Project Title: **A literature survey on glass corrosion and its relationship to mechanical performance**

Submitted to: Bryan Kim, Director of Engineering, Pressure Products Company, Inc.,
4540 Washington Street West, Charleston, WV 25313

Prepared by: Matthew Hall (Consultant), Associate Professor of Biomaterials and Glass Science,
Kazuo Inamori School of Engineering at Alfred University, 2 Pine Street, Alfred, NY 14802

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§ 1. INTRODUCTION

This document is intended to address two principal topics: 1) Corrosion behavior of glasses and 2) The link between glass corrosion and mechanical performance. A general overview will be provided on the factors that commonly influence glass corrosion, including intrinsic factors such as glass chemistry and extrinsic factors such as temperature, pH, electrolytes, *etc.* A thorough treatment of the mechanical properties of glass is beyond the scope of this document, although sufficient background information will be provided in order to appreciate the subsequent discussion of phenomena such as stress corrosion cracking.

As a starting point, it is worth noting that the seemingly simple term "glass" is actually quite misleading. Glass is not a uniform substance – that is, the glass used to fabricate the screen of a mobile phone is not equivalent to the glass used in the windshield of a car, which in turn is not equivalent to a glass fiber that transmits optical communications data, and so on. With that said, general statements can often be made about glasses that fall within particular compositional families. The information in this document will be restricted to silicate glasses – that is, glasses in which SiO_2 is the majority component. Particular attention will be applied to archetypical silicate glasses such as fused silica, sodium lime silicate (SLS) glass, and borosilicate glass. It should be noted that this terminology is somewhat loose. For example, the term "borosilicate glass" may not specifically refer to the exact borosilicate glass employed by Pressure Products in fabricating sight glasses.

§ 2. GLASS CORROSION

§ 2.1. Mechanisms of Glass Corrosion

The specific details of the corrosion processes that take place for a specific type of glass under a specific set of conditions can vary widely from case to case. As a result of this strong dependence on specific conditions, the chemical durability of a glass is not a true, singly valued property like density or refractive index. Nonetheless, several general mechanisms of corrosion are often found to occur – for example:

- Ion exchange – Mobile cations (*e.g.*, weakly bound network modifiers such as Na^+, K^+, *etc.*) can exchange with cations in a corroding medium, including hydronium ions (H_3O^+) that are naturally present in water.
- Network hydrolysis – Network modifiers are not the only component of a glass susceptible to corrosion. The Si-O-Si bonds that comprise the glass network can also be ruptured by a hydrolytic mechanism to produce silanol groups – *i.e.*, hydroxyl groups bound to silicon ions (Si-OH)
- Surface precipitation – In certain cases, the corrosion process can lead to the formation of precipitation products at the glass/solution interface. The driving force for precipitation can arise from more than one source. For example, corrosion products from the glass can be extracted in such great quantities that super-saturation is achieved.

The actual corrosion process that is observed will depend on the rate and extent to which these mechanisms operate. Glass dissolution processes that are observed in practice can be categorized according to five general types (Hench and Clark, 1978):

- Type I – characterized by a very slight reaction with an aqueous environment, resulting in a modified surface that is perhaps on the order of 1 nm in depth. The reaction of fully dense fused silica, a highly durable glass, with water under ambient or near-ambient conditions would generally be characterized as a Type I process.
- Type II – ion exchange reactions between alkali and alkaline earth ions in the glass (*e.g.*, Na^+, Ca^{2+}) with hydronium ions in the aqueous medium characterize first stage of the Type II dissolution process. This leads to the formation of a surface layer that is depleted of network modifier ions and a now hydrated silica-rich “gel layer”. This silica-rich gel layer will also undergo some level of network hydrolysis, although not to an extent that causes significant

network dissolution. Typical examples of Type II processes would include SLS and borosilicate glasses exposed to moderately acidic to neutral pH conditions.

- Type III – a glass undergoing a Type III corrosion process initially exhibits the same features of a Type II process (*i.e.*, ion exchange and network hydrolysis to create a silica gel layer on the surface). However, a Type III process will also exhibit secondary film formation on top of the silica-rich gel layer. This secondary film may form as the result of precipitation at the solution/glass interface. In certain cases, a Type III corrosion event can be desirable since the secondary film helps to passivate the surface by inhibiting further corrosion.
- Type IV – glasses containing an insufficient concentration of network formers (see § 2.1 for more information) or exposed to very high levels of hydronium ions are likely to undergo a Type IV process. In this case, a compositionally distinct surface film is formed, similar to Type II and III dissolution processes. However, the modified surface layer is unstable and does not provide sufficient protection for the underlying bulk glass. As a result, significant attack of the glass network is observed, resulting in eventual total dissolution.
- Type V – also called congruent dissolution, a Type V process is characterized by complete network dissolution of the glass. The corrosion of the glass surface is sufficiently rapid and complete that no compositionally distinct surface layer is formed. Instead, the exposed surface dissolves dissolves fully into the adjacent corroding medium.

§ 2.2. Influence of glass composition

The constituents of glasses are frequently defined on the basis of their oxide equivalents. For example, a typical SLS glass is largely comprised of Na_2O, CaO, and SiO_2 (minority additions frequently include MgO and Al_2O_3). Three generic categories are used to classify the role of these oxide constituents within the structure of a glass: network formers, network modifiers, and intermediates.

Network formers such as SiO_2 and B_2O_3 are capable of forming a glass on their own with relative ease. In the case of pure SiO_2 glass, also called fused silica or fused quartz, the structure of the glass consists of a random network of Si-O-Si bonds. The oxygen anions participating in a bond with two network forming cations such as Si^{4+} are called bridging oxygens (BO). Fused silica is a remarkably rugged substance with many excellent technical properties. Unfortunately, it also difficult to form owing to the high temperatures that are required to bring the viscosity down to a point that is suitable for forming. This extremely high viscosity is correlated with high degree of so-called "network connectivity" that is directly proportional to the BO content of the glass. As a result of the energy intensive processing that is required for melting, the cost of fused silica will also tend to be relatively high.

Network modifiers such as Na_2O, K_2O, MgO, and CaO enable less energy-intensive glass melting by reducing network connectivity through the formation of non-bridging oxygens (NBO) – *e.g.*, the introduction of Na_2O disrupts the BO present in Si-O-Si bonds to form NBO via Na-O-Si bonds. The strength of the bonds containing NBO will generally be lower than BO-based bonds, thereby causing a relative decrease in viscosity of a glass forming melt. The introduction of network modifiers can unfortunately have deleterious effects on other glass properties. In particular, the chemical durability of a silicate glass will generally decrease with increasing network modifier concentration. However, it should be noted that not all network modifiers are created equal. For example, an archetypal SLS glass contains at least two distinct network modifiers (Na^+ and Ca^{2+}) that facilitate melting of the glass under relatively non-challenging conditions. The choice to use a mixture of Na^+ and Ca^{2+} is motivated by the fact that the divalent cation stabilizes the structure of the glass relative to a case in which a purely monovalent modifier such as Na^+ is present. The stabilization that is provided by the Ca^{2+} cation helps to increase the durability of the SLS glass, thereby making possible its use in applications such as windows as food grade containers.

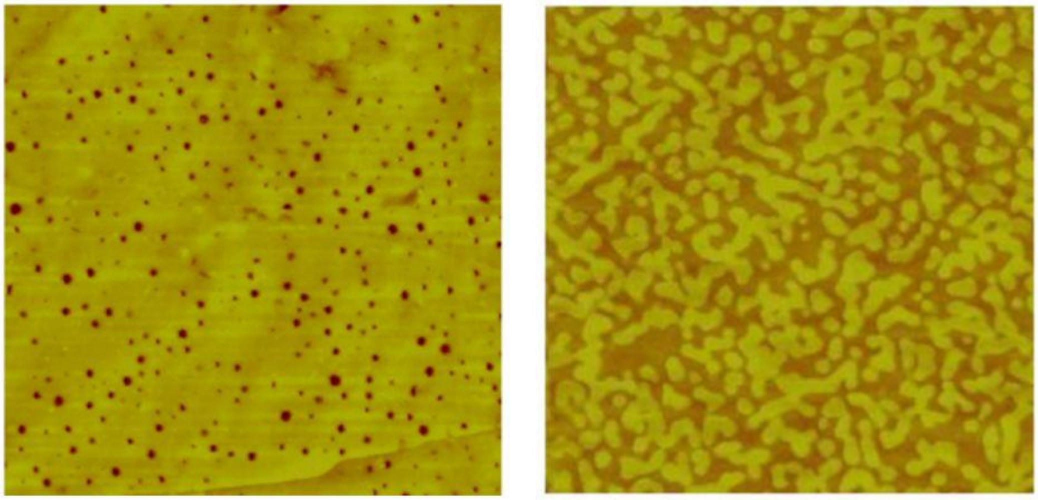
Finally, intermediate oxides such as Al_2O_3, ZrO_2, and TiO_2 are regarded as compounds that enter the glass network (thereby increasing network connectivity), although they cannot readily form a glass in isolation such as SiO_2. In general, intermediate oxides are found in relatively minor levels as additives to glasses containing a majority of a conventional glass network former. The addition of appropriate levels of intermediates such as Al_2O_3 can have any beneficial effects, including careful tuning of thermal properties (*e.g.*, viscosity, coefficient of thermal expansion), resistance to devitrification, and increase of chemical durability.

