quasicrystals in melts. The stability of the aluminate groups are KAlO₂ >NaAlO₂>LiAlO₂>Ca_{0.5}AlO₂>Fe_{0.5}AlO₂>Mg_{0.5}AlO₂ [84]. Qualitatively, the behavior of tetrahedrally coordinated Fe³⁺ resembles that of Al³⁺ in that it requires electrical charge-balance with alkali metals, alkaline earths or ferrous iron [84]. The hierarchy for Fe³⁺ complexes suggested by Mysen [84] is similar to that of the aluminate complexes, e.g., KFeO₂ > NaFeO₂>LiFeO₂>Ca_{0.5}FeO₂>Fe_{0.5}AlO₂>Mg_{0.5}FeO₂. Since both Al³⁺ and Fe³⁺ in tetrahedral coordination need to be charge balanced and the relative stability of the Al³⁺ and Fe³⁺ complexes is considered to be the same, the convention is to first assign cations to the ferric iron complexes.[84]

In HLW glasses such as those being processed in the DWPF, Ellison and Navrotsky [85] concluded that the glass should be composed of the following polymerized silicate groups: (K,Na,Li)AlO₂, (K,Na,Li)FeO₂, (K,Na,Li)BO₂. The excess (K,Na,Li)₂O in this waste glass suggests that network-modifier-rich polymerization dominates over silica-rich polymerization and the hierarchy for polymerization for Na⁺ tetrahedral groups was hypothesized to be NaBO₂>NaFeO₂>NaAlO₂. [85] Experimental evidence for the existence of alkali ferric iron clusters (NaFeO₂ and LiFeO₂ complexes), (Na,K,Li)BO₂ clusters, and NaAlO₂ clusters in HLW glasses is reviewed elsewhere.[86,87] Experimental evidence for transition metal-silicate structures is supported by the Raman spectroscopy and optical absorption spectroscopy conducted by Nelson, Furukawa and White.[88]

Greaves [89] also used Extended X-ray Absorption Fine Structure (EXAFS) to demonstrate that ion exchange occurs along percolation channels that exist in glass. He demonstrated that the percolation channels are defined by the non-bridging oxygens (NBO) atoms at the edges of the highly ordered network regions, which ionically bond to the alkali, alkaline earths or other modifier species in a glass (Figure 4). As the cation species are preferentially leached out of the

channels, the leachant can then preferentially attack the Si–O NBO bond(s). Recent EXAFS studies also demonstrated that such percolation channels exist in European HLW glasses of the rare-earth aluminoborosilicate type containing sodium, calcium and neodymium.[6] The AlO_4 and BO_4 are preferentially charge compensated by low field strength network-modifying cations, e.g., Na^+ while SiO_4 NBO are connected to the higher field strength network-modifying cations, e.g., Nd^{+3} and Ca^{2+} . [6] (Figure 5)

The existence of highly ordered network regions is in agreement with the 1970's calculations performed by El-Shamy [90], which indicate that alkali and alkaline-earth silicate glasses with a silica content of ~67 mol% silica corresponds to a composition at which every silicon atom in the glass becomes associated with a basic ion as a second neighbor. In glasses with < 67 mol% silica, there is always an interconnected path of nonbridging +Si–O⁻ sites that allows exchange of species between leachate solution and the glass. At >67 mol% silica, these sites are isolated from each other by the silica network +Si–O–Si+ groups in the glass that suppress the movement of ions involved in leaching. Most HLW waste glasses contain between 45-67 mol% silica and thus likely have interconnected paths by which non-matrix forming elements can leach.

The percolation channels in glass (Figure 4) are defined by the MRO structure of a given glass. Interestingly, such channels have been experimentally observed at the glass-gel interface when the leached layer is removed with tape (Figure 6). Hess [91] and Bottinga and Richet [92] developed polymerization models for simple and complex silicate glasses by invoking crystalline silicate structural analogues. Marians and Hobbs [93] developed a nomenclature scheme to describe the local topology surrounding the SiO_4 anion groups in glass and their most immediate neighbors, "local clusters or quasicrystals." This enables higher order polymerization modeling of these local clusters into various types of rings, sub-networks, and networks that define the percolation channels [65]. The polymerization scheme is similar in many aspects to the classification of silicate minerals into cyclosilicates (linkage of SiO_4 tetrahedra into rings), sorosilicates (linkage of two SiO_4 tetrahedra sharing an oxygen), ionsilicates (linkage of SiO_4 tetrahedra into linear chains by the sharing of oxygen), etc.[94,95]

Comparative dissolution experiments on the mineral albite ($\text{NaAlSi}_3\text{O}_8$) and on albite glass which share the same MRO structure have been performed.[96] Figure 7 demonstrates that during the durability testing the mineral dissolution is two orders of magnitude less than the mineral glass dissolution as the mineral has both MRO and long range order (LRO). The author states, "it is likely that same mechanisms are operating with both glasses and minerals but at different rates" which demonstrates that the MRO is likely controlling the distribution of ion exchange sites, hydrolysis sites, and the access of water to those sites in both crystalline and vitreous solids.

(2) Advances in Defining the Crystalline Reference State (c.r.s)

The concept of a crystalline reference state (c.r.s.) was presented by Conradt [44,45] for a wide variety of glasses (e.g., window glass, HLW glass, and fiberglass). The MRO clustering and polymerization in glass resembles quasicrystals (or alternatively, mineral moieties).[97] While Conradt used the conditional phases in known silicate containing quaternary oxide systems to define his c.r.s. phases, McGrail developed a mineral moiety model for dissolution which uses

the following simplified suite of mineral species: sodium disilicate, sodium metasilicate, reedmergnerite, albite, nepheline, sodium aluminate, and quartz.[97] For melt rate modeling of window glass, Conradt used the constituent phases in the $\text{Na}_2\text{O}\text{-CaO}\text{-SiO}_2$ system [98,99] as a method to predict the theoretical heat demand of the batch-to-melt conversion for window glass applications, and later confirmed this normative mineral model with calorimetric measurements. For liquidus temperature modeling, Jantzen and Brown [86,87] used the phases (e.g., nepheline, SiO_2 (quartz), alkali di-silicates, acmite, and excess Fe_2O_3) of the basalt quaternary $\text{Na}_2\text{O}\text{-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-SiO}_2$ because high Fe_2O_3 HLW glasses are compositionally similar to alkali basalts (SiO_2 poor basalts also known as ijolites) when the B_2O_3 is normalized out of the composition on a wt% basis.

Recent research on glasses made from stoichiometric mineral compositions has shown that glasses with more atomic % Al^{3+} than Si^{4+} dissolve at higher rates. [58,100] The altered layers of simple glasses with varying Al:Si stoichiometry, e.g., NaAlSiO_4 (nepheline), $\text{NaAlSi}_2\text{O}_6$ (jadeite), and $\text{NaAlSi}_3\text{O}_8$ (albite) composition, were examined by Nuclear Magnetic Resonance (NMR) techniques. NMR shows the dissolution rate was proportional to the Al/Si atomic ratio of the parent glass [100,101,102], e.g., durability decreased from albite to jadeite to nepheline glass as the Al:Si ratio increased from 0.33:1 to 1:1. The correlation of glass durability with the stoichiometry of the parent glass is important as the Al-O-Si linkages in the glass are known to hydrolyze more rapidly than the Si-O-Si bonds [56,58,59,103], e.g., hydrolysis of Al-O-Si bonds becomes more energetically favorable as the number of Al atoms per Si tetrahedron increases [100]. NMR of a BNFL glass has indicated that glasses with more Q^3 than Q^4 silicate groups[†] increase the dissolution rate of HLW glass.[104] The presence of Al, promotes Q^4 , reduces Q^3 , and reduces N_4 (the number of BO_4 tetrahedral groups). The presence of alkali and alkaline earth oxides increases Q^3 .[104] When considering these effects, the higher the fraction of albite c.r.s. in a glass should increase its durability.

For boron-containing c.r.s. species, Conradt used $\text{Na}_2\text{O}\bullet 4\text{B}_2\text{O}_3$, $\text{Na}_2\text{O}\bullet 2\text{B}_2\text{O}_3$, and B_2O_3 [44,98,99]. Ramsey and Jantzen [105] determined that HLW glasses containing reedmergnerite structures leached similarly to glasses containing albite structural units, where B^{3+} in the reedmergnerite structure replaces Al^{3+} in the albite structure.[106] Thus, Jantzen and Pareizs [60] and McGrail et.al. [97] also assumed reedmergnerite structures. Recent studies on the French HLW glass, SON68, have shown that B exists in mixed tetragonal and trigonal forms [107]. The tetragonal form represents ~70% of the B in the glass and is present as reedmergnerite groups. The trigonal B is present as B_2O_3 suggesting that Na only participates with B in the reedmergnerite structure and not in the formation of alkali metaborates or alkali diborates. Recently, an NMR study of a British BNFL mixed alkali borosilicate glass has demonstrated that both reedmergnerite (NaBSi_3O_8) and danburite ($\text{CaB}_2\text{Si}_2\text{O}_8$) groups stabilize $[\text{BO}_4]$ groups in the glass, where danburite is the B analog of anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$). The NMR study indicates that the danburite groups are of the type $[\text{B}(\text{OSi})_3(\text{OB})]$ that are preferentially associated with the presence of large cations (e.g., Cs and La) when Al is present. Reedmergnerite groups of the type $[\text{B}(\text{OSi})_4]$ are preferentially associated with the presence of smaller MgO or Group I alkali oxides. The presence of alkali and alkaline earth oxides increases

[†] The polymerization or extent of MRO of a melt can thus be expressed by calculating or measuring a Q distribution where the superscript designates the number of bridging oxygens.

