

The Effect of Microwaves on Aqueous Corrosion of Glass

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ABSTRACT

Glass corrodes in aqueous environments. The corrosion process is well-understood for many circumstances involving long periods of time at room temperature as well as processes that involve conventional heating, but the effect of microwave energy on glass corrosion has never been fully investigated. It was suspected that microwaves may alter or accelerate the aqueous corrosion processes that occur in glass which contribute to migration into foods or other materials. Lithium disilicate ($\text{Li}_2\text{O}-2\text{SiO}_2$) and commercial soda-lime glass were corroded using both conventional and microwave heating in this study. The results did not clearly show substantial differences in corrosion under the test conditions, but leave open the possibility of an altered mechanism in some circumstances. These findings suggest the need for testing at a lower microwave frequency, specifically 2.45 GHz.

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List of Symbols

In order of appearance within the text* :

$^{\text{TM}}$	Trademark
$^{\circ}$	Degree (as unit of angular measure or temperature)
$\text{\AA}$	Angstrom (0.1 nm)
$\text{\textcircled{C}}$	Copyright
$\equiv$	Implies 3 covalent bonds connecting to glass network
gl	Glass
t	Time
$\tilde{D}$	Interdiffusion Coefficient
D_A	Intrinsic diffusivity of alkali or other species A
D_B	Intrinsic diffusivity of hydrogen or other species B
c_A	Concentration of alkali or other species A
a	Rate of dissolution of glass/water interface
b	Mathematical variable defined in text
y	Distance from glass surface or Boltzmann transform variable
D_H	Intrinsic diffusivity of hydrogen-bearing species
D_{Na}	Intrinsic diffusivity of Na^+
$\tilde{D}_T$	Interdiffusion coefficient, adjusted for changes in to intrinsic diffusivities
α	Empirical constant for fitting diffusion equation, unitless kinetic parameter calculated from the molar ratio of corrosion products ($\text{Li}^+:\text{Si}$), or attenuation factor in depth of penetration equations
C	Instantaneous concentration
C_O	Original concentration
C_H	Concentration of hydrogen-bearing species
c_m	Concentration of mobile water species
c_{im}	Concentration of immobile water species
D_m	Intrinsic diffusivity of mobile water species
K'	Dissociation constant of water
$D_{\text{H}_2\text{O}}$	Diffusivity of water
ε	Unitless kinetic parameter proportional to thickness of leached layer
$[\text{SiO}_2]$	Concentration of silica species dissolved in solution
$[\text{Li}^+]$	Concentration of Li^+ dissolved in solution
ε'	Relative dielectric constant or permittivity
ε''	Loss factor
n	Index of refraction
k	Absorption index
N	Complex index of refraction
W	Wavenumber
N_c	Index of refraction of crystal
N_{sample}	Index of refraction of sample
N_{sc}	Ratio of N_{sample} to N_c
Θ	Angle of incidence

* Does not include SI unit abbreviations, atomic symbols, acronyms, or standard mathematical symbols

ppm	Parts per million (mg of dissolved substance per L of solution)
®	Registered
D_p	Depth of penetration
λ_0'	Free space wavelength
ϵ_{eff}''	Effective relative loss factor
ϵ_0	Permittivity of free space
$\tan\delta$	Ratio of ϵ'' to ϵ'
P	Power of microwave
P_{max}	Microwave power before attenuation
E	Electric field of microwave
E_{max}	Amplitude of microwave electric field
x	Distance variable
z	Distance variable
ω	Angular frequency
β	Phase factor
P_{peak}	Microwave power after attenuation
E_{peak}	Amplitude of microwave electric field after attenuation
$P_{\text{delivered}}$	Power absorbed by material
z_c	Critical distance, also known as depth of penetration
$P_{D_p \frac{1}{2}}$	Power at the depth of penetration

Chapter I: Introduction

Glasses corrode in aqueous environments. This corrosion causes glasses to gradually release constituents into solution (by preferential leaching of alkali ions and degradation of the glassy network) where these dissolved corrosion products can be released into the environment, ingested by humans, or incorporated into industrial or laboratory processes.

Glass is an important food container material as it is routinely used as packaging for beverages, food, or as glaze on ceramic containers. When glass is used as a food or beverage container, the manifestation of corrosion is the migration of glass constituents from the package into the food. Because of its packaging role, it is a potential source of migrating species and is often in contact with food and beverage during microwave heating.

The corrosion process is well-understood for many circumstances involving long periods of time at room temperature as well as processes that involve conventional heating. Corrosion mechanisms are therefore controlled when selecting materials and designing systems for these applications. The microwave effects on glass corrosion, however, are not well-understood. In many non-glass systems, microwave processing is suspected to alter or accelerate kinetics. It is uncertain whether microwave energy has any significant effect on glass corrosion.

There has been very little in the literature on glass corrosion due to microwave heating. In food migration studies, glass has historically been overlooked and assumed to be nearly inert compared to more contaminant-producing polymers. While it is known that glass constituents leach into food, no studies have been performed which rigorously examine the corrosion of or migration from glass when exposed to microwaves. This type of study is very difficult to perform due to the inherent differences between microwave and conventional heating.

Microwave processing, on the other hand, has been studied in several ceramic systems in which kinetics appeared to have been enhanced. If similar enhanced kinetics occur in glass corrosion, the result could be the release of unexpectedly large quantities of glass constituents which are potentially harmful in a number of ways. The current

literature is not sufficient to rule out the possibility and studies in other areas suggest the likelihood of an effect is high.

Hypothesis

The hypothesis is that microwaves cause accelerated aqueous corrosion of glass by enhancing one or more of the responsible mechanisms. The objective of this work is to test the hypothesis by performing corrosion studies on glass using conventional heating as well as heating by microwaves.

In order to investigate the hypothesis, a thorough literature review was conducted. This review provided a basic understanding of glass corrosion mechanisms under conventional heating and was necessary in order to fully understand the mechanisms potentially targeted by microwaves. Furthermore, the literature review provided a summary of the current state of knowledge about microwave interaction with food-contact materials and therefore a basis for the hypothesis. This review is presented in Chapter II.

Experimental work, presented in Chapter III, was carried out on simple binary alkali silicate glass (lithium disilicate, $\text{Li}_2\text{O}-2\text{SiO}_2$) and complex commercial container glass (soda-lime). The experimental work included static corrosion testing using different microwave frequencies and times, with special attention being paid to accurate temperature measurement in both the conventional and microwave ovens. Accurate temperature measurement ensured the comparability of the tests between the microwave and conventional ovens.

The experiments yielded information on the amount and nature of glass corrosion occurring in both environments. Both the corrosion product and corroded surfaces were analyzed. The corrosion product, glass constituents released into solution and solution components removed from solution, were analyzed by inductively coupled plasma and pH techniques. Corrosion surfaces were analyzed by infrared reflection spectroscopy, scanning electron microscopy, and secondary ion mass spectrometry. The experimental results are reported in Chapter IV.

In Chapter V, the experimental results are synthesized to draw all conclusions made possible by the data.

Chapter II: Literature Review

This chapter reviews relevant research and publications in the areas of glass structure, glass corrosion, and migration from food packaging.

Glass Structure

Glasses are amorphous and lack the long-range order which provides other, crystalline, solids with a definite crystal structure. Glasses are formed by several constituents, all of which contribute to the properties and structure of the glass.

The network former, silica (SiO_2) in the case of silicate glasses, is the backbone of the glass [1]. It is the primary glass-forming component and so is responsible for the amorphous nature. In the case of vitreous (glassy) silica, two silicon atoms join together by a single oxygen atom, known as a “bridging” oxygen atom, to which each is covalently bonded. The network is formed by a 3-dimensional continuation of the bridging between silicon atoms.

An important feature of glass structure is the silica tetrahedron, shown in Figure 1. In this representation, oxygen atoms are at the vertices of the tetrahedron while the silicon atom occupies the centroid [1]. In the case of vitreous silica, no network-modifying constituents are added so the glass network is uninterrupted and each oxygen atom assumes the role of bridging oxygen. Each of the four vertices is also the vertex of an adjacent silica tetrahedron and all tetrahedra are connected to four other tetrahedra [1].

A second group of materials that serve as primary components of traditional glasses is comprised of the network modifiers. When a network-modifying oxide, lithia (Li_2O) for example, is incorporated as a glass component, some bridging oxygen bonds are converted to “nonbridging” oxygen bonds in order to accommodate the new compound [1]. The nonbridging oxygen, instead of connecting two silicon atoms, is bonded between a silicon atom and the cation of the oxide. An illustration of the bond structure is shown in Figure 2 [2]. In $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ glass, the stoichiometry is such that there is one nonbridging oxygen for every silica tetrahedron and therefore each silica tetrahedron is connected to only three other tetrahedra [1]. The effect of the addition of a network modifier is to make the glass easier to process.

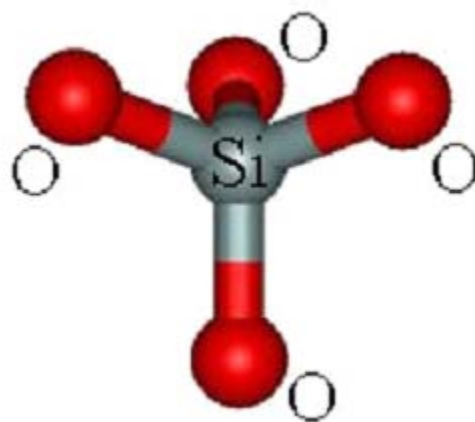


Figure 1: Silica tetrahedron. From [3].

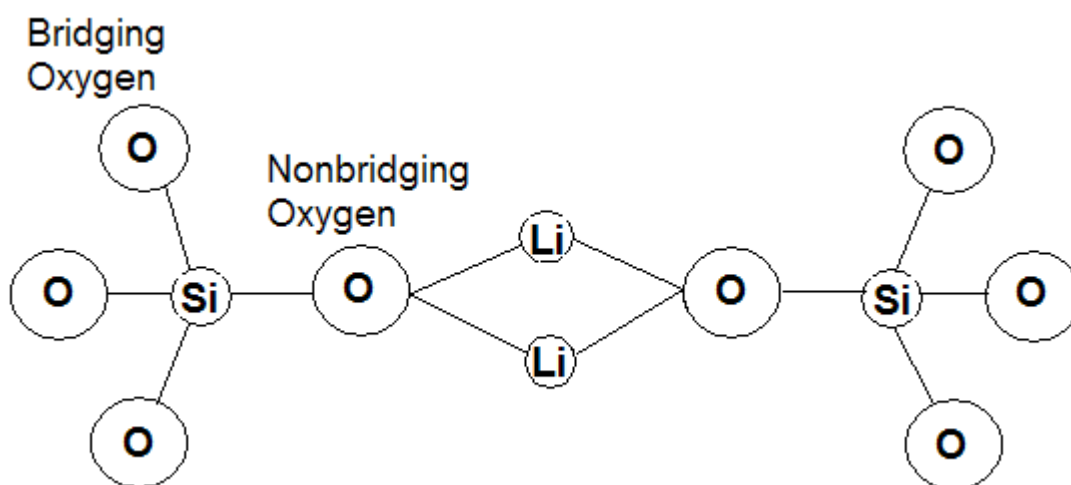


Figure 2: Bond structure of lithium disilicate glass. After [2].

The short-range ordering (the atomic arrangements within a small distance) is similar throughout a glass. The short-range is on the scale of the average separation of silicon atoms, which is 3.6 Å [1]. In vitreous silica, the average angle of the silicon-oxygen-silicon bond is 144°, but there is about 10% variability [1]. This variability in arrangement gives rise to only small differences in orientation over a short-range scale but over the long-range it forces the network into a random orientation. It is the lack of long-range order (at more than approximately 10 Å radius) that inhibits the development of a crystal structure, making glass amorphous [1].

In $\text{Li}_2\text{O}-2\text{SiO}_2$ glass, the atomic arrangements have been shown to be similar to crystalline lithium disilicate [1]. Figure 3 shows the structure of lithium disilicate crystals, with silicon in the center of the tetrahedra, oxygen at the vertices, and lithium represented by the black triangles. It is suspected that $\text{Li}_2\text{O}-2\text{SiO}_2$ glass possesses a short-range order very similar to what is shown, but with variations in bond angles leading to its amorphous nature over the long-range scale [1].

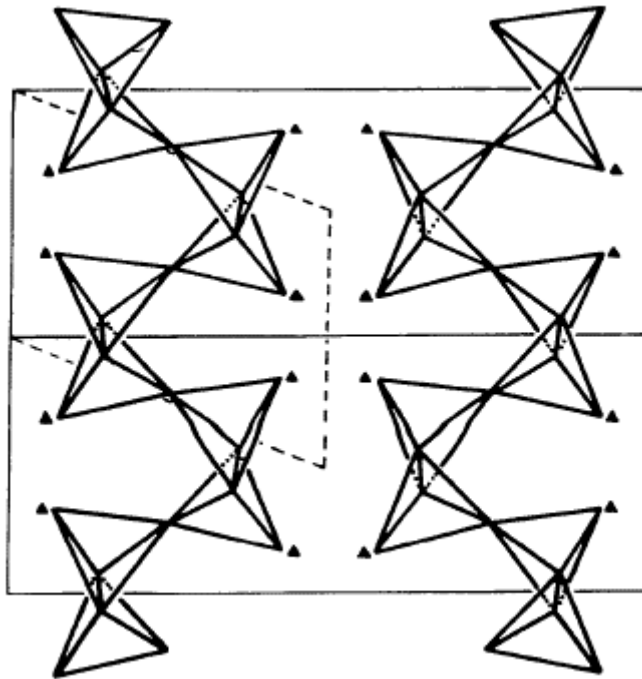


Figure 3: Structure of crystalline lithium disilicate. From [1, 4] (reprinted by permission, ©International Union of Crystallography, <http://journals.iucr.org>).

Glass Corrosion

Glass is not an inert material, yet it is commonly assumed to be at home, in industry, and in laboratories. Glass corrosion in water consists of preferential leaching of ions, degradation of the glassy network, or some combination of these two mechanisms [5]. Corrosion causes glasses to gradually release constituents into solution where the dissolved corrosion products can be released into the environment, ingested by humans, or incorporated into industrial processes. It is that corrosion process which is the focus of this work.

The chemical durability of glass for commercial purposes as well for storing nuclear waste catalyzed research on glass corrosion. Commercial glasses were studied first and most of the investigations into the fundamental mechanisms of glass corrosion were performed on simple laboratory or commercial glasses. Glasses for nuclear waste, on the other hand, benefited from the knowledge gained from simple- and commercial-glass studies. They experience many of the same corrosion mechanisms such as leaching and network dissolution; however, due to their immense complexity, they also experience mechanisms which do not typically affect commercial glasses, such as precipitation from saturated solutions and sorption and colloid formation [6]. The discussion in this chapter will be limited primarily to simple laboratory and commercial glasses because they are most relevant to both $\text{Li}_2\text{O}-2\text{SiO}_2$ and glasses found in food packaging.

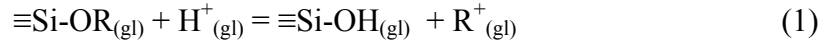
Throughout this work, the term “corrosion” will be used to refer to the whole process of degradation. A subset of corrosion is the “leaching” of ions which involves the preferential removal of cations from glass as well as their release into solution. “Network dissolution” is also a subset of corrosion and refers to the degradation of the glassy network, the backbone of the glassy structure, and the subsequent release of silica into solution. This term is typically reserved for attack on the glassy network specifically. When network dissolution occurs to such an extent that cations are released into solution in the same ratio as they are present in the glass because the silica that keeps them in place is dissolved, the term “congruent dissolution” is typically used. Other types of corrosion, such as weathering, do indeed occur but the primary mechanisms of interest here are leaching and network dissolution. These processes may be considered

independent to some degree [5]. Both are the result of interaction with water and will be discussed in-depth.

Leaching

Leaching is effected by ion exchange. The traditional model, and the one with the widest acceptance, is classical interdiffusion. In this model, hydronium ions from solution, H_3O^+ , diffuse into the glass at the same time that network-modifying alkali ions diffuse out [7]. The migrant alkali ions are released by the glass into solution and hydrogen ions, H^+ , arriving in the form of H_3O^+ , assume the position of the alkali ion in the glass structure. Specifically, in the case of $\text{Li}_2\text{O}-2\text{SiO}_2$, H^+ assumes the position occupied by Li^+ shown in Figure 2. The H^+ ion is then associated with the nonbridging oxygen forming an Si-OH silanol structure [8].

The chemical reaction that describes this phenomenon is given in Equation 1 [1]. The alkali ion is represented by the letter R. In the case of $\text{Li}_2\text{O}-2\text{SiO}_2$, R is Li.



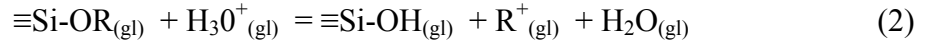
In Equation 1, the reaction is shown so that only one H^+ enters the glass and exchanges with R^+ . In this model, the H^+ is treated as just another alkali ion which diffuses through the glass in a similar fashion to Li^+ , Na^+ , or K^+ . The reality, however, is that the process is too complicated for ion exchange to occur in such a simplistic manner.

A lone H^+ ion cannot be transported through a glass [9]. This prohibition is due to the tight binding between hydrogen and oxygen, resulting from the fact that a proton (H^+) does not have an electron cloud to keep the degree of interatomic separation found between the alkali ions and oxygen. As a result, H^+ cannot be by itself in an ionic solid (or in a solution, for that matter) as an independent ion; it must be attached to something else [9].

In aqueous solution, the hydrogen atom joins with a water molecule (H_2O) and creates the hydronium ion, H_3O^+ . It is interesting to note that a given H_3O^+ lasts for a very short period of time in solution—on the order of a picosecond to a nanosecond [10, 11]. An H_3O^+ ion decays when its proton is given to another water molecule, forming a new H_3O^+ ion. In glass, though, H_3O^+ is not surrounded by other water molecules to which it may transfer the proton and so it is stable and does not decay [10].

In glass, water can be present within the structure in several ways. Hydration exists in the form of silanol (Si-OH), molecular water (H₂O), or H₃O⁺. Protons, which are key to the ion exchange process in leaching, are transported through diffusion of the water species present in the glass (H₂O and H₃O⁺) or via a “shielded diffusive transport” mechanism in which the proton jumps from one Si-O⁻ group to another [9]. The latter mechanism occurs similarly in water and ice, but is less probable in ion exchange because continuous chains of Si-OH groups are required and are initially not present in uncorroded glass [9]. The transport of protons by H₂O diffusion will be discussed later as a theory separate from classical interdiffusion.

Equation 2 gives the equation for ion exchange occurring by H₃O⁺ diffusion [12]. The result is that molecular water is left in the glass after the ion exchange has occurred. The molecular water can remain attached as hydronium or split off, as shown, and dissolve into the glass or phase-separate [10, 11].



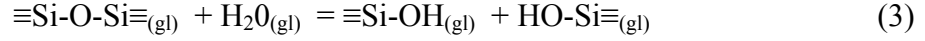
The effect of ion exchange is the removal of cations from a surface layer of the glass, leaving behind an alkali-depleted region called a leached layer. This layer is sometimes similar to a silica gel and contains Si-OH groups [1].

Leached Layer

It has been suggested that the diffusion of alkali ions is significantly enhanced in the leached layer. The calculated diffusion coefficients are in several cases several orders of magnitude higher than the diffusion coefficients measured for the same alkali ions in the bulk glass [8].

It is proposed that the diffusion of alkali ions through the leached layer is sped up in two ways related to the effect of the formation of Si-OH groups [8]. The first is the decreased bond strength of the alkali to nonbridging oxygen. When an alkali ion encounters a Si-OH group, it is attracted only by hydrogen bonding instead of ionic bonding (as it would be to bare Si-O⁻) which allows it to diffuse more freely. The second is the creation of free volume inside the glass structure. When alkali ions are replaced by hydrogen ions, the smaller atomic radius of the hydrogen leaves a void. These voids provide an open channel through which larger ions may diffuse.

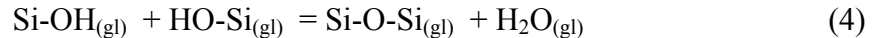
The presence of molecular water (hydration) may also affect the diffusion of alkali ions [8]. Molecular water can hydrolyze bridging oxygen bonds by Equation 3, effectively creating Si-OH groups.



During interdiffusion, as H^+ ions are depleted from solution, the pH increases accordingly. High pH causes network breakdown to predominate. Under static conditions, i.e. the solution is not replenished during the course of corrosion, the pH rises until network dissolution becomes the predominant mechanism. Under dynamic conditions, i.e. the solution is replenished or constantly replaced by new solution flowing through the system, or if the pH is held constant by titration, leaching will continue to predominate. This mechanism will be described in further detail later.

If pH is held constant, the kinetics of leaching sometimes changes from $t^{1/2}$ (diffusion-controlled) to t^1 (interface-controlled) [8], as has been shown to be the case for representative binary alkali silicates as well as other less-durable glasses [8]. It has been argued that the leached layer makes a transition from a structure resembling the original glass network through which ions must diffuse (albeit alkali ions diffuse faster than in the bulk) to a structure that provides very little resistance to diffusion [8, 13]. After this transition has occurred, leaching occurs directly at the bulk glass/leached layer interface and the products are released almost directly into solution instead of at the leached layer/water interface after the alkali have diffused through the leached layer. The altered layer sometimes takes on a gel-like structure.

The gel structure is formed from the leached layer, and is sometimes known in the literature as a “transformed surface layer” [13, 14]. It forms at longer leaching times, when phase-separation between water and silica begins. The water phase likely contains silicic acid, $\text{Si}(\text{OH})_4$ [14]. The proposed mechanism is the result of the condensation reaction of Si-OH groups (Equation 4) [12].



When Si-OH groups recombine, they do not re-form the original silica network. Instead they form phase-separated spheres, much like a silica gel [14]. Evidence of phase separation has been found by small angle x-ray scattering [15] and evidence of silica spheres has been found by transmission electron microscopy (TEM) [14]. The high

concentration of water between the spheres is what allows for rapidly-enhanced diffusion of alkali away from the gel/bulk glass interface.

Interdiffusion Model

The classical empirical explanation for ion exchange was put forth by Doremus [7]. In proposing the model, he improved on the standard analysis of data resulting from glass leaching by using a concentration-dependent diffusion coefficient, shown in Equation 5. Previous work had been performed assuming an ideal concentration-independent diffusion coefficient. His mathematics included a moving interface resulting from the shift in the gel-glass interface during corrosion. In the equation for the interdiffusion coefficient (Equation 5), A is the original alkali ion in the glass, c_A is the concentration of A, and B is the in-diffusing species (in this case, the hydrogen bearing species which was identified as most likely H_3O^+).

$$\tilde{D} = \frac{D_A}{1 + c_A \left(\frac{D_A}{D_B} - 1 \right)} \quad (5)$$

Equation 6 gives the equation for the concentration of A in the glass, where a is the rate of dissolution, $b = \frac{D_A}{D_B} - 1$, y is the distance from the glass surface, D_A is the concentration-independent diffusion coefficient of A, and D_B is the concentration-independent diffusion coefficient of B.

$$c_A = \frac{1 + e^{-ay/D_B}}{1 + be^{-ay/D_B}} \quad (6)$$

The treatment of the data with a concentration-dependent interdiffusion coefficient provided an improved fit to leaching data. Figure 4 shows the experimental and theoretical concentration profiles for a leached lithium glass. The theoretical profile was calculated assuming a constant diffusivity. By contrast, Figure 5 shows the experimental and theoretical profiles of a corroded obsidian specimen using the adjusted interdiffusion model. The agreement between the experimental and theoretical curves results from the use of a concentration-dependent diffusivity. A schematic of the regions of the glass described by the theoretical curves is given in Figure 6.

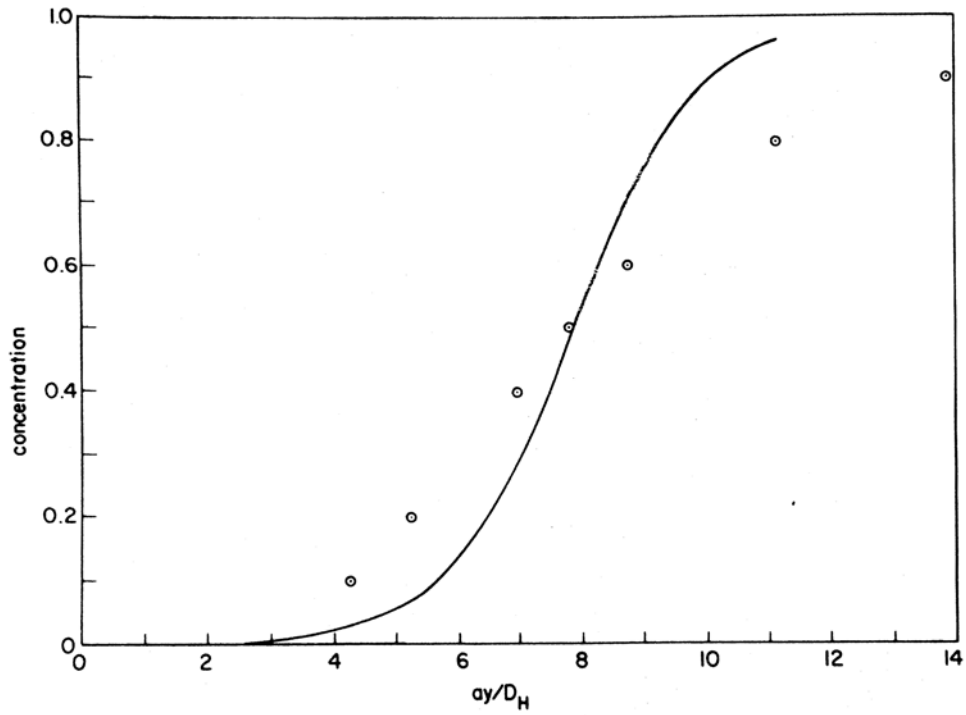


Figure 4: Experimental (dotted) and theoretical (solid) lithium profile for leached lithium silicate glass assuming constant diffusivity. From [7] (reprinted by permission, ©1975 Elsevier).

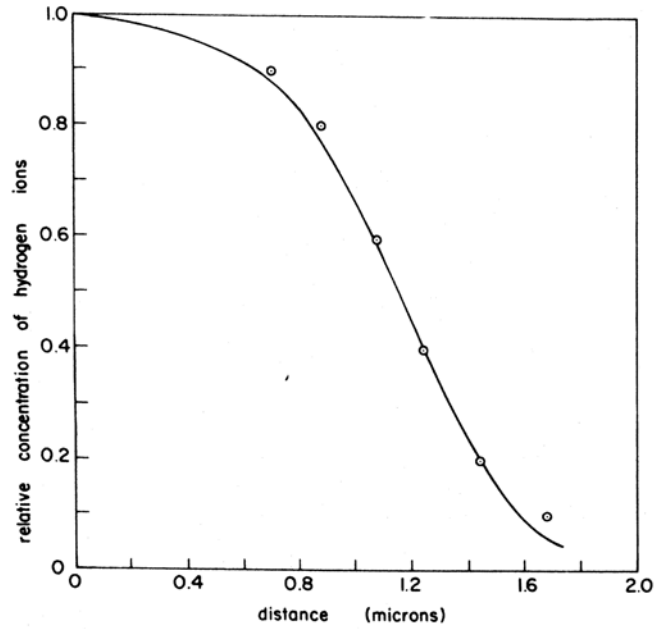


Figure 5: Experimental (dotted) and theoretical (solid) hydrogen concentration profile for leached obsidian. From [7] (reprinted by permission, ©1975 Elsevier).

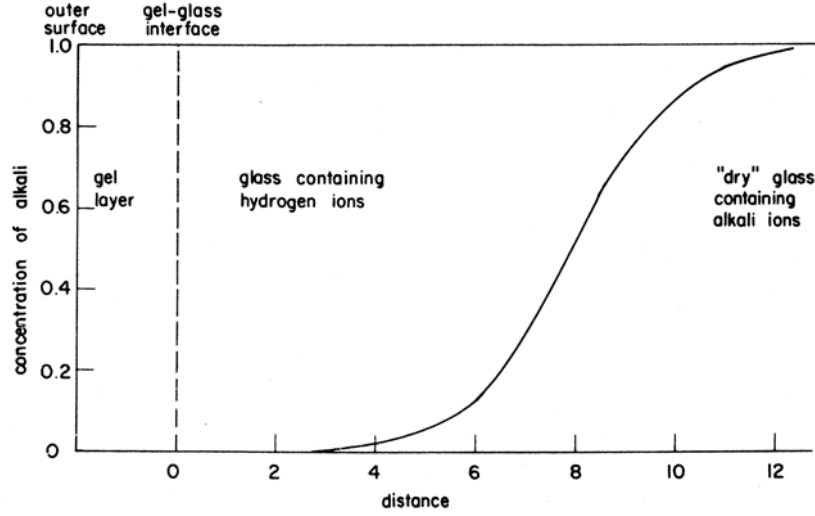


Figure 6: Schematic of the theoretical model describing alkali concentration in leached glass using a concentration-dependent interdiffusion coefficient. From [7] (reprinted by permission, ©1975 Elsevier).

The Doremus interdiffusion model was considered and improved upon for several systems of glasses. Lanford *et al.* corroded a commercial soda-lime window glass and obtained concentration profiles by resonant nuclear reaction techniques [16]. They found reasonable agreement of the Doremus model to experimental results at times where leaching dominated before the rate of silica dissolution caught up to the rate of leaching. However, when corrosion was allowed to proceed until the point of severe silica etching (steady-state) as required by the original Doremus model, the agreement was not as good.

To improve the fit, the authors altered the method of calculation of $\tilde{D}$ based upon the idea that the intrinsic diffusion coefficients for the alkali and the hydrogen-bearing species, (D_A and D_H) might change based upon the changes occurring in the glasses. The approach is shown in Equation 7, where $b = D_H/D_{Na} - 1$ and α is an empirical constant.

$$\tilde{D}_T = \tilde{D} \left(1 + \alpha \frac{C}{C_O} \right) = \left(\frac{1 + \alpha C_H}{1 + b C_H} \right) D_H \quad (7)$$

The authors found that the corrosion data was fit well with a value of $\alpha=1$ for the short-term and $\alpha=10$ for steady state. In solving the equation, they were also required to assume a ratio between the diffusivities of Na and H in order to calculate b. The authors

chose this ratio as $D_{Na}/D_H=1000$. This value fit the data well and the assumptions were in agreement with what little experimental data existed for the system at the time [16].

The short-term data required a smaller value of α because the fit of the Doremus equation was relatively good to begin with, whereas the steady-state data originally had a poorer fit. No direct physical meaning was associated with α , but it was suspected to be related to the stress induced in the leached surface. As degree of leaching increased, the stress in the leached layer increased and further altered D_H and D_{Na} from their original values. Calculating these diffusivities, $D_H \approx 10^{-16} \text{ cm}^2/\text{s}$ and $D_{Na} \approx 10^{-13} \text{ cm}^2/\text{s}$ for both $\alpha=1$ and $\alpha=10$.

The altered approach was also considered for the binary alkali silicate system $\text{Na}_2\text{O}-3\text{SiO}_2$ for short corrosion times [17]. Using the Boltzmann transformation on the adjusted Doremus equation (Equation 7), they obtained Equation 8 (see Appendix A for derivation). Solving the differential equation numerically and plotting against their experimental data, they obtained a good fit with $\alpha=0$.

$$\left(\frac{d^2 C_H}{dy^2} \right) = -2y \left(\frac{1 + bC_H}{1 + \alpha C_H} \right) \left(\frac{dC_H}{dy} \right) + \left(\frac{b - \alpha}{1 + \alpha C_H} \right) \left(\frac{dC_H}{dy} \right)^2 \quad (8)$$

In plotting the data, a value of $D_{Na}/D_H=100$ was required in order to obtain a good fit, which was an order of magnitude smaller than the previous study [16]. This assumption yielded the following values: $D_H=1.48 \times 10^{-12} \text{ cm}^2/\text{s}$ and $D_{Na}=1.48 \times 10^{-10} \text{ cm}^2/\text{s}$, which were several orders of magnitude higher than the previous study. The authors explained this away as a product of the disparate structures and corrosion resistances of the two types of glasses. The calculated value of D_H agreed well with the available data in the literature for soda silicate glass: $D_H=1.528 \times 10^{-12} \text{ cm}^2/\text{s}$ for 15% Na_2O -85% SiO_2 glass [17].

To further improve upon this model, Doremus proposed a transformed surface layer that develops in some less-durable glasses, like the binary alkali silicates and laboratory soda-lime silicates [13]. Taking this surface layer into account helped improve the fit of the model to data for those glasses.

The transformed layer is demonstrated in Figure 7. It is adjacent to the aqueous solution and has a sharp interface with the rest of the glass. It is assumed that the alkali ions in the transformed layer have been almost fully depleted. Next to it is the

interdiffusion layer. This is the layer into which H_3O^+ diffuses but the network structure has not been significantly altered as it has been in the transformed layer. As the concentration of hydrogen in the interdiffusion layer approaches zero and the alkali concentration approaches bulk levels, the interdiffusion layer fades into the bulk glass.