Composition can also pre-dispose a glass to undergo a process known as phase separation in which two or more chemically distinct phases are present. There are two general morphologies associated with phase separation: 1) droplet in matrix and 2) interconnected. A glass exhibiting phase separation with a droplet in matrix morphology will consist of isolated droplets of one composition dispersed throughout a continuous matrix of a different composition (see Figure 1a). A glass exhibiting phase separation with an interconnected morphology will consist of two interwoven continuous phases (see Figure 1b). The composition and thermal history of a glass will dictate the morphology of the phase separation, although adjustment of composition is generally used in practice to control the extent and character of phase separation.

Conventional high durability borosilicate glasses (such as those used in the fabrication of sight glasses) are expected to exhibit a phase separation morphology similar to the example in Figure 1a. In this case, the Na_2O and B_2O_3 components of the glass are primarily sequestered into the droplet phase, while the SiO_2 component makes up a majority of the continuous matrix. This arrangement is the key to the technological performance of borosilicate glasses. The Na_2O and B_2O_3 additions initially facilitate melting at lower temperatures relative to pure fused silica. However, upon cooling, the components that would also degrade properties such as chemical durability are trapped in a silica-rich matrix, thereby limiting access to the external environment. While certainly not equivalent to fused silica, the silica-rich matrix of an appropriately engineered borosilicate glass can also provide excellent thermal shock resistance.

A glass exhibiting the phase separation morphology shown in Figure 1b would not generally be desirable, since the low durability phase is now fully connected and accessible by the external environment. As a result, exposure to a sufficiently corrosive medium would result in rapid dissolution of the low solubility phase, thereby leaving the more soluble phase partially attacked or perhaps largely intact. Porous Vycor glass is an example of one exception in which it is actually desirable to create a glass with interconnected phase separation. In this case, the initial glass is appropriately designed to undergo selective dissolution in a slightly acidic medium to produce a porous, silica-rich “skeleton”. This porous material has several applications, including catalyst supports and filtration.

A change in phase separation from a droplet in matrix morphology to an interconnected morphology can have potentially significant effects on other properties of a glass, including the temperature dependence of key viscosity points such as the glass transition point and the softening point. This observation can serve as a potential line of inquiry when troubleshooting the behavior of glasses that are known to exhibit phase separation.



(a) (b)

Figure . False color images of glass exhibiting phase separation (Wheaton and Clare, 2007): (a) Droplet in matrix type of morphology,(b) Interconnected morphology. A conventional high durability borosilicate glass should be expected to have a phase separation morphology similar to example (a).

§ 2.3. Influence of pH of corrosion medium

The pH of the corroding medium is one of the most critical environmental variables that must be considered within the context of glass durability. Common glasses (*e.g.*, fused silica, borosilicate glass, SLS glass) are all known for being generally stable under low pH conditions. This is not to say that absolutely no corrosion takes places. For example, alkali ions are readily extracted from the surface of a SLS glass in contact with acid via the ion exchange mechanism that was previously discussed. The rapid extraction of alkali is driven by the abundant concentration of hydronium ions in the acidic medium. However, the extraction of alkali is eventually inhibited by the formation of a durable silica-rich surface layer that is depleted in alkali. The stability of silicate glasses is generally compromised under alkaline pH conditions. The hydroxide ion (OH^-) can readily disrupt Si-O-Si bonds, thereby accelerating the network dissolution process. Figure 2 illustrates the effect of pH on the dissolution of fused silica at 80^{o}C. The extent of dissolution as measured by silica extraction) increases with increasing pH (also note that significant dissolution is observed over a relatively short time period at this elevated temperature).

Similarly, Figure 3 shows the sensitivity of a borosilicate glass to changes in the pH of the corrosion medium.

In certain cases, the initial stages of glass corrosion can produce pH changes that will accelerate continuing network dissolution. This is most commonly observed when sodium ions are extracted from the glass at a level that is sufficient to cause a significant increase in the pH of the corroding medium. This effect can be observed in Table 1 using results taken from Clark *et al.* (1976) in which SLS glass was immersed in deionized water at 100°C for up to 216 h. The pH of the water is observed to increase over time and is correlated with the ion exchange reaction that pulls sodium from the glass into solution. Also note the significant increase in the concentration of silicon in solution at long time periods under pH conditions of >10.

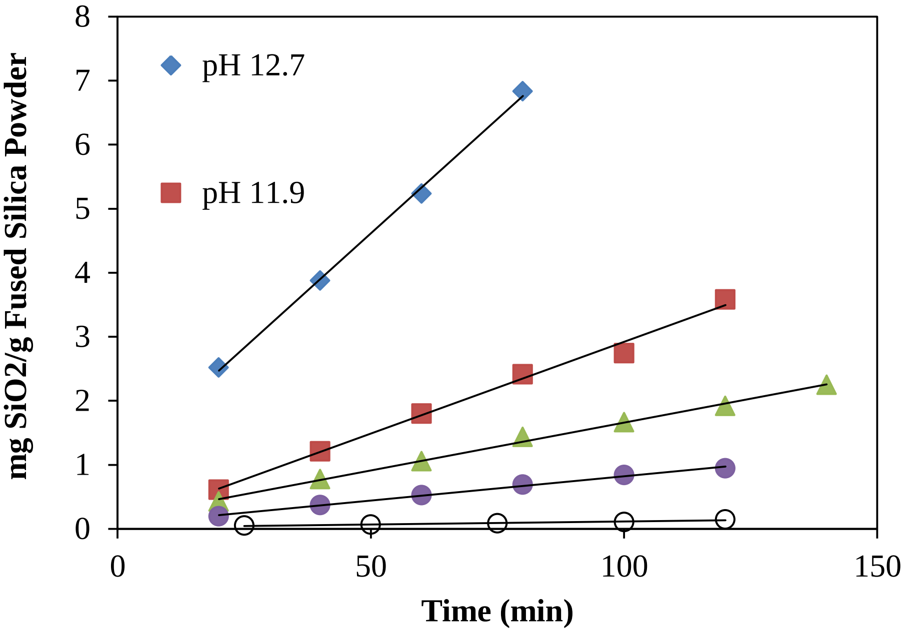


Figure 2. Silica extraction from fused silica powder at 80°C at various pH values (Douglas and El-Shamy, 1967).

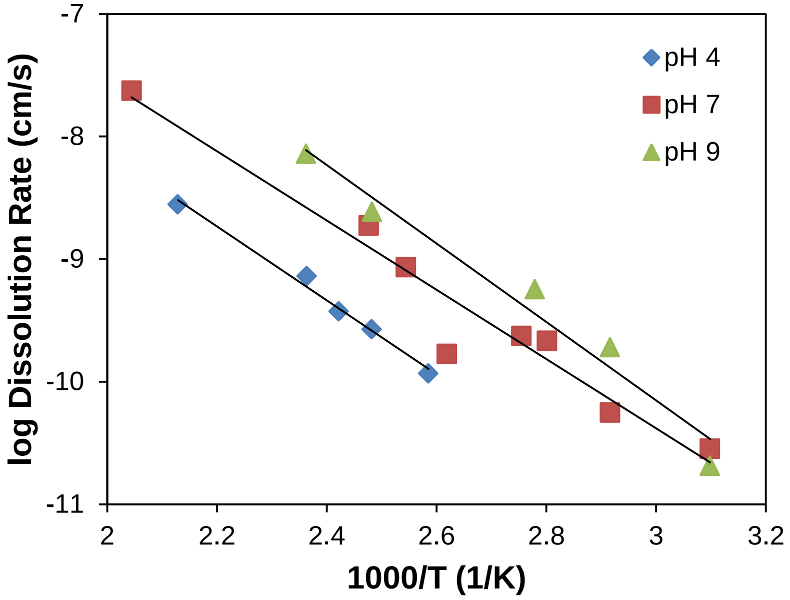


Figure 3. Influence of pH and temperature on the dissolution rate of Pyrex borosilicate glass (Perera and Doremus, 1991).

Table 1. pH and ionic composition of water upon contact with SLS glass at 100°C (Clark *et al.*, 1976).