N₄.[104] These results indicate that increasing the fraction of reedmergerite or danburite c.r.s. in a glass should increase its durability. This structural interpretation may also be related to the boron/alkali retention factor recently added to kinetic models for HLW glass dissolution [108] and to the inverse relationship recently found by Monte Carlo simulation between the Ca content of a HLW glass and the B release to solution. [109]

IV. STAGES OF CORROSION

Current theories of glass dissolution suggest that all glasses typically undergo an initial rapid rate of dissolution denoted as the “forward rate” (Figure 8a). However, as the contact time between the glass and the leachant lengthens some glasses come to “steady state” equilibrium and corrode at a “steady state” rate while other glasses undergo a disequilibrium reaction with the leachant solution that causes a sudden change in the solution pH or the silica activity in solution [110]. The “return to the forward rate” (Figure 8b) after achieving “steady state” dissolution is undesirable as it would cause the glass to return to the rapid dissolution characteristic of initial dissolution.

The initial rate is often referred to as Stage I dissolution in the U.S. literature but it encompasses zones where multiple mechanisms are operative including regimes that are interdiffusion controlled, hydrolysis controlled, and a rate drop that is diffusion or affinity controlled [111]. The “steady state” rate (also known as the residual or final rate) that signals the end of the alteration phase and/or a pseudo-equilibrium between the alteration and re-condensation reactions [107, 111] is known as Stage II dissolution, and the return to a forward rate (or resumption of alteration) is known as Stage III dissolution. Diffusion controlled dissolution of network modifiers and/or radionuclides during Stage I and Stage II normally follow a mathematical function related to the square root of the test duration as observed in many burial studies [39] while other radionuclides are solubility limited, entrapped in the gel layer, or complexed in secondary alteration phases that form from the leachate solution.

A reaction zone is formed as the leached layer solution interface progresses into the glass (Figure 1a). The front of the reaction zone represents the region where the glass surface sites interact with the ions in solution [12]. The top of the gel reaction zone represents the leached layer-glass interface where a counter-ion exchange occurs [12]. The glass dissolution rate is modified by the formation of the hydrated amorphous gel layers and/or secondary precipitates, e.g., metal hydroxo and/or metal silicate complexes that have reached saturation in the leachate and can precipitate on the surface of the gel layer [112,113,114,115,116,117]. These “back reactions” have been attributed to formation of silanol bonds as surface adsorption sites which were modified by changes in solubility of the species in solution and surface (zeta potential) considerations.[117,118]

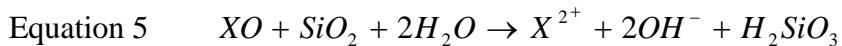
The gel layer may, under certain conditions, act as a selective membrane [114,119] or as a protective/passivating layer [107,108,112, 113, 116, 117, 120, 121, 122, 123, 124]. The slowing of glass dissolution to a steady state rate by solution saturation (affinity) of glass matrix elements or reaction through a surface layer has been referred to as Stage II dissolution including residual rate dissolution, steady state dissolution, or the final dissolution rate. Recent mechanistic modeling of glass durability including the slowing of the dissolution rate due to affinity and/or

surface layer effects was first modeled by Grambow and Muller [125] and is referred to as the GM2001 model. The GM2001 model combines the effect of glass hydration by water diffusion with ion exchange and affinity-controlled glass network corrosion. The slowing of dissolution due to the effect of a growing surface gel layer is represented by a mass transfer resistance for silica by this layer. At the interface between the glass and the gel layer a different “gel layer” is assumed to be hydrated glass that allows diffusion of H₂O in and boron and alkali atoms out of the glass (similar to Figure 1). A 2003 modification of the GM2001 model, known as the GM2003 model [111], treats silica dissolution and silica diffusion through the gel separately from water diffusion and boundary conditions are specified at the gel/diffusion layer and the gel/solution interfaces. Recently, the GRAAL (Glass Reactivity with Allowance for the Alteration Layer) model [37,38] has been proposed which is dependent on the composition and the passivating nature of the gel layer, called the Passivating Reactive Interphase (PRI). The leached layer has been found experimentally to be zoned (5-7 zones) (Section IV.2 and 111) and the GRAAL model assigns various mechanisms to different zones within the PRI.

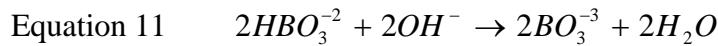
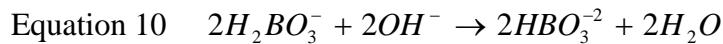
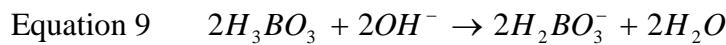
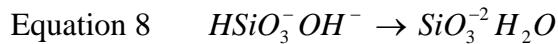
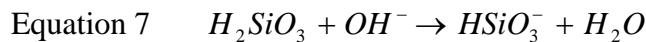
The resumption of alteration (Stage III) causes the long term dissolution rate to reaccelerate to a rate that is similar to the initial forward dissolution rate for some glasses. This unexpected and poorly understood return to the forward dissolution rate has been shown to be related to the formation of the Al³⁺-rich zeolite, analcime, and/or other calcium silicate phases. Moreover, the presence of Al³⁺ and Fe³⁺ in the HLW glass, in the leached layer, and in the leachant has been shown to influence whether a glass maintains Stage II dissolution or reverts to the forward rate of dissolution, e.g., Stage III dissolution. Van Iseghem and Grambow [110] demonstrated that an Al³⁺-rich zeolite (analcime) formed on certain glasses during dissolution but not on others. The formation of analcime in these experiments carried out at 90°C at SA/V conditions of 10, 100, and 7800 m⁻¹ accelerated the glass corrosion by consuming H₄SiO₄ from the leachate solution but did not accelerate the glass corrosion back to the original forward rate, e.g., “the formation rate of analcime is too small to bring the glass dissolution rate back to the forward rate” [110]. Two different glasses were studied, SM58 that contained 1.2 wt% Al₂O₃ and 1.2 wt% Fe₂O₃ and SAN60 that contained 18.1 wt% Al₂O₃ and 0.3 wt% Fe₂O₃. The SAN60 glass, with the higher concentrations of Al₂O₃ and the lowest concentration of Fe₂O₃, formed the analcime reaction product. Van Iseghem and Grambow also demonstrated that a change in solution pH accompanied the return to the apparent forward rate when analcime formed. Likewise, Inagaki [126] demonstrated that solution pH and solution concentrations of Na and K were also involved in the formation of undesirable analcime versus Na-bedellite (a smectite clay). Other zeolites and smectite clays that are rich in Fe³⁺ compared to Al³⁺ do not appear to accelerate glass corrosion [110,127,128].

(1) Strong Base-Weak Acid Equilibria [40,41]

During static leaching in deionized water the glass chemistry causes a [WA]- [SB] equilibrium to occur in the leachant [40,41]. The silicic and boric acids formed from the hydrolysis of the SiO₂ and B₂O₃ in the glass react with the strong bases (OH⁻) formed from hydrolysis of the alkali and alkaline earth species (Li₂O, Na₂O, K₂O, CaO, BaO, etc.) in the glass. The dissolution of an alkali species in the glass via hydrolysis releases one mole of OH⁻ for each mole of elemental alkali or ½ mole of an alkaline earth, e.g., each Na⁺ releases one mole of OH⁻ per Equation 4 or 1/2Ca²⁺ releases one mole of OH⁻ per Equation 5



where M_2O is any alkali oxide and XO is any alkaline earth. The molar strong base [SB] generated by the hydrolysis of the alkali oxides in the leachate solution can be approximated by summing the molar alkalis measured in solution plus the alkaline earths.[40,41] Conversely, Si and B are present in the leachate solution as weak acids (H_2SiO_3 and H_3BO_3) or weak acid salts ($MHSiO_3$ or MH_2BO_3). Each mole of weak acid buffers one mole of strong base via interactions between the hydrolysis reaction(s) (Equation 4, **Equation 5**, and Equation 6) and the neutralization reactions of the weak acids at various pH values (Equation 7 through Equation 11):



The solution electrical neutrality[†] can then be determined. For a HLW durability dataset generated by ASTM C1285 (Product Consistency Test, PCT, static testing) [70] a linear relation was found between the log of the molar leachate strong base concentration, [SB], and the log of the molar weak acid concentration: [WA], $\log_{10}[SB] = -0.09 + 1.08 \log_{10}[WA]$ with an $R^2 = 0.99$.[40,41] The slope of ~1 shown in Figure 10 (top) indicates solution neutrality.

The solubility of the boron and silicon in the glasses studied can be expressed as a leachate concentration versus solution pH. The concentrations of the leachates are expressed as the logarithm of the concentration in millimoles/L of each element in solution. The pH of the leachate solution is influenced by the interaction of the strong bases and the weak acids released during hydrolysis. The PCT leachate chemistry can, therefore, be modeled as a mixture of weak

[†] A similar approach is used by geochemical codes such as PHREEQC and EQ3/EQ6, EQ3NR that calculate solution pH from the total concentration of the cations and anions in solution through the physical requirement that the solution in total must be electrically neutral. It should be noted that pH cannot be accurately calculated from electrical neutrality if the pH is very low (acidic) or very high (where $p_{OH} = -\log_{10}[a_{OH^-}]$ is low and the electrical balance would effectively be constraining OH).

acids (e.g., orthosilicic or boric acid) in equilibrium with their alkali metal salts. [129,130] A weak acid in equilibrium with a salt of that acid are internally buffered solutions that obey the Henderson-Hasselbalch (HH) relationship.^f Indeed, boric acid and NaOH is a commercial buffer solution used over the pH range of 7.8 to 10.0.[131] Substitution of log[SB] for log[base] and log[WA] for log[acid] in the HH relationship allows the relation between the PCT leachant pH and the {log[SB] - log[WA]} concentration to be evaluated where pKa is the equilibrium acid dissociation constant.

The pH of the leachant solution vs. the [WA] and [SB] concentrations should have the shape of a buffer curve when pH is plotted against the fraction alpha, α , the total base divided by the total acid plus base, or $\alpha \equiv [SB] / ([SB] + [WA])$.[40,41] This relationship, for a suite of HLW glass leachates filtered to <45 microns to avoid silica and iron colloid interferences,[40,41] is plotted in Figure 9 that has the shape of a partial buffer curve, e.g., the plateau and region dominated by the strong base concentration. The glasses with solution pH values in the plateau region are releasing equivalent molar [SB] and [WA] while those glasses in the region dominated by [SB] have higher solution pH values and are undergoing accelerated matrix dissolution. The pKa for the homogeneous glasses shown in Figure 9 is approximately 10.5. The theoretical pKa values for silicic and boric acids are 9.8 and 9.2, respectively. This indicates that the effective pKa of the PCT leachate solutions are being affected by the second dissociation constants for silicic and boric acid where the pKa values are 12.0 and 12.7, respectively.