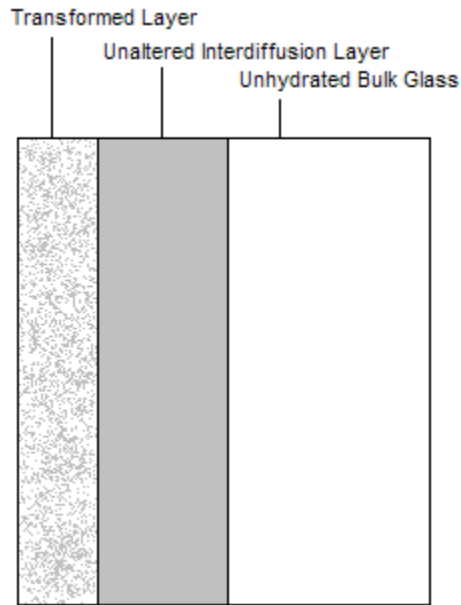


Figure 7: Schematic illustration of the transformed layer appearing in less-durable glasses.

In the transformed layer, the diffusivities are much higher than in the rest of the glass and are not taken into account in the model. The higher diffusivity in the transformed layer was attributed with making it easy to pump out water in a vacuum, a phenomenon which makes experiments requiring a vacuum difficult. This will be discussed in greater detail later.

The interdiffusion model is only applied to the “unaltered” interdiffusion layer, in which it was assumed no significant structural changes had taken place and interdiffusion proceeds as expected in the previous publications. This restriction is illustrated in Figure 8, a hydrogen profile for a low-durability laboratory soda-lime-silica glass, where the vertical line at normalized distance 0.27 represents the beginning of the interdiffusion layer. From 0 to 0.27 comprises the transformed layer and the interdiffusion model is not applied. The fit of the model to the data farther than 0.27 into the glass is shown.

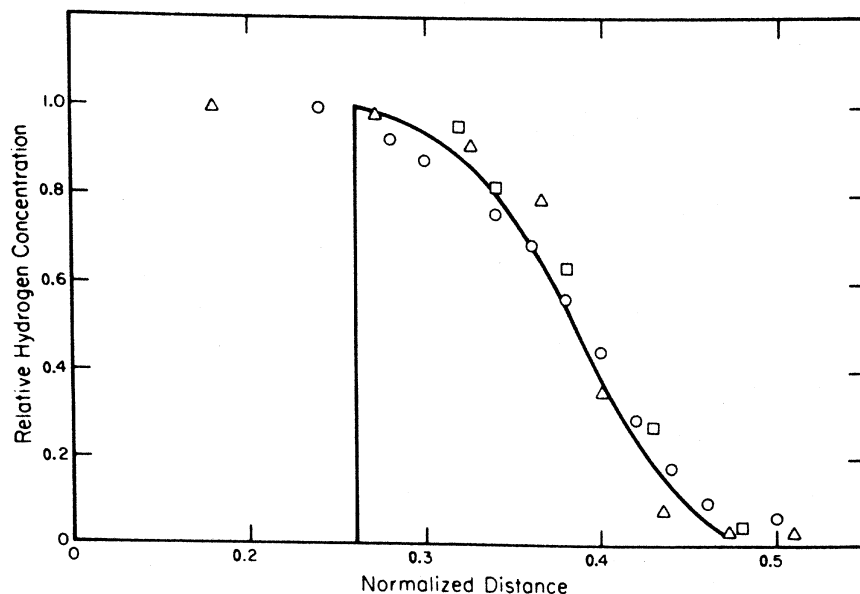


Figure 8: Application of interdiffusion model to low-durability glass using the transformed layer methodology. From [13] (orig. Fig 13, reprinted with kind permission of Springer Science and Business Media, ©1975 Springer).

In applying the interdiffusion model as it originally appeared in [7] (with no concentration effects on D_H or D_{Na}), good fits were found for all glasses tested. The more durable glasses, such as those containing calcium and cesium, did not require a transformed layer to improve the fit. The less-durable glasses, those with only small amounts of calcium, did require a transformed layer. This finding supported the validity of the interdiffusion model in regions of the glass where the network structure was substantially unaltered by hydration. It also elucidated the possible mechanism making some glasses less-durable than others: a layer with little or no resistance to diffusion.

Phase separation in the transformed layer was supported by the work of Tomozawa and Capella [15]. Doremus suggested the high diffusivity in the transformed layer may be due to a high-diffusivity phase resulting from phase separation, though he stopped short of calling the transformed layer a gel in later publications.

Hydrogen-to-Alkali Ratio

The interdiffusion model requires that H_3O^+ replace the constituent alkali atoms. Therefore, it is expected that in fully-leached layers, the ratio of the number of hydrogen atoms to the nominal composition of alkali in the glass would be 3:1 because 3 hydrogen atoms replace every 1 alkali ion. This was indeed the case for soda-lime window glass

used in Lanford *et al.*, as measured by a resonant nuclear reaction technique [16]. This was not the case, however, in the study performed by Houser *et al.* on less-durable Na₂O-3SiO₂ glass, where the ratio was found to be 1.75:1 [17].

Tsong *et al.* found by sputter-induced photon spectrometry (SIPS) that in two commercial soda-lime glasses, the ratio was near 3:1 but for a laboratory (less-durable) soda-lime glass, the ratio was approximately 2:1 [18]. The results for the more-durable and less-durable glasses were in agreement with the previous two studies.

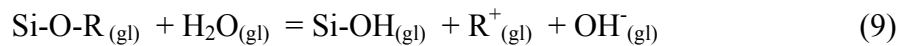
The 2:1 ratio for the less-durable glasses is at odds with the interdiffusion model. The authors postulated two realistic theories for these results and therefore suggested the role of alternative leaching mechanisms: the interdiffusion of a mixture of H⁺ and H₃O⁺ with the alkali ions or the interdiffusion of molecular water with the alkali.

The alternative to this idea, however, is that the low measurement of hydrogen is due to nearly unavoidable removal of water from the transformed layer in the vacuum required by the techniques [19]. Schnatter *et al.* took great pains to ensure rapid cooling of the glass after leaching and cooling during testing in the vacuum [19]. They tested both a soda-lime glass suspected of forming a transformed layer as well as a soda-lime glass which did not. They found an approximate hydrogen-to-alkali ratio of 3:1 in each.

When they tested a similarly corroded glass without these precautions, they found a hydrogen concentration drop of nearly half in the glass with the transformed-layer and no drop in the glass without the transformed layer. These results suggest the validity of the interdiffusion model and the inaccuracy of the hydrogen profiles in glasses with a high-mobility transformed layer which do not prevent the escape of molecular water in a vacuum.

Molecular Water Model

As an alternative to interdiffusion involving H₃O⁺, the second major theory of leaching from glass involves the in-diffusion of molecular water, H₂O, instead of H₃O⁺ [20]. In this theory, the rate-limiting factor is the diffusion of molecular water into the glass. The reaction with the glass occurs as shown in Equation 9 [20]:



This theory was devised for several reasons. First, the authors fit their secondary ion mass spectroscopy (SIMS) data for their less-durable soda-lime and soda-potassium-

lime glass with the interdiffusion model. The only good fit achieved required very low values of D_H and D_{Na} compared to those obtained by electrical conductivity measurements and therefore the authors concluded they were nonphysical. A diffusion model attributing H_2O to be the diffusing species did, however, fit the data. The model requires that the molecular water be immobilized by non-bridging oxygen, as shown in Equation 9. Glasses lacking non-bridging oxygen, such as those containing Al_2O_3 , are not susceptible to this mechanism and therefore are subject to conventional (and slower) interdiffusion as proposed by Doremus.

The theory hinges upon a modification of Fick's 2nd Law to accommodate water immobilized by non-bridging oxygen (Equation 10) [20]. The variable c_m is the concentration of mobile (water) species, c_{im} is the concentration of immobilized (water) species, and D_m is the diffusivity of the mobile (water) species. Equation 11 results after assuming that there is a one-to-one correspondence between non-bridging oxygen and immobilized water, where K' is the dissociation constant of the water. After assuming that the concentration of mobile water is much less than the concentration of immobilized water ($c_m \ll c_{im}$), Equation 12 may be derived. Finally, after using a Boltzmann transformation with $y = \frac{x}{\sqrt{4D_m K' t}}$, Equation 13 may be derived and solve numerically for a given set of experimental data. Appendix A contains the mathematical details of the derivation.

$$\frac{\partial c_m}{\partial t} + \frac{\partial c_{im}}{\partial t} = \frac{\partial}{\partial x} \left(D_m \frac{\partial c_m}{\partial x} \right) \quad (10)$$

$$c_m = \frac{K' c_{im}}{c_A} = \frac{K' c_{im}}{1 - c_{im}} \quad (11)$$

$$\frac{\partial c_{im}}{\partial t} = \frac{\partial}{\partial x} \left(\frac{D_m K'}{(1 - c_{im})^2} \frac{\partial c_{im}}{\partial x} \right) \quad (12)$$

$$\frac{d^2 c_A}{dy^2} = -2y c_A^2 \frac{dc_A}{dy} + \frac{2}{c_A} \left(\frac{dc_A}{dy} \right)^2 \quad (13)$$

In solving the equation and obtaining a fit for the data, the authors found a value of $D_m = 8 \times 10^{-17} \text{ m}^2/\text{s}$ ($8 \times 10^{-13} \text{ cm}^2/\text{s}$) and $K' = 2 \times 10^{-3}$.

In order to test the theory of molecular water diffusion versus ion interdiffusion, Smets and Lommen tested a series of $20\text{Na}-(80-x)\text{SiO}_2-x\text{Al}_2\text{O}_3$ glasses with varying concentrations of Al_2O_3 [21]. At low concentrations of Al_2O_3 , the Na was bonded with both the nonbridging oxygen and the AlO_4^- tetrahedra. At high Al_2O_3 concentrations, the Na was bonded exclusively with the AlO_4^- tetrahedra. The H_2O model was expected to apply for those glasses where Na was bonded with nonbridging oxygen and the ion interdiffusion model was expected to apply for those glasses where Na was only bonded AlO_4^- tetrahedra. The concentration of Na was measured by profiling with SIMS.

At low Al_2O_3 concentrations, the authors found good agreement between the H_2O diffusion model and the experimental data. Leaching occurred more rapidly than would be expected on the basis of the ion interdiffusion model alone. The authors calculated a value of $D_{\text{H}_2\text{O}}=2.3 \times 10^{-13} \text{ cm}^2/\text{s}$ and $D_{\text{H}_2\text{O}}=3.5 \times 10^{-14} \text{ cm}^2/\text{s}$ for 5 and 10% Al_2O_3 , respectively. Correspondingly, at high Al_2O_3 concentration, good agreement was obtained when the ion interdiffusion model was applied. The SIMS profiles of Na and the agreement of the model are shown in Figures 9 and 10.

The variation of the experimental data from the model near 0 (the water-glass interface) can be explained by the slower, supplementary action of ionic interdiffusion to the removal of Na. When analyzed using the interdiffusion model, $D_{\text{Na}}=1.6 \times 10^{-15} \text{ cm}^2/\text{s}$ and $D_{\text{H}}=1.6 \times 10^{-16} \text{ cm}^2/\text{s}$ for that region, the former in good agreement with separate tracer data.

In an expansion of their work, Smets and Lommen published another paper investigating the effects of H_2O concentration on the molecular water model [22]. Instead of assuming $c_m \ll c_{\text{im}}$ and obtaining Equation 13, they allowed c_m to be large and in doing so obtained Equations 14, convertible to Equation 15 using Boltzmann's transformation.

$$\left(1 + \frac{K'}{(c_m + K')^2}\right) \frac{\partial c_m}{\partial t} = \frac{\partial}{\partial x} \left(D_m \frac{\partial c_m}{\partial x} \right) \quad (14)$$

$$\frac{d^2 c_m}{dy^2} = -2y \left(1 + \frac{K'}{(c_m + K')^2} \right) \frac{dc_m}{dy} \quad (15)$$

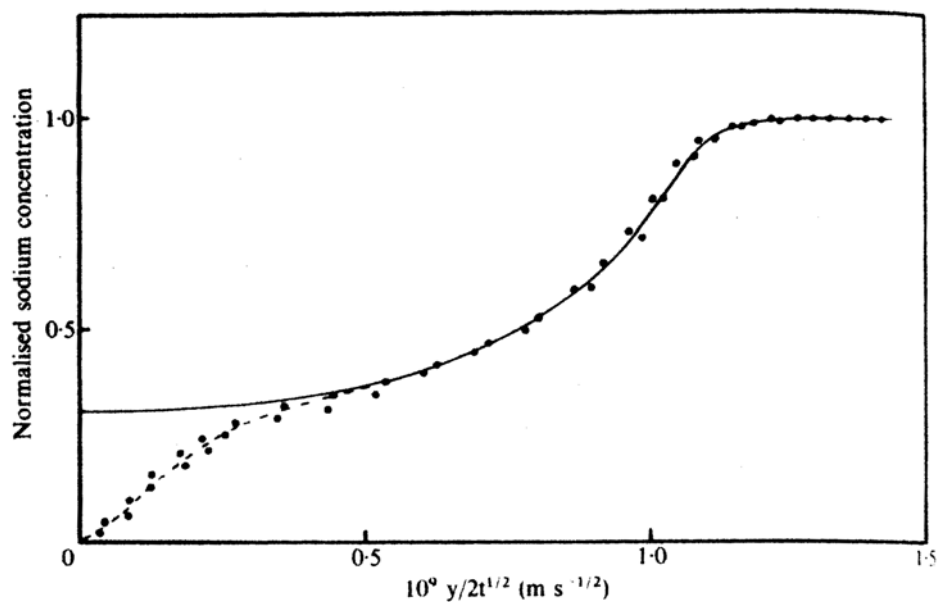


Figure 9: Experimental Na concentration data and theoretical curve predicted by molecular water model for $20\text{Na}_2\text{O}-5\text{Al}_2\text{O}_3-75\text{SiO}_2$ glass. From [21] (reprinted with permission, © 1982 Society of Glass Technology).

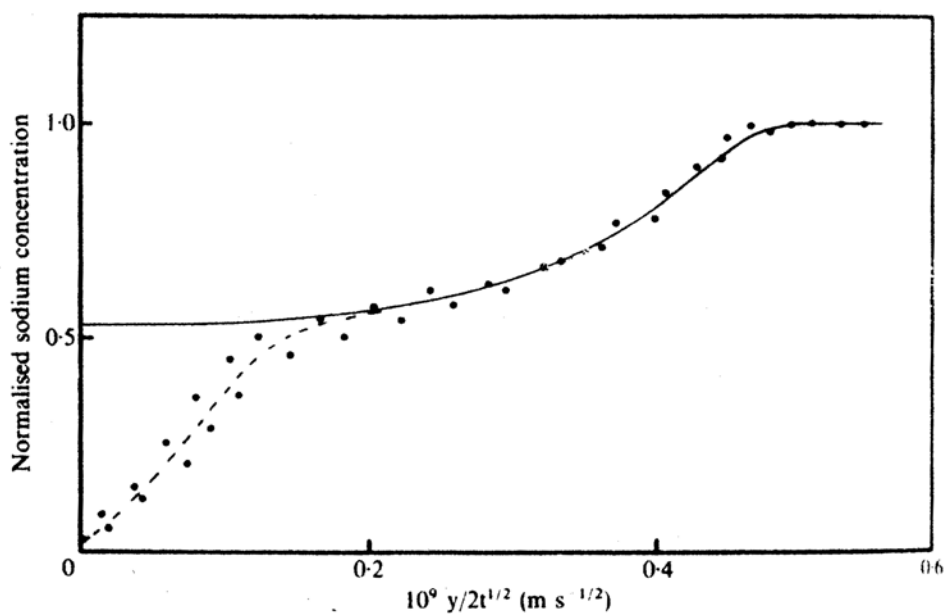


Figure 10: Experimental Na concentration data and theoretical curve predicted by molecular water model for $20\text{Na}_2\text{O}-10\text{Al}_2\text{O}_3-70\text{SiO}_2$ glass. From [21] (reprinted with permission, ©1982 Society of Glass Technology).

As c_m increased, the theoretical curves did not vary significantly, with only slight changes resulting in K' and D_m . The authors argued that this result was proof of the accuracy of the model and that different glasses had different compositions of water in the leached layer, as obtained in the SIMS profiles discussed in the previous section.

In another paper, the molecular water model successfully predicted the sodium and hydrogen profiles determined experimentally by SIMS for a series of soda-lime-silicate glasses [23]. In taking the hydrogen profile by SIMS, the loss of water due to the vacuum was taken into account and treated appropriately. No cooling was performed but the authors claimed sufficient time was not given for a significant decrease in hydrogen concentration. The agreement between the experimental and theoretical curves is shown in Figure 11.

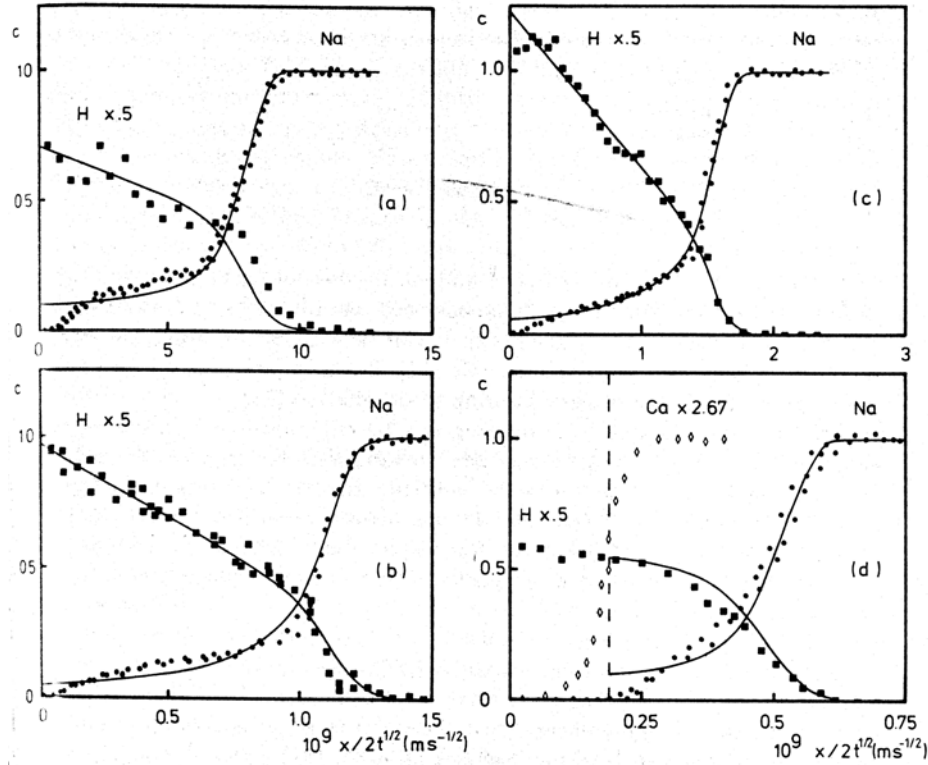


Figure 11: Hydrogen (H) and sodium (Na) concentration profiles for $20\text{Na}_2\text{O}-y\text{CaO}-(80-y)\text{SiO}_2$ glasses with a) $y=0$, b) $y=5$, c) $y=10$, and d) $y=15$. From [23] (reprinted by permission, ©1984 Elsevier).

In addition to calculating profiles, the authors generated several other conclusions. First, they calculated an approximate hydrogen-to-alkali ratio ranging from 1.3 to 2.5 depending on the calcium concentration. Also, they hypothesized that the diffusivity of H₂O decreases as divalent cations are added because the divalent cations block interstices used in the diffusion of H₂O molecules.

To extend the theory to accommodate network dissolution, Equation 10 was modified to include the rate of network dissolution, a (Equation 16) [24]. Using the standard Boltzmann transformation, it was converted to Equation 17, which could be solved numerically to fit experimental data. The hydrogen concentration was expressed as $c_H = 2c_m + c_{im} = 2c_m + (1 - c_{Na})$.

$$\frac{\partial c_m}{\partial t} + \frac{\partial c_{im}}{\partial t} = \frac{\partial}{\partial x} \left(D_m \frac{\partial c_m}{\partial x} \right) + a \left(\frac{\partial c_m}{\partial x} + \frac{\partial c_{im}}{\partial x} \right) \quad (16)$$

$$\frac{d^2 c_m}{dy^2} = -2 \cdot [y + a\sqrt{(t/D)}] \cdot \left(1 + \frac{K'}{(c_m + K')^2} \right) \frac{dc_m}{dy} \quad (17)$$

Equation 17 fit experimental data from 20Na₂O-10CaO-70SiO₂ glass well at low pH (4.7-5.0), moderately well at high pH (8.8-9.1), and poorly at very high pH (12.8-13.0).

The solution kept at high pH was buffered by KOH. Unlike low-pH leaching, the layer of sodium depletion was very thin, much thinner than predicted by the model. Data provided by SIMS showed the layer penetrated by hydrogen to be three times thicker than the layer of sodium depletion. Usually, the two layers are on the same order of thickness. Had ion exchange between H₃O⁺ and Na⁺ been responsible, this result would not have been possible.

The authors concluded that at high pH the diffusion of alkali through the glass was the limiting factor. Therefore, Equation 17 failed to take this into account and could not predict the proper concentration profile. They attributed the limited Na⁺ diffusion to the dissociation of Si-OH in the presence of strong base, leaving Si-O⁻ which trapped the Na⁺ at the nonbridging oxygen site and slowed diffusion.

There were two other findings in this paper relevant to diffusion mechanisms. The first was an approximate surface concentration determined by SIMS of a hydrogen-to-alkali ratio of 2.5 ± 0.5 . The second was the finding that K⁺ from the buffered

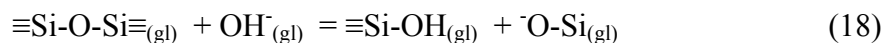
leaching solution penetrated into the glass much slower than hydrogen, as determined by SIMS. This finding is significant because H_3O^+ and K^+ are of similar size and would be expected to diffuse into the glass at nearly the same rate. Since K^+ diffused much slower than the hydrogen-bearing species, it suggests H_2O was responsible for leaching instead of H_3O^+ .

Despite the agreement with experimental evidence, several serious questions remain about the physical viability of the molecular water mechanism [25]. Chief among them was that the theory required alkali and OH^- to diffuse rapidly to the surface of the glass and into solution, which cannot be taken for granted. Additionally, since network dissolution occurs quickly in high-pH solutions, the ability of OH^- to migrate through the lattice without reacting was called into question. Additional doubts included accelerated diffusion in an electric field and high ionic conductivity in the leached layer, both of which are possible in the ion interdiffusion model.

Molecular water can diffuse through the glass structure in one of two ways [26]. The first method is direct transport of molecular water through interstices. The second is via a hydrolysis and condensation reaction where the water molecule hydrolyzes a bridging oxygen bond, then condenses, moves, and hydrolyzes another bond. All oxygen atoms and hydrogen atoms in the glass are eligible to take part in this reaction [27]. In the early stages of leaching, interstices are usually too small to allow for H_2O transport but grow as leaching continues. This enhancement of direct transport of H_2O helps explain the higher diffusivities in the leached layer.

Leaching is not a simple process. There is a significant amount of conflicting data to support two competing mechanisms and problems with both theories [28]. It is likely that both the classical interdiffusion mechanism as well as the molecular water-based mechanism play a role [8, 12, 28].

A novel theory was put forward by Ernsberger that sought to combine both mechanisms and in doing so eliminate the problems with both [28]. One primary assumption was that OH^- , as it occurs in the molecular water theory, does not diffuse through the lattice and back into solution. Instead it reacts quickly with the silica network, as shown in Equation 18.



Equation 9 and Equation 18 completely describe the role of molecular water. It reacts with the nonbridging oxygen, freeing OH^- and Na^+ . Then, the OH^- reacts with the silica network. Finally, the free Na^+ is immobilized by the Si-O^- , forming Si-O-Na . The Na^+ is leached later by H_3O^+ . The net result of the process is Equation 3 since only two new silanol groups are formed. By this process, the glass network is restructured substantially. The rise in pH of a static solution and $t^{1/2}$ dependence of Na^+ release are the result of Equations 2 and 9 occurring simultaneously.

Four distinct regions of the glass are proposed by this unified theory, shown in Figure 12. The quenched layer is adjacent to solution and is very porous. This layer has been restructured and contains gel. Solution is free to penetrate within the layer. The second layer is the neutralization layer. In this layer, the structure has been significantly altered to be composed of some gel and allow much quicker passage of diffusants. The H_3O^+ is responsible for ion exchange as shown by Equation 2 and the near complete removal of Na^+ from the layer. The final distinct leached layer is the restructuring layer in which H_2O is responsible for restructuring the silica network as shown by Equations 3, 9, and 18 and described previously. The final layer is the bulk glass in which no leaching has occurred.

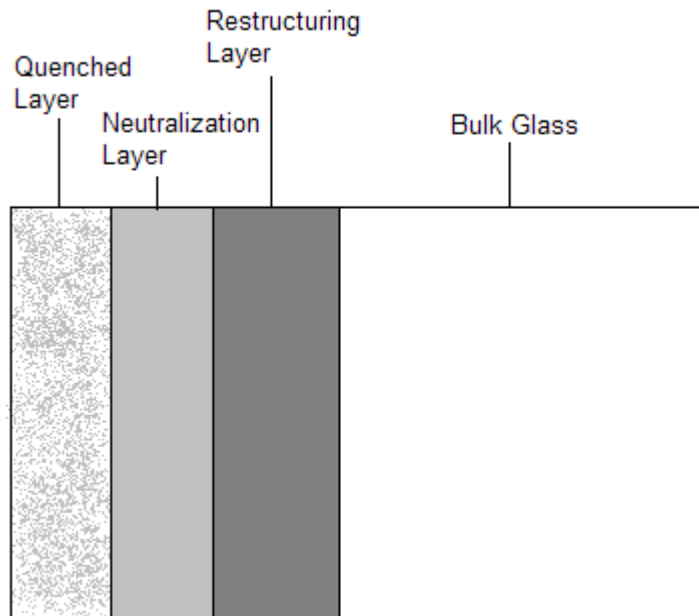


Figure 12: Schematic diagram of the 4 layers of the Ernsberger combined leaching model.

This theory resolved the outstanding problem of OH⁻ diffusion from the molecular water theory and it also solved the problem of the application of the electric field. According to Ernsberger, when an electric field is applied, the diffusion of H₃O⁺ is accelerated to a higher rate than the H₂O and therefore is entirely responsible for leaching. When this occurs, the quenched layer and restructuring layer do not occur because the entire leached layer consists of the neutralization layer. This neutralization layer has very high resistivity, in agreement with experimental evidence [28].

Little research was performed to support or refute this theory. One study, which claimed evidence for pure interdiffusion with a transformed layer, found no evidence for the combined theory [19]. However, the concept of a combined interaction of H₂O and H₃O⁺ leaching mechanisms, though perhaps not exactly aligned with the previous theory, is generally regarded as true [12, 26]. No generalized theory of leaching mechanisms has ever been validated in such a way as to be regarded as definitive.

Network Dissolution

Silica dissolution occurs throughout the corrosion process but dominates after the pH has risen to a high level. Initially, the release of silica into solution is diffusion-controlled because it obeys $t^{1/2}$ kinetics (release is dependent upon the square root of time) and so it is diffusion-dependent [1]. At long times, the control is by t^1 .

The release of silica was first modeled empirically by Rana and Douglas (Equation 19) [29]. The variable Q is the amount of silica released with time, A and B are constants, and t is time. When the corrosion time is short, Q is dominated by the $t^{1/2}$ term but when sufficient time has passed, the t^1 dominates.

$$Q = A\sqrt{t} + Bt \quad (19)$$

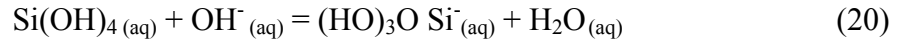
The likely culprit for the initial silica release phenomenon is the diffusion of H₂O into the glass network and subsequent reaction with the network (Equation 3). The diffusion of H₂O into the glass and eventual release of silica obeys the $t^{1/2}$ kinetics required for it to diffuse out.

A model developed by Harvey *et al.* based on the diffusion of H₂O into glass agreed quite well with experiments using Vycor®, a soda-lime silicate, and two borosilicate glasses [29]. Using this model, they derived a diffusivity of H₂O of $D_{H_2O} = 1.3 \times 10^{-13} \text{ cm}^2/\text{s}$ in the soda-lime-silicate glass which agreed fairly well with the

values estimated using the molecular water model [20, 23]. The depth of penetration of water also agreed reasonably well [20].

The reaction occurs until all bridging oxygen associated with a given silicon atom have been hydrolyzed. This is illustrated for a surface reaction in Figure 13 but is analogous in the bulk. The silica is then released in the form of silicic acid: $\text{Si}(\text{OH})_4$ [1]. Diffusion-control is explained by the theory that water diffuses into the glass network, reacts with the silica, and then the products diffuse out.

At low pH values, the $\text{Si}(\text{OH})_4$ remains intact. Across all pH levels, the amount of $\text{Si}(\text{OH})_4$ soluble in water does not change significantly, a fact that is illustrated by the relatively constant region from pH =1 to 9 in the solubility diagram for silica shown in Figure 14 [30]. When the pH rises to approximately 9, more silica is allowed to dissolve into the system by means of the reaction in Equation 20 [30]. The same amount of $\text{Si}(\text{OH})_4$ is dissolved in the system at high pH values, but the overall solubility of silica is increased by reaction of $\text{Si}(\text{OH})_4$ (which would otherwise precipitate) to form $(\text{HO})\text{Si}_3\text{O}^-$.



The silica network is also attacked by OH^- as shown in Equation 18 and Equation 20 [31]. The attack on the silica network increases in severity at high pH due to the increased solubility. When this mechanism takes over, dissolution of the silica at the interface between the glass and water occurs. The kinetics are no longer $t^{1/2}$, or diffusion-controlled. Instead they become interface-controlled and are proportional to t^1 [31].

Another theory of the $t^{1/2}$ dependence of initial silica release was given by Isard *et al.* [32] This theory postulates that there is a local pH increase very near the interface of the glass and water due to H_3O^+ depletion (ion exchange). The OH^- , left uncompensated by H_3O^+ , attack the silica network (Equation 18). The diffusion dependence is due to the concentration gradient set up in the aqueous solution, causing H^+ to diffuse to the interface. As leaching slows, network dissolution slows too because there is less H^+ depletion. Eventually, as solution pH increases to the critical level, t^1 control begins as the solution is flooded with OH^- . The authors were successful in modeling the release of silica and alkali into solution for three disparate glasses, each simulating a natural glass, a nuclear waste glass, and simple laboratory glass, respectively.

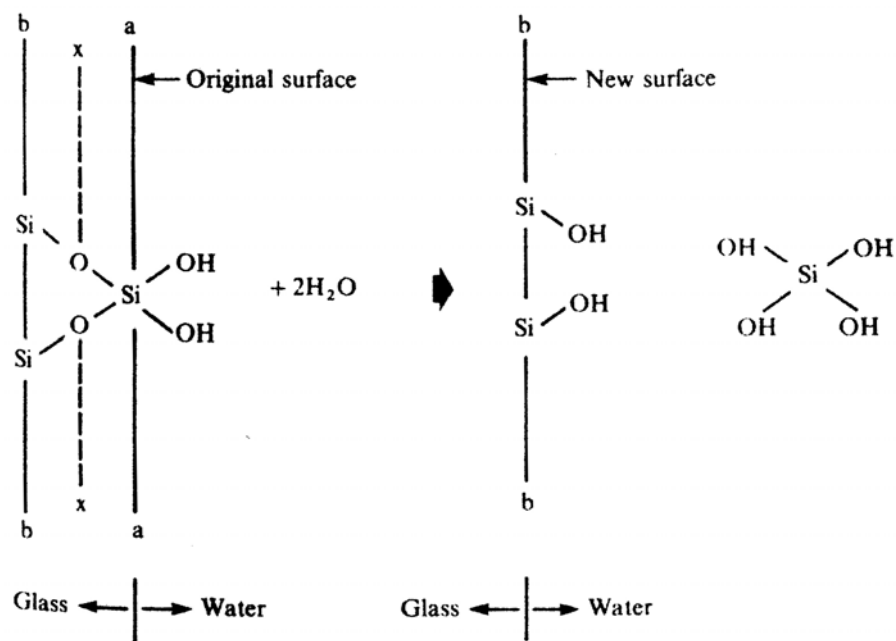


Figure 13: Schematic of H_2O reaction with bridging oxygen bonds and subsequent release of $\text{Si}(\text{OH})_4$. From [29] (reprinted by permission, ©1986 Society of Glass Technology).

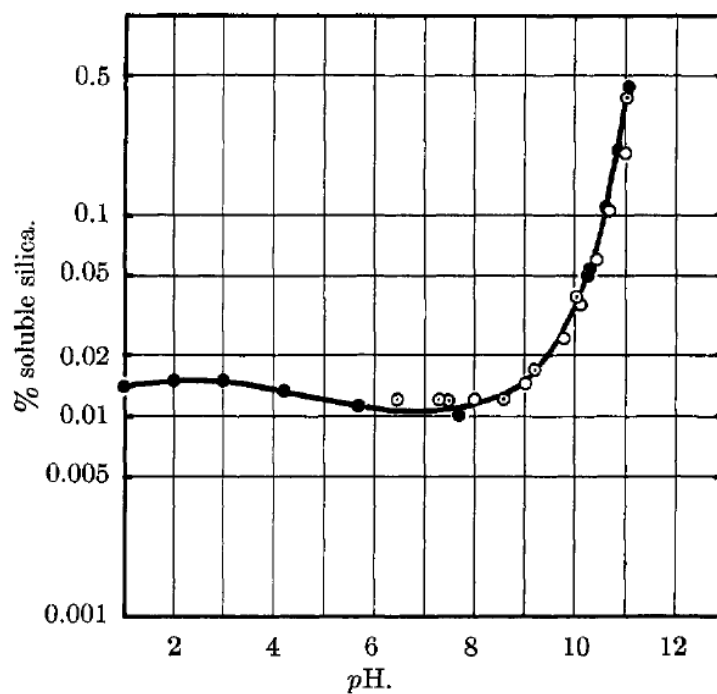


Figure 14: Silica solubility versus pH. From [30] (reprinted by permission, ©1954 American Chemical Society).