Time (h)	**pH**	**Elemental Concentration in Solution (ppm)**		
		Na	Ca	Si
0.167	6.5	10.4	4	9.7
1	7.6	33.5	3	7.4
3	8.0	38.0	11	26.8
12	9.7	73.3	37	50.0
48	10.1	500	47	143
216	10.8	566	108	566

The long-term use of any silicate glass at a pH of ~10 or higher is generally not recommended. At a minimum, the optical clarity of the glass will be compromised as a result of corrosion. It should also be noted that "alkaline resistant" glasses are available for specific purposes – this increased resistance is generally accomplished through the addition of small amounts of ZrO_2 to the glass composition (Sihman, 1983). Alkaline resistant glasses are typically used as fibers for the reinforcement of cement, a high pH environment that would rapidly corrode less durable glasses.

§ 2.4. Surface Area to Volume Ratio

The surface area to volume (SA/V) ratio is defined by the surface area of glass that is in contact with a given volume of medium that may react with the glass. As the SA/V ratio increases, the rate at which a given glass corrosion process proceeds should also increase.

At first glance, the SA/V ratio would not seem to be a significant factor for the sight glasses. The glass component of the sight glass is a low surface area part. However, the SA/V ratio can take on added significance when the glass is exposed to a vapor phase that is capable of condensing on the surface. For example, a thin, stagnant film of water condensate may form on the window of a sight glass that is exposed to a steam atmosphere. The volume of this thin film of water is quite low, thereby translating into a high SA/V ratio. As a result, the extraction of even small amounts of network modifiers such as sodium from the glass via the ion exchange reaction with the vicinal water layer can be sufficient to dramatically increase the localized pH. As previously mentioned in § 2.3, the corrosion of silicate glasses is enhanced under strongly basic conditions. In addition, the dissolution products extracted from the glass under such conditions frequently form hydroxide and carbonate crystalline deposits on the glass surface. This so-called “weathering” process consisting of a combination of corrosion and deposit formation will often lend a hazy white appearance to the glass that can impair optical transparency.

A similar effect can sometimes be observed in double pane windows in which the seal that serves as a vapor barrier has been compromised, thereby allowing moisture to condense inside the window. The stagnant environment inside the window allows the condensed film to gradually corrode the interior surfaces of the window. This is in contrast to the window surface that is in contact with the external environment. Exposure of the external surface to water can result in minor corrosion. However, corrosion products that accumulate at the glass surface are generally rinsed away by rain such that neutral pH conditions are maintained.

§ 2.5. Solutes

Examples of fundamental studies on glass corrosion in pure water may be found in the literature. While such work provides useful information, an aqueous medium contacting a glass is rarely pure in practice and will instead contain dissolved solutes of varying chemical identity and concentration. These solutes can potentially increase the extent and rate of glass corrosion. Relevant examples include, but are not limited to:

- Ray (1970) reported on the effect of phosphoric acid on the corrosion of SLS glass. Phosphoric acid is unique in that the acidic orthophosphate unit may polymerize in solution to form higher molecular weight species. The extent of polymerization of the orthophosphate is dependent on concentration, temperature, and time. It was found that the corrosion rate of SLS glass was directly proportional to the temperature and the concentration of the orthophosphosphate specie (refer to Figure 4). As an interesting side note, the corrosion reaction produced surface deposits that improved resistance of the SLS glass to HF acid.
- The addition of neutral salts such as LiCl, NaCl, KCl, *etc.* can have a significant effect on the dissolution rate of glasses (Scholze, 1985; Scholze, 1988; Wickert *et al.*, 1999). For example, Figure 5 shows the effect of NaCl content on the dissolution rate of a SLS glass at room temperature. Although there is no universally applicable trend for all salt/glass combinations, it is generally observed that increasing salt additions will often increase the extent of glass corrosion.
- As previously mentioned, HF acid attack on silicate glasses is a special case brought about by the chemical activity of the fluorine anion. The speciation of the fluorine anion is dependent on the HF concentration and temperature. For example, Judge (1971) studied the potency of HF and HF_2^- species in buffered solutions produced by mixing HF and NH_4F in various proportions. Regression modeling of experimental data produced the following relationship for corrosion rate, R, as a function of fluorine speciation and temperature:

  $$R\ (\text{Å/sec}) \approx 5.0\times10^{7}\,[HF_2^-]e^{0.0091/RT} + 2.2\times10^{6}\,[HF]e^{0.0081/RT} + 0.025\,(T - 292)$$

  where $[HF_2^-]$ and $[HF]$ correspond to the molarities of the HF_2^- and HF species, respectively, R is the universal gas constant, and T is temperature. This relationship suggests that the HF_2^- specie is the more chemically aggressive form of the fluorine anion. Tso and Pask (1982) performed a systematic study of the dissolution rate of silica glass in pure, non-buffered HF solutions. Not surprisingly, the corrosion rate increased significantly with both increasing HF concentration and temperature (refer to Figure 6). The addition of any network modifier and/or intermediate to pure SiO_2 glass will reduce resistance to HF acid, as shown in Figure 7 (Spierings, 1991).

- Species that specifically complex ions within the glass can also enhance the rate and extent of corrosion. For example, a conventional chelating agent such as ethylenediaminetetraacete (EDTA) is known to form stable complexes with a number of divalent and trivalent cations such as Mg^{2+}, Ca^{2+}, and Al^{3+}, all of which are commonly found in various technical glasses. Other compounds such as catechol are thought to form stable complex with Si^{4+} and other tetravalent cations. Figure 8 shows the enhancement of corrosion that can be achieved with various chelating agents as a function of pH (Ernsberger, 1959).

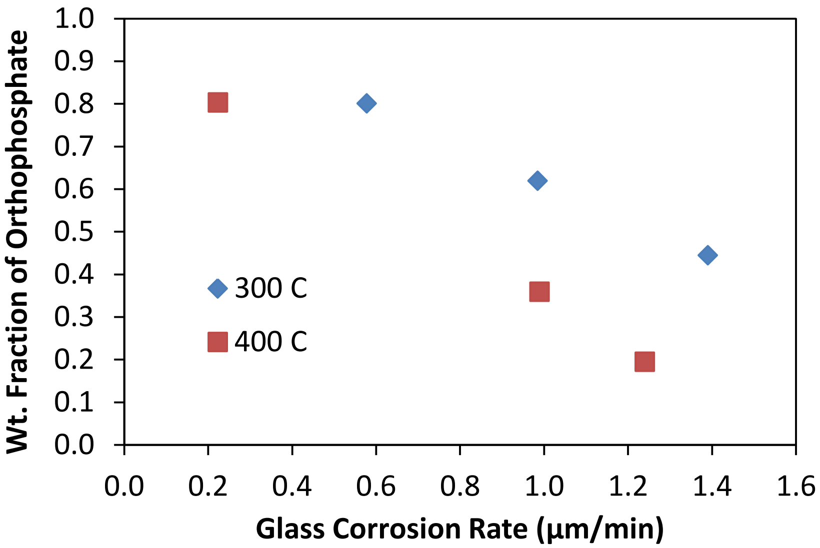


Figure 4. Effect of orthophosphate content (*i.e.*, “non-polymerized” phosphoric acid) on the corrosion rate of SLS glass at temperatures of 300°C and 400°C (Ray, 1970).

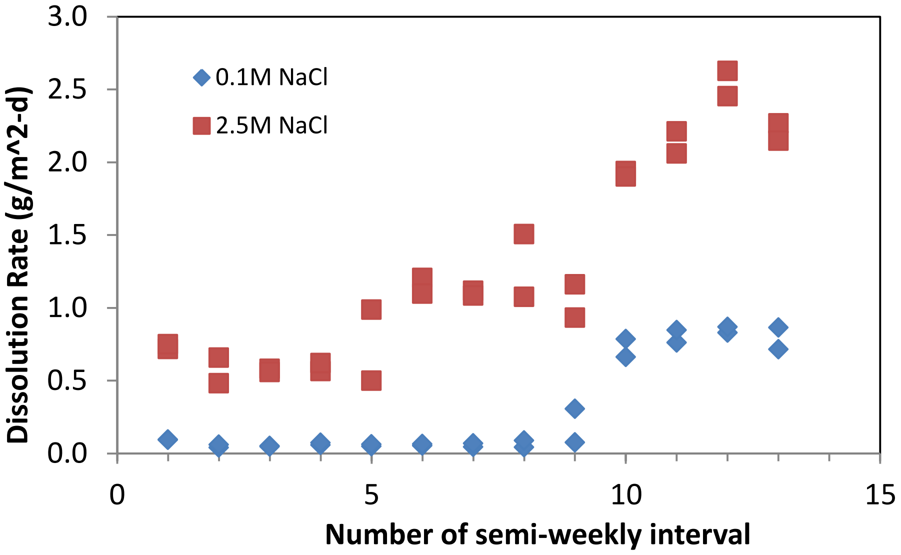


Figure 5. Dependence of SLS glass dissolution rate on NaCl concentration (Wickert *et al.*, 1999).