The PCT leachate concentrations can also be expressed in terms of excess [SB] as [SB]-[WA]. A plot of [SB]-[WA] versus measured pH indicates the same steep rise in pH when the buffer capacity of the leachate solution weak acids is exceeded (Figure 10), e.g., for glasses of poorer durability. For durable glasses, the leachates are buffered at a neutral [SB]-[WA] of ~0 until experiencing a sharp break in the pH versus [SB]-[WA] curve at pH of ~10.8. This pH corresponds to the pH in the vicinity of the defense HLW high iron (Purex) glasses, while the EA glasses are in the pH range where excess base, [SB]_{ex}, dominates. The pH values corresponding to the loss of the [WA] buffer capacity in leachates, e.g., the pH where the break in the [SB]-[WA] versus measured pH curve occurs, are almost identical to the pKa calculated for the same glass leachates in Figure 9.

In summary, the [SB]-[WA] equilibrium drives the leachate pH that is manifested in the pH dependency of the leached layer and the phases that form, thereafter, by Ostwald ripening. Ostwald [132] suggested that the solid first formed from solution would be the least stable polymorph and that during the course of transformation of the unstable (or metastable) solid into a stable one, the system does not go directly to the most stable state (corresponding to the modification with the lowest free energy) but prefers to reach intermediate stages (corresponding to other metastable modifications) having the closest free energy to the initial state. This can be explained on the basis of irreversible thermodynamics, structural relationships, or a combined consideration of thermodynamics and structural variation with temperature and/or solution pH. Ostwald's rule is not a universal law but is only a possible tendency in nature. Therefore glass

^f $pH = pK_a + \log \frac{[base]}{[acid]}$

dissolution in a static or near static environment is pH dependent and so is the subsequent Ostwald ripening. Both the initial gel layer formation and the Ostwald ripening of that gel into secondary phases needs to be modeled as separate pH dependent processes during glass dissolution.

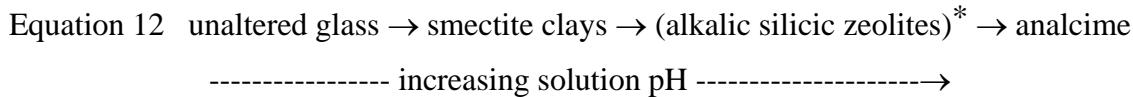
(2) Aging of Amorphous Gel Layers and the Return to the Forward Rate [40,41]

Experimental aging of the hydrated gel layers formed during Stage II glass dissolution has shown that the gel layer components age “in-situ” into either clay mineral assemblages or zeolite mineral assemblages [133,134,135,136,137]. To understand the aging of a leached glass (or glass ceramic GCM) gel layer into either clay or zeolite mineral assemblages, it is important to recognize that the hydrated gel layer exhibits acid/base properties that are manifested as the pH dependence of the thickness and nature of the gel layer [138]. The alteration of aluminosilicate gels (artificial or natural) to clay or zeolites is also pH dependent, with clay formation favoring less basic aging environments than zeolites [139]. Thus, if the solution pH changes while the gel ages, clay mineral species may convert into zeolite mineral species in response to an increase in pH.

The “in-situ” aging of aluminosilicate-rich leached layers in HLW glasses mimics the aging of aluminosilicate gels including artificially produced gels or those found in nature.

Aluminosilicate gels that were co-precipitated under controlled laboratory conditions were aged into a variety of natural clays (smectites, beidellites, saponites, saucanites and montmorillonites) [140,141,142]. Aluminosilicate gels found in natural geothermal systems in an alkaline environment were harvested and then aged in a laboratory to the zeolite analcime [143]. The alteration of aluminosilicate gels (artificial or natural) to clay or zeolites is pH dependent. Aging of leached gel layers in natural environments (e.g., weathering of altered rhyolitic (acidic) volcanic glass, has been shown to alter “in-situ” to both zeolites (clinoptilolite) and clays (smectite, montmorillonite), and sometimes opal (hydrated silica)).[143,144,145]

Conversely, sequential aging of nuclear waste glass gel layers that were enriched in iron under controlled laboratory conditions produced montmorillonite clay [146] and the “in-situ” formation of smectite clays has been determined to be dependent on the iron content of the dissolving glass [147]. The similarity of the gel layer formation and dissolution mechanism of iron-containing borosilicate waste glasses and natural basalt glasses containing iron has been noted by several researchers including Morgenstern [148], Ewing [149], Malow [150], Allen [151], and Jantzen [152]. In particular, the work of Allen [151] indicated that the alteration layer on basalt glass is formed of cryptocrystalline iron-rich clays grouped under the term “palagonite.” Likewise, the geochemical modeling (EQ3/EQ6) performed by Bourcier [153] on an iron-rich waste glass gel layer composition predicted the formation of notronite ($\text{Fe}_2\text{Si}_2\text{O}_7 \bullet 2\text{H}_2\text{O}$) the iron analogue of the Al-rich clay mineral kaolinite ($\text{Al}_2\text{Si}_2\text{O}_7 \bullet 2\text{H}_2\text{O}$). Additional comparisons of the aging sequences of basaltic glasses and nuclear waste glasses tested by the Vapor Hydration Test (VHT) have indicated the following aging sequences (paragenic trends) [136, 137]:



which upon further aging, including dehydration, may form anhydrous feldspars (i.e., K-rich and Na-rich species such as albite). Often the alkalic silicic zeolite phases do not appear to form and smectite clays are found to be in contact with analcime. The paragenetic sequence shown in Equation 12 occurs as the solution becomes more basic and more saturated with silica and alumina during static durability testing.

Recent studies by Muller [128] have characterized the clay (nontronite) and zeolite (phillipsite) on long-term (15 year) PCT testing. The analyzed composition of the nontronite was analyzed as $(\text{Na},\text{K})_{0.8}(\text{Fe},\text{Mg})_{1.3}(\text{Al},\text{Si})_4\text{O}_{10}$ and the phillipsite as $(\text{K},\text{Na},\text{Ca}_{0.5})_{1.2}(\text{Si},\text{Al})_8\text{O}_{16}\bullet 6\text{H}_2\text{O}$. In all cases the glasses exhibiting nontronite only leached at a steady state rate while glasses exhibiting zeolite formation returned to the forward rate. A higher leachate pH was found to favor zeolite formation as discussed above. Another important finding of this study was that the higher the pH the lower the Si/Al ratio in the zeolite phase (see Section V.2).

The waste glass gel layers are zoned (5-7 zones) and the paragenic sequences of the layers follow the sequence shown in Equation 12 depending on the pH. [136, 137] The smectite clays are always in contact with the unaltered glass while analcime is further removed [136, 137, 154]. Glasses rich in K are found to form KAlSi_3O_8 (orthoclase) in the surface layer and glasses rich in Ca form $\text{Ca}_4(\text{Si}_6\text{O}_{16})(\text{OH})_2\bullet 3\text{H}_2\text{O}$ (gyrolite), $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ (Hydroxy apatite), and/or $\text{Ca}_5(\text{OH})_2\text{Si}_6\text{O}_{16}\bullet 4\text{H}_2\text{O}$ (tobermorite) [155, 154]. For glasses containing U, a uranium silicate often forms such as $\text{K}_2(\text{UO}_2)_2(\text{Si}_2\text{O}_5)_3\bullet 4\text{H}_2\text{O}$ (weeksite) [154] or $\text{KNa}_3(\text{UO}_2)_2(\text{Si}_4\text{O}_{10})_2(\text{H}_2\text{O})_4$ [156].

(4) Donnan Membrane and Electrochemical Considerations

The gel layers that form during water-saturated durability tests appear to exhibit selective cation exchange (Donnan equilibrium, see 40 and 157) and entrap large positively charged cations such as Ca^{+2} , Nd^{+3} , U^{+4} in the negatively charged silicate gel layer (e.g., HLW glass zeta potentials are negative at all pH values greater than 2 as indicated in Figure 12). The Donnan equilibrium is pH dependent, the electrochemical charge on the gel layer is pH dependent, and condensation reactions of hydrated Si-OH and Al-OH bonds are likely pH dependent. In addition, any excess strong base $[\text{SB}]_{\text{ex}}$ can either stabilize or destabilize the gel layer. If the gel layer is destabilized in response to $[\text{SB}]\text{-}[\text{WA}]$ equilibria in the solution, the gel layer can begin to dissolve releasing Al^{+3} , Ca^{+2} , Nd^{+3} , U^{+4} to solution.

The results of a variety of studies [27, 40, 158, 159, 160, 161, 162, 163, 164, 165, 166, 167, 168] that examined glass leached layer compositions found the following:

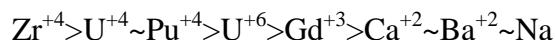
- Silica species are soluble in the leachate but also concentrate in the solution-gel

* These phases were sometimes but not always observed, e.g. Na-chabazite ($\text{Na}_2\text{Al}_2\text{Si}_4\text{O}_{12}\bullet 6\text{H}_2\text{O}$) or chabazite ($\text{CaAl}_2\text{Si}_4\text{O}_{12}\bullet 6\text{H}_2\text{O}$).

amorphous interface and in the gel reaction zone (from a combination of surface and sub-surface enrichment)

- Most alkaline earth species (Ca^{+2} , Sr^{+2} , Ba^{+2}), transition metal species (Mg^{+2} , Ni^{+2} , Fe^{+2} , Mn^{+2} , Co^{+2}), and other highly charged cations (Zr^{+4} , U^{+4} , Pu^{+6} , U^{+6} , Gd^{+3} , Fe^{+3} , Al^{+3} , Ce^{+4} , Nd^{+3} , Ce^{+3} , Cm^{+3} , Ti^{+4} , and Zn^{+2}) usually participate in glass surface layer formation as surface enrichment, sub-surface enrichment, or a combination of the two

This led to an empirical ranking of the elemental distribution of cations between the ionic field strength ($F = Z/r^2$ where Z is the atomic charge and r is the cation-oxygen atomic radius) in the gel reaction zone [157] and the retardation of certain species during leaching and the known sorption capacity onto silica gel.