Static Corrosion of Li₂O-2SiO₂ Glass

Ethridge performed a very detailed analysis of the overall corrosion process of binary alkali silicate glasses, including Li₂O-2SiO₂ glass [31]. In this analysis, he tracked a variety of critical parameters to determine the nature of the corrosion of binary alkali silicate glasses. These parameters included solution data and infrared reflectance spectra of the glass surfaces.

Figure 15 and Figure 16 show the concentration of Li⁺ and silica released into solution, respectively, during corrosion at 50°C with a glass surface area to solution volume ratio (SA/V) of 0.77 cm⁻¹. In both figures, Li₂O-2SiO₂ glass is denoted 33L, shorthand that refers to the fact that there is approximately 33 mol% Li₂O in the composition. Similarly, 20L refers a glass with the composition 2Li₂O-8SiO₂ and likewise for the other curves labeled in the graphs.

The graphs show that the release of both Li⁺ and silica into solution is greater for glasses with higher Li₂O content at any time of exposure to solution. From the rest of Ethridge's work, it is true in general that as alkali content increases, durability decreases and consequently more alkali and silica are released into solution for a given corrosion time. Furthermore, it is noted from Figures 15 and 16 that the release of Li⁺ and silica has a slope initially of ½ on the log-log plot, thus indicating that the corrosion is proportional to $t^{1/2}$ and therefore diffusion-controlled. For 33L, as time increased past 300 minutes in Figure 16, the concentration of silica changed by a slope of 1, indicating t^1 , or interface-controlled, kinetics. No similar change is shown for the lithium-silicates within the timeframe shown in Figure 15, but the transition was found for less-durable sodium- and potassium- silicates. The change in alkali leaching kinetics occurred after the change in silica release kinetics.

The kinetics were also described in terms of two parameters, α and ϵ , defined in Equations 21 and 22. The first, α , describes the balance between preferential leaching and network dissolution using the concentration of Li⁺ and silica in solution. A value of 0 indicates pure leaching of Li⁺ whereas a value of 1 indicates pure congruent dissolution (attack on the silica network so severe it dismantles the silica bonds and releases Li⁺ as the network disappears). The second parameter, ϵ , is proportional to the thickness of the leached layer.

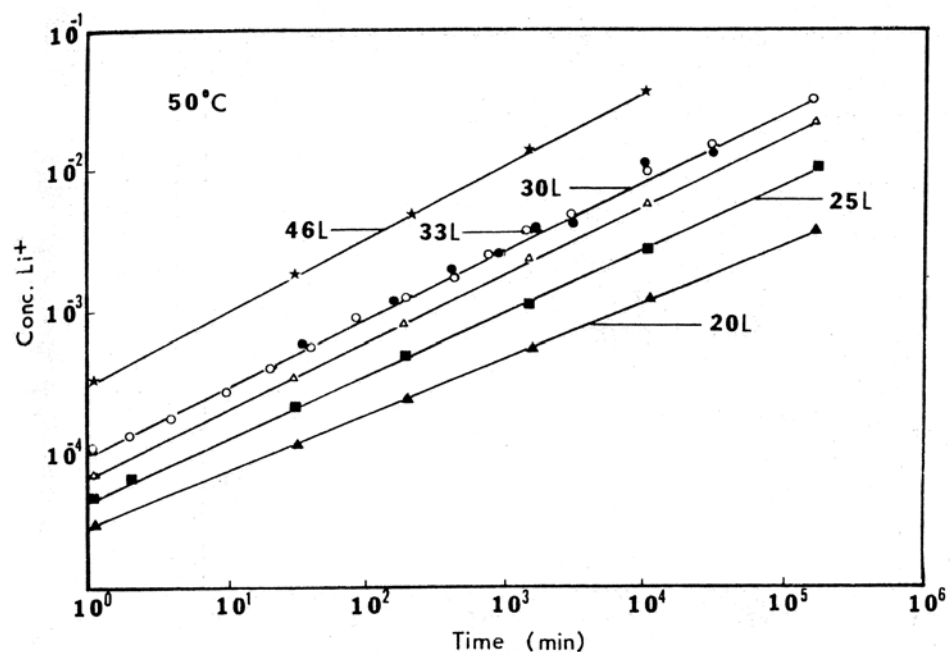


Figure 15: Li^+ released into solution (mol/L) during corrosion at 50°C for various lithium-silicate glasses. From [31] (reprinted by permission, ©1977 E.C. Ethridge).

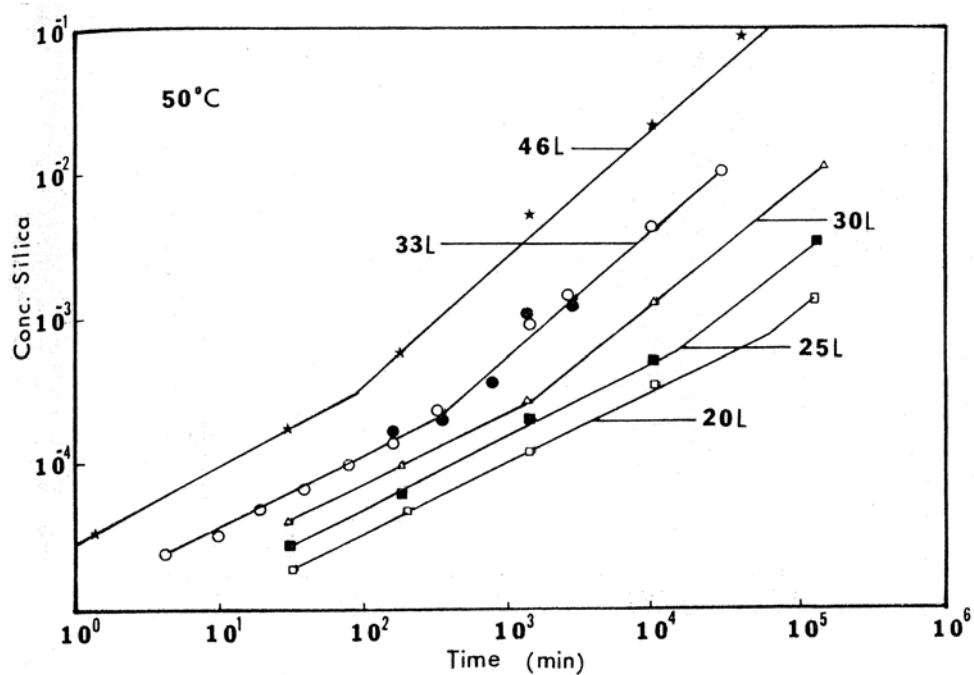


Figure 16: Silica released into solution (mol/L) during corrosion at 50°C for various lithium-silicate glasses. From [31] (reprinted by permission, ©1977 E.C. Ethridge)..

$$\alpha = \frac{[SiO_2]}{[Li^+]} \quad (21)$$

$$\varepsilon = [SiO_2] \cdot \left(\frac{1-\alpha}{\alpha} \right) \quad (22)$$

Figure 17 and Figure 18 show how α behaves. Less-durable glasses (those with higher alkali content) exhibit α -values which rise more quickly due to more severe leaching, shown in Figure 17. The reason given for this phenomenon is that as H_3O^+ is depleted from solution and replaced with Li^+ , the pH rises and network dissolution by OH^- attack occurs more quickly. As temperature increases, Figure 18, the reactions occur more quickly and a high α -value is achieved in less time.

The trend associated with ε is shown in Figure 19. As time increases, leaching occurs and ε increases. Since ε is proportional to the thickness of the leached layer, the leached layer increases in thickness during the process. Eventually, as shown for 46L glass, ε reaches a maximum value and then drops precipitously. Thus, after a time, the leached layer reaches a maximum thickness and then decreases rapidly to 0. Given enough time, the 33L glass, whose ε -curve had almost reached its maximum, would have displayed the same behavior.

The study was also accompanied by a series of wavelength dispersive infrared reflectance spectra of the surface of the glasses. Figure 20 shows the spectra from 33L glass corroded for up to 3 weeks at 100°C. The spectra start similarly to the freshly abraded surface (f.a.), progress and become similar to vitreous silica after approximately 1 hour (1h) to 1 day (1 d). Then, they slowly become more similar to the freshly abraded surface, until appearing nearly identical after 3 weeks (3 w).

Based on this data, Ethridge concluded in general that the corrosion of binary alkali silicates occurs in a multi-step process, illustrated by Figure 21. First, preferential leaching occurs, leading to the release of Li^+ (or other alkali) into solution and the depletion of a surface layer of Li^+ (leached layer). Then, as pH increases past approximately 9, network dissolution accelerates and for a time, both preferential leaching and the dissolution of the leached layer occur. Finally, the rate of leached layer dissolution catches the rate of leaching and overtakes it, leading to a decrease in thickness of the leached layer. Then, after further attack, the leached layer is fully etched away,

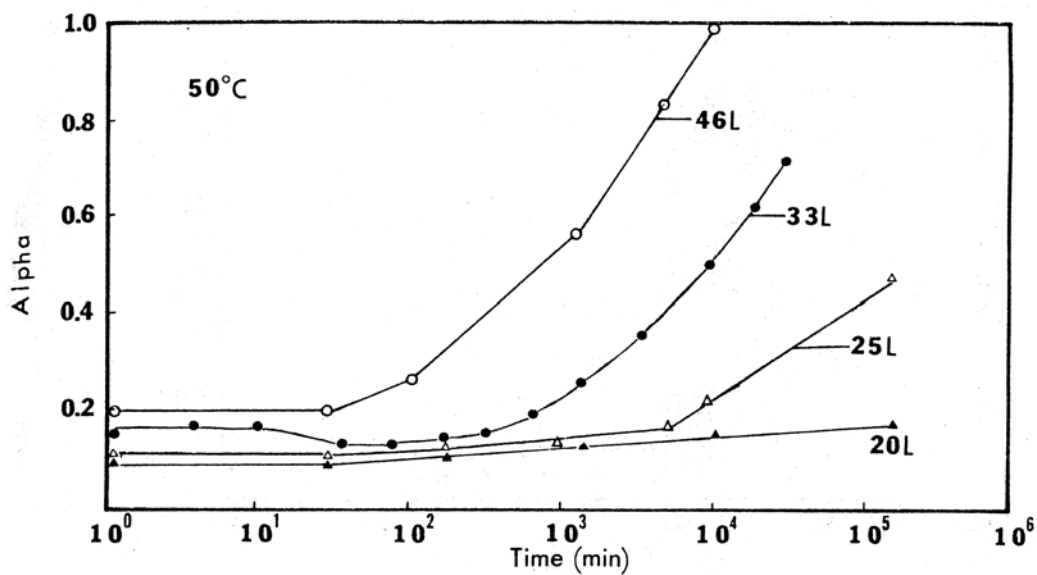


Figure 17: Trend of the parameter α with time for various lithium-silicate glasses. From [31] (reprinted by permission, ©1977 E.C. Ethridge).

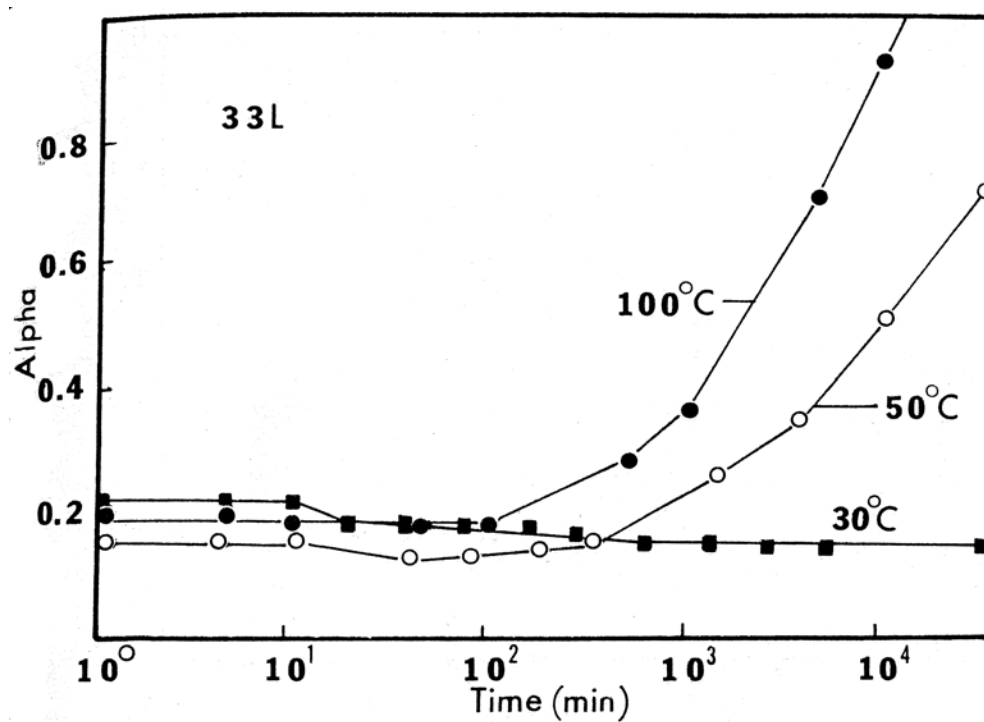


Figure 18: Trend of the parameter α with time for various corrosion temperatures. From [31] (reprinted by permission, ©1977 E.C. Ethridge).

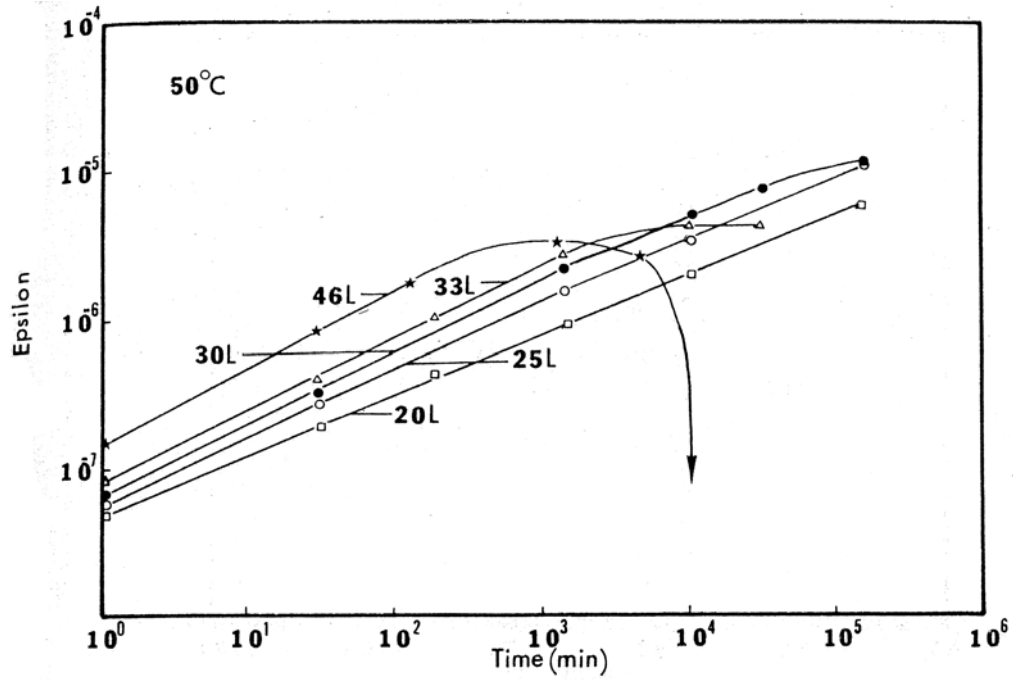


Figure 19: Trend of the parameter ϵ with time for various lithium-silicate glasses. From [31] (reprinted by permission, ©1977 E.C. Ethridge).

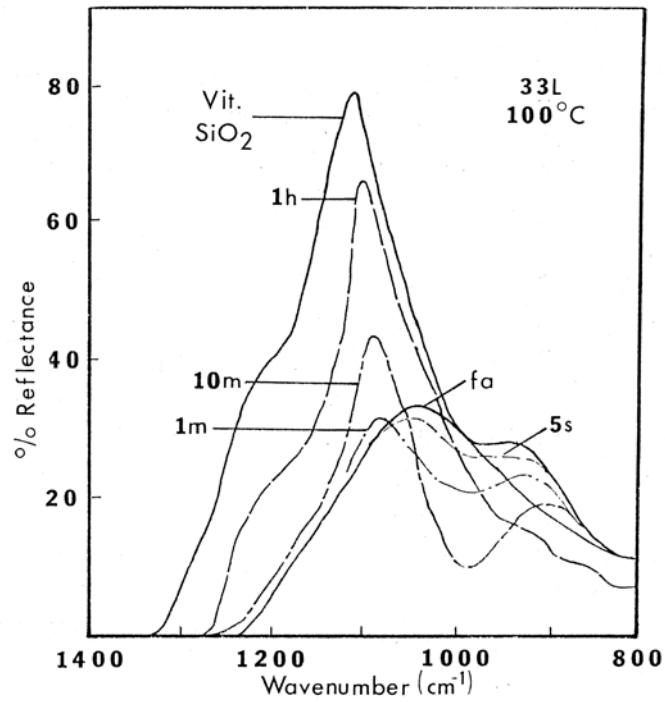


Figure 20: Wavelength dispersive infrared reflectance spectra of 33L glass surface for various corrosion times. From [31] (reprinted by permission, ©1977 E.C. Ethridge)..

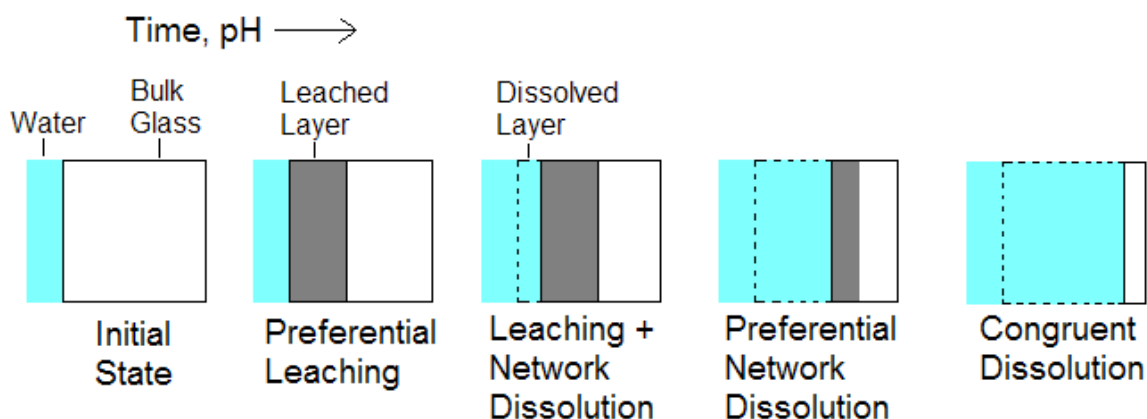


Figure 21: Schematic diagram of the steps occurring in static corrosion of binary alkali silicate glasses. After [31].

leaving fresh bulk glass surface to be dissolved by solution (congruent dissolution). This process is auto-catalytic and will occur by itself given sufficient time in a static solution.

Corrosion of Commercial Glasses

There are a variety of glasses that are commonly used for food packaging and preparation applications. Due to the lack of durability of a simple binary alkali silicate glass, most food-related glasses contain other modifying elements to increase the chemical durability. Chief among these additional elements is calcium, Ca, which forms soda-lime-silicate glass when added to a soda-silicate glass.

In this study, consumer soda-lime glassware was examined for chemical durability in the microwave oven. The selected glass contained a small percentage of elements besides Si, Na, and Ca. For this reason, the corrosion mechanisms of soda-lime-silicates as well as the effect of minor alloying additions such as K_2O , Al_2O_3 and B_2O_3 will also be reviewed here, though the selected glass may not have contained all of these minor additions.

Soda-Lime Glass

Corrosion of simple laboratory soda-lime-silicate glass proceeds in much the same manner as corrosion of binary alkali silicates, but the rate is substantially slower [33]. Clark reported similar infrared reflection spectra resulting from $20Na_2O-80SiO_2$ glass corroded in water at $100^\circ C$ for 1 hour and $20Na_2O-10CaO-70SiO_2$ glass corroded in water for 2 days [33]. After 12 hours of corrosion, the $20Na_2O-80SiO_2$ glass surface was

roughened and cracked severely. The surface of the 20Na₂O-10CaO-70SiO₂ glass did not display comparable damage severity after 9 days in the same environment.

Solution analysis indicated that for the 20Na₂O-10CaO-70SiO₂ glass, Na was leached preferentially at first, while Ca and Si were released at approximately the same rate. After several days, the rate of release of Ca and Si increased, indicating an increase in network dissolution. Electron microprobe analysis showed that a Na-depleted layer was formed during initial corrosion, but as corrosion proceeded, a Ca-rich layer formed within the leached layer. This layer was attributed with increasing corrosion-resistance of the glass at longer times by serving as a diffusion barrier. This barrier also increased the resistance of the glass to network dissolution in high-pH solutions [34].

If the concentration of Ca and Na are too great, then the result could be decreased durability. For instance, if there is more than 20 mol% Na₂O, a glass containing 20 mol% CaO is less resistant to corrosion than a glass containing 10 mol% CaO [34].

The Ca in the glass structure helps to “increase the coupling interaction between the Na ions and the glass network.” [34] Furthermore, “commercial additives to soda-lime-silica glasses improve glass durability by further tightening the glass structure and increasing the coupling interaction between the Na ion and the glass network.” [34] Shelby argued that the Ca atom is positioned similarly to alkali atoms in alkali silicate glasses, except its +2 charge dictates that it must be closely associated with two nonbridging oxygen sites instead of only one [35]. Instead of the nonbridging oxygen sites acting as terminations of the glass network, the nonbridging oxygen actually become linked [35]. In taking this position, the Ca atom takes the place of two alkali atoms [35]. The nature of this bonding leads to higher bond strength and lower mobility of the Ca atom than found in the case of alkali [35]. Molecular dynamic simulations confirm that Ca²⁺ do tend to be distributed next to nonbridging oxygen sites [36].

In addition to CaO, MgO is also used to increase the chemical durability of glass. This compound produced similar effects, though the leached layer is approximately 25% larger when MgO is used [23]. The compound ZnO, though Zn is not an alkaline earth metal, is also used for a similar effect because of its +2 ionic charge [23].

Addition of K

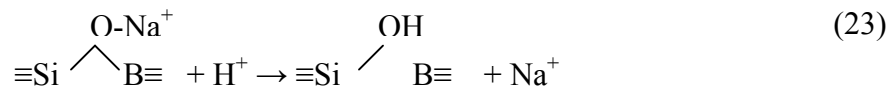
Potassium is another alkali atom, one row down from Na in the periodic table. Its behavior is very similar to that of Na within glasses. Molecular dynamics calculations show it occupies the same sites as Na within a glass [36].

Addition of B₂O₃

The compound B₂O₃ is a glass-former, akin to silica, and is capable of forming a vitreous network with no other constituents besides itself [1]. Instead of the tetrahedral structure of vitreous silica, the default structure is a planar triangle [1]. Thus, each B atom is associated with 3 oxygen atoms instead of the 4 oxygen atoms associated with Si. However, upon the addition of alkali to a borate glass, some B adopts four-fold oxygen coordination and takes on a tetrahedral structure [1]. The tetrahedron, denoted (BO₄)⁻, has an overall negative charge due to the +3 charge of the B as opposed to the +4 charge of Si [37]. As a result, alkali ions are attracted to the tetrahedron.

In a glass with a relatively small percentage of B and large percentage of alkali, the B will be present in both 3-fold and 4-fold coordination. The alkali present in the glass will either be bonded to the B-tetrahedra or to nonbridging oxygen belonging to silica tetrahedra [38].

As a result, in neutral solutions, the alkali bonded to the nonbridging oxygen atoms leach in a manner typically associated with binary alkali silicates with an equivalent number of alkali bonded to nonbridging oxygen [38]. The alkali bonded to the B-tetrahedra do not leach as readily [38]. At high pH, uniform network dissolution dominates [38]. At low pH, leaching of alkali atoms associated with B-tetrahedra occurs in addition to those associated with nonbridging oxygen. Because of this, B is more readily leached due to the effect of H₃O⁺ exchange on Si-O-B bonds (Equation 23) [38]. This effect is called proton-catalyzed hydrolysis wherein the Na⁺ is loosely associated with the oxygen between the Si and B and is replaced with hydrogen. The hydrogen becomes closely associated with the oxygen and therefore fulfills one of the oxygen's bonds and results in the separation of B from the Si.



When the molar concentration of B_2O_3 and Na_2O is approximately equivalent, the durability of borosilicate glass is the best [39]. This effect is modeled simplistically by each Na^+ being associated with a $(BO_4)^-$ tetrahedron [40]. If Na_2O exceeds B_2O_3 , Na^+ in excess of the number of $(BO_4)^-$ tetrahedra is bonded to nonbridging oxygen in the silica network [39]. In actuality, however, it is believed that all B does not exist with fourfold coordination. Instead, some B exists with threefold coordination regardless of the actual Na content. For example, in a $30Na_2O-10B_2O_3-60SiO_2$ glass, approximately 20% of the B has threefold coordination [38].

When Na_2O exceeds B_2O_3 , some threefold-coordinated B (triangular) are left in the glass, with the Na^+ distributed between $(BO_4)^-$ tetrahedra and nonbridging oxygen [41].

Finally, if B_2O_3 exceeds Na_2O , a large number of the B exists with threefold coordination [39]. It was shown for this case that no Na^+ is associated with silica groups [41].

The presence of Ca in addition to alkali causes some $(BO_4)^-$ tetrahedra to be associated with Ca^{2+} [35]. Each Ca^{2+} is associated with 2 tetrahedra in order to offset the single negative charges. This coordination increases the connectivity of the glass network.

Addition of Al_2O_3

Alumina (Al_2O_3) is incorporated into glass and forms $(AlO_4)^-$ tetrahedra similarly to B in borosilicate glasses [38, 42]. In an experiment comparing two sodium-aluminosilicate glasses, one with composition $Na_2O-0.2Al_2O_3-2.8SiO_2$ (having 5 nonbridging oxygen sites for every 10 silica tetrahedra) and the other with composition $Na_2O-0.8Al_2O_3-2.2SiO_2$ (having 1 nonbridging oxygen site per 10 tetrahedra), the effect of alumina incorporation was illustrated [42]. In the glass with more alumina, Na^+ was almost entirely associated with $(AlO_4)^-$ groups and very little (1 atom for every 10 silica tetrahedra) was associated with silica. This glass exhibited network dissolution without the formation of a leached layer at low pH due to the low-pH solubility of Al^{3+} . It also exhibited much-improved resistance to both leaching and network dissolution at high-pH due to lack of solubility of $Al(OH)_3$. The other glass, with more Na^+ associated with nonbridging oxygen sites in the silica network, exhibited more severe leaching in both

acidic and basic solutions and was more resistant to network dissolution in low-pH solution.

These results supported the Smets and Lommen model for the role of H₂O in leaching [21, 42]. When Na⁺ is associated with (AlO₄)⁻ groups, H₂O was suspected not to react with the tetrahedra and was not expected to be a major player in leaching. Hence all leaching was restricted to either H₃O⁺ ion exchange with Na⁺ associated with (AlO₄)⁻ or standard leaching of the few Na⁺ associated with silica nonbridging oxygen. In high pH solution, where less H₃O⁺ was available, leaching was significantly slowed in the glass containing more alumina. Leaching was quicker for the glass containing less alumina, suggesting that H₂O was instrumental. Low pH data was not meaningful, as network dissolution occurred due to Al(OH)₃ solubility.

Wassick and Doremus, however, noted that Al₂O₃ does decrease the dissolution rate of glass but attributed the leaching characteristics not to lower H₂O mobility and reactivity but rather to decreased structural openness which suppressed the diffusion of H₃O⁺ [43]. They claimed that the transformed layer, detailed earlier, was not formed because Al₂O₃ held the structure together better. They based this claim on diffusivities calculated using the classical interdiffusion model. The diffusivities for the Al₂O₃-containing glass agreed with those reported for uncorroded, bulk glass.

A further theory of the contribution of Al₂O₃ comes from Dilmore *et al.* [44] This study observed the beneficial effect of adding Al₂O₃ and speculated that a surface film of approximately 50 nm thickness precipitated over long times in a static solution. They made this conclusion based on decreased Al³⁺ concentration in solution at long times and increased Al³⁺ concentration on the surface of the glass at the same times. Wassick and Doremus did not find evidence of a similar surface film in a soda-lime aluminosilicate glass, however. [43] The true mechanism of improved corrosion resistance due to Al₂O₃ is still somewhat unclear, but it is generally accepted to be similar to that described earlier [21, 42, 43].

In soda-lime compositions with B₂O₃ and Al₂O₃ as minor components, the concentrations of Na₂O and CaO dominate. Some of the bonding discussed for the former additions will be present, but the network structure will be dominated by Si, Ca, and Na. The additional elements do, however, play an important role in increasing

durability through their effect on the network structure. Thus, they should be taken into consideration when considering glass corrosion.

Methods of Characterization

Infrared Reflection Spectroscopy

Infrared spectroscopy is a common tool used in a variety of fields because it provides valuable information on the bonds present in a solid, liquid, or gas. Infrared absorption and transmission spectroscopy have been important to the study of silicates and understanding their structure.

Sanders first proposed the use of wavelength dispersive infrared reflection spectroscopy to study polished glass surfaces [45]. He favored this option for studying glass corrosion over traditional transmission or absorption because thin samples were not required and depth of penetration could in principle be tailored (maximum of 0.5μ , minimum approaching 0μ) using angle of incidence. Also, resulting spectra were characteristic of bonds in the same way that the spectra resulting from the more standard transmission and absorption techniques yielded characteristic spectra. In practice, the technique allowed an understanding of the surface reactions taking place by monitoring bonds because of its nondestructive, room-temperature and atmospheric-pressure nature (i.e. no vacuum required).

In order to use infrared reflection spectroscopy in a quantitative and definite manner, Sanders *et al.* investigated the spectra resulting from different compositions of alkali. The series of spectra for varying concentrations of Li_2O is given in Figure 22 for the range of $800\text{-}1300\text{ cm}^{-1}$. In general, as Li_2O content increased, the spectra looked less like the spectrum of vitreous silica. As Li_2O concentration increased, the tall peak at approximately 1100 cm^{-1} for vitreous silica decreased in intensity and shifted to lower wavenumbers. The satellite peak at 1250 cm^{-1} also vanished. At about 20 mol% Li_2O , a second peak developed at approximately 950 cm^{-1} . In general, the distortion from vitreous silica increased as the molar mass of the alkali element increased.

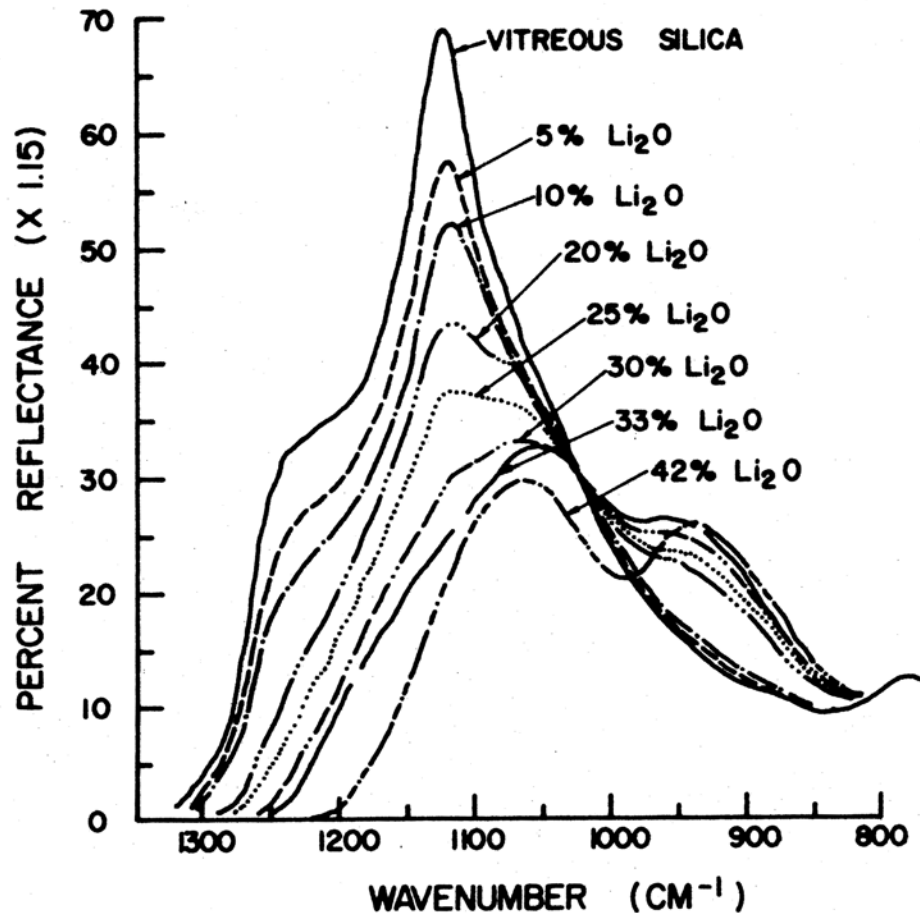


Figure 22: Wavelength dispersive infrared reflectance spectra for various compositions of lithia-silica glass. From [46] (reprinted by permission, ©1974 Society for Applied Spectroscopy).