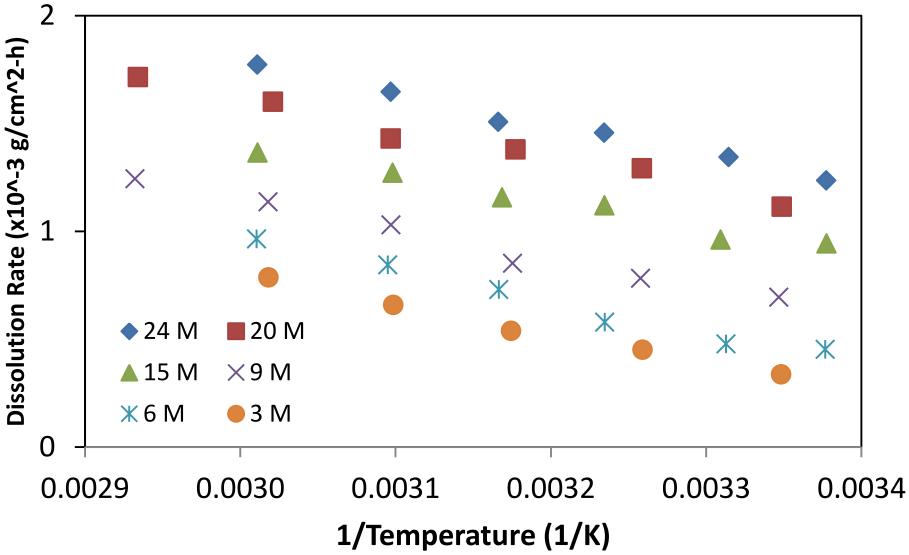


Figure 6. Dissolution of silica in HF acid of varying concentration as a function of temperature (Tso and Pask, 1982).

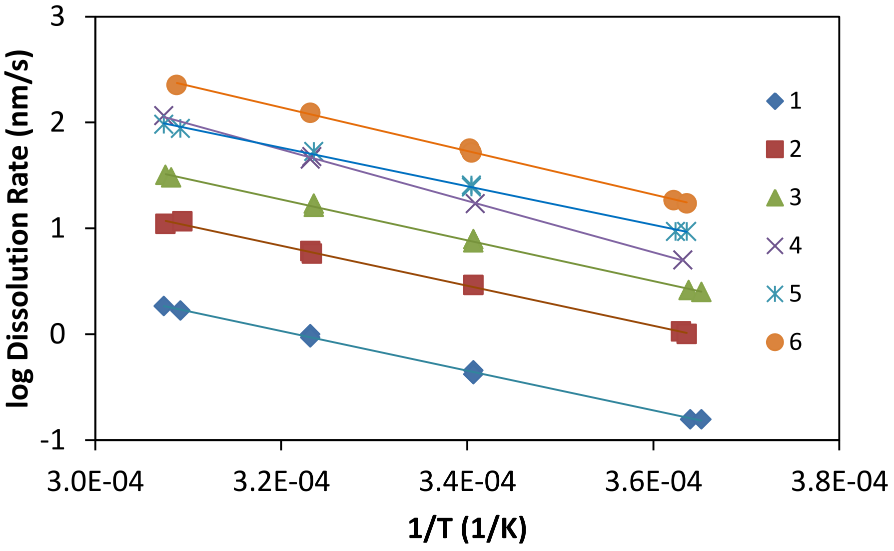


Figure 7. Corrosion of various glasses in 2.9M HF solutions as a function of temperature: 1. Fused silica, 2. 11Na_2O-11B_2O_3-78SiO_2 (mol%), 3. 15Na_2O-15B_2O_3-70SiO_2, 4. 30Na_2O-70SiO_2, 5. 15Na_2O-15CaO-70SiO_2, and 6. 12.5Na_2O-12.5ZnO-12.5Al_2O_3-62.5SiO_2 (Spierings, 1991).

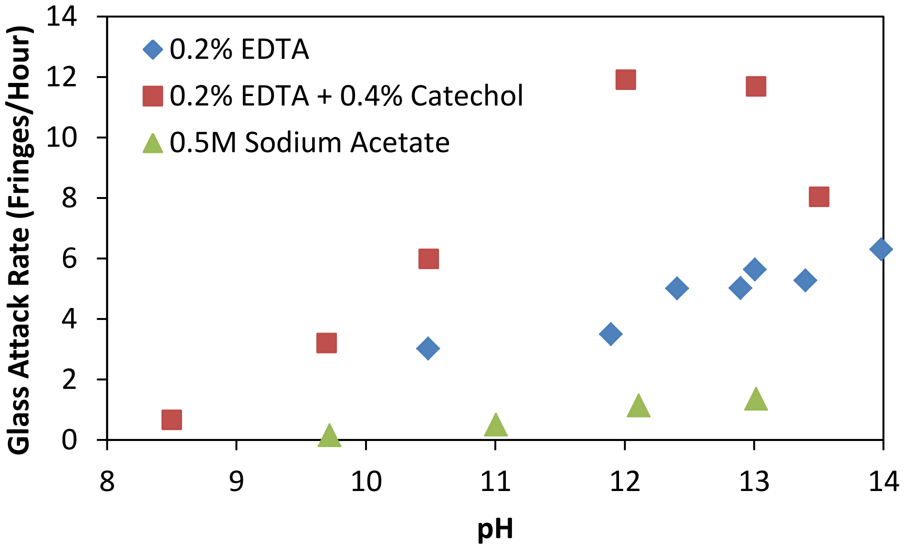


Figure 8. Corrosion of a borosilicate glass as a function of pH in solutions containing various chelating agents. The ordinate unit scheme (Fringes/Hour) refers to an optical interferometry method used to characterize the corrosion rate (Ernsberger, 1959).

The previous discussion presented examples in which the presence of solutes enhance glass corrosion – however, this does not translate to a universally applicable effect. For example, Buckwalter and

Pederson (1982), demonstrated that the introduction of dissolved lead ions (Pb^{2+}) into an aqueous medium can inhibit the corrosion of a glass. The mechanism behind this inhibitory effect was explained by the chemisorption of Pb^{2+} onto reactive, negatively-charged sites on the glass surface. Le Chatelier's principle can also be applied to the concept of glass corrosion. For example, Baillif *et al.* (2000) found that the addition of soluble silica to the corroding medium can decrease the extent of corrosion (refer to Figure 9), presumably in part because the driving force for silicon extraction from the glass is reduced.

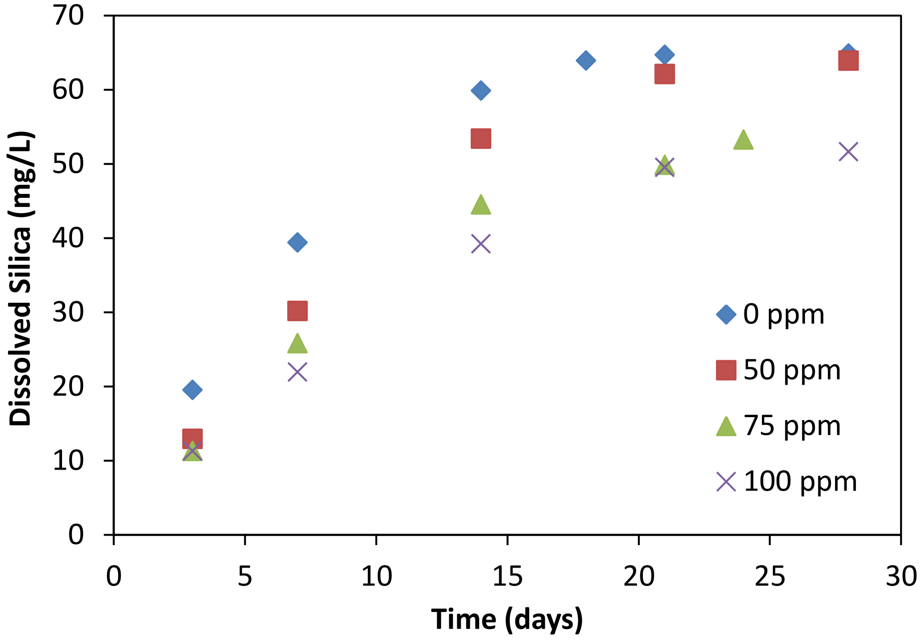


Figure 9. Dissolution of silica from a borosilicate glass as a function of time. The addition of soluble silica to the initial solution at varying concentrations (50 ppm, 75 ppm, and 100 ppm) depresses glass dissolution. The reported concentration of dissolved silica represents the final silica concentration minus the initial silica concentration (Baillif *et al.*, 2000).