Clearly, the composition and structure of the gel layer needs to be investigated further as the gel layer redefines the distribution of ion exchange sites, hydrolysis sites, and the access of water to those sites. Condensation reactions may drive the gel layer to exhibit Donnan equilibrium and retain the high Z/r^2 cations or the cations may merely be retained by electrochemical forces, e.g., zeta potential.

V. MODELING USING GLASS MRO STRUCTURE

(1) NORMCALC™: PREDICTING GLASS MRO

The c.r.s. species chosen for HLW glass are based on the basalt natural analogue system, $\text{Na}_2\text{O}\text{-SiO}_2\text{-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$ where Li^+ and K^+ are assumed to substitute for Na^+ . [60] The c.r.s. species are also consistent with known measurements and/or molecular dynamic (MD) simulations in simple three and four component glass systems. A computer model, NORMCALC™, was developed [60] to calculate the c.r.s. components of waste glasses based on the basalt analogue system. The NORMCALC™ program is based on the principle of normative mineral calculations used in geochemistry (e.g., the CIPW calculation) for calculating the hierarchy of mineral species that would form from a molten magma if it were allowed to completely crystallize. Adaptations were made for the boron species in HLW glasses that are not normally present in natural magmas and glasses.

NORMCALC™ was used to demonstrate that the c.r.s. mineral species in the glass (solid) are related to the elements in each glass when the composition is expressed in terms of atomic ratios. Geochemical modeling of the leachate (solution) chemistry for the same glasses calculates what phases are saturated in the leachates and most likely to form in the leached surface layers. These phase assemblages are then related to the same atomic ratios in the glass that were predicted from NORMCALC™. This establishes a relation between the glass (solid) composition and the leachate (solution) composition and the leached layer formation based on the atomic ratios in the parent glass. The coupled geochemical and NORMCALC™ modeling was then applied to both

short-term and long-term PCT (ASTM C1285) to demonstrate that the relationship holds for both short-term and long-term glass dissolution.

The stoichiometry of the c.r.s. (in terms of atomic ratios of species such as Al and Si) is proportional to the stoichiometry of the activated surface complexes[†] that form on the glass during dissolution. For comparison, the Al:Si stoichiometry of the activated complexes found by Helgeson et. al. [53] on crystalline albite had the same atomic ratios as the parent albite. Similarly, in 1996 Gin [169] determined that the dissolution kinetics of a simulated HLW glass were related to an (Si-Al) complex in solution (modeled as the IAP, $a\text{Si}^{0.88} \times a\text{Al}^{0.12}$, where the ratio of Si:Al in the IAP was related to the Si:Al ratio in the glass (normalized to 1). Thus, it is likely that the determination of the c.r.s. stoichiometry using NORMCALC™ can provide a link to the surface reactions and complexes that are controlling HLW glass dissolution rates. See also the discussion below of the simplified SON68 glass with 36% albite c.r.s. compared to the chemical analysis of the gel layer which when modeled with NORMCALC™ indicated ~41-44% albite (Section V.3).

(2) ACT™: PREDICTING GLASS DURABILITY FROM ACTIVATED COMPLEXES

Another computer model, Activated Complex Theory (ACT™), was developed to model the proton exchange between a solid (glass) and the solution (leachate), as governed by the law of mass action. ACT™ was coupled with NORMCALC™ in the following manner: ACT™ expresses the glass composition as atomic ratios, e.g., Al/Si, Fe/Si, and B/Al, where higher fractions of more polymerized albite c.r.s. in the glass would have an Al/Si of 1/3 while higher fractions of more soluble nepheline c.r.s. in a glass would have an Al/Si of 1/1; the activated complexes should retain a similar atomic stoichiometry. [53] NORMCALC™ modeling and the geochemical modeling have shown that the glass composition expressed as atomic ratios link the solid and solution chemistry. Therefore, an ACT™ atomic ratio model was developed [60] to determine short-term HLW glass dissolution. It is of interest to note that ACT™ would predict that glasses with a lower Si/Al ratio, e.g., more nepheline than albite c.r.s., would be less durable and the pH would contain excess [SB] in agreement with the findings of Muller et. al. [128] that glass leachates with a higher the pH formed zeolite phases with a lower Si/Al ratio which implies that these zeolites had aged from a gel and glass with a corresponding composition containing lower Si/Al c.r.s. phases.

In ACT™ [60] composition ratios were also found to be related to long-term glass durability, e.g., leach layer formation and the tendency of a glass to dissolve linearly by steady state kinetics

[†] Activated complex control of glass durability treats glass dissolution as a rapid removal of univalent and divalent cations from the near surface by ion exchange followed by the slower exchange of Al^{3+} for 3H^+ protons in solution. The Al^{3+} proton exchange does not destroy the glass framework but it partially liberates three adjoining silica tetrahedra to which it is bonded. It is the detachment of the partially liberated silica that is the rate determining step, i.e. partially detached silica dissolves more readily than bonded or “attached” tetrahedral silica. The glass dissolution is, therefore, proportional to the concentration of partially detached glass structural species, which is linked through the law of mass action to the relative concentration of atomic species in a glass via the cation/proton exchange reactions.

or non-linearly by returning to the forward rate of dissolution. This was found by relating the phases predicted by geochemical modeling of filtered leachate solutions to the atomic ratios of key glass constituents, e.g., Al, Fe, and Si. In this manner atomic ratios were used to distinguish between those glasses whose dissolution will slow to a steady state rate (those enriched in Fe_2O_3 that primarily form smectite clay leached layers) versus those that may return to a high forward dissolution rate over time (those glasses high in Al_2O_3 with certain favorable Na/Al ratios for analcime or zeolite formation) as shown in Figure 11. These predictions are also in agreement with the experimental determinations of Muller et. al. [128] on 15 year PCT tests of HLW glasses.

(3) ACT™: PREDICTING OSTWALD RIPINING AND THE RESUMPTION OF DISSOLUTION

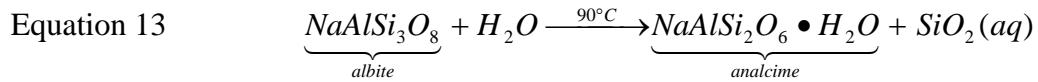
The concentrations of c.r.s. mineral moieties such as albite ($\text{NaAlSi}_3\text{O}_8$), reedmergnerite (NaBSi_3O_8), jadeite ($\text{NaAl}_2\text{Si}_2\text{O}_6$), nepheline (NaAlSiO_4), and acmite ($\text{NaFeSi}_2\text{O}_6$) in a HLW glass are estimated from the glass composition using NORMCALC™. These compositions can be expressed on a ternary phase diagram composed of the end members Si, Al, and Fe in atomic % when there is sufficient alkali in the glass to form any of the potential mineral moieties. A ternary of Si, Al, and Fe in atomic % is shown in Figure 11 for 217 glass compositions. The compositions of several Belgian/French, Russian, and US HLW glasses are overlain on Figure 11.

Figure 11 demonstrates that glasses with high concentrations of albite (Ab) and acmite (Ac) c.r.s. are predicted to form ferrosilicate clay minerals on the leached glass surface and these glasses should not return to the forward rate because aluminosilicate phases are not predicted to form. Glasses with low concentrations of albite (Ab) have more jadeite (Jd) c.r.s. and insufficient Si to form acmite c.r.s. In other words, the Al:Si ratio of the glass and the activated surface complexes are more favorable to the formation of analcime (zeolite) that has the same Al:Si ratio as Jd. Those glasses with more Jd or Ne component are thus more likely to return to the forward rate of dissolution (Stage III; Figure 11). Most of the Belgium/French, and the Russian and US burial glasses all have sufficient Si (at%) relative to Al (at%) and Fe (at%) to maintain steady state dissolution.

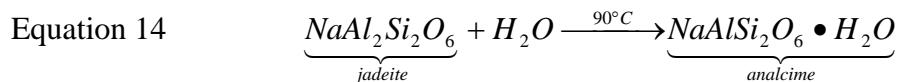
The simplified SON68 HLW glass studied by Munier and Crovisier [170] is a particularly interesting example as glass and gel composition data are available. NORMCALC™ predicts this simplified glass to be highly polymerized containing ~ 36 wt% albite and 50 wt% reedmergnerite. The gel layer composition calculated (using a geochemical code known as KINDIS) from the 30-180 day leachate data coupled with NORMCALC™ demonstrates that the gel is ~42-44 wt% albite and 56-58 wt% residual SiO_2 . This implies that the HLW gel retains the Al:Si ratio of the c.r.s. albite but loses Na from the albite and the reedmergnerite c.r.s. to solution and loses B from the c.r.s. reedmergnerite to solution leaving a gel layer composed of albite and silica gel residua. In Figure 11 only the SAN60 and SM527 glasses are predicted to return to the forward rate (Stage III dissolution) and both SAN 60 [110] and SM527 [171] have been experimentally shown to do so.

Another interesting glass durability study is the fractured roman glass block altered for 1800 years in seawater that was studied in 2008. [172] The leached layer was analyzed and found to be composed of stevensite^f (an Mg rich smectite clay). Clay formation would be predicted from the glass bulk composition given in 172 when plotted on Figure 11 and NORMCALC predicts that albite/orthoclase, (Na,K)AlSi₃O₈, and excess Na₂SiO₃, CaSiO₃, and residual SiO₂ c.r.s. are the predominant polymerized c.r.s. mineral moieties with ~ 1 wt% acmite (NaFe₂SiO₆). Because this composition is silica rich and alumina poor it will not form jadeite or nepheline c.r.s. and thus will not be prone to form analcime or other zeolites as demonstrated below.