To understand the meaning of the resulting spectra, the vibration of each type of bond motion was calculated and assigned to an infrared frequency. Two principle mathematical methods were used for this assignment—the Wilson GF matrix technique and lattice dynamics simulations—both of which yielded similar results and were summarized by Sanders *et al* [46]. Figure 23 gives the Fourier transform infrared (FTIR) reflectance spectra for vitreous silica and freshly abraded $\text{Li}_2\text{O}-2\text{SiO}_2$ glass (author's data) with major peaks labeled according to the assignments shown graphically in Figure 24.

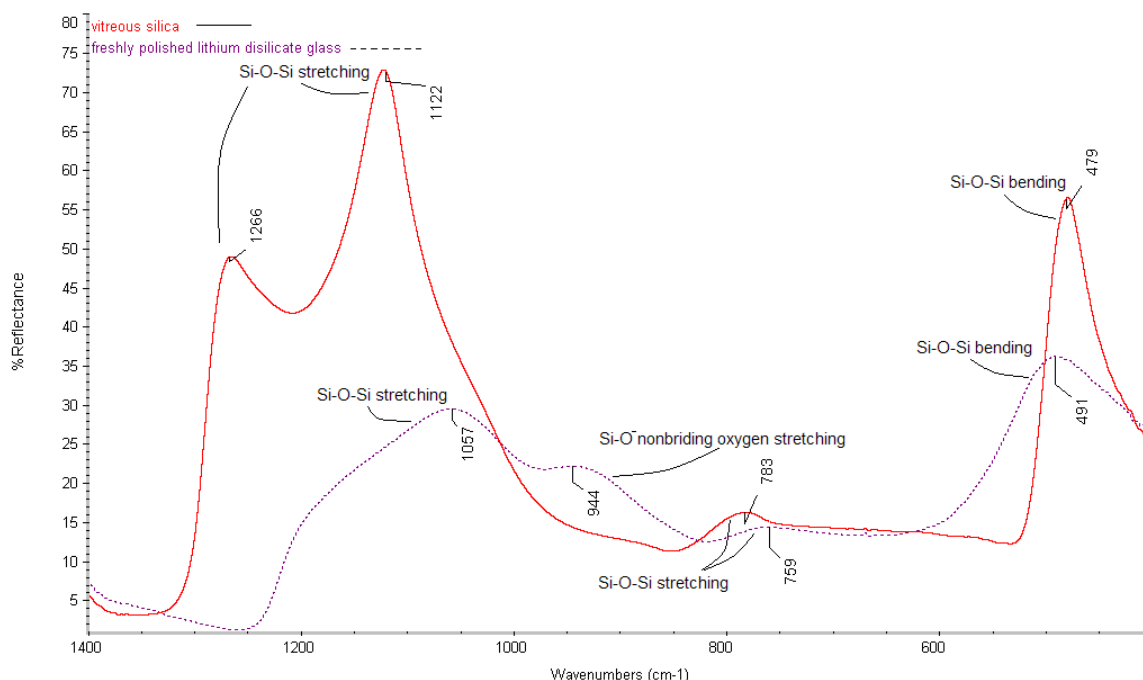


Figure 23: Fourier transform infrared (FTIR) reflectance spectrum for vitreous silica and $\text{Li}_2\text{O}-2\text{SiO}_2$ glass with major peaks identified (Author's own data).

The graphical representation of peak assignments in Figure 24 is a correlation diagram between various modes of atomic vibration for vitreous silica (those vibrations found in the T_d vibration point group column), disilicates (C_{3V} point group column), and metasilicates (C_{2V} point group column). In vitreous silica, the F_2 modes are highly infrared-active and the A_1 mode is slightly infrared-active. The F_2 modes comprise both asymmetric Si-O-Si bridging oxygen bond stretching vibrations and O-Si-O bending vibrations. The A_1 mode consists of symmetric Si-O-Si bridging oxygen stretching. The asymmetric Si-O-Si stretching vibrations are assigned to $\sim 1100 \text{ cm}^{-1}$. The O-Si-O bending vibrations are assigned to approximately 500 cm^{-1} . The Si-O-Si symmetric stretching vibration is assigned to approximately 500 cm^{-1} , but is very weak [47].

For disilicates, the assigned modes are given in column C_{3V} , with both the A_1 and E modes being infrared-active. Both the symmetric (A_1) and asymmetric (E) Si-O-Si bridging oxygen stretching bonds are assigned to $\sim 1050 \text{ cm}^{-1}$. Nonbridging Si-O $^-$ bond stretching in the presence of an alkali is assigned to $\sim 950 \text{ cm}^{-1}$. Finally, the various bending modes are assigned to $\sim 500 \text{ cm}^{-1}$. The widening of all peaks as alkali is added to glass is attributed to the additive effect of these various vibration modes [46].

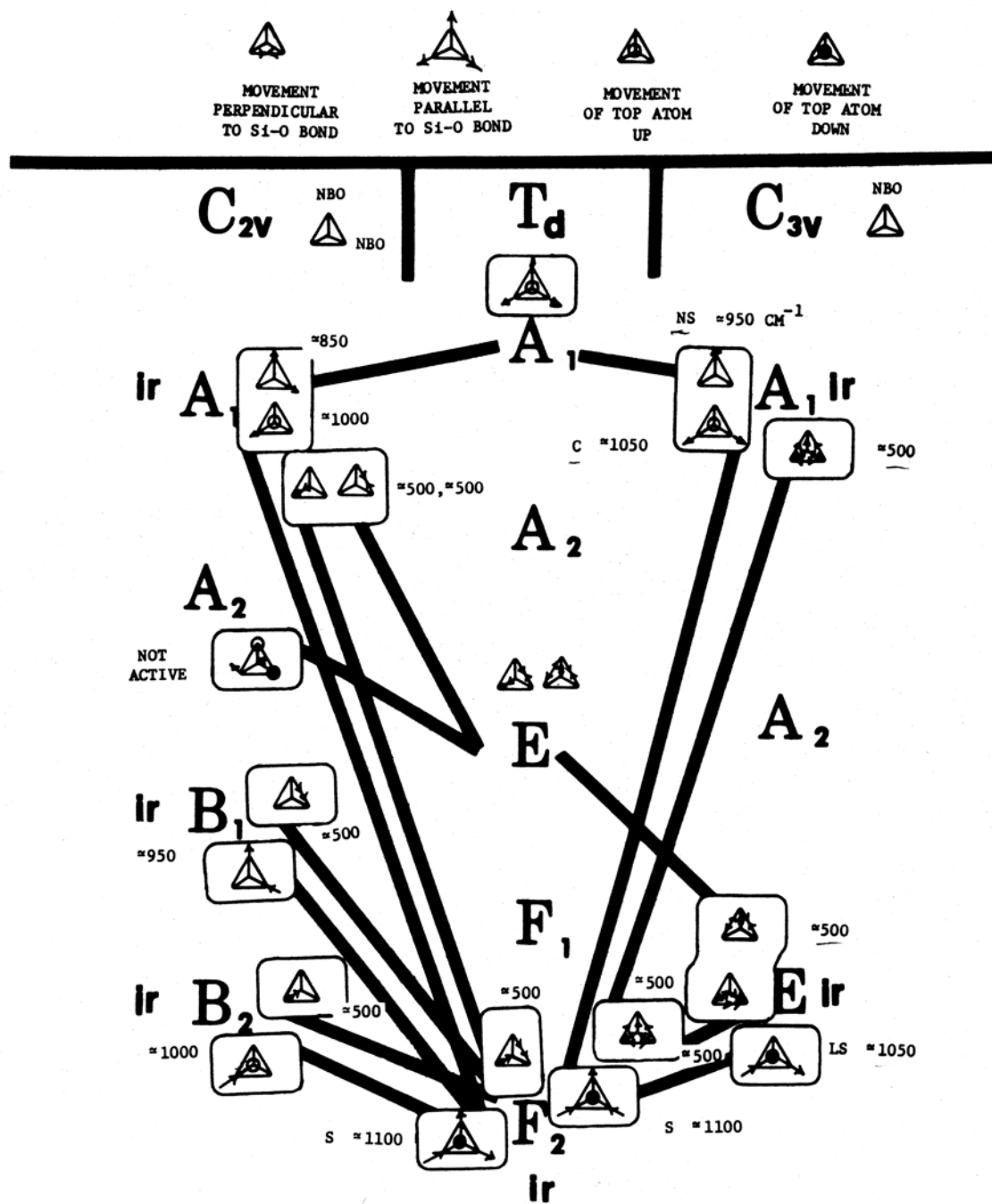


Figure 24: Correlation diagram showing bond vibrations and IR wavelength for vitreous silica (center), binary alkali disilicates (right) and metasilicates (left). From [46] (reprinted by permission, ©1974 Society for Applied Spectroscopy).

Sanders *et al.* also addressed the problem of phase separation in binary alkali silicates through the glasses' infrared reflection spectra [46]. They found that the reflectance of the Si-O-Si stretching peak decreased in intensity as the concentration of alkali increased. There was, however, a slope change in the location where the glasses changed from phase-separated to non-phase-separated. For lithia-silicate glasses, this break occurs at 33 mol% Li₂O, or the composition of Li₂O-2SiO₂ glass. At less than 33%, the glass tended to phase-separate into silica-rich regions (SiO₂) and Li₂O-rich regions (Li₂O-2SiO₂). Thus, the spectrum in the region between 0 and 33 mol% Li₂O was determined by the summed contributions of the SiO₂ and Li₂O-2SiO₂ spectra, with the contributions determined by the lever rule.

Other peaks in vitreous silica have also been identified. The satellite peak at 1266 cm⁻¹ was attributed to the longitudinal optical (LO) mode of the Si-O-Si asymmetric stretching vibration whereas the 1122 cm⁻¹ peak was attributed to the transverse optical (TO) asymmetric stretching vibration [48, 49]. The TO and LO modes are optical phenomena associated with variations of dielectric parameters (ϵ' and ϵ''), index of refraction (n) and absorption index (k) in reflection [50]. Therefore, these two peaks are the result of anomalous behavior of optical parameters.

Also, the peak at 783 cm⁻¹ was assigned to Si-O-Si stretching in rings of silica tetrahedra [48, 49]. Finally, a peak that does not appear in Figure 23 but is of importance later is located at approximately 960 cm⁻¹. It is assigned to Si-OH stretching (analogous to Si-O⁻ nonbridging stretching in the presence of alkali responsible for the peak at 944 cm⁻¹) [48, 49].

The infrared reflection technique was used successfully to monitor changes to Li₂O-2SiO₂ glass surfaces exposed to a variety of conditions, including acid, base, hydrofluoric acid, a desiccator, and corrosion solutions with different SA/V ratios [51]. The changes that occurred in the spectra shed light on the leaching and/or network dissolution taking place on the surface of the glasses.

The information gained by studying the concentration effects on infrared spectra is useful for qualitatively and quantitatively tracking processes involved in corrosion and evaluating extent of corrosion. Ethridge used reflectance data to qualitatively track corrosion [31]. Clark *et al.* used infrared reflection spectroscopy to quantitatively track

the position of the Si-O-Si stretching peak in the region of 1050-1100 cm^{-1} for 20Na₂O-80SiO₂ and 20Na₂O-10CaO-70SiO₂ glasses [52]. As leaching proceeded, the peak's location (wavenumber in cm^{-1}) increased as the square root of time. This result confirmed the role of leaching in the glass system and also provided a tool to determine the extent of corrosion.

The spectrum of a silica gel resembles that of vitreous silica, but is not identical. The primary difference is that the Si-O-Si nonsymmetric stretching peak at $\sim 1122 \text{ cm}^{-1}$ appears at lower wavenumbers due to residual tension on the bonds [53]. Corroded glass surfaces appear similar to vitreous silica as well as silica gels. As corrosion proceeds on a glass surface, the spectrum's peaks shift from that of the bulk glass surface to resemble that of vitreous silica. However, the spectrum never quite reaches that of vitreous silica in terms of peak position (which stays at lower wavenumbers) or reflectivity. The appearance is therefore also characteristic of a silica gel. The same peaks are present and identified with the same vibrations, but the surface structure is not equivalent with vitreous silica and probably resembles a gel, as described previously.

Recently, the applicability of this approach to all glasses was called into question [54, 55]. The estimated maximum depth of penetration for the infrared beam into an SiO₂ surface layer is typically approximated to be 0.5 μ with an angle of incidence of 25° from the normal to the surface, assuming attenuation of the infrared radiation to 1/e of its initial strength [56]. Figure 25 shows the calculated depth of penetration for vitreous silica and generic soda-lime glass, assuming attenuation to 1/e. For attenuation to 10%, the calculated depths should be multiplied by 4.6 [54].

For SiO₂ films on glass substrates, such as those developed during leaching, it was shown that a layer approximately 2 μ thick was needed to eliminate interference from the substrate with a near-normal angle of incidence, assuming attenuation to 10% of the beam's original strength [55]. The interference caused by the substrate affected the location and intensity of the main stretching band ($\sim 1100 \text{ cm}^{-1}$) as well as the location and intensity of the $\sim 950 \text{ cm}^{-1}$ band (which is assumed to be caused by Si-O⁻ stretching in an alkali environment or Si-OH stretching). The authors concluded that, at least when using reflection spectroscopy at a near-normal angle of incidence, the traditional chemical interpretations of the resulting spectra were probably valid for the less-durable

alkali silicates which form leached layers on the 2- μ scale, but might need to be reconsidered for more-durable commercial glasses that form thinner leached layers.

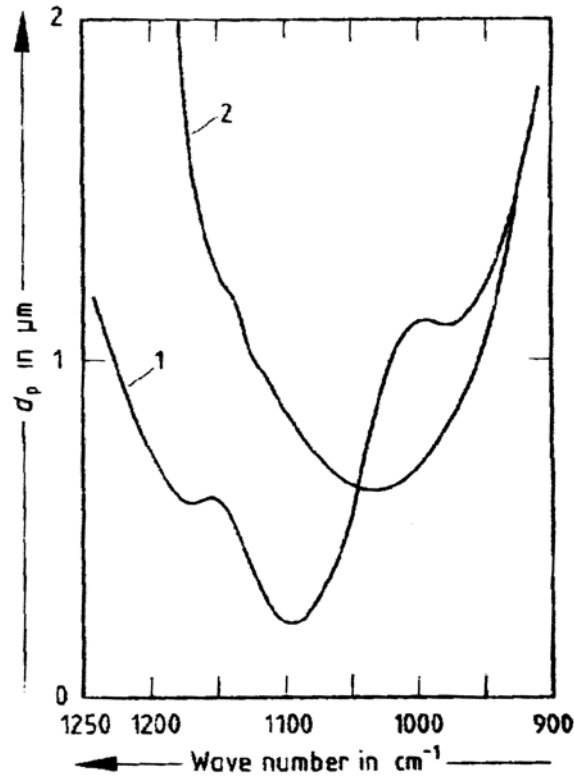


Figure 25: Calculated depth of penetration for vitreous silica (line 1) and generic soda-lime glass (line 2). From [54].

The authors suggest that the purely chemical interpretation of the reflection spectra is inappropriate on the basis that essentially the same sequence of spectra can be generated by depositing layers of SiO_2 of varying thickness on a soda-lime glass substrate [54]. As layer thickness increased, the resulting sequence of reflection spectra resembled that which would be expected for the leached layer of a glass as leaching proceeds. The spectrum of zero thickness SiO_2 appeared as the bulk glass and as the SiO_2 thickness increased, the main Si-O-Si asymmetric stretching peak moved to the left (higher wavenumbers) and the nonbridging peak decoupled and moved to the right (lower wavenumbers) and decreased in intensity. Eventually between 1 and 3 μ , the reflection spectrum resembled that of bulk vitreous silica. This effect was further confirmed by computer simulation [54].

The best fit to experimental data was achieved when the components of the complex index of refraction, N (where the components are the real index of refraction, n , and the absorption coefficient, k , such that $N=n+ik$) were varied between that of soda-lime glass and vitreous silica. Initially, with no silica layer, N was equivalent to that of bulk soda-lime glass. As the thickness of the layer increased, N was set to intermediate values between the two. Finally, when the thickness was at the critical value determined experimentally, N was set to the value of vitreous silica. Throughout this process, the sequence of spectra displayed was equivalent to what would be generated by leaching of a soda-lime glass.

These studies demonstrate that the reflection spectra are dependent on the thickness of the leached layer as well as the optical properties of the leached layer and the bulk glass. Thus, they cannot be used to estimate the concentration of alkali within the leached layer as previously supposed but they can be used to demonstrate relative degree of leaching. Both the thickness of the leached layer and its optical properties are dependent upon the leaching process, so corrosion can be studied comparatively.

An important element of the work described above is the depth of penetration as related to the angle of incidence. The authors used a near-normal angle of incidence and report all results as such. To calculate depth of penetration at other angles, the equation for $1/e$ attenuation is given in Equation 24 below [57]. In this equation, W is the wavenumber, N_c is the refractive index of the crystal used in the equipment, N_{sc} is the ratio between the refractive index of the sample and the crystal (N_{sample}/N_c), and Θ is the angle of incidence.

$$D_p = \frac{1}{2\pi W N_c (\sin^2 \theta - N_{sc}^2)^{1/2}} \quad (24)$$

As angle of incidence increases, where the angle is measured from the vector normal to the plane of the sample, depth of penetration decreases. Therefore, the depth of penetration for an angle of incidence of 45° , such as the angle used in this study, is much less than for nearly 0° (near-normal) or even the 25° used in older calculations.

Thus, the estimate of $2\text{-}3\mu$ thickness of the leached layer from [55] is an overestimation for what is required to eliminate the influence of the substrate in $\text{Li}_2\text{O-SiO}_2$ glass in this work. The actual depth of penetration into $\text{Li}_2\text{O-}2\text{SiO}_2$ is probably

more on the order of 0.5-1.5 μ due to the high angle of incidence used in this study. Significant interference from the bulk is likely an issue only in the initial phase of leaching before the leached layer builds up much thickness. However, the spectra obtained in this study are very representative of comparative corrosion even if the bulk glass interferes with the spectra because the spectra are only compared to one another and no attempt will be made to quantify the amount of lithium in the leached layer using infrared reflection spectroscopy.

Secondary Ion Mass Spectrometry

Secondary ion mass spectrometry (SIMS) is another tool for the characterization of a corroded glass surface. This technique is a destructive technique requiring a vacuum that allows both the characterization of surface composition as well as depth profiling [58]. The generation of a depth profile is known as dynamic SIMS and generates curves such as Figure 4 and similar plots.

A depth profile is achieved by means of sputtering away the surface of a sample with accelerated ions [6]. As the accelerated ions, known as primary ions, impact the surface, they ionize some fraction of all elements present. The ionized surface elements, called secondary ions, are then analyzed by mass spectrometry.

A beam of primary ions only ionizes a portion of all atoms present on a surface [59]. Sputtering is achieved because the rest of the atoms from the surface are simply knocked loose by the high energy ions. All the atoms from a surface, both charged and uncharged, are drawn away from the sample. The uncharged atoms are then filtered from the secondary ions and the secondary ions are analyzed using mass spectrometry.

The data that results from mass spectroscopy is in counts per second, i.e. only the numbers of secondary ions per second are counted. Unfortunately, each element ionizes at its own rate which, among other things, is dependent upon its chemical environment and varies greatly from material to material [58, 59]. For instance, if $\text{Li}_2\text{O}-2\text{SiO}_2$ glass is analyzed by SIMS and x counts per second of Li-bearing ions are measured and x counts per second of Si-bearing ions are also measured, the ratio of Li to Si is not 1 to 1 even though equal number of secondary ions of each species are measured. It is simply a coincidence that the numbers happen to be the same. Therefore, data in counts per

second cannot determine chemical concentration alone. The profiles, however, can be used to infer changes in relative concentration of a particular element.

In order to allow concentration to be quantified, a standard of known concentration must be used to calibrate the curves [59]. If no standard is available, no quantitative chemical analysis is possible. This fact makes the quantitative analysis of hydrogen very difficult, as hydrogen is not available as a solid and it is very difficult to achieve a set hydrogen concentration in a real material.

Conducting samples easily conduct away charge and so the buildup of potential is not a problem. However, insulating materials, like glasses, do not conduct away charge and the buildup of potential may lead to migration of cations and other species within the sample and invalidate any data gained by performing the technique [59]. To alleviate this problem, they are coated with a thin film of conducting material (similar to preparation for scanning electron microscopy) [58]. A charge neutralization gun may also be used [59]. This apparatus discharges an electron beam of equal and opposite current to the beam of positive secondary ions. These methods allow a glass to remain electrically neutral and yield good, reliable SIMS profiles useful for analyzing glass corrosion [58].

Migration

Glass is an important food container material. It is routinely used in packaging as a stand-alone material or as glaze to coat surfaces in contact with food or beverage. Because of this role, it is often in contact with food during microwave heating.

A primary concern for food contact materials is that of migration. For glasses, migration is the release of corrosion product into food. Migration is defined as “mass transfer from an external source into food in physical contact with it by sub-microscopic processes.” [60] Since a wide variety of materials are used to contain food, migration is known to be a concern for plastics, rubber, metals, paper and paper products, and glass [60]. Oligomers, monomers, polymerization aids, and catalyst residue are known to leach from polymers [61]. From glasses, silica and component species may migrate [62]. Migration is particularly troublesome at high temperatures where the kinetics of diffusion are enhanced. The problem is most severe for polymeric food contact materials, as is evidenced in the large volume of literature devoted to the subject.

Glass is typically not given significant consideration as a potential hazard because it is known as “amongst the most inert of common substances.” [62] Silica is under investigation as a buffer coating on plastics to prevent more severe migration into foods [63].

In 1974, a study was performed on container glass manufactured in the United States [64]. The test was performed using distilled water and acetic acid as extracting solutions heated in an autoclave at 121°C for 1 hour. The conditions of the tests simulated the room-temperature migration from the containers that would be expected over the course of several months [65]. The solution analysis revealed the presence of 27 species. The expected migrants, SiO₂, CaO, MgO, Na₂O, and K₂O, were present in solution, but other species were found in trace quantities including Al, Ti, V, Cr, Mo, Sn, Pb, Mn, Ni, Cu, Sr, Ba, B, As, Sb, Se, Fe, F, Co, Zn, Cd, and Hg. Despite the unexpected migrants, all containers tested were found suitable for water and acidic aqueous solutions according to the proposed limits at the time of the US Food and Drug Administration [64].

Another migration test was performed on container glass from the United Kingdom in 1989. It mimicked the thermal treatment of the first study (121°C for 1 hr.) [62, 65]. Similarly, the analysis revealed the presence of 27 leached species, some of which were known migrants—SiO₂, Na, K, Ca, Mg, and Al—and some of which were unexpected migrants and potentially harmful, though very dilute—Sb, Ba, Mo, Se, Sn, T, V, Cd, Cr, Co, Fe, Pb, Li, Mn, Ni, Sr, and Zn [62]. All glass articles studied conformed to the European Union’s proposed migration standard of 10 mg/dm² of food-contact surface [65].

Lead oxide is often an additive to glass used for standalone articles or as glaze for ceramicware. The leaching of lead from this type of glass has been known for some time and standards to limit lead leaching continue to increase in scope [62]. The goal is the continual reduction of lead migrants.

Through studies similar to these, the chemical durability of most types of container glass is understood and controlled under room-temperature and conventional heating conditions. However, no significant investigation into the microwave effects on migration from glass has been performed.

The idea that microwaves enhance migration is not new, but has only been studied with any degree of rigor in polymeric materials. In one study, the migration of seven common species—oligomers, acetyltributyl citrate, dilaurylthiodipropionate, benzene, toluene, ethylbenzene, and Irganox 1076—from five common polymers—crystalline poly(ethylene terephthalate), poly(vinylidene chloride)/poly(vinyl chloride), poly(4-methyl-1-pentene), polyester, and polypropylene—was studied using heating both by microwaves and a conventional oven [66]. The measurement accuracy was somewhat low, specifically $\pm 25\%$ for the specific migrants of interest from crystalline poly(ethylene terephthalate) and polyester and $\pm 12\%$ for those migrants of interest from poly(vinylidene chloride)/poly(vinyl chloride), poly(4-methyl-1-pentene), and polypropylene [66].

The data indicated no significant microwave enhancement, but the conclusion was not that there was no microwave effect; rather the authors concluded that if any effect were present, it was insignificant. Even if a microwave effect as large as $\pm 25\%$ was present, the data obtained conventionally was declared good enough for migration testing and therefore “migration testing of plastics materials for the purposes of examining for compliance with regulations can be conducted in conventional laboratory oven, as is already the case with other food contact materials.” The authors acknowledged that “it is not possible to demonstrate unequivocally whether or not microwave energy itself exerts any effect on migration from plastics...there are far too many classes of materials and types of components to individually examine every circumstance...nevertheless [results can be] used to make generalized statements about the effect of microwave energy.”

A later study sponsored by industry performed by de Kruijf and Rijk also investigated the effect of microwaves on migration from food contact materials [67]. Several different plastics and one glass pot were studied. Neither the composition of the glass, nature of the glass migrant, nor any other information about the glass was specified. Tests were performed in the four different types of food simulants: water, 3% acetic acid, 15% ethanol, and olive oil. Instead of matching temperature profiles, the authors tested the materials conventionally using European and Dutch standards and tested the materials heated by microwaves by simulating actual use conditions [67].

The conventional tests were much longer in duration than the microwave tests. Furthermore, the maximum temperatures did not quite match the maximum temperatures attained by microwave heating. For instance, the glass tested with water conventionally was filled with hot water and placed in an oven for an hour. The maximum measured temperature of the water was in the range 92-96°C. The glass tested using microwave heating had a total exposure of 7 minutes and experienced a maximum temperature of 100°C, as measured by a thermocouple.

In this particular test, the migration values for the glass exposed to microwaves were lower: 0.6 mg/dm² compared to 2.3 mg/dm². However, after exposure to identical test conditions as water, the acetic acid test resulted in a migration value that was higher for the microwaved sample, 1.0 mg/dm² compared to 0.9 mg/dm², despite being exposed for only 11.6% of the total time at a slightly higher temperature than the conventional sample. The authors concluded that any differences between migration conventionally and with microwaves were small and therefore conventional test conditions could be used to test materials, both plastic and glass, intended for microwave use [67]. The authors did not make any investigation into migration from exposure times and temperatures that were equal for both heating methods as this type of test is very difficult to perform (typical home microwaves are not equipped to monitor temperature and vary power output; equipment with such capability is very expensive and rare).

In another study, the authors tested six polymers using four heat treatments [68]. The first three treatments were conventional: 40°C for 10 days, 80°C for 30 minutes, and 121°C for 30 minutes. The fourth treatment involved microwave irradiation at 800 W for 3 minutes. Separate tests were carried out using 100 ml of 3 aqueous simulants—water, 3% acetic acid, and 15% ethanol—by filling pouches of test material. Though no attempt was made to monitor temperature in the microwaved samples, the overall migration after 3 minutes of exposure to microwave radiation from polyvinyl chloride (PVC) was shown to be greater than migration from PVC caused by the 3 conventional treatments [68]. Being aqueous simulants, it is not likely that the bulk temperature exceeded 100°C during the 3 minutes of microwave exposure, which puts the severity of the microwave test into perspective. No other polymers tested exhibited significant differences due to microwave exposure [68].

The generalized conclusion that microwaves do not affect migration from plastics at a level significant enough to mandate special accommodations has become the conventional wisdom in the migration community [61]. The United States Food and Drug Administration (FDA) requires only a conventional test of microwave food contact materials to be performed when qualifying a new product [69]. The temperature of this test is determined only by the maximum measured temperature experienced by any part of the product while in a microwave oven.

The FDA's required tests make use of an "estimated daily intake" (EDI) figure [69]. This value is based on the idea that a toxic substance, if present at a sufficiently low concentration, poses a negligible health risk [70]. In order to qualify a product, the amounts of specific migrants present after what is expected to be average daily use must be shown to be safe. This documentation through various toxicological studies is provided with other pertinent information to the FDA [71]. Therefore, no specific limits exist on migrants, but levels of migrants present must be demonstrated to be safe. In Europe, where migration legislation is much more restrictive, the proposed overall migration limit for glasses and glass ceramics is 60 mg/L (60 ppm), with limits on specific migration from lead and cadmium of 5 mg/L (5 ppm) and 0.25 mg/L (0.25 ppm), respectively [70].

Thus, it is possible in theory to qualify a product in the United States even if microwaves do accelerate migration. The first reason this might be possible, and the one most relevant to the pertinent regulations, is that testing is done conventionally and so no effect would appear. Furthermore, even if some acceleration of migration were known, it might be considered negligible if what migrates is less than the ADI specifies regardless of how it relates to conventional leaching. This information would not be required to be shared with the FDA or the migration community.

While the absence of a microwave effect has been accepted as the physical reality, it is supported by only a few studies performed on polymers. There has been very little in the literature specifically on glass migration due to microwave heating. In fact, glass has been praised as an ideal microwave material due to its resistance to *conventional* migration [72].

The focus on glass in microwave ovens has been one of mechanical stability and non-uniform food heating. Several papers have been published that report microwaving food in glass does not cause thermal stresses severe enough to damage the mechanical integrity of the glass [73-75]. Corning recommended for microwave use any glassware labeled “ovenware” or similar designation because these types of glass have been tempered to withstand thermal stresses [76, 77]. Other concerns are the buildup of hotspots within the food which can cause local boiling and violent splattering [63].

Another criterion for glass use in the microwave is microwave absorption. Corning recommended against using glazed glass-ceramic ware in the microwave because certain components of the glass glaze may be more absorbing, causing rapid heating and failure due to thermal stress [76, 77]. Furthermore, Corning recommended a test for ceramic ware which called for placing a container of water inside a ceramic dish and heating both in the microwave. If the dish got hot but the water stayed cool, the dish was not recommended for use in the microwave because it absorbed too much microwave energy [77].

These two criteria, mechanical stability and non-absorption, serve as the principal requirements for the designation “microwave safe.” A major distributor of consumer microwave-safe glassware conducts tests, the nature of which are proprietary, to ensure the glass will not break under rapid and nonuniform heating conditions in the microwave oven [78]. The absorption test described previously is also commonly recommended as the appropriate method for testing an article if it is not labeled as such [79]. Therefore, for the designation “microwave safe,” the article must pass the mechanical stability/heating tests (it may be inferred also that the article must conform to migration standards at the appropriate conventional temperature as described previously). There is no universal standard for labeling a glass product “microwave-safe.” [78]

The studies that do evaluate the effects of microwaves on migration have not been comprehensive. In one study, ceramic dinnerware manufactured between 1920 and 1940 with lead-glass glaze was bought secondhand [80]. The items were filled with 4% acetic acid or 0.5% citric acid and heated for 2 and 5 minutes in a microwave, respectively. Microwave heating studies indicated that enough lead had leached so that “eating a single meal microwaved in one of the test dishes could result in the ingestion of amounts of lead

approaching or exceeding the 3.0-mg permissible weekly limit for adults.” No attempt was made to compare these results with conventional heating, but large amounts of lead were also found to have leached when the acid solutions were allowed to stand in them for 24 hours at room temperature.

In another study, the author cooked beans and tomato juice in recently manufactured lead-glazed vessels by an open-flame method and by microwave heating [81]. The data indicated that more lead was released by the open flame method; however, the cooking time in the microwave was shorter and no attempt was made to monitor temperature in either setup.

The experimental conditions in comparative migration studies obscured the fundamental mechanisms that govern glass corrosion. It is clear from the first study that leaching occurs when microwave heating is used. It is also clear from the second study that under those particular conditions (including the specific glaze composition, the flame-cooking method as “conventional,” the fact that different times were used for the two methods, and no temperature control), the glaze did not leach as much when microwaves were used. The literature that exists on the effects of microwaves on migration from glass does not provide an unequivocal conclusion.

Microwave-Enhanced Kinetics

Microwave processing has been studied on several systems in which kinetics appeared to have been enhanced. These apparent enhancements provide the basis for concern that microwaves accelerate glass corrosion.

The superconductor yttrium barium copper oxide (YBCO) was sintered and annealed with microwave energy [82]. The time and apparent temperature required were less than that required by conventional processing. Alumina was also sintered to 95% density with microwave energy at an apparent temperature which was 75-200°C less than conventional [83]. In another study, microwaves promoted better densification of alumina when microwave-processed samples were held at the same temperatures and times as samples fired conventionally [84]. It has been the subject of debate whether these effects were purely thermal, resulting from microwave absorption, or resulted from a nonthermal, enigmatic “microwave effect.”

It has been suggested that microwaves enhance diffusion of certain cations into glass [85]. In this particular study, the diffusion of cobalt ions into Pyrex™ was studied both conventionally and by microwave heating. For conventional heating, a Pyrex™ cylinder was packed with cobalt oxide in a crucible and heated to 935°C for 1 hour. The total time from the start of the initial ramp to cooling back to room temperature was approximately 3.8 hours.

For the microwave heating, a thin layer of cobalt oxide was deposited from a solution of cobalt nitrate when the solution was heated with microwave radiation [85]. Microwave heating was performed using 2.45 GHz microwaves at 1.6 kW.

The sample was heated to 750°C, determined by optical pyrometry, over 15 minutes at which time heating was stopped and the sample allowed to cool. Room temperature was achieved in an additional 20 minutes, for a total time of 0.6 hours from start to finish.