§ 2.6. Influence of temperature and pressure

The temperature and/or pressure to which a glass is subjected can have a significant effect on the rate and extent of corrosion. As shown in a number of previous examples addressing chemical effects (*cf.* Figure 7), the corrosion rate is expected to increase with increasing temperature. There is much less in the way of systematic information in the open literature on the effects of pressure on glass corrosion. Nonetheless, glasses are known to degrade under steam and supercritical water conditions. For example, Sun *et al.* (2008) subjected SLS glass beads to supercritical water under 16 MPa of hydrostatic pressure at temperatures ranging from 150^{o}C to 300^{o}C. Extensive corrosion of the glass beads under all conditions was observed after just 1 hour(refer to Figure 10). Sigoli *et al.* (2003) demonstrated the porous materials could be produced by subjecting Pyrex-type borosilicate glass to an autoclave treatment at 450^{o}C for 3 hours. For the sample sizes/geometries studied, this treatment was sufficient to corrode the entire glass part (see Figure 11).

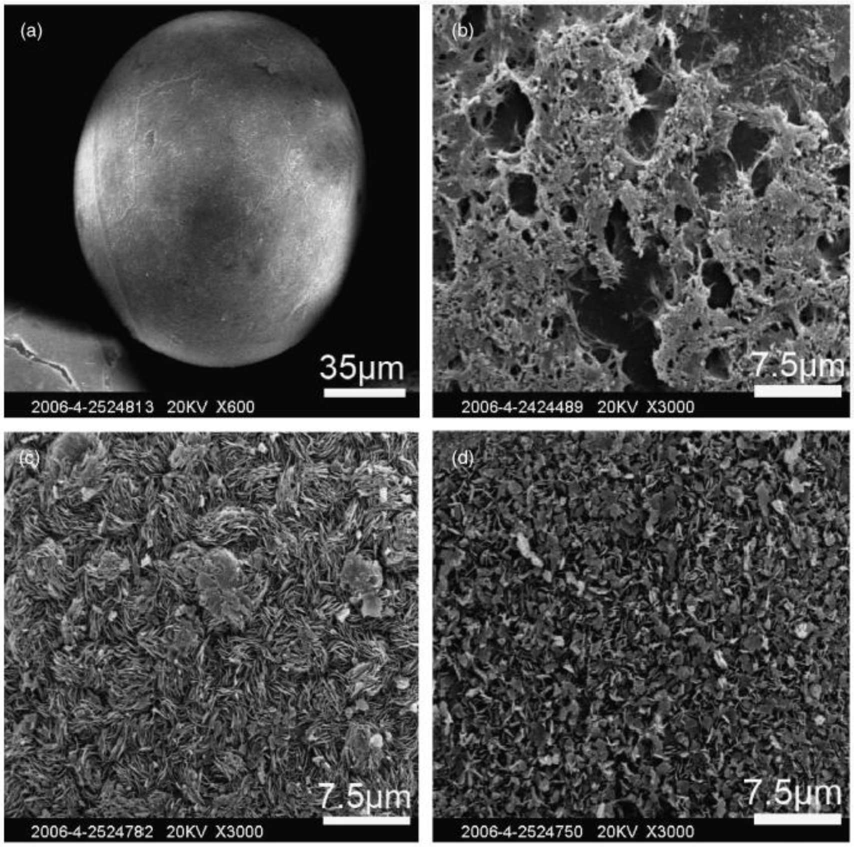


Figure 10. Scanning electron microscopy images of SLS glass beads treated with water at different temperatures and 16 MPa for 1 h: (a) 150C, (b) 200C, (c) 250C, (d) 300C (Sun *et al.*, 2008).

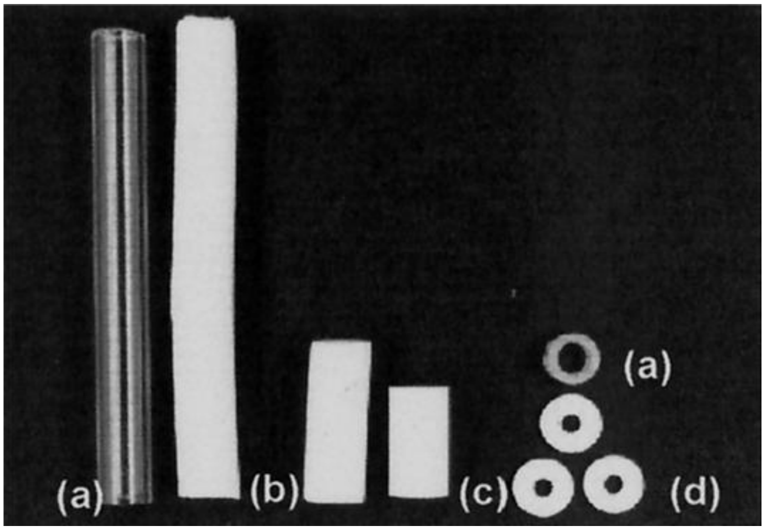


Figure 11. Images of (a) Untreated Pyrex glass tube and disk, (b,c) Porous silica tube, and (d) porous silica tubes (Sigoli *et al.*, 2003).

§ 2.7. Surface Modifications

The intrinsic performance constraints that are placed on a glass by its composition can be circumvented to some extent by surface modifications that can increase corrosion resistance. For example, flame polishing of a SLS glass surface can selectively volatilize network modifiers such as sodium, thereby creating a silica-rich surface that is more chemically durable relative to the bulk glass. Silica-rich glass surfaces can also be created by chemical means such as high temperature treatment with sulfate salts that extract sodium.

Coatings are commonly used as an alternative to the direct modification of the underlying glass surface. Coatings for corrosion resistance can be fully inorganic or organic in nature. For example, SCHOTT offers a specialty borosilicate glass vial (Type I plus®) in which the interior vial surface has a silica coating that can significantly increase chemical durability and prevent undesirable reactions with aggressive pharmaceutical formulations. A variety of methods can be used to apply inorganic coatings for corrosion resistance, although many approaches tend to be cost prohibitive for low volume production. Organic polymer coatings represent a potentially cheaper alternative to inorganic coatings. In addition, polymer coatings can impart resistance to higher pH conditions that cannot be tolerated by inorganic materials. Unfortunately, polymeric coatings suffer from key limitations such as reduced thermal stability and abrasion resistance relative to inorganic coatings. In addition, long-term aging can reduce the optical transparency of polymeric coatings, a property that is generally critical for sight glass applications.

§ 3. GLASS CORROSION AND MECHANICAL PERFORMANCE

§ 3.1. Surface flaws and the stress concentration effect

As previously stated, a complete treatise on the mechanical properties of glass is beyond the scope of this document, although selected information will be presented to help appreciate what is to follow. First, it is critically important to understand that the strength of glass is not a single value that can simply be found in a table of material property data (although such tables certainly do exist). The stress at which a glass may fail in practice is more correctly defined as a probability distribution that has a minimal dependence on the specific glass composition. Instead, the practical strength of glass is controlled by the presence of surface flaw, also known as “Griffith flaws”, that can dramatically reduce the intrinsic strength of pristine glass. Surface flaws in glass can arise from a number of sources, including but not limited to handling damage, abrasion, machining, *etc.* The severity of surface flaws can be reduced by the use of appropriate polishing methods, although the presence of flaws can never be fully eliminated.

Surface cracks weaken glass through a mechanism known as stress concentration – *i.e.*, applied stresses within the vicinity of a crack are amplified at the crack tip. To a simple first approximation, the stress concentration effect can be described by

$$\sigma_{crack} = 2\sigma_{applied}\left(\frac{c}{\rho}\right)^{\frac{1}{2}} \tag{1}$$

where σ_{crack} is the stress at the crack tip, $\sigma_{applied}$ is the applied stress that is amplified by stress concentration, c is the crack length, and ρ is the crack tip radius. The critical crack length, c^*, that produces a crack tip stress sufficient for failure, σ_f, is estimated as

$$\sigma_f = \left(\frac{2\gamma E}{\pi c*}\right)^{\frac{1}{2}} \tag{2}$$

where γ is the surface energy and E is the elastic modulus. The population of flaws on a glass surface is assumed to be heterogeneous, meaning that a distribution in the value of c/ρ is expected. As a result, a “weakest link” argument can be used in considering what flaw will propagate under a tensile load, thereby leading to brittle failure.