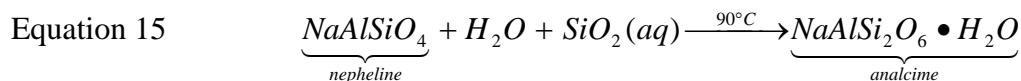
The aging of the c.r.s. mineral moieties in a glass can also be examined using thermodynamics. If a glass is primarily an albite glass, it cannot form analcime by reaction with water as the free energy of the reaction is not energetically favored, e.g., the free energy of formation of Equation 13 at 90°C is +23.5 kJ/mol.



If a glass is primarily jadeite, it is energetically favored ($\Delta G_{\text{fm}} = -9.8$ kJ/mole at 90°C) to form when reacted with water (Equation 14). Note also that the Al:Si ratio of Jd and analcime are the same so it is also structurally favored.



If a glass is primarily nepheline, a source of aqueous SiO₂ is needed for the formation of analcime in addition to H₂O (Equation 15) and the reaction is energetically favored ($\Delta G_{\text{fm}} = -38.2$ kJ/mole at 90°C)

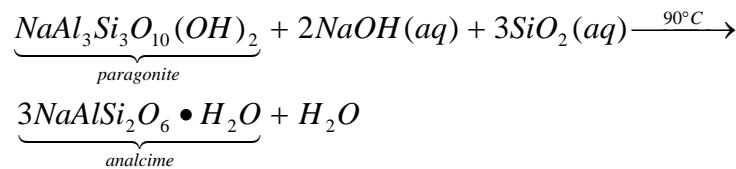


In the presence of excess OH⁻, nepheline glass moieties can form paragonite (Equation 16) where the formation of paragonite from nepheline is energetically favored ($\Delta G_{\text{fm}} = -139$ kJ/mole at 90°C). In turn, paragonite can form analcime by reaction with more base and a source of aqueous SiO₂ (Equation 17) and this reaction is also energetically favored ($\Delta G_{\text{fm}} = -170$ kJ/mole at 90°C).

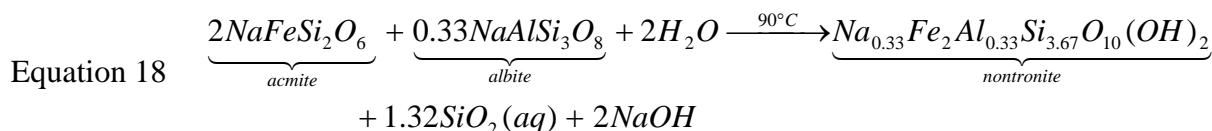


^f For this glass calcite (CaCO₃) was also found to be co-precipitated and calcite is strongly related to the mineral dolomite (Ca,Mg)CO₃. According to thermodynamic calculations, stevensite is stable at the expense of dolomite in a silica-rich and CO₂-poor environment.[174]

Equation 17



However, if a glass has sufficient acmite c.r.s. in it and enough of a highly polymerized albite c.r.s. then the formation of nontronite (a Fe-rich clay mineral) is highly energetically favored ($\Delta G_{fm} = -604$ kJ/mole at 90°C) and the glass should continue to leach at steady state rate (Equation 18). No excess aqueous SiO₂ is needed for this reaction to occur.



Thus glasses with insufficient Si to form albite moieties form jadeite or nepheline moieties and are more susceptible to forming analcime and returning to the forward rate of dissolution via Equation 14 to Equation 17 than glasses with sufficient Si to form albite and sufficient Fe to form acmite (Equation 13 and Equation 18) that remain at the steady state of dissolution.

VI. CONCLUSIONS

The durability of glass in aqueous solution is a complex but dynamic equilibrium controlled by the composition and molecular structure of a glass. The molecular structure controls the glass durability by establishing the distribution of ion exchange sites, hydrolysis sites, and the access of water to those sites. In turn, the glass composition controls the molecular structure.

Thermodynamic models are evolving to include the effects of glass MRO in the form of crystalline reference states (c.r.s.) on glass dissolution. The c.r.s. can also be used to determine if a clay-like or zeolite-like Ostwald ripening of the gel layer formed during dissolution will occur. Kinetic models have remained mostly mechanistic but are also now evolving to include the activation energies associated with MRO bond hydrolysis.

What remains problematic is the nature and structural control that the altered gel layer provides; it redefines the distribution of ion exchange sites, hydrolysis sites, and the access of water to those sites. The in-situ aging of the gel layer by Ostwald ripening produces more stable mineral assemblages on the glass surface versus the unstable or metastable gel. The more stable mineral forms (clay or zeolite) will have a lower solubility (e.g., lower K_{sp}) than their precursors and the concentrations of the final mineral components will be significantly depleted in the leachate. Thus, the equilibrium between the aged (ripened) gel layer and the leachate is re-established and the dissolution may return to a rate similar to the forward rate. If the final stable mineral form contains strong base precursors (Na, P, Ca, Mg), then the leachate pH may be increased or decreased. If excess strong base is available then the pH will increase which is associated with the return to a rate similar to the forward rate. Knowledge of the types of final mineral form

assemblages, and their respective K_{sp} values is needed to enable a determination of whether a specific HLW glass will return to the forward rate (e.g., evaluation of the K_{sp} of **Equation 13** to **Equation 18** presented above).

It should be noted that the process of dissolution, aging of the gel, and the formation of stable minerals from the gel, will eventually result in a final mineral assemblage that is more stable than the original glass. Clearly more research is needed in terms of the composition and structural nature of the gel layer, how it ages, and whether the mineral assemblages formed sequester and/or sorb the radionuclides of concern to the environment. This would eventually allow the final mineral phases, which have inherently low solubility, to be used to model long-term environmental release for thousands of years.

VII. ACKNOWLEDGEMENTS

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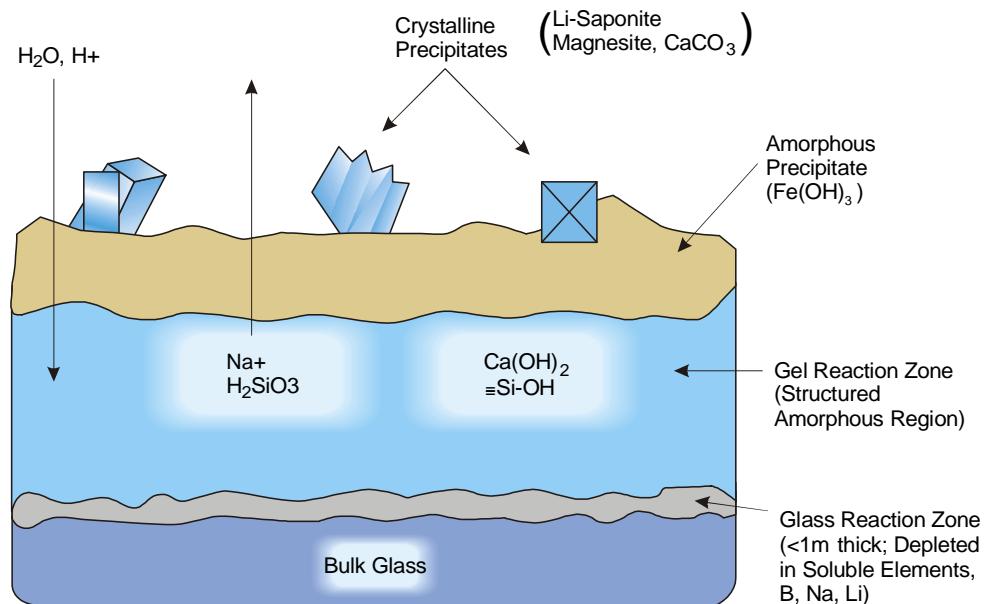
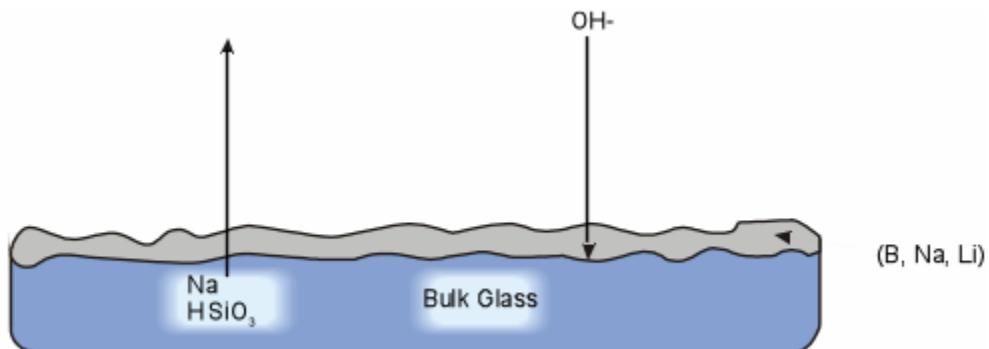


Figure 1 a Schematic diagram of glass dissolution mechanisms (ion exchange and matrix dissolution) in aqueous solution, coupled with both hydrated amorphous surface layer formation and crystallization/precipitation from solution [27, 173].



- b Schematic diagram of the glass dissolution mechanism known as “accelerated matrix dissolution.” In this mechanism, the excess strong base in the leachate released by the ion exchange mechanisms attacks the glass surface layers, including the gel layer, and makes the glass appear to have little or no surface layer.