After treatment, the diffusion distance of cobalt into the glass was measured by back-scattered electrons (BSE) for both samples and the diffusivity of cobalt was estimated in both cases. The authors concluded that cobalt diffusion was enhanced by the microwave field. The authors also reported formation of additional phases in the microwave-treated glass which did not occur in the sample treated conventionally. After similar testing and comparison with data available in the literature, they concluded that the diffusion of sodium was not enhanced [85].

It has also been suggested that microwaves are capable of accelerating diffusion in polymers. Evidence was provided in a paper published in 1988 which detailed the diffusion of ethylene oxide (EO) out of poly(vinyl chloride) (PVC) medical tubing [86]. According to standard medical procedures, PVC tubing is sterilized with EO but during the sterilization, EO diffuses into the plastic. A subsequent heat treatment in air is required to drive off the EO through diffusion to the surface and out into the air. In this study, desorption was performed by the standard conventional process and by a microwave process designed to mimic it. In the conventional process, hot air (55°C) was flowed over the tubing. In the microwave experiment, the tubing was heated directly to 55°C with microwaves while cooler air (23°C) was flowed over it.

The authors reported that the time to reach an average EO concentration of 100 ppm was significantly decreased (250-450%) by the microwaves with an accompanying decrease in activation energy. They attribute this effect to microwave disruption of hydrogen bonds between the EO molecules and PVC polymer chains [86].

Their conclusions have been called into question on the basis of temperature measurement [61]. The authors used an infrared thermometer to remotely measure temperature on the surface of the PVC tube [86]. However, it is possible that the surface was cooled by convection and was not representative of the internal surface temperature [61]. If the internal temperature were higher than 55°C, it could have been responsible for enhanced diffusion [61].

Microwave Chemistry

Microwave chemistry involves the use of microwaves to heat solutions in pressure vessels. The solutions are typically very acidic and digest samples for chemical analysis. Fused quartz is one of the most frequently used pressure vessels in this application [87].

Over time, these vessels become badly corroded [87]. Two vessels that had been used in the laboratory for a long time were also investigated, one used conventional digestion and one used in microwave digestion. The researchers found no obvious qualitative differences between the microstructures of the conventional and microwave vessels that had been used in the laboratory, but no record was kept of how many digestions each experienced and no rigorous method was employed to evaluate microstructural features and so it was impossible to make the type of comparison that this study attempts.

Summary

Glass is an important food packaging material. As such, it is capable of releasing migrants into food and is also commonly exposed to microwaves. The corrosion processes that introduce migrants are relatively well understood under conventional heating conditions but the effects on glass corrosion when exposed to microwave fields have historically been under-explored. It is unknown what, if any, effects microwave have on migration from glass.

Glass corrosion occurs by leaching and network dissolution. Both of these processes release glass components which can make their way into foods or other environments. Each is essentially aqueous, being effected by H_3O^+ , OH^- , and H_2O . Because microwaves couple strongly with water, these processes may be influenced by microwave heating. Furthermore, microwaves have been shown to possibly influence the kinetics of a number of ceramic systems.

The goal of this study is to make an initial investigation into glass corrosion by microwaves in order to fill the gap in knowledge by revealing a microwave effect on the fundamental mechanisms of corrosion, if present.

Chapter III: Experimental Procedure

Methods of Characterization

Fourier Transform Infrared (FTIR) Reflection Spectroscopy

Fourier transform infrared (FTIR) reflection spectroscopy with a 45° angle of incidence was used to analyze the surface of the samples. The equipment was a Nicolet Avatar 330 FT-IR with Smart SpeculATR reflectance attachment by Thermo Electron Corporation (Figure 26). The region of interest was the mid-infrared [57], from 1400 to 400 cm^{-1} . Samples were prepared by polishing their surfaces to 1000 grit, enough to make the surface mirror-like so that specular reflectance techniques were possible [57].

The FTIR works by generating an interferogram based on an optical path difference between two infrared beams which either pass through a sample (transmission and absorbance) or are bounced off of a sample (reflectance) [57]. The interferogram is then transformed into an infrared spectrum using a Fourier transform algorithm. The resulting spectrum then shows the transmittance, absorbance, or reflectance of the sample, depending on the technique used. In this case, all FTIR spectra were generated by reflectance techniques.

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)

Inductively coupled plasma optical emission spectrometry (ICP-OES) was used to determine the concentration of corrosion products in solution. The instrument was a Spectroflame FTMOA85D by Spectro Analytical Instruments, Inc.

ICP-OES is a sensitive chemical analysis technique, useful for determining precise concentrations of even trace elements. The ICP-OES introduces a test solution to a plasma (8000K) by means of a nebulizer and the plasma excites the components of the solution, ionizing them [88]. The atoms present in the solution emit light at a characteristic wavelength, which is then used to fingerprint atoms present in solution. The intensity of the characteristic light emitted is used to quantify the amount of a particular atom present and determine precisely its concentration [89]. Table 1 shows the range of concentrations for which it is possible to get an accurate reading for elements relevant to this study [90].

The ICP-OES equipment returns concentration values in units of parts per million (ppm), a common abbreviation for mg of solute per liter of solution (mg/L) [88]. In determining ppm, the ICP-OES takes into account only the particular atom desired, *not*



Figure 26: FTIR reflection spectroscopy equipment.

Table 1: ICP-OES analytical range for relevant elements. From [90].

Element	Minimum Concentration (ppm)	Maximum Concentration (ppm)
Li	0.002	10000
Si	0.006	3000
Na	0.015	1000
B	0.002	600

any other element that it is complexed with. For instance, Si is present in solution as $\text{Si}(\text{OH})_4$ or $\text{Si}(\text{OH})_3\text{O}^-$ [30]. The ICP-OES determines concentration in terms of ppm of Si and not ppm of the entire species [88]. In order to convert from ppm to moles per liter (mol/L) of Si, the molar mass of Si is used to calculate from mass Si per liter to number of moles Si per liter.

pH

Measurements of pH were taken using a double junction pHTestr3+ meter by Oakton Instruments. The meter was calibrated daily using standard pH 10.00 buffer solution from Fisher Scientific.

Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) was used to examine corroded glass surface morphology. Images were taken with a Leo 1550 scanning electron microscope at an accelerating voltage of 5.00 kV. Energy dispersive spectroscopy (EDS) analysis was performed with an attached IXRF Systems, Inc. Iridium Microanalysis System with an accelerating voltage of 20.00 kV. All samples were sputter-coated with 10 nm of a gold-palladium alloy.

Secondary Ion Mass Spectroscopy (SIMS)

Secondary ion mass spectroscopy (SIMS) was performed at the North Carolina State University Analytical Instrumentation Facility using a Cameca IMS 6f with charge neutralization gun. The primary ion was O^{2+} with an accelerating voltage of 9.23 kV, energy of 5.5 keV, current of approximately 200 nA, and impact angle of 42° . Samples were coated with gold prior to analysis [59].

Sample Preparation

Lithium disilicate glass frit was melted in a covered platinum crucible at 1100°C for 1 hour and fired (small bubbles removed) at 1400°C for 4 hours. The melted glass was then cast into a cylindrical graphite mold, which had been pre-heated to 400°C , to form cylinders of approximately 18 mm diameter and 77 mm length. The glass, still inside the mold, was annealed for at least nine hours at 400°C to relieve thermal stresses. The schematic temperature profile is shown in Figure 27.

Following casting, the cylinders were sectioned using a diamond wafering saw. The faces of the samples were ground and polished using silicon carbide paper up to 1000 grit (approximately 10 μ average particle size) [91].

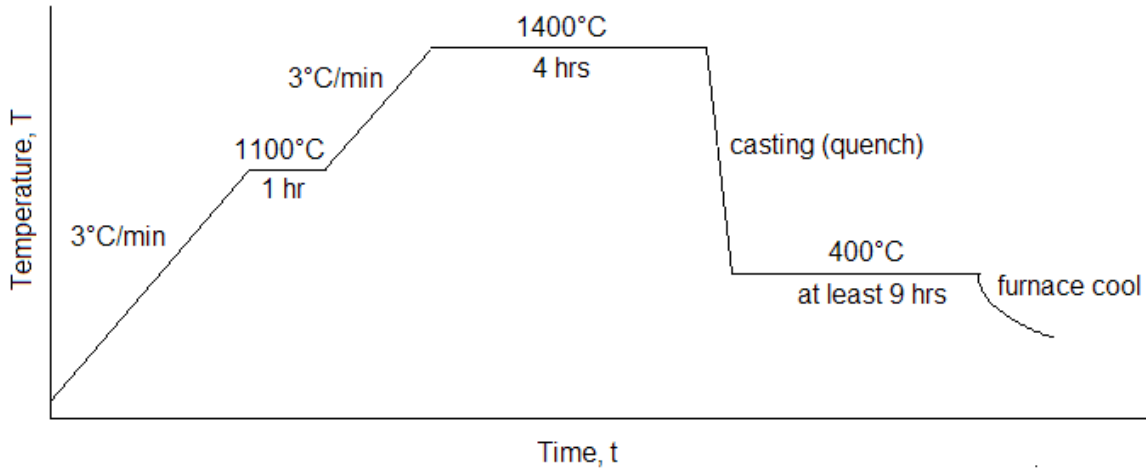


Figure 27: Temperature profile for casting Li₂O-2SiO₂ glass.

Heating

Two types of heating were used: conventional and microwave. A Lab-Line Imperial V laboratory convection oven was used for conventional heating. To monitor the temperature of the water bath, a thermocouple (type K inconel-shielded or type T) was inserted through an exhaust port of the oven and into the container in some tests. The temperature of the oven was controlled using a Eurotherm programming device.

A Lambda Technologies Vari-Wave Model 1500 variable frequency microwave oven, with a frequency range of 6.5-18 GHz, was used for microwave heating. Temperature was monitored by a Luxtron Corporation STF Teflon[®]-sheathed optical temperature probe with optical SMA-style connector. This probe was transparent to microwaves in the frequency range and the Vari-Wave was controlled by the reading from the probe.

Figures 28 and 29 are photographs of the Vari-Wave oven and also show the configuration of corrosion cell within the microwave cavity. Figure 30 is a photograph of the tip of the Teflon[®]-sheathed optical probe.

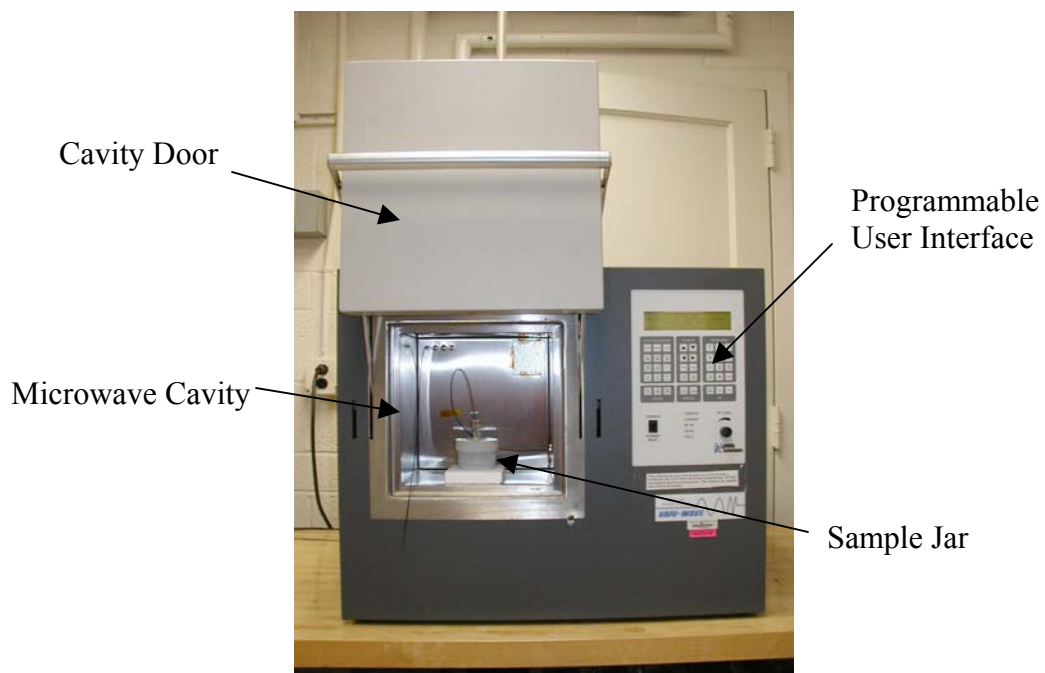


Figure 28: Vari-Wave variable frequency microwave oven (cavity door open and sample jar inside).

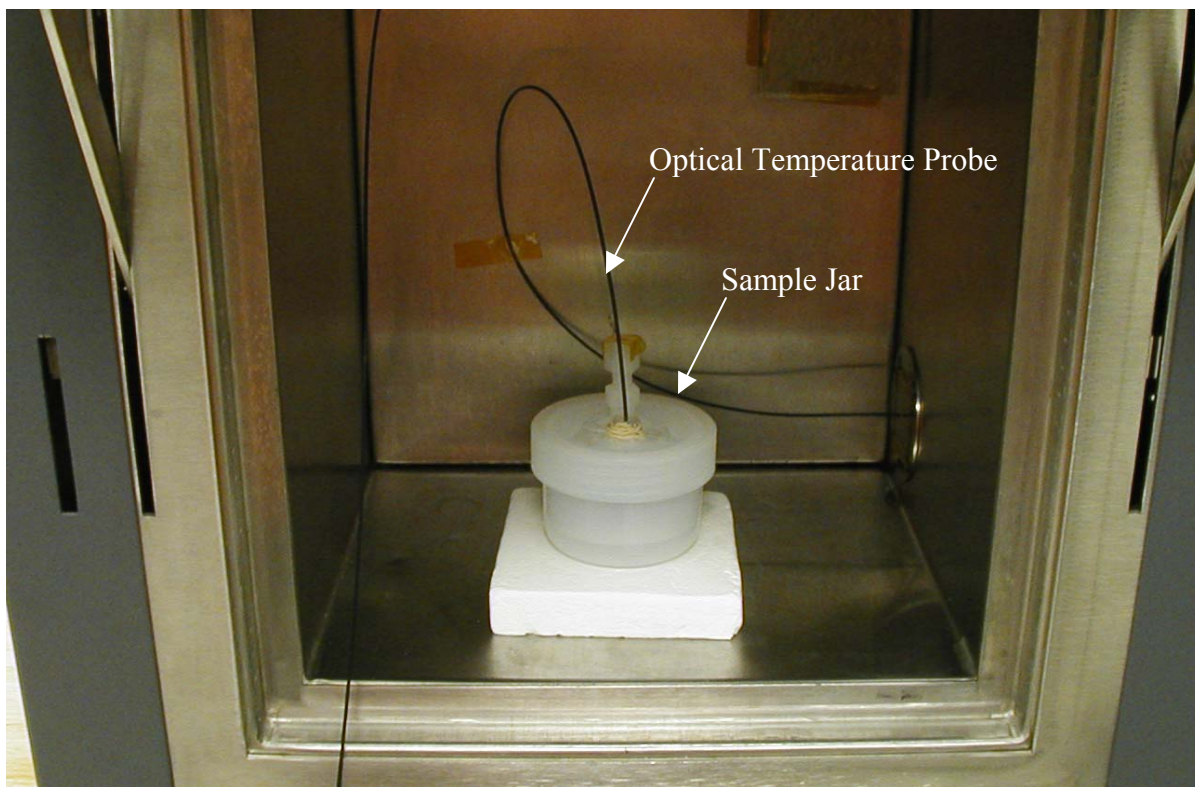


Figure 29: Sample configuration in Vari-Wave microwave cavity. Temperature probe is inserted into sample jar.

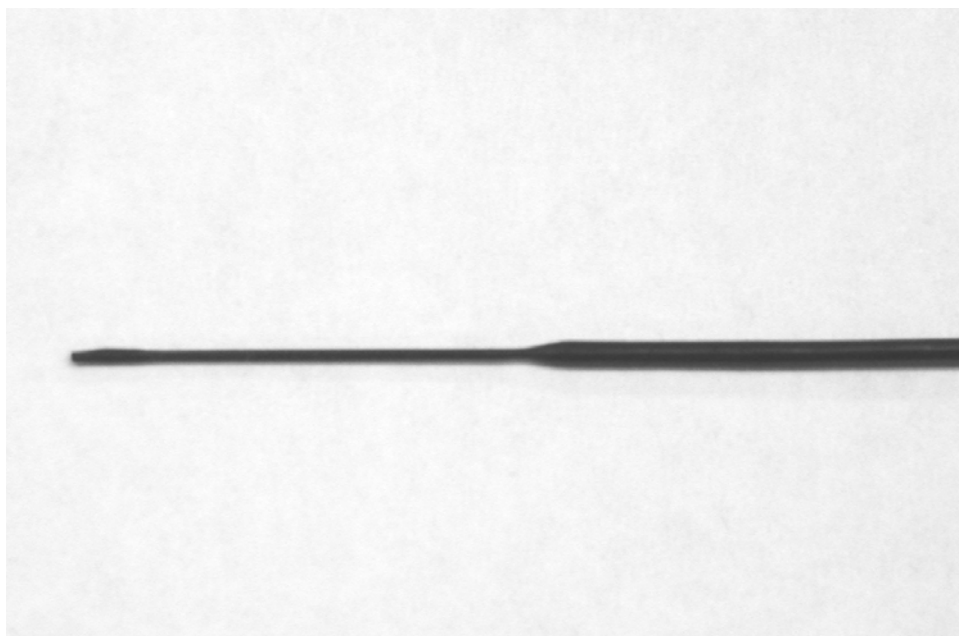


Figure 30: Tip of optical temperature probe.

The Vari-Wave oven could be programmed to maintain a constant temperature for a specific length of time. The temperature of baths in the microwave was monitored using the optical probe and microwave energy was applied to maintain a setpoint.

Conventional Experiments

Conventional experiments were carried out in a Teflon[®] perfluoroalkoxy (PFA) jar manufactured by Savillex. The volume of the jar was approximately 120 ml, with an inside diameter of 60 mm and height of 53 mm. It had two holes in the lid into which threaded PFA tubes were screwed. These screws were useful for guiding temperature measurement devices into the container. Two PFA rings were used to keep the glass specimen from touching the bottom of the jar. The rings were cut from a threaded PFA tube and were 2 mm in diameter with a thickness of 1-2 mm.

A schematic drawing of the setup is shown in Figure 31. In this drawing, the thermocouple is inserted into the bath. The optical device in the microwave was inserted in a similar manner. Prior to use, the jar was washed thoroughly with detergent and rinsed with deionized water.

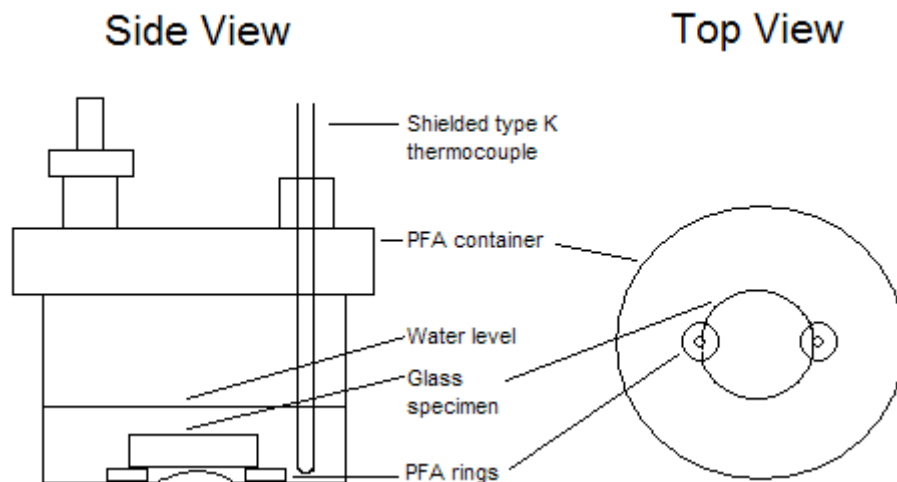


Figure 31: Schematic diagram of the initial test setup.

Conventional Temperature Measurements Series

To determine the nature and extent of corrosion in the glass at the temperatures and times of interest, a sequence of conventional tests was performed. This testing provided a baseline to which corrosion in a microwave field could be compared. A glass specimen immersed in 25 ml deionized water was ramped from room temperature to temperatures ranging from 40 to 90°C. The total time of each test was 4 hours. Upon the conclusion of the trial, the sample was removed, washed with deionized water, and blotted dry. For this series of tests, one glass specimen was used. After exposure and characterization of the flat face, the sample was repolished with 1000 grit silicon carbide paper. To ensure that the entire corroded layer had been polished away, a new FTIR scan was taken, revealing the spectrum of a fresh surface.

Depth of Penetration Calculations

To ensure microwave radiation would reach the glass-water interface of the samples, the depth of penetration of microwaves into water was estimated. Based on these calculations, the water level surrounding samples was carefully controlled.

When an electromagnetic field is incident upon a dielectric material, both the amplitude of the electric field associated with the wave and, as a consequence, the power contained by the wave are attenuated at a rate that depends on the dielectric properties of

the material. The energy lost is absorbed by the material. This phenomenon is illustrated by Figure 32 [92].

In order to observe microwave effects on glass corrosion, it was critical for microwaves to reach the interface between the glass and water because all corrosion mechanisms act on or near the interface. Water strongly couples with microwaves at the frequencies used. Without proper experimental design, the water far away from the interface would have absorbed most microwaves and the corrosion that occurred at the glass-water interface would have been due almost solely to temperature of the water. Therefore, the experimental setup was designed around the depth of penetration of microwaves into water to guarantee exposure of the glass-water interface to microwaves.

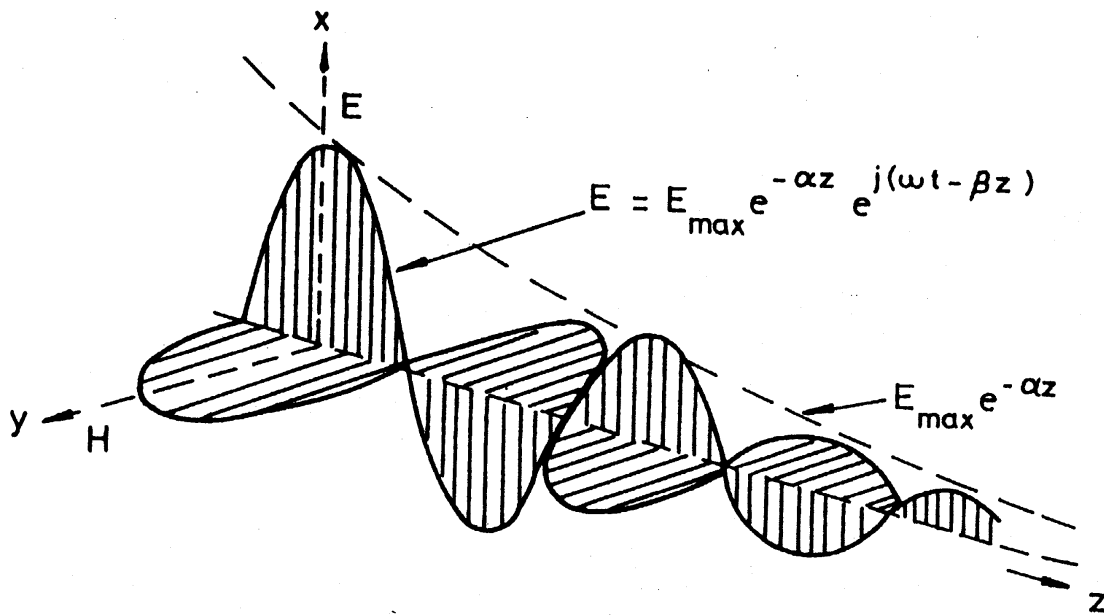


Figure 32: Electromagnetic field attenuation along the z-axis. From [92] (reprinted by permission, ©1983 Institution of Engineering & Technology).

The depth of penetration (D_p) relationship is given in Equation 25 [92]. This relationship may be used to calculate the distance into which the incident power of a microwave field penetrates into a dielectric material before the power contained in the wave is attenuated to $\frac{1}{e} \approx 0.368$, or 36.8%, of its original value. At this power

attenuation, the electric field is attenuated to $\sqrt{\frac{1}{e}} \approx 0.607$, or 60.7%, of its original value.

The variables in the equation are λ_0' , the free space wavelength of the microwave radiation, ϵ' is the relative dielectric constant, and ϵ_{eff}'' is the effective relative loss factor.

$$D_p = \frac{\lambda_0'}{2\pi(2\epsilon')^{1/2}} \left[\left(1 + \left(\frac{\epsilon_{\text{eff}}''}{\epsilon'} \right)^2 \right)^{1/2} - 1 \right]^{-1/2} \quad (25)$$

Equation 26 gives the equation for the depth of penetration for the power to be attenuated to 50% of its power (instead of 36.8% in Equation 24) [93]. At this depth of penetration, the electric field is attenuated to $\sqrt{\frac{1}{2}} \approx 0.707$, or 70.7% of its original value.

In this equation, λ_0 is the free-space wavelength of the microwave radiation, ϵ' is the real dielectric constant of the material, ϵ_0 is the permittivity of free space, and $\tan\delta = \epsilon''/\epsilon'$. The value of ϵ'/ϵ_0 in this equation is essentially the relative dielectric constant found in Equation 25. To design experiments with this equation is more conservative because it incorporates a stronger electric field at the D_p . Appendix B gives the details of the electric field calculations for both equations.

$$D_p = \frac{3\lambda_o}{8.686(\tan \delta) \sqrt{\frac{\epsilon'}{\epsilon_o}}} \quad (26)$$

Using data from [92], [94], [95], and [96], D_p values were calculated. Figure 33 shows some of these calculated values and their variation with temperature. As temperature increased, so did depth of penetration (due to changes in ϵ' and ϵ''). As wavelength increased (frequency decreased), depth of penetration increased as well (as is shown in Equations 25 and 26). Figure 34 shows the published depth of penetration for several lower frequencies, including 2.45 GHz (2450 MHz) [92]. The agreement at 60°C between D_p calculated using Equation 25 for 3 GHz and D_p published in Figure 34 for 2.45 GHz confirms the validity of the methodology.

Table 2 shows dielectric property data for water obtained from various sources and the calculated D_p using either Equation 25 or Equation 26. The relative value of the power and electric field are shown also for clarity, along with the source of the dielectric property data. The frequencies shown are in the neighborhood of 7 GHz. At 55°C, the

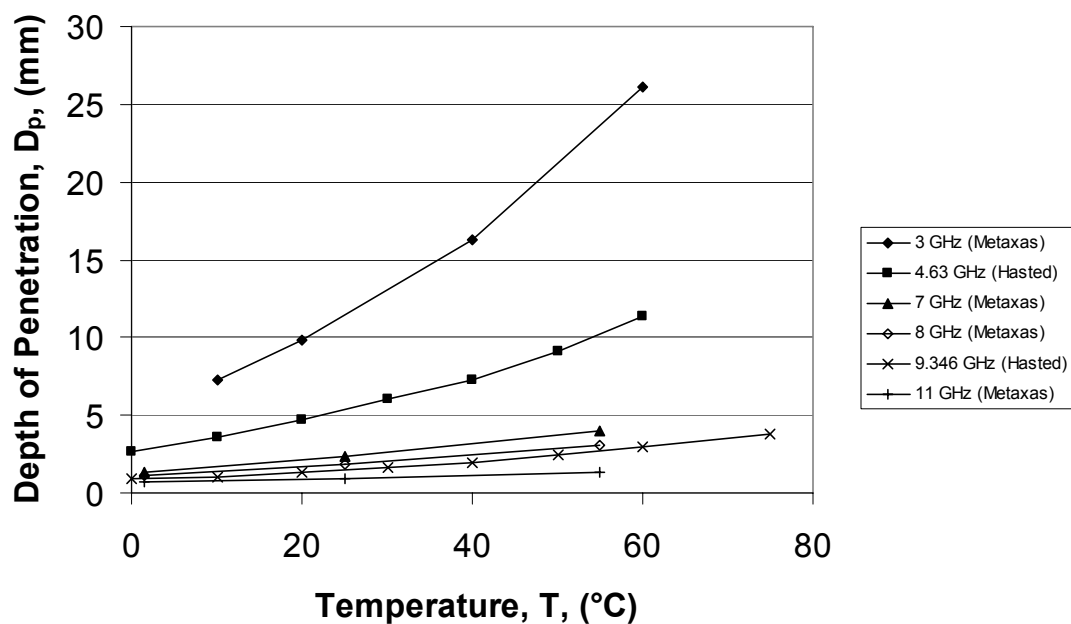


Figure 33: Calculated depth of penetration of microwaves into water versus temperature for several frequencies.

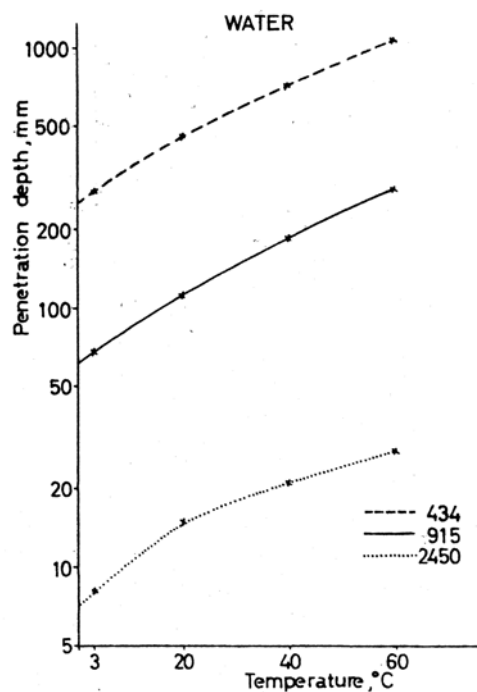


Figure 34: Depth of penetration into water for frequencies including 2.45 GHz (2450 MHz). From [92, 97] (reprinted by permission, ©1974 International Microwave Power Institute).

Table 2: Dielectric properties of water from various sources and calculated D_p for various frequencies of microwave radiation.

Frequency (GHz)	Temp. (°C)	ϵ'	ϵ''	Dielectric Prop. Ref.	Equation	P/P _{max}	E/E _{max}	D _p (mm)
4.63	60	66.3	7.4	[94]	25	0.369	0.607	11.36
5.341	35	71.7	14.57	[94]	25	0.369	0.607	5.22
6	55	67	10	[92]	25	0.369	0.607	6.53
7	55	66	16	[92]	25	0.369	0.607	3.98
7.7075	50	67.2	14.49	[94]	25	0.369	0.607	3.52
9.141	60	63.5	13.5	[94]	25	0.369	0.607	3.10
9.346	50	64.93	17.56	[94]	25	0.369	0.607	2.37
9.346	75	60.7	10.51	[94]	25	0.369	0.607	3.80
9.355	90	56.9	7.56	[95]	25	0.369	0.607	5.10
9.368	50	65.6	16.9	[94]	25	0.369	0.607	2.46
9.375	50	64.5	17	[94]	25	0.369	0.607	2.43
9.39	50	64.6	17	[94]	25	0.369	0.607	2.42
10	55	60	21.6*	[96]	26	0.500	0.707	1.18
10	85	54	14.0 [†]	[96]	26	0.500	0.707	1.73
11	55	60	25	[92]	25	0.369	0.607	1.37

* $\tan\delta=0.36$

[†] $\tan\delta=0.26$

calculated depth of penetration for 11.00 GHz is 1.37 mm. For 7 GHz, the depth of penetration is 3.98 mm. Appendix B gives a sample calculation for the 7 GHz value.

In some initial experiments, 11.00 GHz was used. Therefore, the thickness of the water layer over the glass sample may have inhibited a substantial amount of microwave energy from actually getting to the glass/water interface because the water covered the surface by approximately 4 mm. Though some 11.00 GHz microwaves would have gotten to the interface at that thickness, it was thought that using 7.00 GHz, the lower limit of the frequencies available on the Vari-Wave, would allow the microwaves to better reach the interface and expose the microwave effect, if any existed.

Systematic Bulk Testing

The procedure used to obtain the vast majority of the results is presented in this section. Some initial experiments were carried out before the systematic testing and their procedure and results are given in Appendix C. These experiments are not presented in this chapter because they do not contribute greatly to the overall discussion.

Calibration

Before beginning testing, the type T (copper-constantan) thermocouple was calibrated to the optical probe by adjusting the ZERO setting of the thermocouple readout. A small laboratory beaker was filled approximately 1/4 full with deionized water and placed on a hot plate. Both the tips of the optical probe and the thermocouple were submerged in this bath to their approximate depths during actual testing (as shown in Figure 35). The tips were kept very close together for accuracy. Bath temperature was kept close to 90°C, as read by the optical probe, by controlling the power knob of the hot plate. The thermocouple's zero point was adjusted until it read almost identical to the optical probe's measurement. The results of this calibration are given in Appendix D.

After calibration, the temperature of the conventional oven required to heat a bath to a temperature corresponding to 90°C was somewhat less than 90°C as measured by the oven's thermocouple. All references to 90°C are specific to the temperature supplied by the optical probe in the microwave oven. The actual temperature setting of the conventional oven can be found in Appendix D.

Corrosion Cell Configuration

The corrosion cells used were two 120-mL capacity PFA jars (see Figure 29). Before beginning the tests, they were cleaned with solutions of hydrofluoric and nitric acids to remove contaminants, had any been present. Between trials, deionized water was boiled inside the jars for approximately 45 minutes (poured out and replenished every 15 minutes) to remove adsorbed Si and Li.