While the Griffith flaw approach is a useful first step in considering the effects of damage on the practical strength of glass, it is not without limitations. In particular, it ignores a time dependent phenomenon known as static fatigue in which the strength of glass under an applied load can diminish over time. Under appropriate conditions, this degradation of strength can lead to eventual catastrophic failure (also called “delayed failure”) of the loaded glass. It should also be noted that conditions of cyclic loading lead to another distinct phenomenon known as dynamic fatigue that is beyond the scope of this review.

§ 3.2. Introductory fracture mechanics and stress corrosion cracking

The time dependency of failure may be considered through basic fracture mechanics. We start by defining the stress intensity factor, K, as

$$K = \sigma_{applied}(\pi c)^{\frac{1}{2}} \tag{3}$$

and, by extension, the critical stress intensity factor, K_c, as the condition in which the crack length has reached a length of c^*:

$$K_c = \sigma_f(\pi c^*)^{\frac{1}{2}} \tag{4}$$

There are several modes in which cracks may propagate under an applied stress. For the sake of simplicity, consider a crack that is propagating directly perpendicular to the direction of the applied tensile stress, so called “Mode I” behavior. Under these conditions, the nomenclature for the stress intensity factor and the critical stress intensity factor becomes K_I and K_{Ic}, respectively. It should be noted that the K_{Ic} parameter is also termed the fracture toughness – *i.e.*, the resistance to propagation of a flaw.

The phenomenon of static fatigue in glass can now be approached by considering the dependence of crack growth velocity, V, on the stress intensity factor. From an experimental standpoint, this information is typically obtained through the use of a double cantilever beam specimen as shown in Figure 12. In this configuration, a constant tensile load, P, is applied to a pre-notched beam – the resulting crack growth velocity is then measured using a traveling microscope to track the moving crack front.

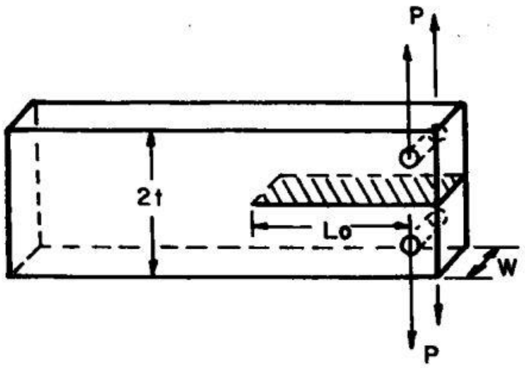


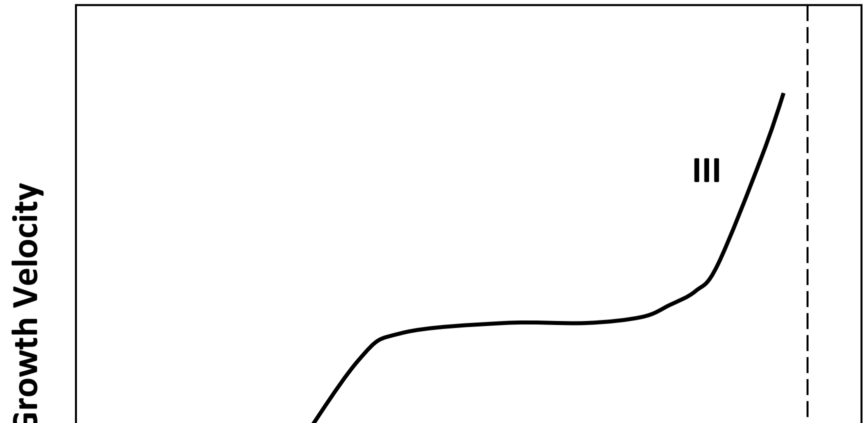
Figure 12. Double cantilever beam specimen for measuring crack growth velocity as a function of stress intensity factor (Wiederhorn, 1967).

A schematic diagram of a standard V(K_I) diagram for a silicate glass is illustrated in Figure 13. By convention, the ordinate axis (*i.e.*, crack growth velocity) is typically presented on a logarithmic scale, making the V(K_I) a semilog plot. The V(K_I) is broadly subdivided into three zones of behavior generally referred to as Region I, Region II, and Region III.

Region I is often of primary interest since glasses that exhibit delayed failure contain surface flaws that undergo a majority of their growth in this regime. The slope of the plot in Region I can vary depending on glass composition. The V(K_I) behavior may also be strongly influenced by relative humidity; this dependence has been formally expressed by:

$$V = a\left(\frac{P_i}{P_o}\right)^n exp(bK_I) \tag{5}$$

where *a* and *b* are constants, P_o is the vapor pressure of pure water at the temperature of interest, P_i is the vapor pressure of water in the gas or the equilibrium vapor pressure over the solution, and *n* is the order of the chemical reaction between water and glass. It is worth noting that systems with relatively low water solubility (*e.g.*, mineral oil, fluorinated hydrocarbons, *etc.*) cannot be ignored since it is the relative humidity, P_i/P_o, that is the governing factor as shown in Equation 5.



II

I

IB

IA

Applied Stress Intensity, K_I K_{Ic}

Figure 13. Schematic representation of crack growth velocity, V, as a function of the applied stress intensity, K_I.

Wiederhorn (1967) was the first to systematically measure the importance of relative humidity on crack growth velocity, as shown in Figure 14. The results suggest that the slope of Region I remains constant and essentially independent of relative humidity. However, the entirety of Region I for the $V(K_I)$ plot shifts upwards with increasing relative humidity –*i.e.*, for a constant stress intensity factor, cracks grow more quickly upon exposure to increasing levels of water vapor. Also note that the rate of change of crack growth has a highly nonlinear dependence on relative humidity, particularly considering the semilog nature of the $V(K_I)$ diagram.

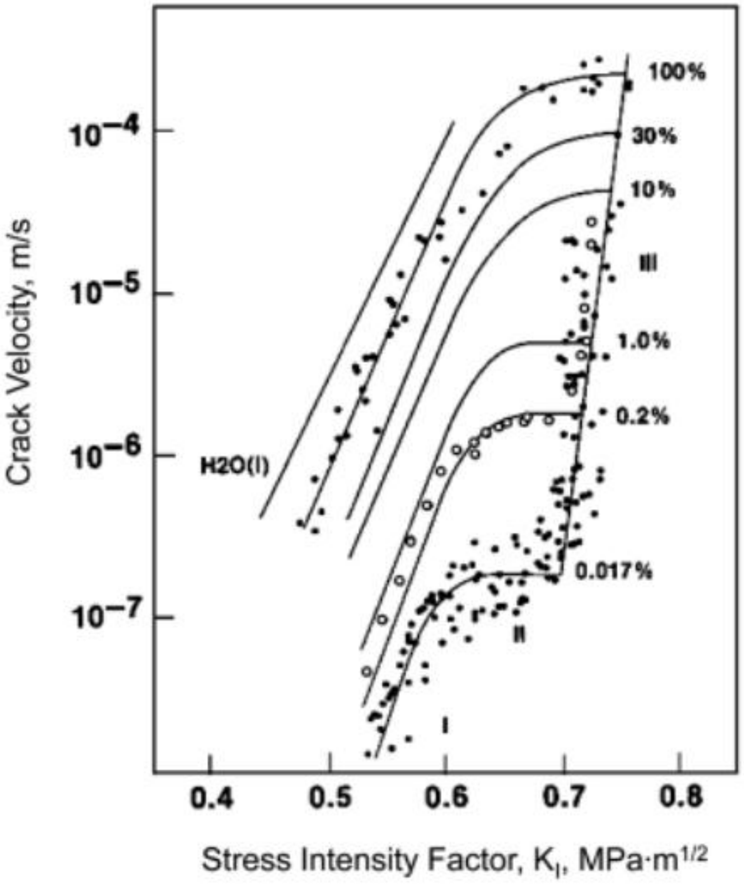


Figure 14. Crack growth velocity in SLS glass as a function of stress intensity factor and varying relative humidity of water (Wiederhorn, 1967).

Environmentally assisted stress corrosion cracking ("stress corrosion cracking" for short) lies at the foundation of the relationship between the results shown in Figure 14 and the static fatigue of glass that may ultimately result in time dependent failure. As previously mentioned, the crack tip region can experience increased tensile loads due to the stress concentration effect. At an atomistic scale, this effect translates into a stretching of Si-O-Si bonds within the glass structure. Sufficiently strained bonds can become susceptible to nucleophilic attack by water molecules, resulting in rupture of the Si-O-Si bond to produce to produce two silicon-bonded hydroxyl groups (also called silanol groups), as illustrated in Figure 15. This stress-enhanced corrosion phenomenon bears a similarity to the network hydrolysis mechanism for glass corrosion discussed in §2 – other linkages between general principles of glass corrosion and stress corrosion cracking will be discussed later in this section. Within the specific context of stress corrosion, the rupture of strained Si-O-Si bonds is thought to help sharpen the crack tip. As shown in Equation 1, this sharpening of the crack tip reduces the applied load needed for crack propagation due to increased stress concentration.