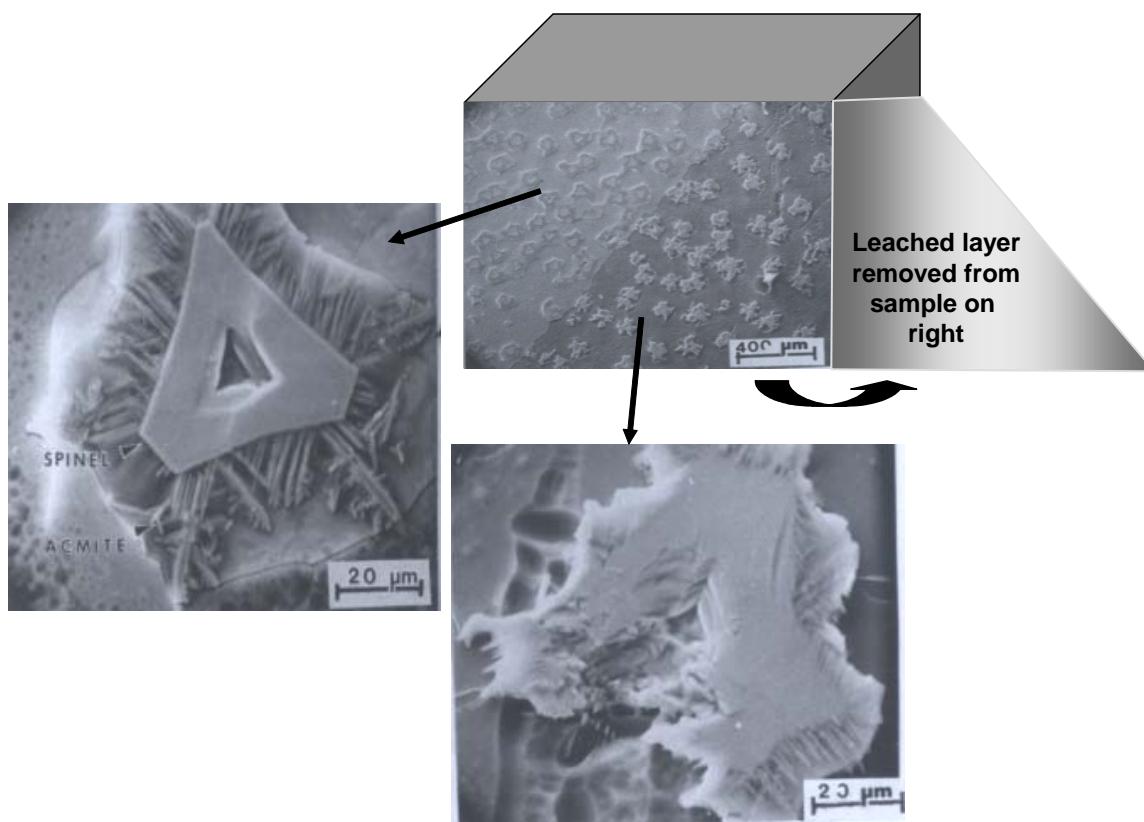


Figure 2. Devitrified glass after 28 days leaching in deionized water (ASTM C1220). Leached layer removed by tape to expose the preferential grain boundary dissolution around iron ferrite spinel crystals in a simulated HLW glass (after 61).

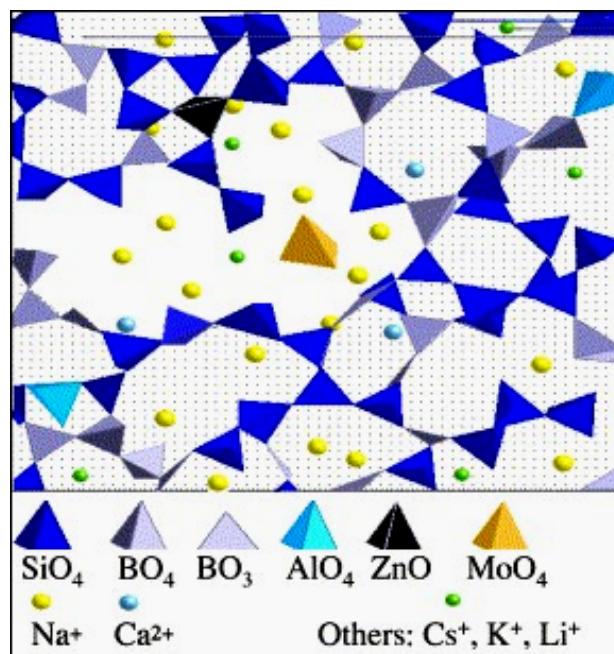
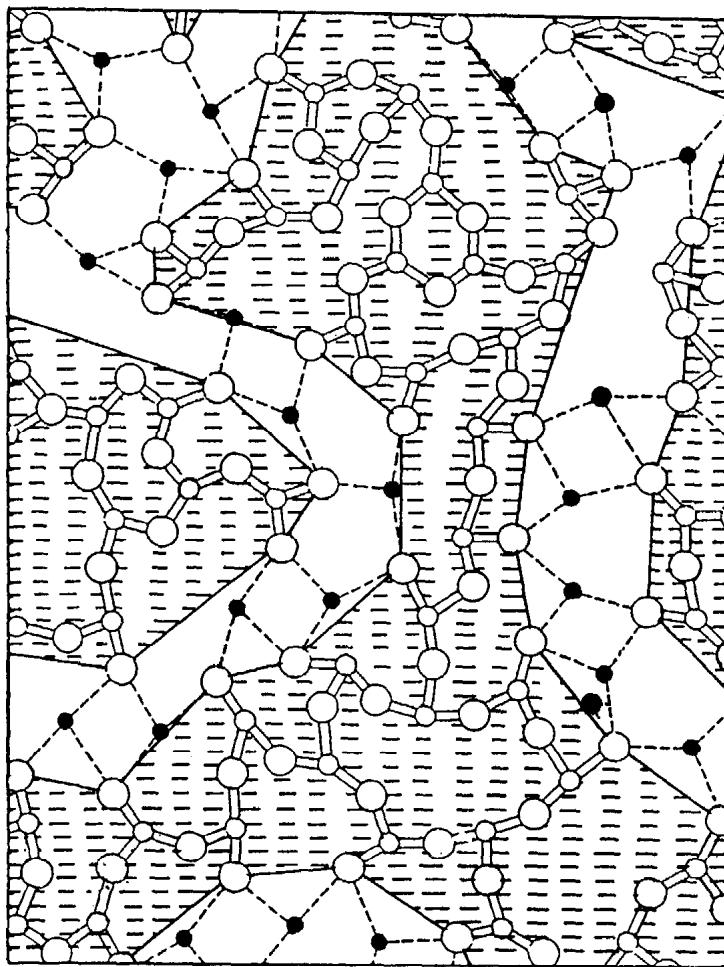


Figure 3. Polymerization of SRO and MRO in the atomic structure of glass. Unshaded region shows formation of an alkali molybdate cluster [from 81].



● Modifying Cations (M) ○ Network Formers (G) ○ Oxygen atoms

Figure 4. A modified random network (MRN) for a glass of nominal composition $M_2O_3(G_2O_3)_2$, where M represents the modifying cations and G represents the tetrahedral cations. Covalent bonds are shown by the solid lines and ionic bonds by the dotted lines. The dashed regions are defined by the boundary which runs along the G–O (i.e., non-bridging) bonds. The undashed regions represent the percolation channels defined by the M–O bonds that run through the glass network (from Greaves, 89).

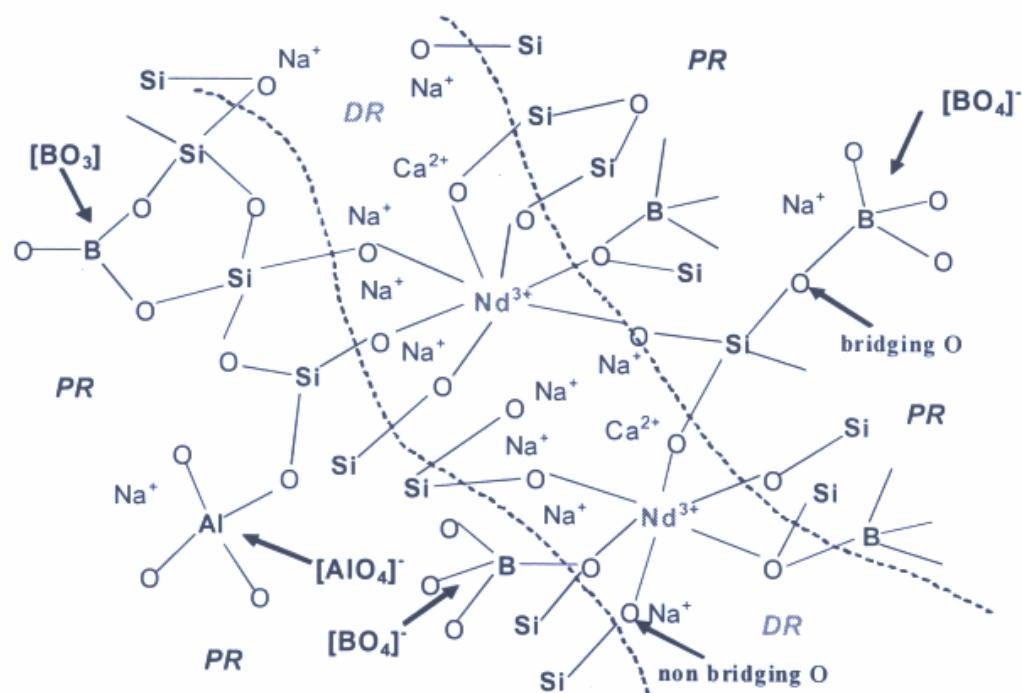
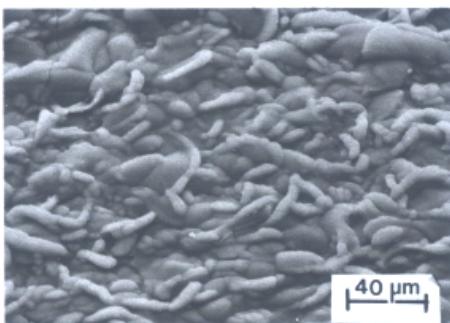


Figure 5. Proposed polymerization of SRO and MRO in the atomic structure of a French HLW rare earth bearing aluminoborosilicate glass . Na^+ , Ca^{2+} and Nd^{3+} exist in the proposed percolation channels [from 6].