Samples, which were prepared as described previously and had an average thickness of approximately 5.66 mm, rested on the bottom of the jar. Deionized water was added at a volume of 18 mL, which covered the samples with a layer of water 1-2 mm deep. The samples were placed near the side of the jar to allow microwave exposure from the side as well as the faces. Figure 36 shows a schematic diagram of this setup.

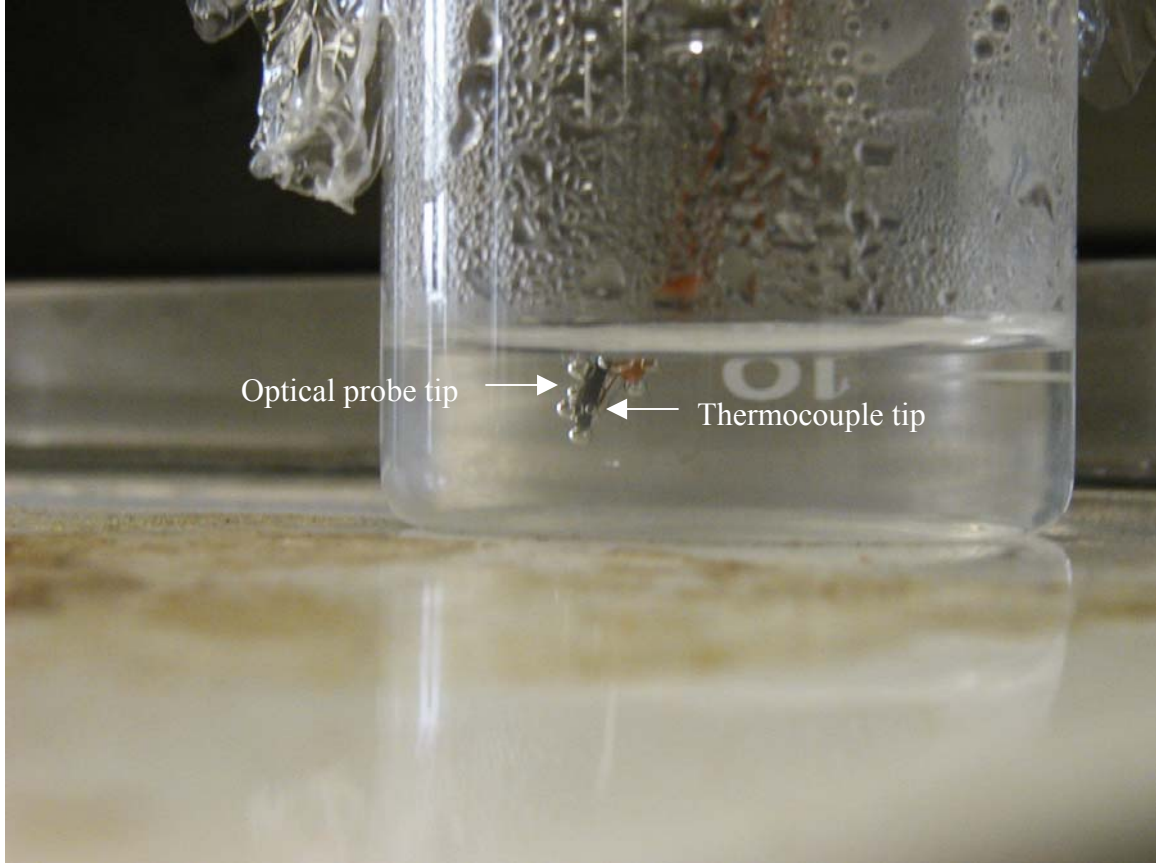


Figure 35: Thermocouple calibration.

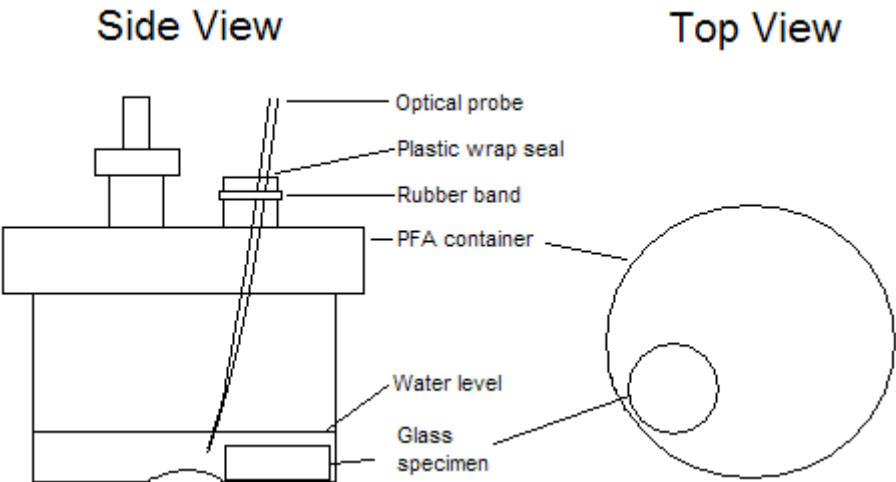


Figure 36: Experimental setup for bulk testing.

Both jars were sealed in the same way. Three squares (each approximately 1 in. x 1 in.) of plastic wrap were cut and layered one on top of another, covering the vent of the jars. A rubber band was stretched around the circumference of the vent, effectively sealing it with the plastic wrap. To allow insertion of the optical probe, a hole was punched with a sewing pin. The hole was small enough to allow the entry of the tip of the probe, but narrow enough to seal around the thicker body of the probe when it was fully inserted (see Figure 30). This seal allowed minimal escape of water vapor from the system even in the longer tests.

In order to make confident statements about the temperature of the baths during testing, the baths were pre-heated to 90°C before samples were inserted. Before this pre-heat, the appropriate amount of water (18 mL) was added to the test jar using a pipette.

The jar was then sealed as described and heated in the Vari-Wave up to 90°C and held for several minutes (500 s total, including the ramp and the hold). The jar was then removed, the plastic wrap seal was replaced, and the jar was placed in the conventional oven for 1 hr. This step allowed the bath to be initially heated to the approximate temperature in the microwave oven and then homogenized to the proper temperature over the course of an hour in the conventional oven, ensuring the bath was at 90°C when glass samples were added.

Representative heating was measured with a “dummy bath” because the thermocouple was not directly inserted into any of the actual test solutions. It took approximately one hour for the thermocouple in the dummy bath to read within several tenths of 1°C of 90°C after the pre-heat in the microwave. This length of time is explained by heat lost in transferring the jar from the microwave oven to the conventional oven. All subsequent tests were performed assuming 1 hr was the time required to bring the bath to a homogeneous 90°C.

To begin the trial, the jar was removed from the conventional oven and the sample was inserted as shown in Figure 36. The jar was either replaced in the conventional oven or loaded quickly into the Vari-Wave oven to minimize loss of temperature by the bath.

Three trials were performed for each of four lengths of time: 100, 250, 500, and 1000 min. Glass from the same casting was used for the conventional and microwave tests for each length of time.

In order to establish whether differences observed between the microwave and conventional samples were purely thermal or in fact the result of a microwave effect, similar tests were run conventionally for 250 min at 91 and 92°C and 1000 min at 91°C. These higher temperatures provided data resulting from a range of conventional temperatures. The samples tested in this manner were not from the same castings as the other samples.

The Vari-Wave oven malfunctioned after testing 3 durations (100, 250, and 1000 min). To fix the problem, the optical probe was replaced by a new, longer probe. The new probe was used exclusively after the fix but it read temperatures several degrees higher than the old probe. Therefore, setting the Vari-Wave to hold at 90°C with the new probe actually meant that it was holding at 87 or 88°C when compared to the previous probe. Subsequent tests were performed at the new “90°C” and the conventional oven was calibrated appropriately to compensate (see Appendix D). Appendix E gives the details of this equipment issue.

One systematic bulk trial was performed with this new setup. The duration was 500 min and three repetitions were performed.

Secondary Ion Mass Spectrometry (SIMS)

To measure profiles of Li, Si, and H within the glass, secondary ion mass spectrometry (SIMS) measurements were taken. Significantly different sample geometry from previous tests was required due to the size limitations of the SIMS sample chamber. The samples were required to be square-shaped with a maximum edge length of 10 mm and a maximum thickness of 4 mm.

Discs of $\text{Li}_2\text{O}-2\text{SiO}_2$ glass were cut in the usual manner from castings, but with a thickness of 4mm instead of 6.2 mm. Each disc was ground into a square using 60-grit SiC paper and, when having approached the correct dimensions, was polished with 180-, 400-, and 1000-grit SiC paper. The average dimensions of each sample were 9.40 mm x 9.60 mm x 3.60 mm, with variations from any dimension being measured as no more than 0.05 mm.

Trials were performed in heavy water (99% D₂O). Since the deuterium (D) atom is very easy to distinguish from the H atom by SIMS, performing corrosion tests in D₂O ensured that the water species that entered the glass during the corrosion tests would be easily distinguishable from water that had entered the glass during melting, casting, polishing, or storage.

Though a large isotope effect occurs in the diffusion of D versus H, there was no reason to believe that the effects of microwaves would be any different for D₂O than for H₂O. Using dielectric data from [95], the depth of penetration of 9.355 GHz microwave radiation into D₂O at 90°C was calculated to be 4.34 mm, as compared to 5.10 mm for H₂O. For 7.00 GHz microwave radiation, the frequency used in the test, the depths of penetration were expected to be greater, as previously discussed.

Testing was performed in the PFA jars used previously with identical sealing procedures. A total volume of 13 mL of D₂O was used for each test, as opposed to 18 mL used previously for the thicker samples, to ensure that the top surface of each thinner sample was covered with approximately 1 mm of solution. For each trial, the corrosion solution was pre-heated for approximately 2 hrs and 15 min in the conventional oven. One trial was performed in the Vari-Wave with a setpoint of 90°C, 1 trial was performed in the conventional oven with a setpoint of 90°C, and 1 trial was performed in the conventional oven with a setpoint of 92°C. Each trial lasted for a total of 43.5 min.

After completing the microwave trial, FTIR spectroscopy was performed on the sample surfaces and solution analysis was carried out. The samples were then transported to the Analytical Instrumentation Facility at North Carolina State University and analyzed by SIMS. In addition to the three corroded samples, one polished but uncorroded sample was analyzed to provide a comparison to the bulk.

Low-Frequency Bulk Testing

In order to perform tests at a lower fixed frequency, several experiments were carried out at Lambda Technologies, Inc. (Morrisville, N.C.) using a MicroCure[®] 2100 microwave oven (Figure 37) with accompanying control software. The MicroCure[®] was similar to the Vari-Wave microwave oven with several notable exceptions. The first was that the microwave cavity was larger than the cavity of the Vari-Wave, with the approximate dimensions being 1.5 ft to a side. The temperature probe (Figure 38), while

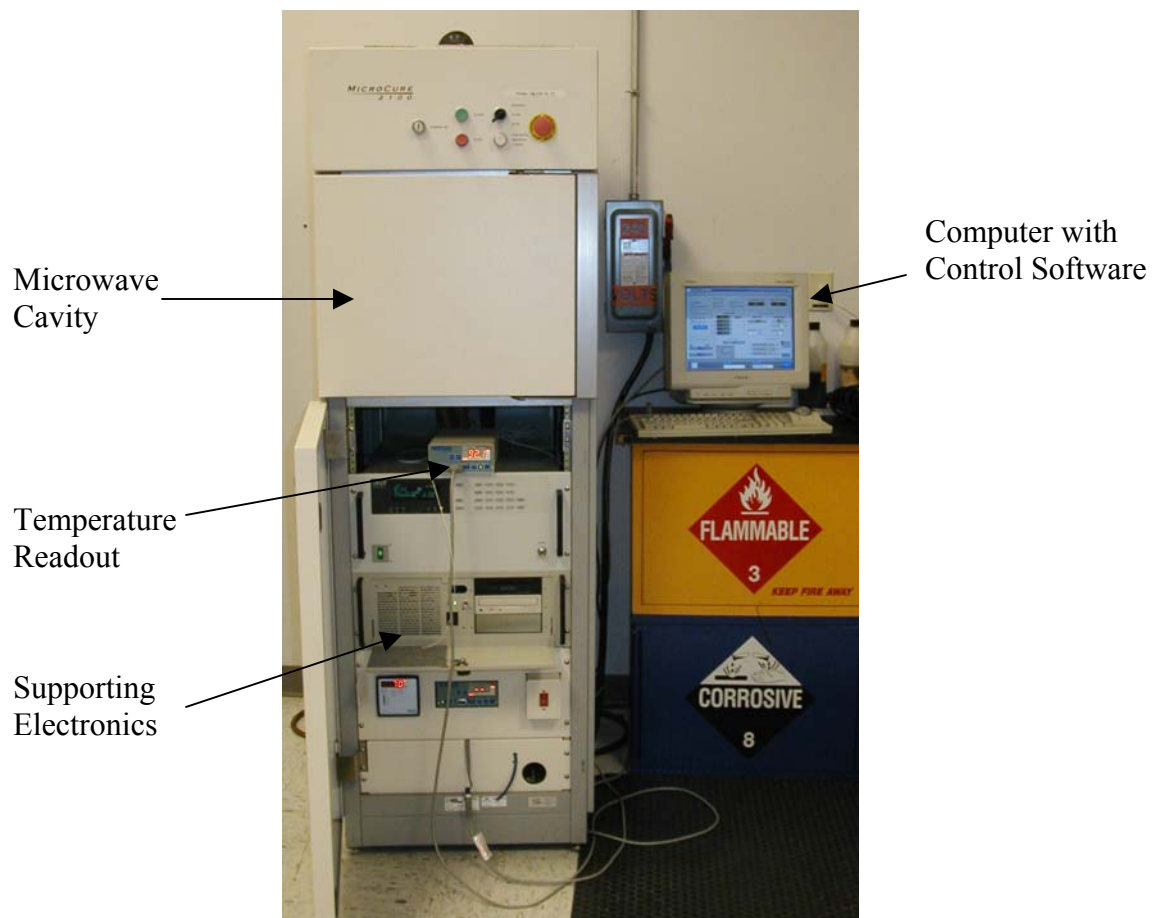


Figure 37: MicroCure® 2100 microwave oven system at the laboratory facility of Lambda Technologies, Inc. in Morrisville, N.C.

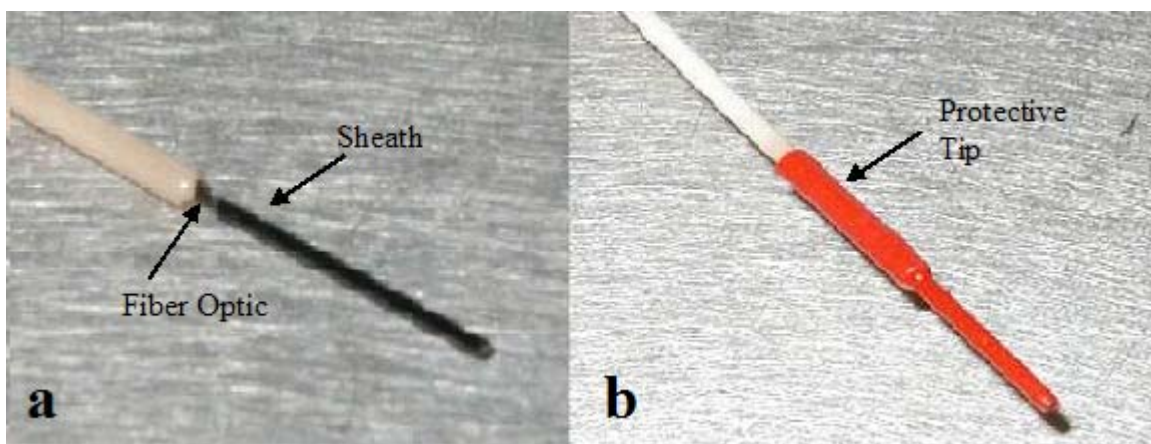


Figure 38: MicroCure® 2100 temperature probe, without protective tip (a) and with protective tip (b).

also having a fiber-optic wire and relaying temperature data to the microwave oven in essentially the same manner, had a thinner Teflon sheath and also had an accompanying plastic tip for mechanical protection of the fiber-optic material.

Samples of $\text{Li}_2\text{O}-2\text{SiO}_2$ glass were cast, cut, polished, and cleaned in the same manner as previously described with the average thickness of each sample being 5.50 mm. Teflon PFA jars were filled with 18 mL of deionized water and the one glass sample per trial was placed in the water. The jars were sealed with plastic wrap held in place by a rubber band as described previously. The temperature probe was inserted through a hole punched by pin in the plastic wrap. Since the protective tip of the probe was larger than the diameter of the white lining of the probe, the protective tip was removed prior to insertion. After insertion, the protective tip was replaced and the top of the jar was screwed on. This provided a good seal as well as use of the protective tip during the trial.

The experimental configuration was similar to that in the Vari-Wave oven and is shown in Figure 39. The PFA jar sat on an insulating layer of ceramic tile. The jar was brought closer to the center of the cavity by a solid, cylindrical piece of Teflon[®]. Care was taken to place the jar, the temperature probe, and the glass sample in the same approximate location for every test. For each trial, there was approximately 1-2 mm of surface coverage above the top of the sample.

Before performing any trials, the PFA jars were cleaned with solutions of hydrofluoric and nitric acid to eliminate possible contaminants, if any. Between each use, the jars were filled with deionized water and boiled for approximately 40 min. The protective tip of the optical probe was also rinsed with deionized water.

Deionized water (18.3 M Ω -cm) was transported because none was available at the test site. The use of deionized water from the filters which had produced the deionized water used in the rest of this work also ensured consistency of the experiments. Eight 1-gallon high-density polyethylene (HDPE) jugs were ordered from United States Plastic Corporation (Lima, Ohio). The jugs were rinsed thoroughly with deionized water prior to transport by partially filling with water, shaking vigorously, emptying, and repeating several times. The jugs were also filled completely with 1 container volume and allowed to stand at room temperature for several hours before emptying. The jugs were then

rinsed again and finally filled with deionized water. Four jugs were used for testing on-site and, to ensure consistency, the remaining water was used for conventional testing.

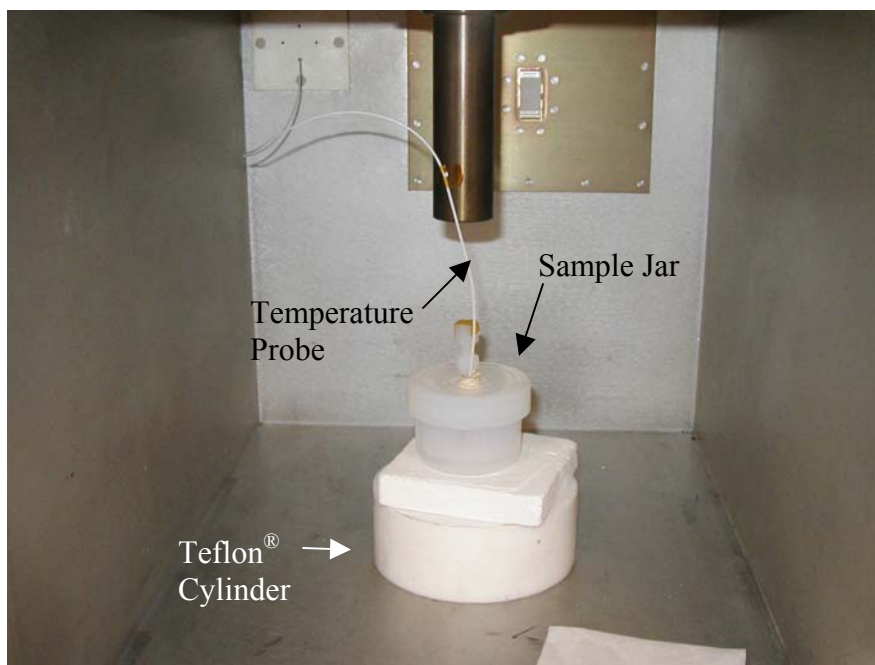


Figure 39: Experimental configuration in MicroCure® 2100 microwave cavity.

Microwave testing was performed at 90°C, as measured by the temperature probe of the MicroCure®, using 5.860 GHz (± 3 MHz) microwave radiation. Testing included 3 trials at 100 min, 3 trials at 250 min, and 1 trial at 1000 min. Instead of a pre-heat step, the samples were placed in solution and then the trial was started. The timer for the 90°C hold was not officially started until the solution reached 90°C, which took 2 min. The time required to ramp up to 90°C was the same as that typically elapsing during the course of placing the glass sample into the pre-heated solution, configuring the experimental setup in the Vari-Wave, and starting the trial. Therefore, no significant error was expected to be generated by the lack of a pre-heat step.

To provide a basis for comparison with conventional heating, a type T thermocouple was calibrated to the temperature measurement of the MicroCure® in the same manner as described previously with the Vari-Wave. The temperature corresponding to “90°C” as measured by the MicroCure® was approximately 5°C higher than “90°C” as measured by the Vari-Wave. The temperature of the conventional oven

was adjusted accordingly to compare to the MicroCure[®] reading. Identical trials were repeated in the conventional oven.

Commercial Soda-Lime Experiments

The purpose of this test was to use glass as an actual container material instead of immersing it in a bath. This arrangement provided this study with an increased element of realism, as it took advantage of the intended use of microwave-safe bowls available for consumers' home use. A microwave effect, if any, may have been more likely to appear if the microwaves did not have to travel through a layer of water to get to the glass/water interface.

Commercial soda-lime glass dessert bowls were purchased from a retail distributor. These bowls each had 275 mL capacity. Clearly indicated on the packaging was the phrase "ideal for microwave use" and the bottom of each bowl was labeled "microwave safe." The bowls were selected from the myriad of commercial glass vessels because of their availability and likelihood of consistency of composition (there was a greater chance for compositional fluctuation in glassware sold by a retail distributor that is unlabeled as to manufacturer or trademarked brand).

To prepare the bowls for experimentation, each bowl was thoroughly rinsed, inside and out, with deionized water. To remove organics, the interiors of the bowls were sprayed with ethanol which, once sprayed, was sloshed around on the inside of the bowl for approximately 1-2 minutes. Following the ethanol cleansing, the bowls were once again rinsed inside and out with deionized water and allowed to air dry. No physical scrubbing was employed in order to avoid damaging the glass surface or adding additional contaminants.

Following cleaning, each bowl was filled with either 30 mL or 250 mL of deionized water.

To pre-heat the water baths, they were heated in a 2.45 GHz Galanz home microwave for short times in order to bring the baths to approximately 80-85°C rapidly. The 30-mL baths were heated for 30 s and the 250-mL baths were heated for 120 s on the intermediate "beverage" setting. Once heated, the bowls were removed, covered in plastic wrap, and placed in the conventional oven at 90°C. The 30-mL baths were allowed 1.5 hrs to homogenize to a uniform 90°C and the 250-mL baths were allowed 2.5

hrs to homogenize. The times required to reach 90°C were measured experimentally by a Type T thermocouple placed in 30- and 250-mL test baths, respectively.

After the pre-heat and homogenization steps, the actual corrosion test began. Each test lasted for 100 min. The samples which were to be exposed to microwave energy were removed from the conventional oven and placed in the Vari-Wave oven at which time the 100-min. test was begun. The samples which were to be corroded by conventional heating were simply left in the conventional oven and the timer was started.

While the pre-heat and homogenization steps caused some corrosion to occur, all samples were treated in a like manner. That is, the corrosion that occurred in the pre-heat and homogenization steps was expected to be the same for both microwave and conventional samples. Therefore, the total concentration of migrants in solution following the test were the result of pre-heat, homogenization, and either conventional or microwave corrosion, but any *differences* were to be attributed to the final step.

Each bowl was covered in plastic wrap to keep water vapor from escaping to the atmosphere. Three sheets were laid one on top of another and pressed together before being placed on the bowls. When placed on the bowls, 2 rubber bands were stretched around the lip of the bowls to provide a good seal. Excess plastic wrap was cut off.

The plastic wrap on the microwave-heated bowls required an additional step in order to be secured. During initial testing, it was found that the plastic expanded vertically as it responded to the increasing vapor pressure of the water. This expansion caused the temperature probe to be lifted out of the water and no longer take an accurate reading of the bath temperature. To secure it, microwave-transparent mica tape was stretched across the top and stuck to the side of the glass bowl. The tape was applied just after putting on the plastic wrap and before the homogenization step. The vertical displacement of the plastic wrap did not occur to as great an extent in the conventional oven and so mica tape was not used.

During testing in the microwave oven, water vapor condensed on the plastic wrap, decreasing solution volume. The phenomenon did not occur in the conventional oven. There was very little condensation on the plastic wrap in the conventional oven, but a large number of droplets had condensed on the interior of the plastic wrap in the microwave oven.

The temperature probe was used to maintain the bath at 90°C in the microwave oven. To insert it, a small hole was poked in the plastic wrap with a pin and the probe was pushed through. Care was taken to ensure a good seal. The probe was pushed just far enough into solution to allow its tip to be submerged.

Chapter IV: Results and Discussion

This chapter presents experimental results in a holistic manner. First, the corrosion mechanisms detailed in Chapter II are related to the FTIR, ICP, pH, SEM, and SIMS data from conventional testing. The data from conventional tests are also compared to existing data from the literature. Next, the data resulting from microwave heating are compared to the conventional data and conclusions about the microwave effects are drawn.

Conventional Temperature Measurements Series

Prior to running conventional tests, the infrared reflection spectra of vitreous silica and $\text{Li}_2\text{O}-2\text{SiO}_2$ glass were recorded as a basis for comparison. The vitreous silica was a highly-polished sample used as a calibration standard for the FTIR. The lithium disilicate glass was a freshly polished specimen. The spectra of these two samples are shown in Figure 40.

The peaks present in Figure 40 were consistent with those in the literature. The peak due to Si-O-Si stretching in vitreous silica occurred at 1122 cm^{-1} , while the Si-O-Si bending peak occurred at 479 cm^{-1} . The satellite peak at 1266 cm^{-1} and Si-O-Si silica ring stretching peak at 783 cm^{-1} were also present.

In the lithium disilicate glass, the Si-O-Si stretching peak was at 1057 cm^{-1} , shifted from 1122 cm^{-1} , and the Si-O-Si bending peak occurred at 491 cm^{-1} , shifted from 479 cm^{-1} . The peak at 783 cm^{-1} in vitreous silica was shifted to 759 cm^{-1} in the lithium disilicate glass. Finally, a new peak due to the Si-O^- nonbridging oxygen stretching vibration in the presence of Li^+ appeared at 944 cm^{-1} in the $\text{Li}_2\text{O-SiO}_2$ glass.

The conventional temperature series experiments consisted of immersing lithium disilicate glass samples in 25 mL of deionized water and heating the bath from room temperature to various setpoints in the conventional oven, the procedure for which is given in Chapter III. To avoid the confusion resulting from too many intersecting curves on one graph, the resulting FTIR spectra have been broken up into three groups and are shown in Figures 41-43. The temperature profiles experienced by the bath during each run are shown in Figure 44.

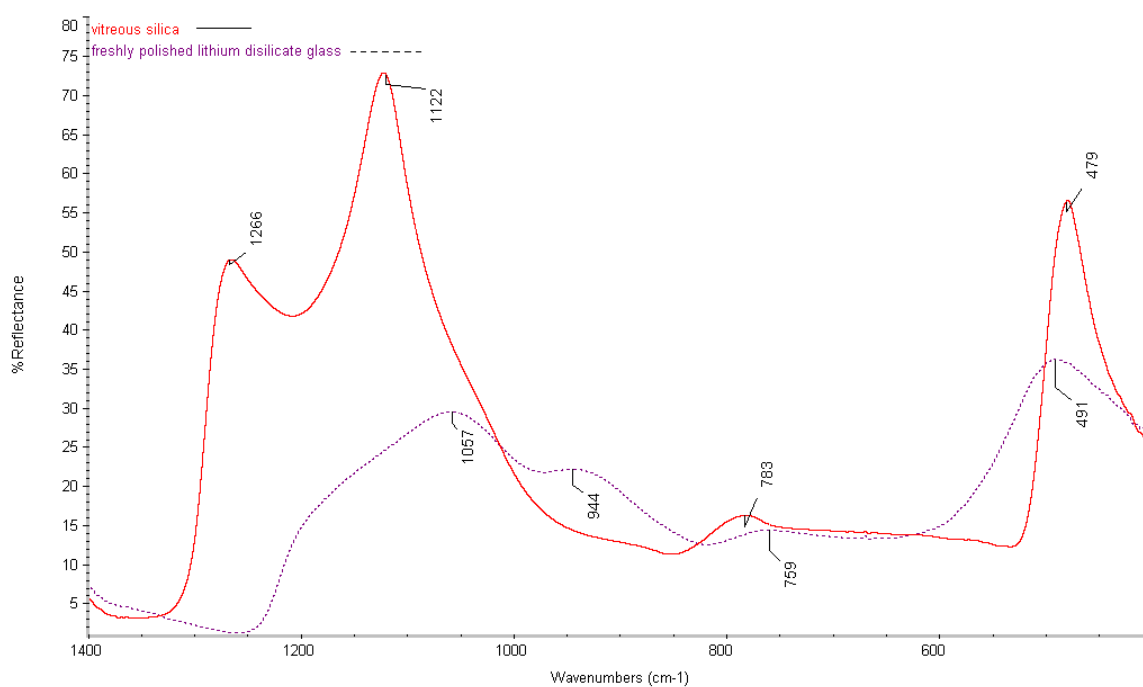


Figure 40: FTIR spectrum of vitreous silica and freshly polished $\text{Li}_2\text{O-SiO}_2$ glass.

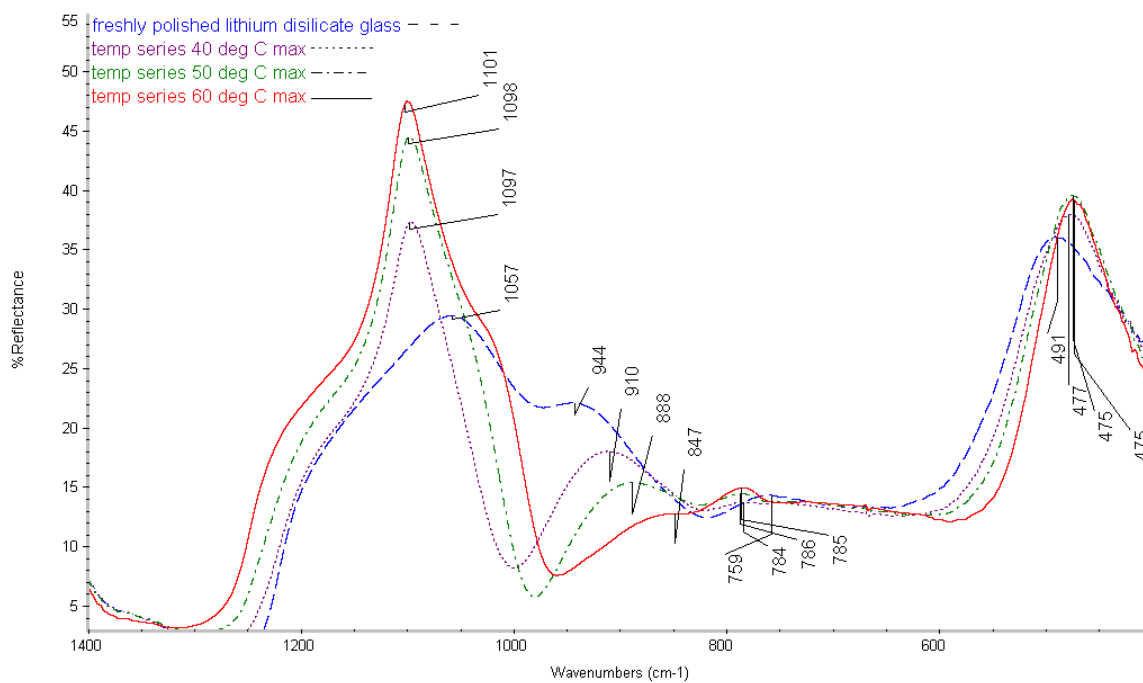


Figure 41: Low-temperature conventional temperature series FTIR spectra.

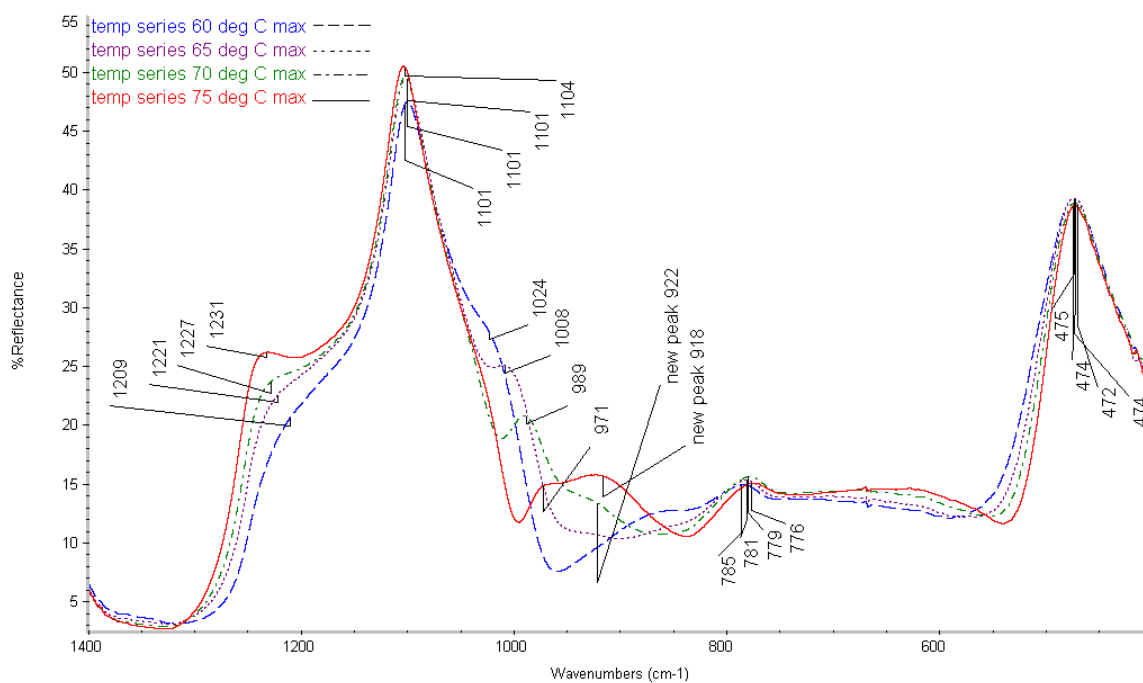


Figure 42: Medium-temperature conventional temperature series FTIR spectra.