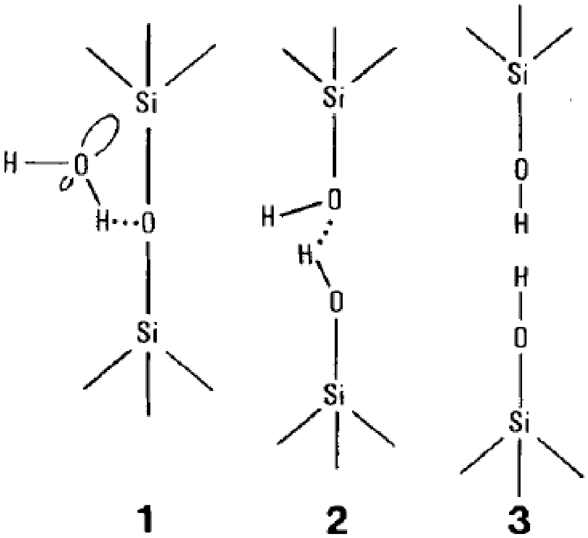


Figure 15. Representation of proposed reaction between water molecular and a strained Si-O-Si bond: 1) Oriented adsorption of water molecule, 2) Concerted acid/base reaction between water molecule and Si-O-Si bond, and 3) Rupture of Si-O-Si bond to form hydroxyl groups (Michalske and Frieman, 1983).

Region I behavior is known to be dependent on the composition of the glass being tested. For example, Figure 16 shows $V(K_I)$ data for a series of commercial glasses tested in water at 25°C (Wiederhorn, 1975). SLS glass exhibited the highest crack growth velocity over a majority of the evaluated range. This result is correlated with the fact that, within the range of glasses tested, SLS glass has the poorest hydrolytic resistance and is therefore most susceptible to stress enhanced corrosion by water.

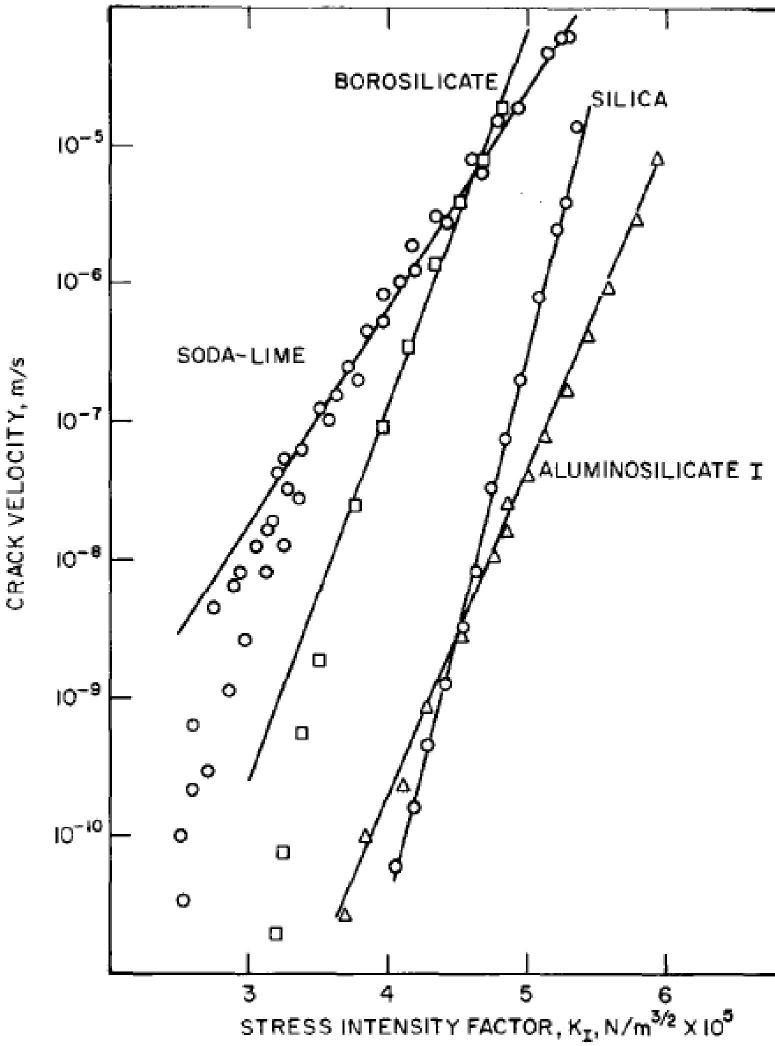


Figure 16. Crack growth velocity for various commercial glasses tested in water at 25°C (Wiederhorn, 1975).

Regions IA and IB represent further refinements to conventional Region I behavior. The nearly vertical response seen in Region IA is observed for particular glasses (*e.g.*, SLS glass) and suggests the possibility of a stress corrosion limit (Michalske, 1983). Region IB is thought to occur in selected alkali silicate glasses that may form corrosion products within the crack tip region. The buildup of these corrosion products are thought to create a "wedging effect" that can enhance the driving force for crack growth (Simmons and Freiman, 1981).

Region II behavior is characterized by a plateau in crack growth velocity that is essentially constant and independent of K_I. The relatively constant value of Region II suggests that the processes associated with stress corrosion cracking are transport limited instead of reaction rate limited. As crack growth velocity increases, a velocity can be reached in which the rate at which the reactive species is depleted (*e.g.*, H_2O molecules reacting with strained Si-O-Si bonds at a crack tip) will exceed the rate at which the reactive species can diffuse to the crack tip from the external environment.

The connection between mass transport processes and stress corrosion cracking has been experimentally demonstrated in a variety of studies. For example, Michalkse and Freiman (1983) measured crack growth velocity of fused silica in regular water and deuterated water (D_2O); the results are shown in Figure 17. Although the difference was slight, the crack growth velocity was found to be systematically higher in H_2O compared to D_2O. This observation was explained by the higher molecular weight of D_2O relative to H_2O, which in turn would lead to a lower diffusivity.

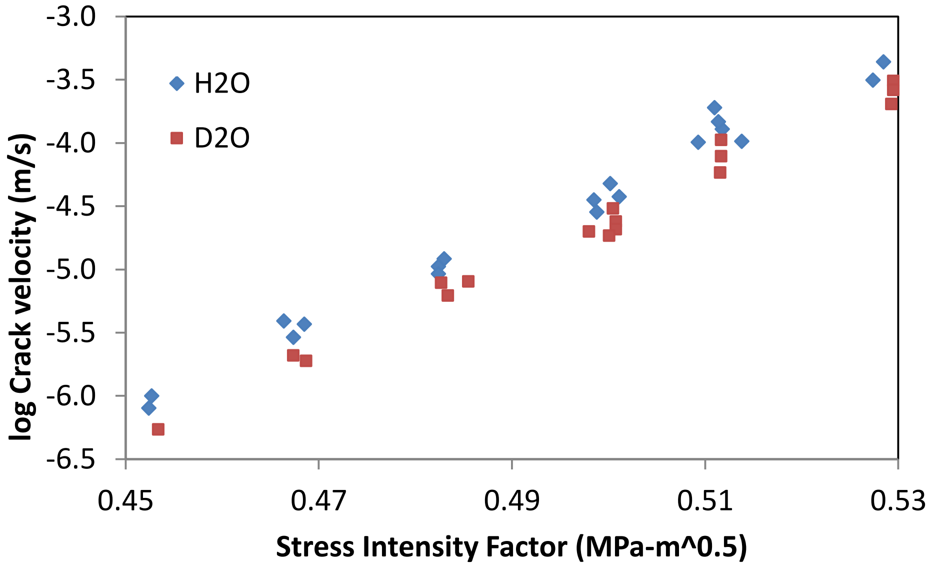


Figure 17. Crack growth velocity versus stress intensity factor in vitreous silica immersed in H_2O and D_2O. The slight downward shift in the D_2O data set demonstrates the dependence of stress corrosion on the molecular weight of the reactive species (Michalske and Frieman, 1983).

The prior discussion of stress corrosion cracking was entirely presented within the context of reaction with water. However, other agents capable of forming activated complexes with strained Si-O-Si bonds can contribute to the stress corrosion. Figure 18 is a $V(K_I)$ diagram for fused silica immersed in various media. Ammonia, formamide, and hydrazine are all shown to be effective enhancers of stress corrosion processes relative to a chemically inert medium such as dry nitrogen. The criteria for considering whether a particular agent may contribute to stress enhanced corrosion include:

- Size – Effective stress corrosion processes require that the reactive species be quickly transported to the crack tip. As such, stress corrosion is more likely to occur for smaller molecules. In addition, steric constraints can also inhibit larger reactive molecules from effectively penetrating into the narrow crack tip region.
- Bonding configuration – The bonding configuration of the reactive species should mimic the water molecule – *i.e.* the molecule should possess a proton donor site opposing a lone-pair orbital. This arrangement enables the nucleophilic attack of silicon and subsequent rupture of Si-O-Si bonds.