GEL LAYER AT GEL-GLASS
INTERFACE



GLASS AT GEL-GLASS
INTERFACE

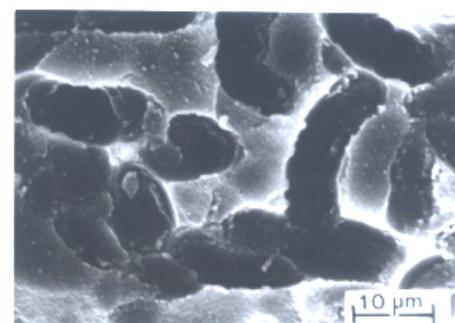
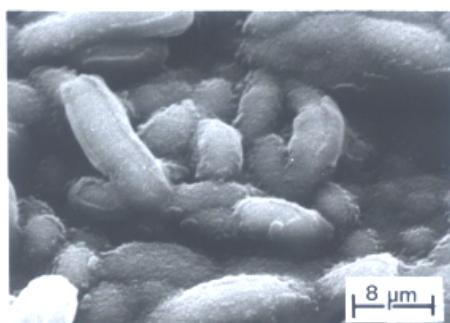
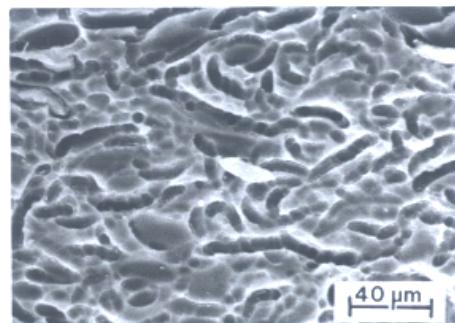


Figure 6. Glass morphology and gel morphology after leaching simulated HLW glass SRL 131 for 28 days in ASTM C1285 deionized water. Dissolution appears to follow percolation channels in the glass (right upper and lower figures). The leached layer had been removed with tape exposing the leached glass interface with the gel layer and allowing the underside of the leached layer that adhered to the tape to be studied (left upper and lower figures).

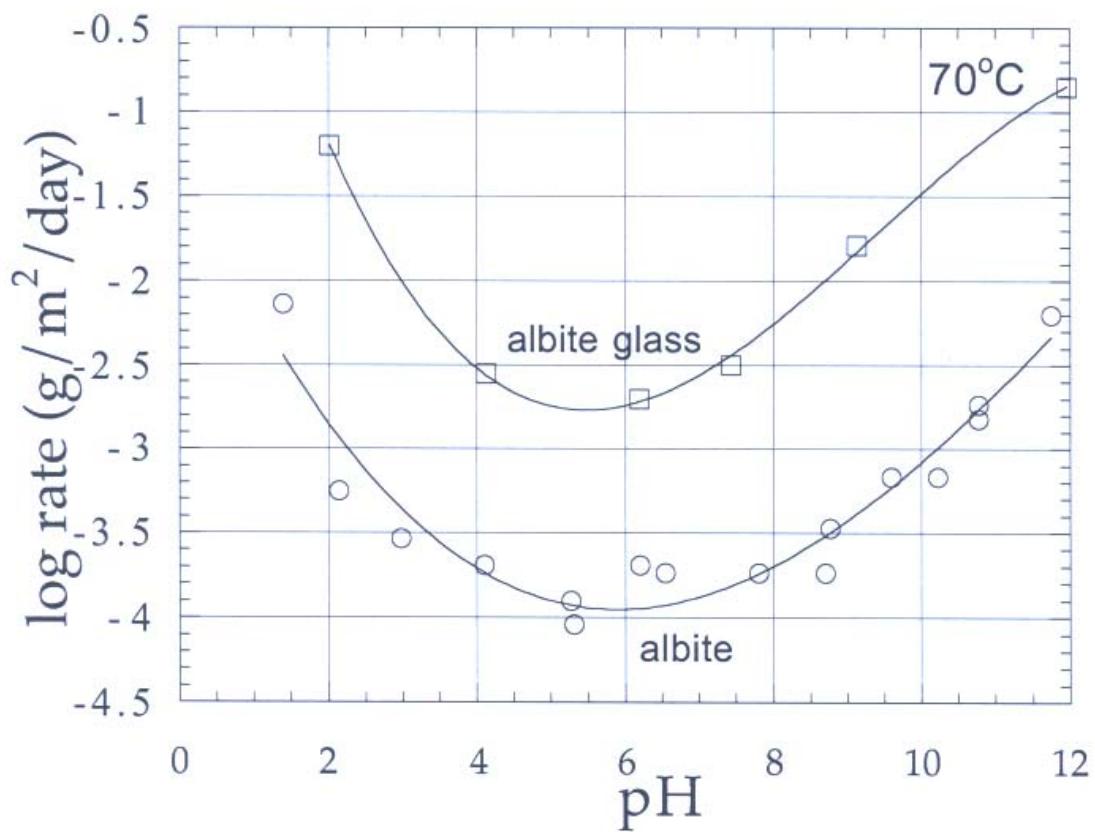


Figure 7. Comparison of dissolution rates of crystalline albite vs. albite glass from SPFT testing. [96]

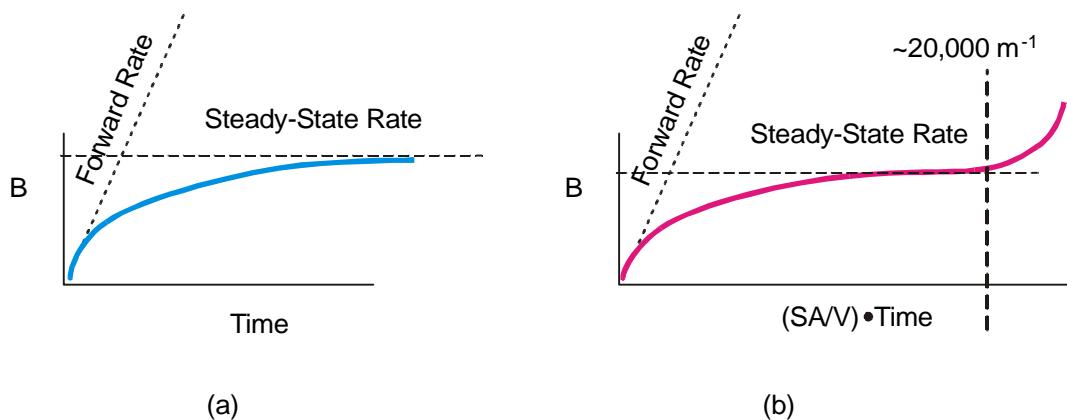


Figure 8. (a) Parabolic behavior of the diffusion of a soluble species out of the glass through an increasingly thick surface layer [114] (b) Acceleration of glass durability tests using glass surface area (SA), leachant volume (V), and time. Acceleration appears to follow parabolic diffusion kinetics until SA/V is $\sim 20,000 \text{ m}^{-1}$ when the glass dissolution mechanism appears to change reverting to a rate similar to the forward rate but likely controlled by precipitation of secondary phases.

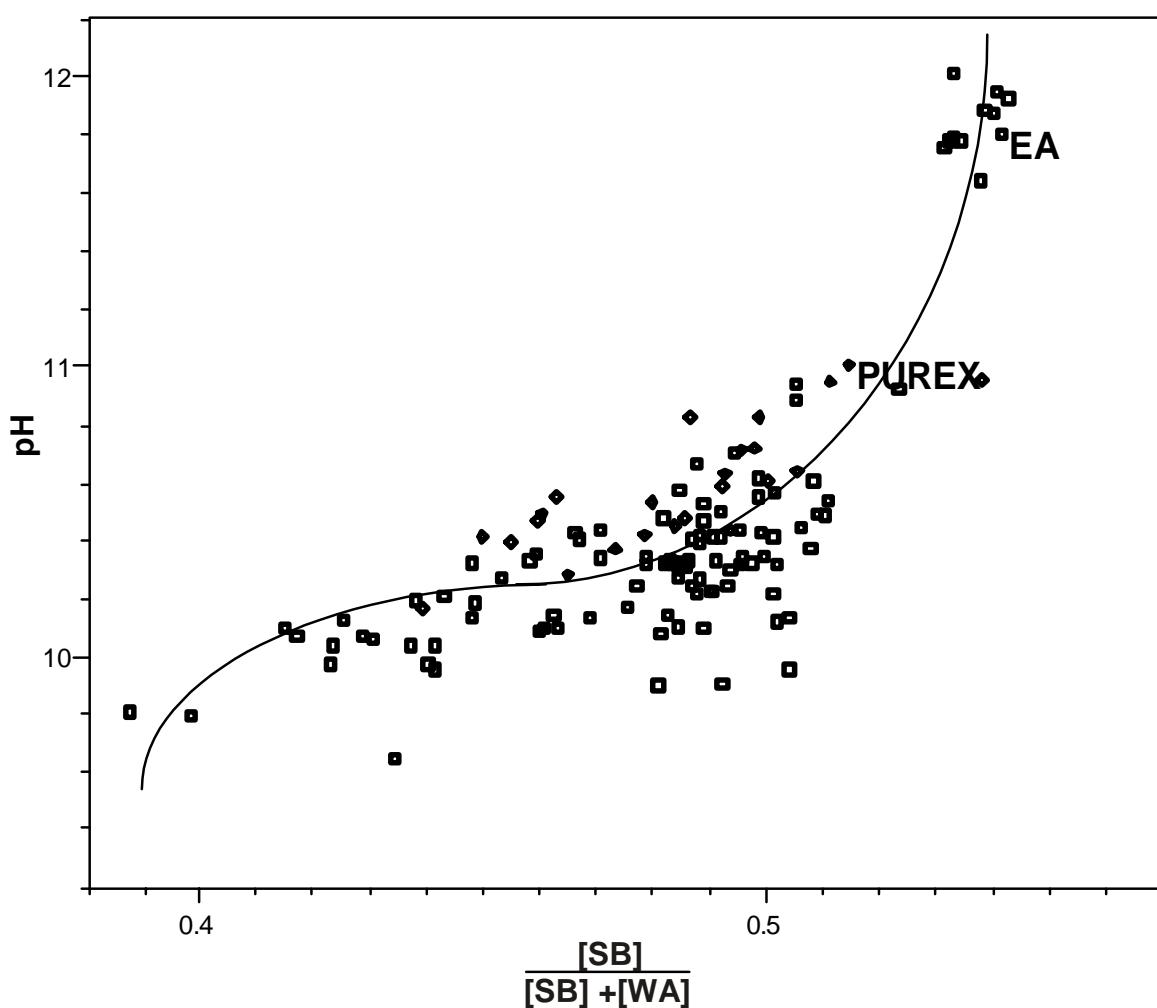


Figure 9 PCT leachate concentrations for HLW glasses from 40 expressed as the measured leachate pH versus the parameter α defined as $\alpha \equiv [\text{SB}]/([\text{SB}] + [\text{WA}])$ in millimoles/L versus. Note that the concentration-pH diagrams take on the general shape of a buffer curve. Note that the effective pK_a of the leachate equilibria can be estimated at $[\text{SB}]/([\text{SB}] + [\text{WA}]) = 0.5$.