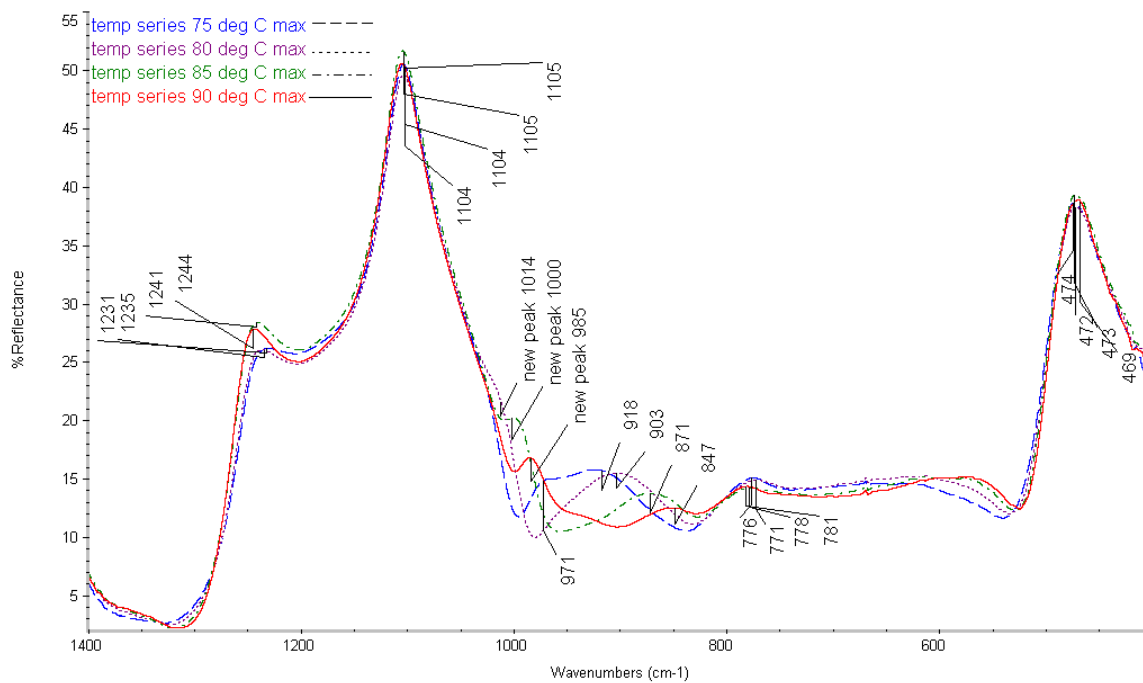


Figure 43: High-temperature conventional temperature series FTIR spectra.

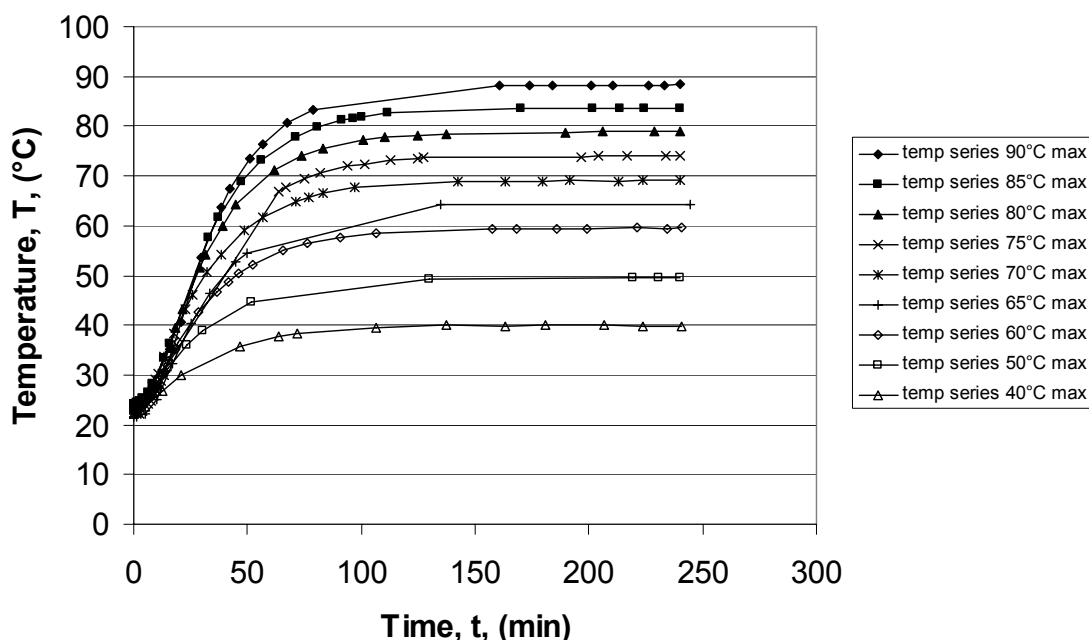


Figure 44: Bath temperature versus time profiles for conventional temperature series.

The spectrum of uncorroded lithium disilicate glass is juxtaposed with the low-temperature setpoint samples (40-60°C) in Figure 41. The medium-temperature (60-75°C) and high-temperature (75-90°C) sample spectra are shown in Figures 42 and 43, respectively. The spectrum resulting from the highest temperature from the previous group is displayed in each figure to give some basis for comparison between the curves. In some of the plots, it is difficult to distinguish which peak wavenumber corresponds with which curve. When this is the case, the wavenumber corresponding to the lowest temperature is on the left. The temperature setpoint increases from left to right.

In Figure 41, as the corrosion temperature increased, the Si-O-Si bridging oxygen peak shifted from 1057 to 1101 cm^{-1} and increased in intensity. The nonbridging oxygen peak in the presence of Li^+ at 944 cm^{-1} decreased to 847 cm^{-1} and lost intensity (a phenomenon sometimes called decoupling). It was completely extinguished in subsequent high-temperature tests. Also, the Si-O-Si bending peak decreased from 491 to 475 cm^{-1} . The peak at 759 cm^{-1} increased to 785 cm^{-1} .

The behavior of both the bridging and nonbridging stretching peaks was highly characteristic of preferential leaching in the outer layer of the glass (Equation 2 and 9), where a silica-rich layer results from alkali depletion. The trend resulting from different

corrosion temperatures follows that demonstrated by Ethridge for $\text{Li}_2\text{O}-2\text{SiO}_2$ glass corroded for different times (Figure 20). Since (from a kinetic standpoint) increasing the corrosion temperature and increasing the corrosion time have essentially the same effect on the corrosion kinetics, the trend of the spectra resulting from this test agrees with what has been presented in the literature when time is varied (Figure 20) for a binary alkali silicate in the early stages of corrosion (preferential leaching) [31]. It should be noted, however, that the spectra presented here are much more detailed than those presented in the literature. This difference is due to the fact that the FTIR technique is capable of resolving much greater detail than the older wavelength dispersive technique.

As the temperature increased, the degree of leaching increased. As degree of leaching increased the bridging and nonbridging peaks decoupled to a greater extent. This behavior was brought on by the decreased presence of Li^+ in the surface layer, a condition manifested in the nonbridging peak extinguishing and the bridging peak gaining in intensity. As leaching proceeded, the FTIR reflection spectra increasingly resembled that of vitreous silica.

In Figure 42, the Si-O-Si bridging stretching and bending peaks were shifted from their original $\text{Li}_2\text{O}-2\text{SiO}_2$ glass locations, but there was very little difference between these main peaks for any of the corrosion temperatures represented in the figure. Also, very little difference existed between the samples for the peak near 780 cm^{-1} . This similarity of spectra most likely indicates a large degree of similarity of structure of the silica-rich layers in the samples resulting from all corrosion temperatures.

Though the main peaks varied little, there were significant differences between the spectra. As temperature increased, a satellite peak to the left of the Si-O-Si stretching peak developed from a shoulder into a distinct, separate peak at 1231 cm^{-1} . Similar behavior occurred with the same peaks for the high-temperature curves in Figure 43. This peak represents the interplay between the LO and TO modes, as described previously.

Somewhat unpredictable behavior occurred in the region of 1050 to 800 cm^{-1} . At the 60°C setpoint, the sample spectrum developed a shoulder to the right of the Si-O-Si stretching peak. At 65°C , this shoulder became a distinct peak at 1008 cm^{-1} . The spectrum from the 70°C sample showed that this peak was shifted from 1008 to 989 cm^{-1} .

At the 75°C setpoint, this peak further decreased in intensity and shifted to 971 cm⁻¹. The shift was also accompanied by the development of a new peak at 918 cm⁻¹ which joined the original to form a doublet. The beginnings of this new peak may be seen at 922 cm⁻¹ in the spectrum belonging to the 70°C sample as it forms a shoulder.

As the setpoint was further increased to 80°C, the original peak which was last seen at 971 cm⁻¹ disappeared. The peak at 918 cm⁻¹ in the 75°C sample shifted to 903 cm⁻¹. As the setpoint increased further, this peak shifted to 871 cm⁻¹ for the 85°C sample and then to 847 cm⁻¹ for the 90°C sample, decreasing in intensity every time and appearing to extinguish in a manner similar to the Si-O⁻ nonbridging oxygen peak (in the presence of Li⁺).

A new peak was also observed developing in the 80°C sample spectrum and maturing in the 85 and 90°C sample spectra. A new shoulder off the Si-O-Si stretching peak first appears at around 1014 cm⁻¹ for the 80°C setpoint. The shoulder became a distinct peak at 1000 cm⁻¹ in the 85°C sample. It shifted to 985 cm⁻¹ at 90°C.

The behavior in the 800-1000 cm⁻¹ range with respect to this shifting peak was not readily explained. The most probable explanation is that this peak is due to Si-O⁻ stretching in the presence of hydrogen. A very rarely studied Si-OH stretching vibration was reported in the literature in the region of 1000 cm⁻¹ [49, 50, 53]. As corrosion severity increased, “water” content could have varied and therefore the peak may have shifted. Alternatively, it may have shifted due to residual stresses in the gel layer. The influence of residual stress on infrared spectra peak location in silica gels has been reported for the primary peaks [53]. The authors reported the presence of this specific peak but did not examine its mobility, because the paper was focused on the primary peaks. Furthermore, it may have been due to leached layer thickness [54]. To the author’s knowledge this type of mobile behavior with respect to this particular peak has never been reported in the literature (possibly due to the inability to resolve it using the older wavelength dispersive technique).

A second theory is that this peak is actually a re-emergence of the Si-O⁻ nonbridging vibration in the presence of Li⁺ which shifts due to variation of Li⁺ concentration. This cause seems more likely as the explanation for the doublet that appeared at 922 cm⁻¹, as the frequency is more characteristic of the nonbridging vibration

in the presence of Li^+ . The peak was extinguished in a manner similar to the original nonbridging peak. It does not, though, seem to explain the peak that appeared at 1008 cm^{-1} .

The reason that these peaks shift and then seem to reemerge could be explained by removal of surface material as corrosion progresses. The original nonbridging peak was extinguished at a lower temperature, indicating that the leached layer was depleted of Li^+ ions. As the peak was extinguished, the “new” peak originated at 1008 cm^{-1} . The timing suggests that a nonbridging vibration in the presence of H^+ could be responsible because these ions replaced the Li^+ ions in the leached layer. As corrosion continued to progress, the leached layer may have been removed into solution, exposing a fresh surface to the infrared beam. The doublet that then developed was due to the nonbridging vibration in the presence of Li^+ that was again expressed. As corrosion progressed on that layer, the same cycle occurred.

Another possible explanation for these transient peaks is the deposition of another compound from solution. This theory is supported by the presence of a milky white compound which was occasionally present on some portions of the corroded surface of the glass. After taking a spectrum from several areas of the sample, with and without the film, though, it was found that the film had a very minimal impact upon the spectrum. Furthermore, the solubility limits of Li^+ and Si in water were not reached, so precipitation was unlikely.

Regardless of its explanation, the location of the peak can certainly be used as a tool for relative comparison between samples because it is so sensitive to temperature. Throughout experimentation (in this test and throughout this work) the behavior was very consistent. Even small differences in corrosion time or temperature influenced the relative location of this peak.

In an attempt to explain the behavior, two samples were dried at 110°C . The first sample was dried after the 40°C conventional series test. After drying, its surface was cracked, characteristic of the classic “parched” appearance of leached surfaces. The parched appearance indicated that water had been driven off from the surface. The FTIR reflectance spectrum is given in Figure 45. Upon drying, the Si-O-Si peak increased in intensity due to the condensation reaction given in Equation 4. The nonbridging oxygen

peak from the original spectrum, which had not yet been extinguished due to the low corrosion temperature, decreased in intensity and shifted to a lower wavenumber.

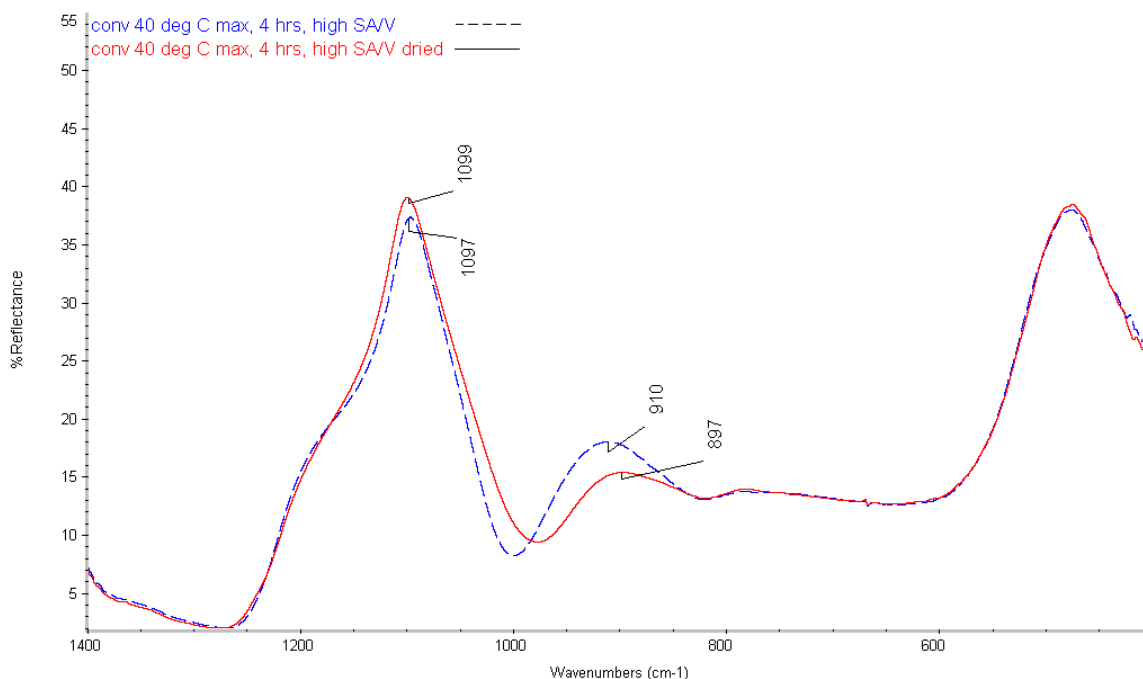


Figure 45: FTIR reflectance spectrum of sample dried after 40°C conventional temperature series test.

To get the second sample, the flat surface of the first sample was ground and then used over again to replicate the 75°C conventional temperature series test. Upon drying, as shown in Figure 46, the Si-O-Si stretching peak increased in intensity and the 1220-1230 cm^{-1} peak became more defined. The doublet at 925 and 979 cm^{-1} appeared to have merged into one peak between at 960 cm^{-1} . In this case, the effect of removing water seems to be the increase in intensity of the silica peak and the movement of what is probably the Si-OH stretching peak to lower wavenumbers. This may be an indication that the condensation reaction (Equation 4) that increases the intensity of the Si-O-Si bridging peak also affects the location of the Si-OH peak as Si-OH groups are depleted by condensation.

By conducting these tests, it has been shown that the $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ glass used in this work follows the typical mechanisms associated with the early stages of static corrosion of binary alkali silicates. Preferential leaching is clearly evidenced by the

expected changes in FTIR reflection spectra. Furthermore, these tests have served to verify FTIR reflectance spectroscopy as a sensitive analytical tool for the type of glass corrosion performed in this work that may be used to examine even small differences which are present between microwave- and conventionally-heated samples.

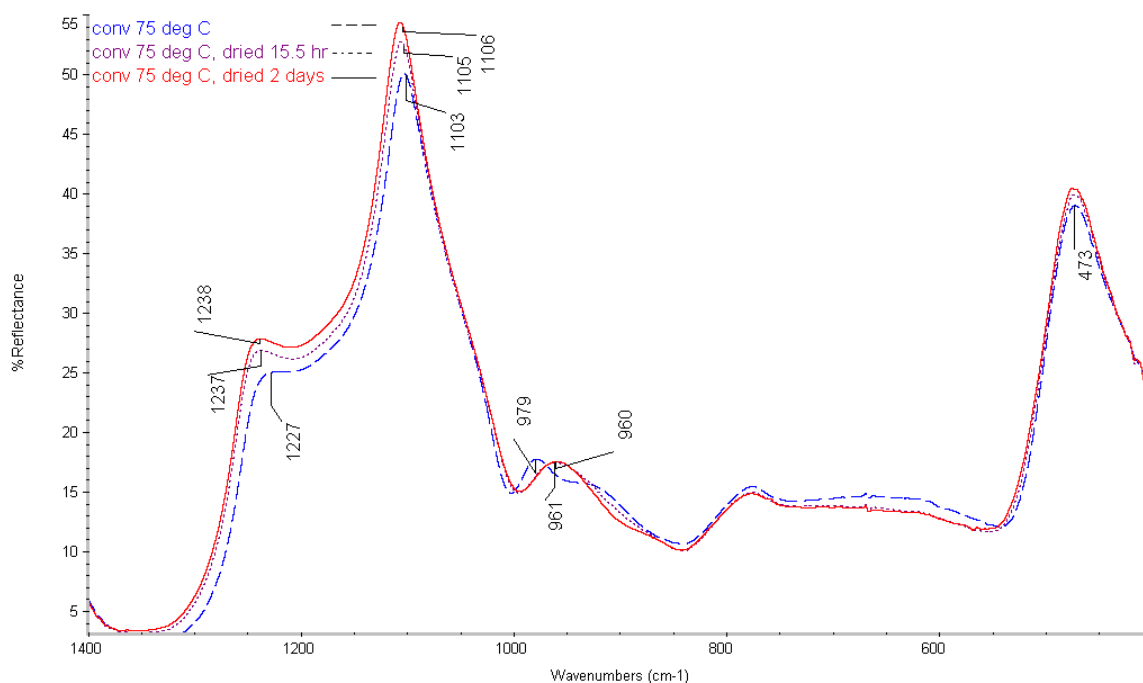


Figure 46: FTIR reflectance spectrum of sample dried after replication of 75°C conventional temperature series test.

Characterization of Conventional Corrosion by Systematic Bulk Testing

The systematic bulk testing detailed in Chapter III provided data from the conventional tests that agreed with what was expected for corrosion of $\text{Li}_2\text{O}-2\text{SiO}_2$ glass in a preheated static solution held at 90°C for the relatively short times studied (100, 250, 500, and 1000 min). Solution data, FTIR spectra, SEM micrographs, and SIMS profiles showed that at short times, leaching predominated and as time increased, network dissolution increased relative to leaching.

Solution data, both ICP and pH, are presented in Figures 47-50. In Figures 47 and 48, the Li^+ and Si released into solution form monotonic increasing curves with time. Both species are present in relatively small amounts. As corrosion time increased, the molar ratio between Si and Li^+ in solution, α , increased as well (Figure 49), indicating that more silica was released into solution with time*. This increase in α corresponded to the increase in pH of the static solution as time increased (Figure 50)†. The release of Li^+ is characteristic of preferential leaching (Equations 2 and 9). The release of Si is characteristic of competing network dissolution (Equations 3, 9, and 18).

Representative FTIR spectra of the top faces of the corroded samples are shown in Figure 51. The sample corroded for 100 min showed the least corrosion and closely resembled the spectrum belonging to the 70°C conventional temperature series sample described above. The satellite peak at approximately 1230 cm^{-1} had not yet completely developed and the transient peak in the $800\text{-}1000\text{ cm}^{-1}$ region was in a similar position.

The samples corroded for 250, 500, and 1000 min in the preheated 90°C solution exceeded even the most severe condition in the conventional series (90°C resulting from a 240-min ramp from room temperature). Their FTIR spectra did resemble some of those belonging to the conventional series. The resemblance, though, is only coincidental: the spectra are caught at various points in the cyclic behavior of the suspected Si-OH peak in the $800\text{-}1000\text{ cm}^{-1}$ region. The position of the Si-OH peak from each sample therefore bears no relationship to the position of the peak from the other samples.

The positions and intensities of the main Si-O-Si stretching and bending peaks were exactly as expected for a leached-layer that is rich in silica. Because the spectra of

* During systematic bulk testing, a problem occurred with the temperature measurement system of the Vari-Wave (see Appendix E). After replacing the probe and reconfiguring the system, the Vari-Wave read several degrees higher than it did before the fix. As a consequence, the actual temperature corresponding to a hold at “90°C” was lower than before the fix. The conventional oven was calibrated accordingly. The 500-min sample tests were performed after this occurred. Therefore, all data resulted from a temperature difference of several degrees. This produced only a small effect on the release of Li^+ and Si individually, but the combined effect caused α to be lower than it otherwise would have been. Had the 500-min tests been done before the adjustment, the corresponding average value of α would be expected to be just slightly higher, perhaps 0.080, and fit in with the general increasing trend in Figure 49 better than it does.

† The average value of pH resulting from the 500-min trials was not included in Figure 50 because it did not at all fit the trend. It is expected that changes to the pH meter, including aging of the glass membrane and careful calibration just prior to 500-min testing, as well as the slight difference in temperature due to equipment problems contributed to the difference. Since it was expected that the 500-min data did not fit the trend due to equipment issues and not differences in corrosion mechanisms, the 500-min data is not included in the plot.

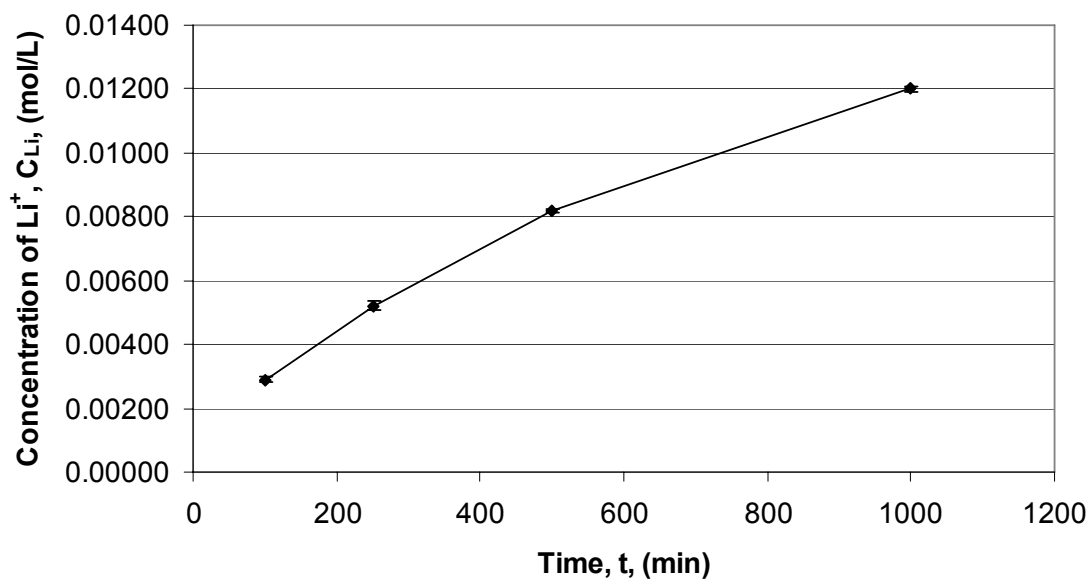


Figure 47: Average concentration of Li^+ released into solution by conventional heating during systematic bulk testing.

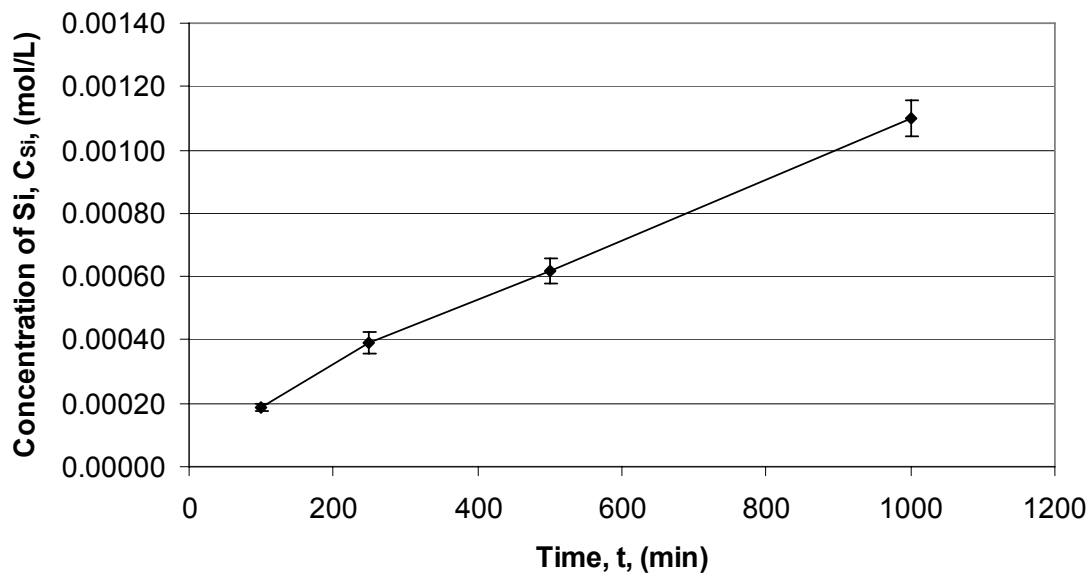


Figure 48: Average concentration of Si released into solution by conventional heating during systematic bulk testing.

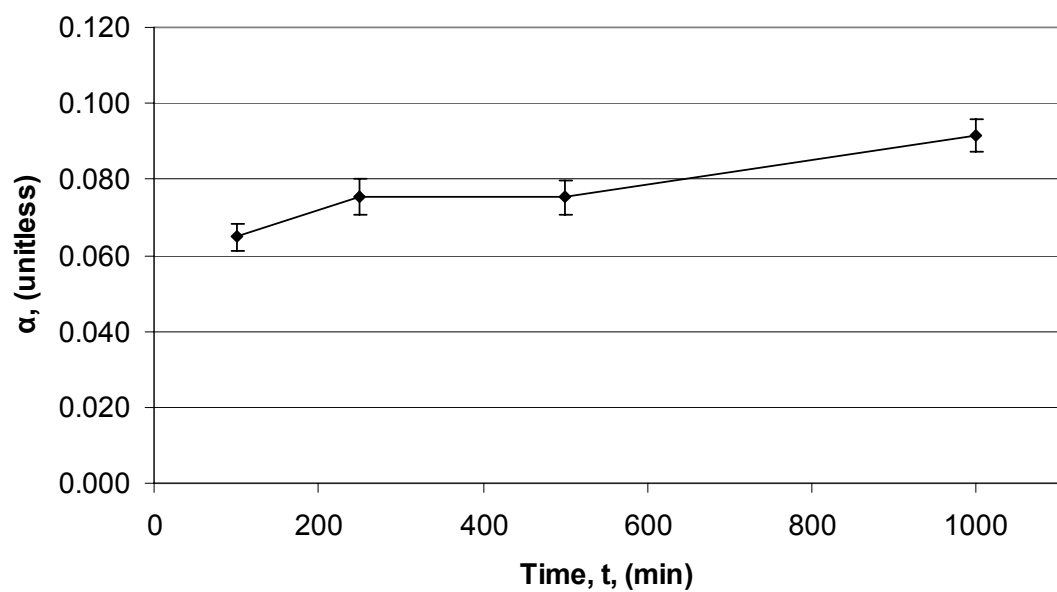


Figure 49: Kinetic parameter α calculated from released Li^+ and Si resulting from conventional heating during systematic bulk testing.

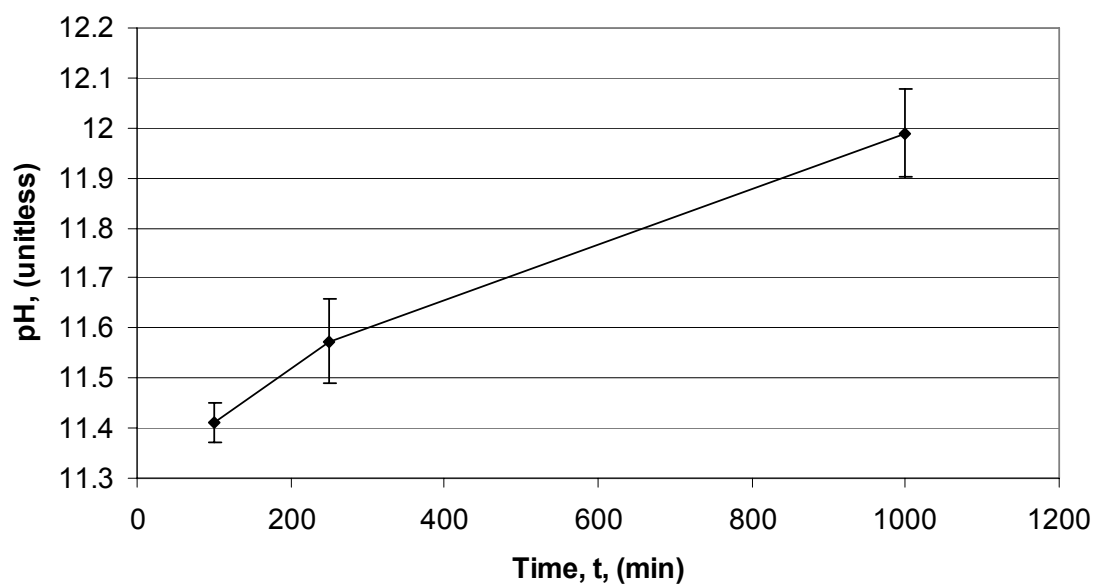


Figure 50: Average pH versus time resulting from conventional heating during systematic bulk testing.

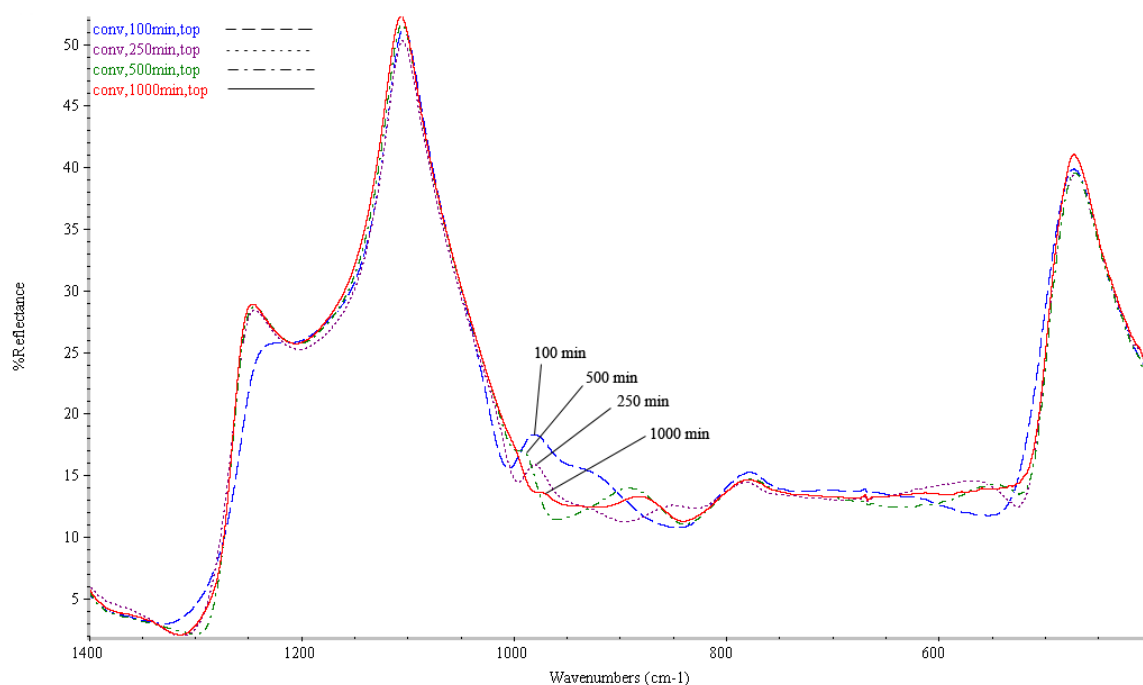


Figure 51: FTIR spectra from conventionally-heated samples held at 90°C in static solution during systematic bulk testing.

the samples corroded for 250, 500, and 1000 min closely resembled each other in regards to these primary peaks (neglecting the 800-1000 cm^{-1} region where the primary peaks were not in existence), it may be inferred that similar leached layers were present on all the samples. Furthermore, since the 100-min sample's 1250 cm^{-1} satellite peak was underdeveloped in comparison to these other spectra, the 100-min sample did not have a fully-formed leached layer. This difference may have been due to either a chemical effect, i.e. the presence of Li^+ in the leached layer, or the thickness of the leached layer, i.e. it may not have been thicker than the depth of penetration of the infrared radiation [52, 54].