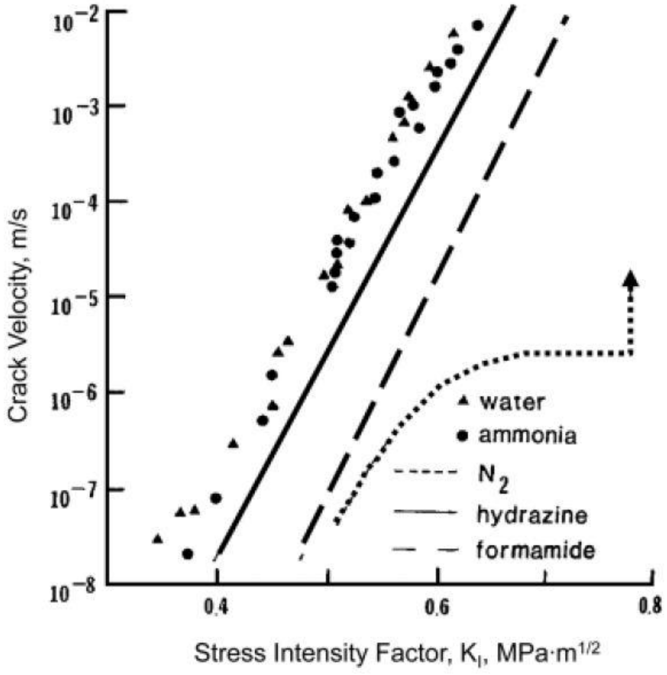
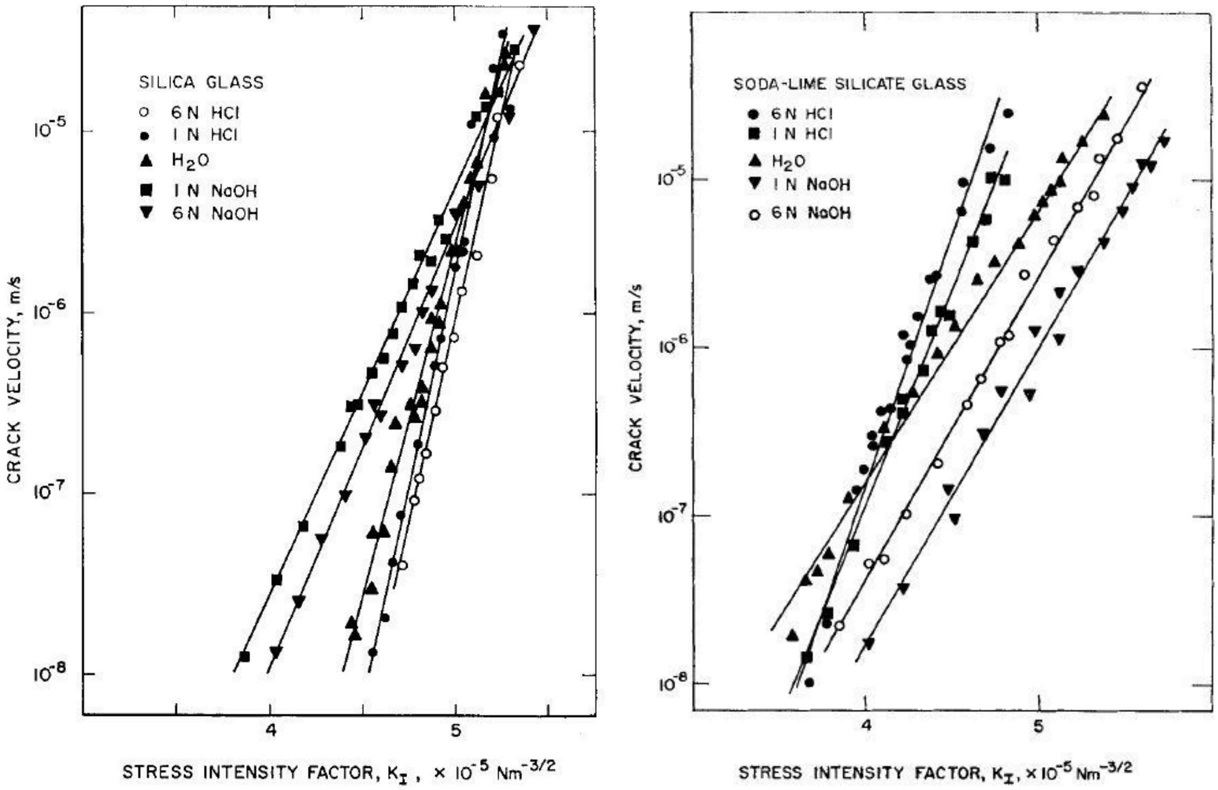


Figure 18. Crack growth velocity as a function of stress intensity factor for fused silica immersed in various liquids.

The transition to Region III behavior is thought to occur when the crack growth velocity begins to greatly exceed the ability of reactive species to reach the crack tip. It is characterized by rapid crack growth that is primarily influenced by the electrostatic properties of bonds within the glass structure and the dielectric properties of the medium in contact with the crack tip (Wiederhorn *et al.*, 1982). In general, Region III behavior for a given glass is shown to converge to a common curve with increasing stress intensity factor.

§ 3.3. Additional aspects of glass corrosion and stress corrosion cracking

As previously mentioned in §2, there are various solution parameters such as electrolyte content and pH that can influence the extent and rate of glass corrosion. These parameters are also found to have measurable effects on stress corrosion cracking and static fatigue of glass. For example, crack growth velocity is found to increase in fused silica when immersed in solutions of increasing pH for low stress intensity levels, as shown in Figure 19a (Wiederhorn and Johnson, 1973). The V(K_I) diagram for SLS glass evaluated in solutions of varying pH shown in Figure 19b is significantly more complex and highlights the potential interplay between ion exchange reactions (*e.g.*, the exchange of hydronium ions in solution with sodium ions in the SLS glass) and network hydrolysis reactions.



(a) (b)

Figure 19. Crack growth velocity as a function of stress intensity factor for (a) fused silica and (b) SLS glass in solutions of varying pH (Wiederhorn and Johnson, 1973).

Given the direct relationship between temperature and glass corrosion, it is perhaps not surprising to observe that increasing temperature can also enhance crack growth. Figure 20 is a V(K_I) diagram for SLS glass tested in water at temperatures of 2°C, 25°C, and 90°C (Wiederhorn and Bolz, 1970). Although the resolution of the data is somewhat low, it also suggests that temperature may influence the lower limit for static fatigue.

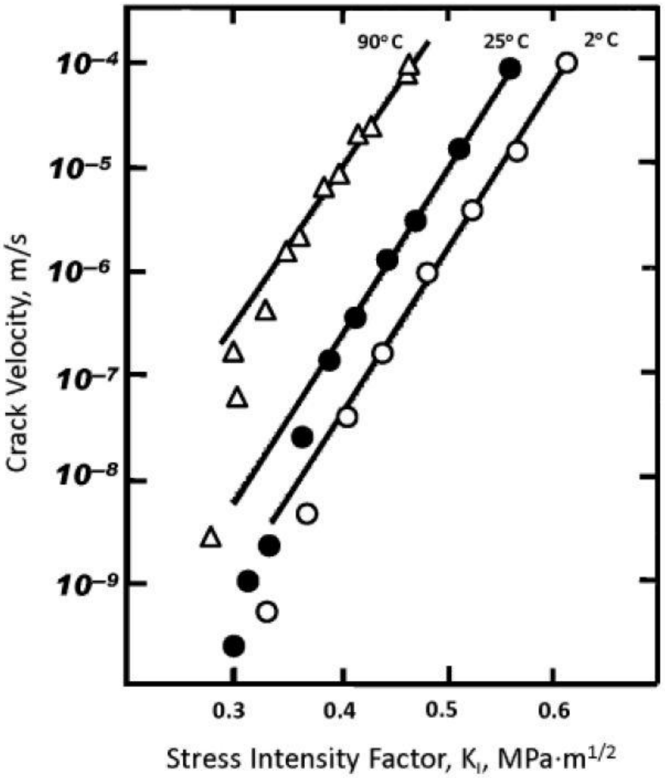


Figure 20. Crack growth velocity as a function of stress intensity factor for SLS glass in water a various temperatures (Wiederhorn and Bolz, 1970).

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