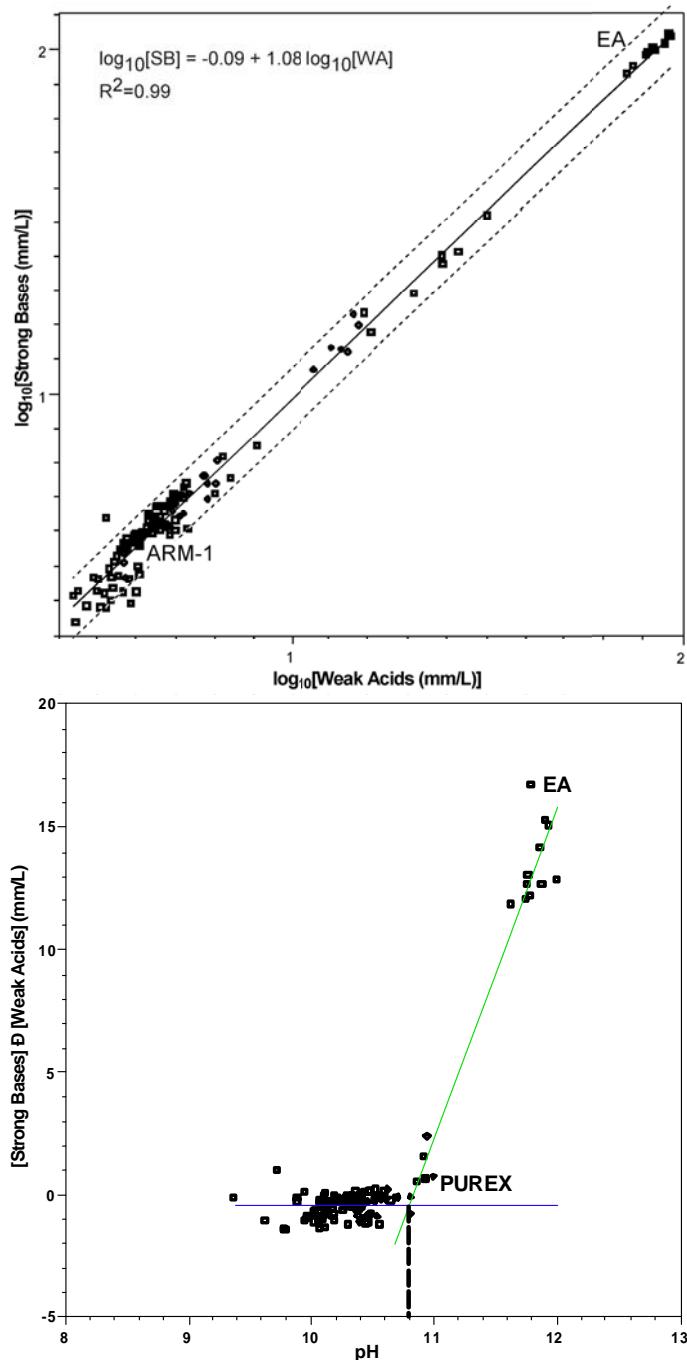


Figure 10 (top) Electrical neutrality between strong base (OH^- generators) and weak acids (H^+ generators) in 131 HLW glass leachates tested using the PCT (ASTM C1285). The dotted lines are the individual 95% Upper Confidence Limits (UCL) and the 95% Lower Confidence Levels (LCL). (bottom) Graphical representation of the effects of excess leachate strong base, expressed as moles $[\text{SB}] - [\text{WA}]$, on the measured pH of 131 HLW glasses. [39] For homogeneous glasses the leachates are buffered at a neutral $[\text{SB}] - [\text{WA}]$ of ~ 0 until a sharp break in the pH versus $[\text{SB}] - [\text{WA}]$ curve occurs at pH of ~ 10.8 .

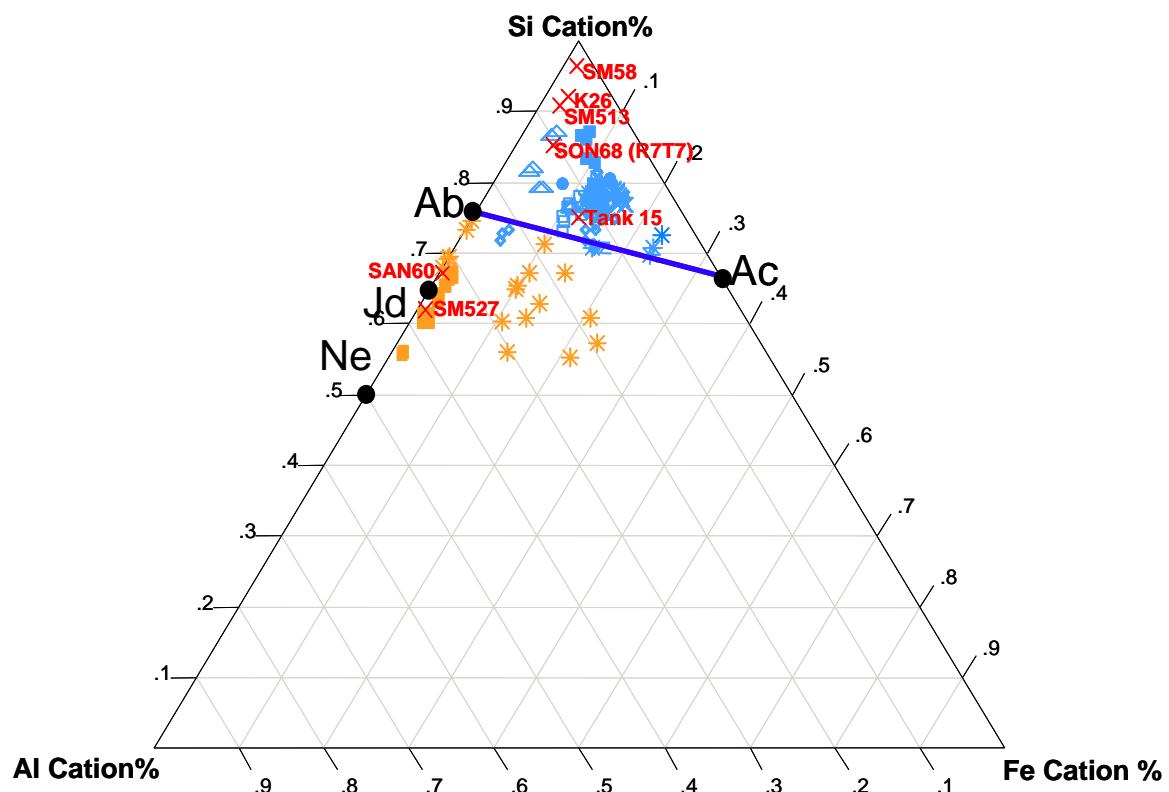


Figure 11 Predicted performance of the burial glasses in terms of the return to an apparent forward rate. Glasses below the Albite (Ab)-Acmite (Ac) join are predicted to form analcime or paragonite and return to the forward rate (Stage III) while glasses above the Ab-Ac join are predicted to form nontronite clays and/or ferrite phases and leach at steady state (Stage II) rates.

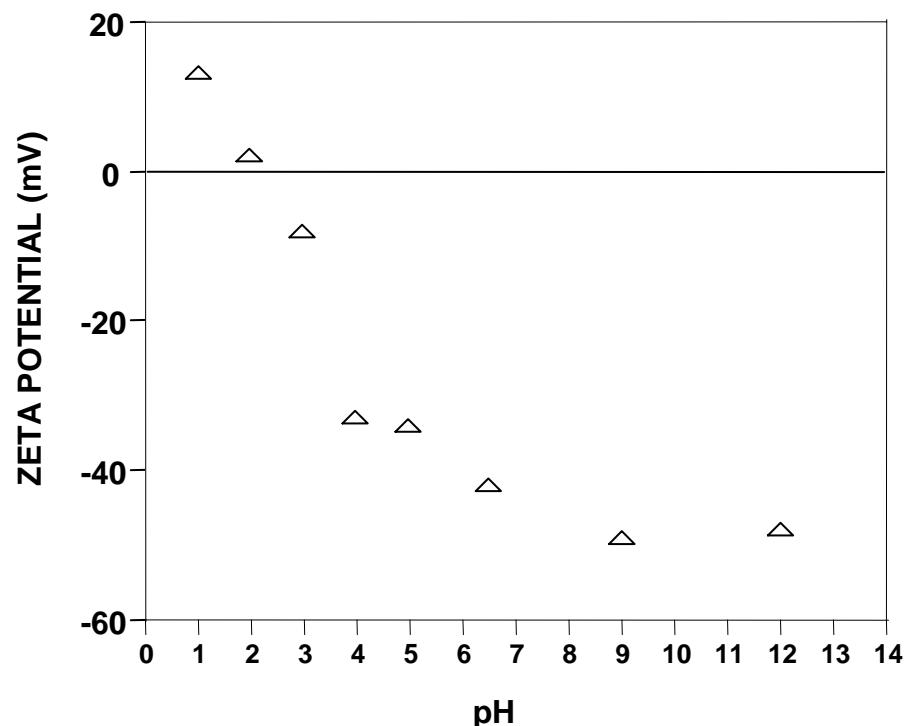


Figure 12. Zeta potential for crushed (37-45 micron) SRL 165 glass measured in water adjusted with HCl (acidic) and NaOH (basic) to create different pH regimes.

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