It should be noted that FTIR reflectance spectra are not useful for comparing degree of corrosion resulting from radically different times or temperatures if these times or temperatures are sufficient to allow the primary stretching or bridging peaks to become fully developed. The principal differences between the spectra of the 250-, 500-, and 1000-min samples were in the 800-1000 cm^{-1} region. As noted, however, the behavior in the 800-1000 cm^{-1} region is cyclic. Differences of 5-10°C or a few minutes may be

successfully monitored by comparing the relative position of the peak in the 800-1000 cm^{-1} region, but conditions that cause the peak to cycle several times cannot be judged reliably from FTIR data. In comparing microwave versus conventional heating, this fact was important to take into consideration and all comparisons were made taking careful note of other corroborating data.

Representative micrographs of the top faces of samples were also taken and are shown in Figures 52-55. From these micrographs, changing morphology may be observed. On the surface of the freshly abraded glass sample (polished with 1000-grit SiC paper), the primary visible microstructural features are the sharp polishing tracks. Figure 52 shows a large polishing track centered in the frame (labeled as I), with other, smaller, tracks visible (labeled as II). The tracks have well-defined features and are segmented along their length, as might be expected if a sharp object skips while being dragged along a surface. Another component of the microstructure is a region with the appearance of a collection of flakes (labeled as III).

Corrosion had a marked effect upon the morphology of the surface. Specifically, it affected the size and shape of the polishing tracks. The changes in morphology may be used as a tool for examining type and severity of corrosion.

In Figure 53 (100 min), the polishing track centered in the frame (I) has maintained most of the sharp features associated with the freshly abraded surface. However, some of the smaller polishing tracks (II) nearby expanded and their features softened, taking on a more rounded appearance. The region with the flaky appearance is less prominent (III).

Figure 54 shows a slightly different morphology belonging to the sample corroded for 250 min. Instead of the mixture of large, sharp features and small, dull features, the features in this case are all rounded. The larger holes (I), previously sharp, retained their size but became open with dull, ellipse-shaped edges. The smaller features (II), which were rounded after only 100 min, appear much shallower. The flaky region (III) does not appear.

Finally, the morphology belonging to the 1000-min sample is given in Figure 55. The features which were at one point large and well-defined (I) at 100 and 250 min were

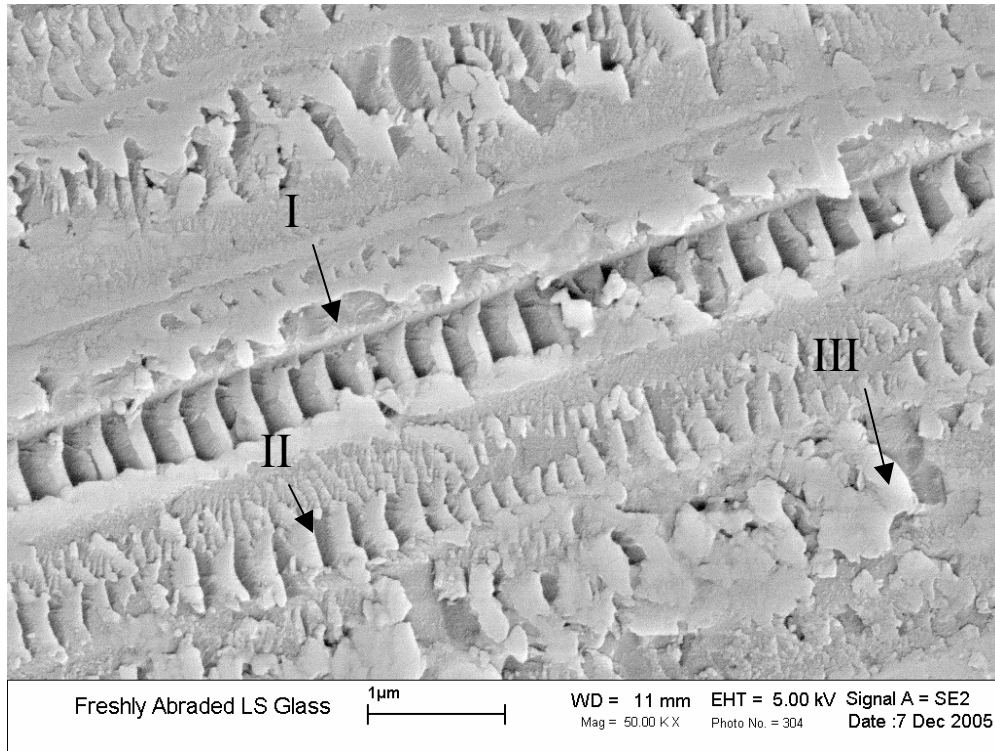


Figure 52: SEM micrograph uncorroded $\text{Li}_2\text{O}-2\text{SiO}_2$ glass after polishing with 1000-grit SiC paper.

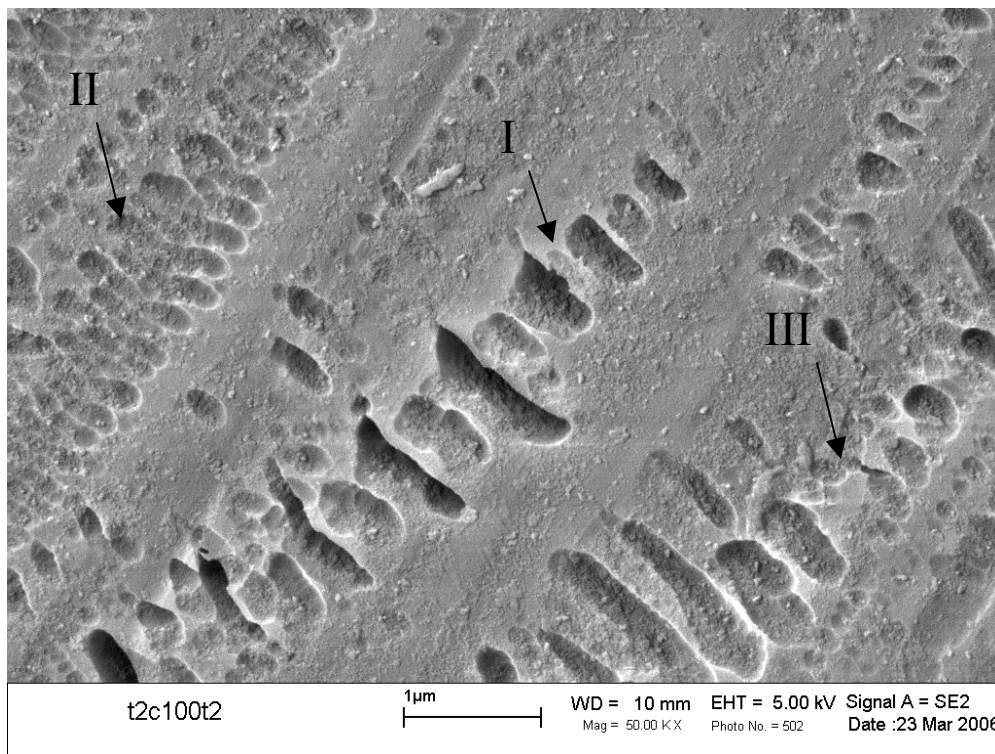


Figure 53: SEM micrograph of $\text{Li}_2\text{O}-2\text{SiO}_2$ glass sample corroded using conventional heating for 100 min in a preheated 90°C static solution during systematic bulk testing.

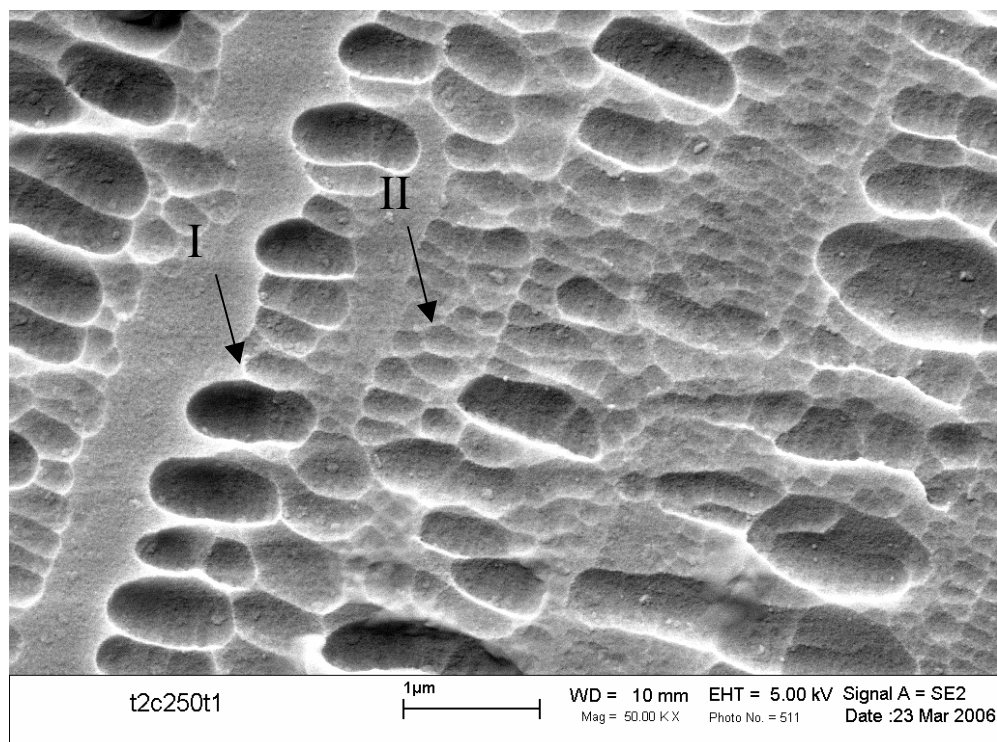


Figure 54: SEM micrograph of $\text{Li}_2\text{O}-2\text{SiO}_2$ glass sample corroded using conventional heating for 250 min in a preheated 90°C static solution during systematic bulk testing.

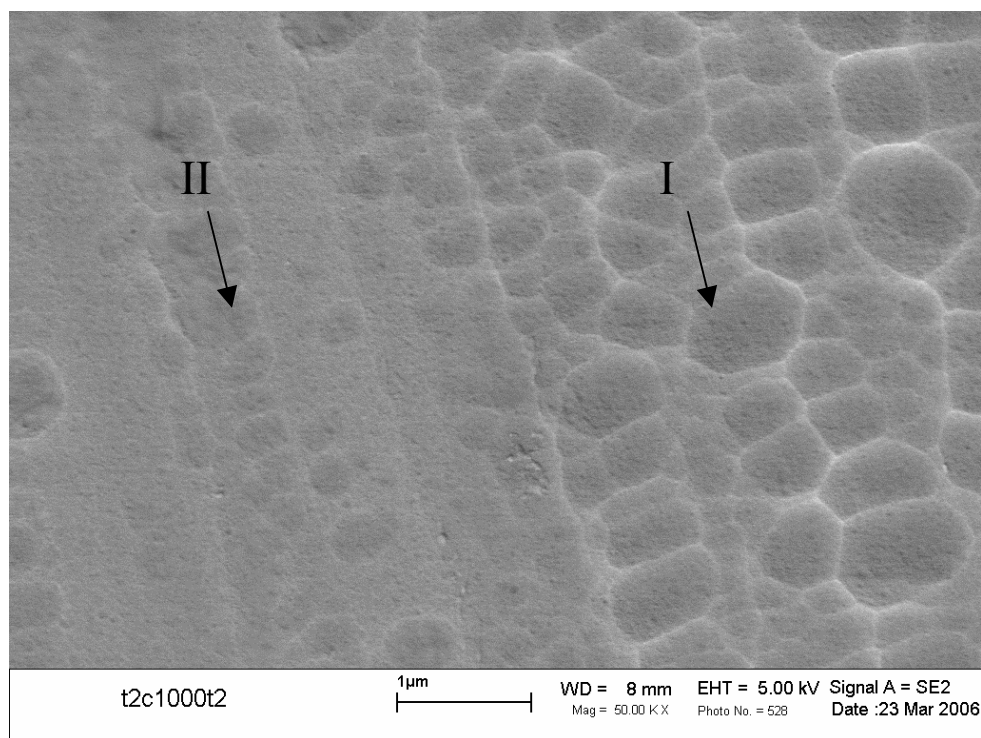


Figure 55: SEM micrograph of $\text{Li}_2\text{O}-2\text{SiO}_2$ glass sample corroded using conventional heating for 1000 min in a preheated 90°C static solution during systematic bulk testing.

completely rounded and very shallow. The smaller tracks (II) almost completely disappeared. The flaky region still does not appear (III).

As observed in the ICP data, both Li^+ and Si were steadily released into solution throughout the process of corrosion. The release of Li^+ was associated with the leaching reaction (Equations 2 and 9). The release of Si was associated with network dissolution, either occurring through the diffusion-controlled reaction of H_2O (Equations 3 and 9) or with the network or the direct attack of OH^- (Equation 18).

Had only Li^+ been released, a value of $\alpha=0$ would have resulted from the ICP data. It would be expected that there would be little, if any, rearrangement of the glassy network and hence no change in the morphology of the polishing tracks. This, however, was not the case. The radical microstructural changes that took place as corrosion time increased were the result of the glassy network being broken down and dissolved into solution via the network dissolution reactions. As corrosion time increased, more and more Si was removed and the sharp features grew rounder and shallower until they had almost disappeared in Figure 55.

Throughout this time, the plane of the leached layer progressed into the glass. For 100 min, the leached layer was nearly completely formed when the polishing tracks began to coarsen. The FTIR spectra in Figure 51 show that the leached layer below the surface had similar characteristics at 250, 500, and 1000 min, indicating that the leached layer was at least some critical thickness as the features coarsened and the surface silica dissolved.

To further evaluate the process of leaching, SIMS profiles were taken. Different test procedures and sample configurations from the previous data were used and are detailed in the previous chapter. SIMS profiles for the $\text{Li}_2\text{O}-2\text{SiO}_2$ glass are shown in Figures 56 and 57. Figure 56 gives the profile for the freshly abraded $\text{Li}_2\text{O}-2\text{SiO}_2$ glass. After some initial noise at the surface, the levels of Li^+ and Si eventually settled at constant values. It is simply coincidence that these values appear to be nearly the same because, as discussed in Chapter II, each species present ionizes at different rates depending on the matrix. It is also apparent that H is in the glass matrix before corrosion, probably entering during the melting, fining, or polishing stages.

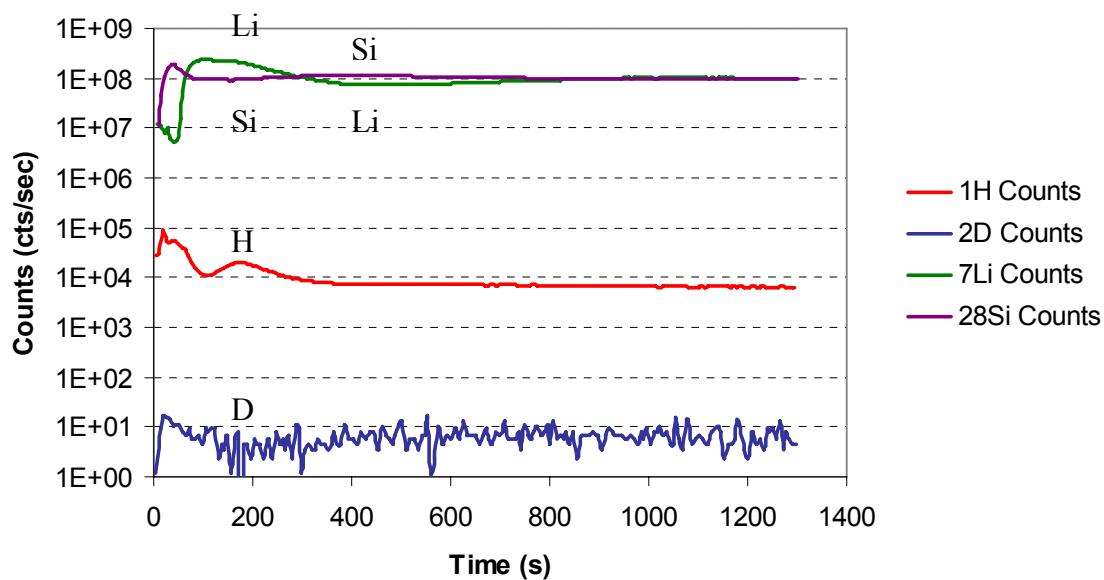


Figure 56: SIMS profile of freshly abraded, uncorroded $\text{Li}_2\text{O}-2\text{SiO}_2$ glass.

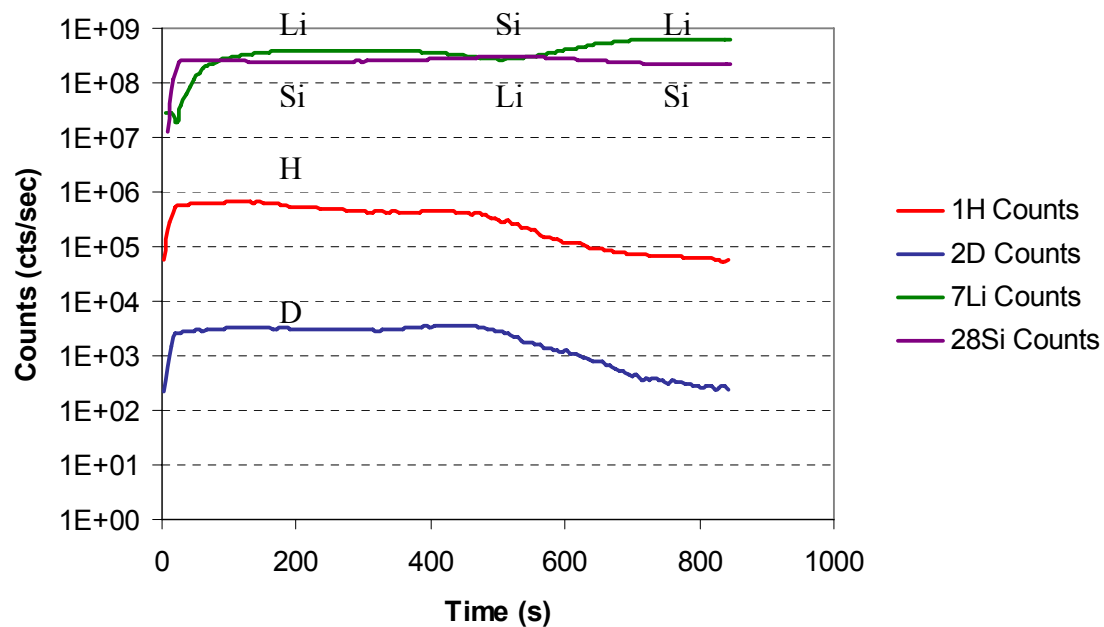


Figure 57: SIMS profile from $\text{Li}_2\text{O}-2\text{SiO}_2$ glass corroded for 43.5 min in a preheated 90°C static solution of D_2O .

Figure 57 gives the profile for a sample heated conventionally in a 90°C static solution of D₂O for 43.5 min. In this plot, the Li concentration starts high, dips, and then increases in the S-shaped curve as sputtering time increases. The opposite behavior is seen for Si. This S-shaped curve was expected for glass corrosion (see Chapter II) and the initial high value near the surface, though unexpected, was attributed to surface roughness^{*}. The roughness is illustrated by a surface roughness profile in Figure 58.

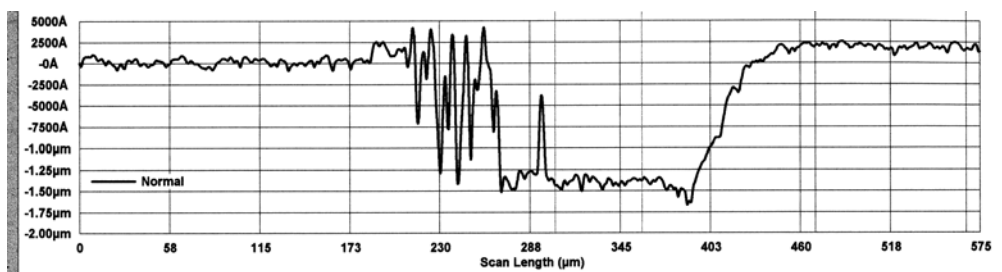


Figure 58: Surface roughness profile of sputtered region of Li₂O-2SiO₂ glass sample.

The presence of the S-shaped curve after sputtering the glass indicated that there was a depletion of Li⁺ at the surface and an increase in its concentration to the bulk level as the beam sputtered into the glass. This Li⁺ concentration profile is characteristic of a leached layer.

The FTIR spectrum in Figure 59 is from the surface of the sample corroded in D₂O at 90°C. It contains a nearly-extinguished Si-O⁻ nonbridging stretching peak (in the presence of Li⁺) at approximately 875 cm⁻¹, an incompletely developed Si-O-Si stretching peak at approximately 1100 cm⁻¹, and bears resemblance to 60°C spectrum in the conventional temperature series (Figure 41).

Solution data (Table 3) shows that the sample released an expected amount of Li⁺ and Si, with a value of α of 0.041. This low value of α indicates the sample was in the very early stages of corrosion, with more inclination towards preferential leaching (versus network dissolution) than the 100-min sample in the systematic bulk test.

^{*} The surface was too rough because it was prepared using 1000-grit SiC paper. This paper produced polishing tracks smaller than the spot size of the primary ion beam. As a result, the profile contained information from the corroded surface and the bulk simultaneously.

Taken together, this data (ICP, pH, FTIR, SEM, and SIMS) indicates that preferential leaching occurred at short times and as time increased, network dissolution increased in relative importance. The morphology of the surface features tends to become rounder and shallower as silica from the glassy network is dissolved into solution. The leached layer remains somewhat intact throughout the process. The trends seen in this data are characteristic of corrosion of binary alkali silicate glasses corroded in a static solution reported in the literature [31].

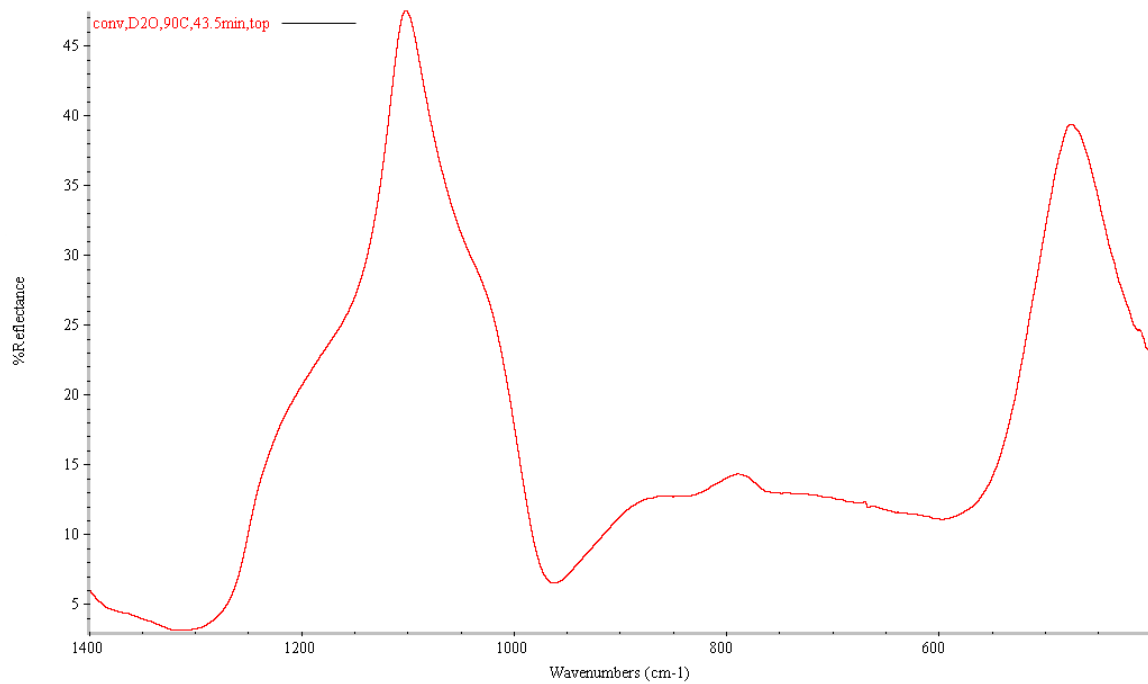


Figure 59: FTIR spectrum of $\text{Li}_2\text{O}-2\text{SiO}_2$ glass corroded for 43.5 min in a preheated 90°C static solution of D_2O .

Table 3: ICP data from $\text{Li}_2\text{O}-2\text{SiO}_2$ glass sample corroded in a 90°C preheated D_2O static solution for 43.5 min.

	[Li] (mol/L)	[Si] (mol/L)	α ([Si]/[Li])
Conventional, 90°C	0.000757	0.000031	0.041

By verifying that the characterization techniques (ICP, pH, FTIR, SEM, and SIMS) and an effective experimental setup produced results in agreement with the literature, it was confirmed that the well-known processes of glass corrosion were being observed. This confirmation signified that microwave radiation could be used as an alternative form of heating and that its effects on the actual glass corrosion mechanisms would be apparent. Furthermore, the sensitivity of the characterization techniques demonstrated their applicability to the study of the influence of microwave effects.

Microwave Heating Effects

Verifying that the well-known processes of glass corrosion were observable with the experimental setup and characterization techniques in question permitted the introduction of microwave energy for heating corrosion solutions. This section details the results of microwave tests and discusses their significance.

Systematic Bulk Testing at 7.00 GHz

Solution Data

Results from ICP solution analysis are given graphically in Figures 60-62. Except for the release of the Si at 100 and 250 min, the microwave samples released more Li^+ and Si at all times than did the conventional samples.

The kinetic parameter α , derived from Li^+ and Si concentration, for the microwave samples was smaller at short times and greater at longer times than the conventional samples. At both 100 min and 1000 min, the α -values for the conventional and microwave samples were significantly different (>90% confidence by ANOVA). The 250-min samples were not significantly different, as the confidence was only just over 85%, and the 500-min samples were even less so. The differences that do exist are possibly due to experimental error but may be indicative of microwave acceleration of leaching at short times and network dissolution at longer times.

Measurements of the pH are given in Figures 63-64*. The pH of the solutions resulting from conventional heating appeared to be higher on average, as illustrated by the error bars, but not significantly so when tested by ANOVA. However, when the

* The average pH measurements from the 500-min trials are not included in Figure 63 for the reasons described previously, though they are included in Figure 64 because relative comparison is valid and useful in that figure.

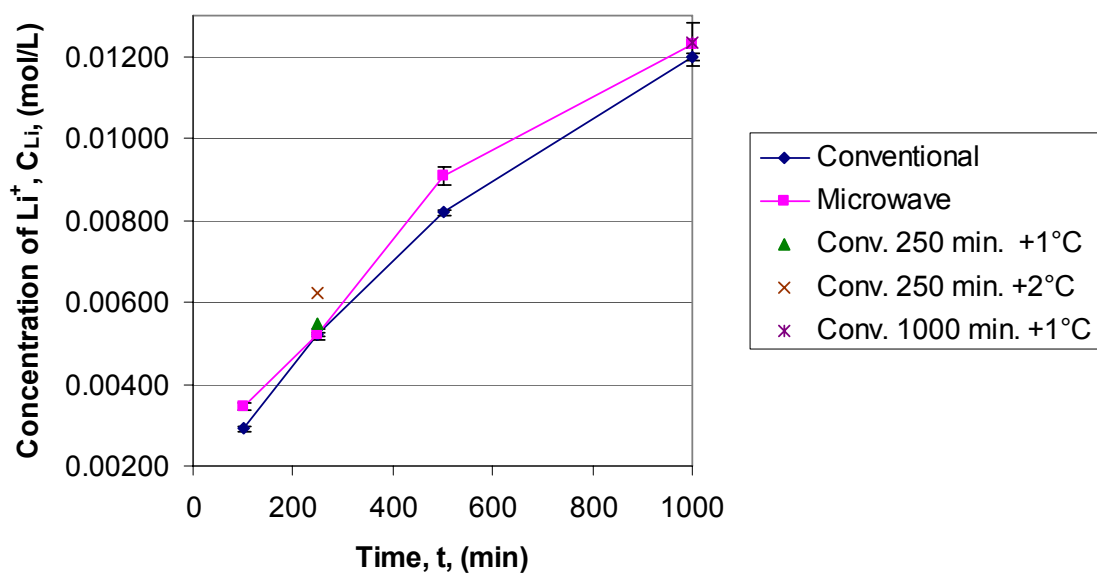


Figure 60: Li^+ released into solution during bulk testing, including conventional tests at 91 and 92°C

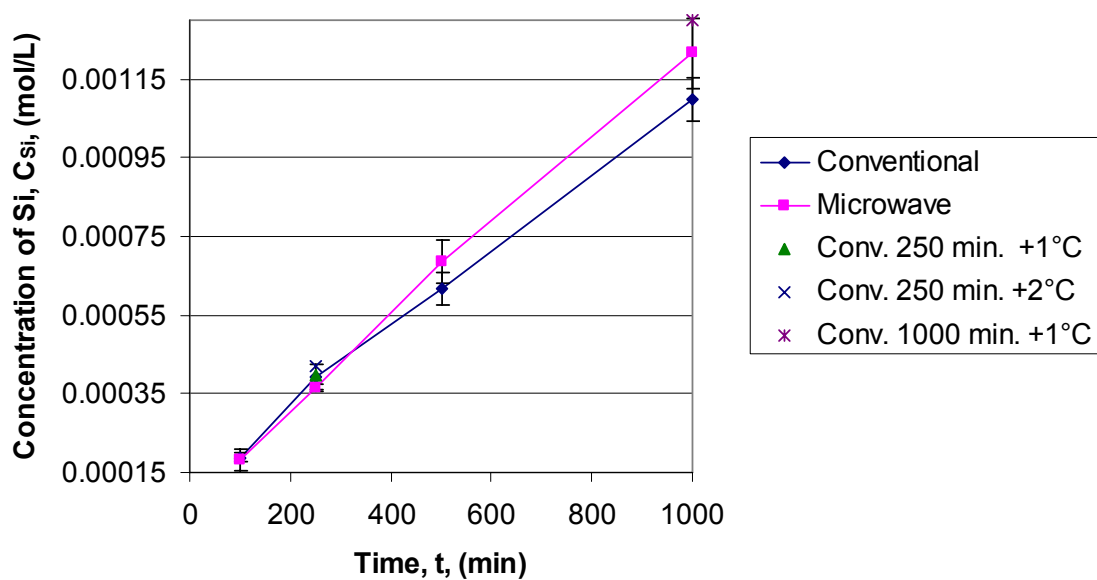


Figure 61: Si released into solution during bulk testing, including conventional tests at 91 and 92°C.

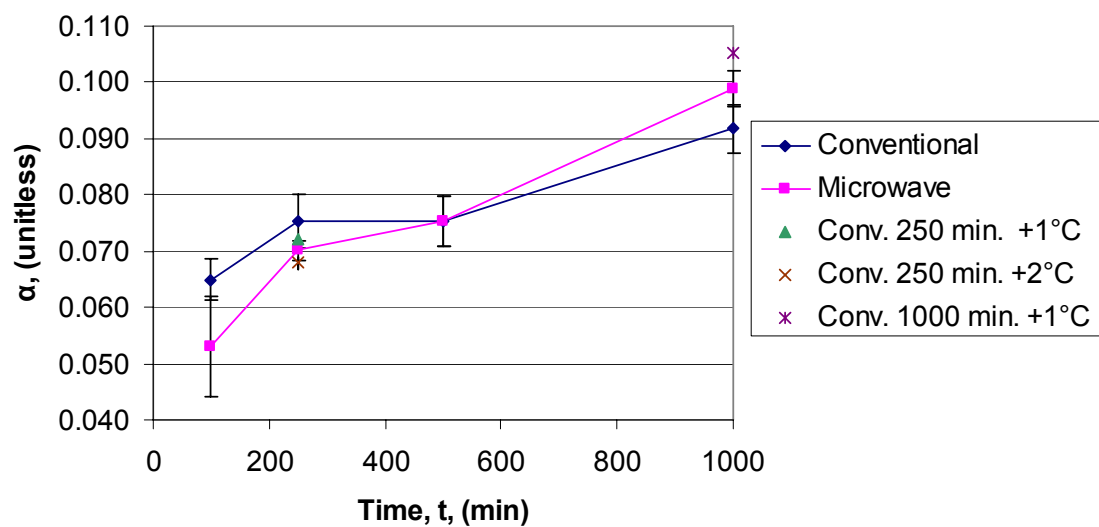


Figure 62: Kinetic parameter α calculated from solution data resulting from bulk testing, including conventional tests at 91 and 92°C.

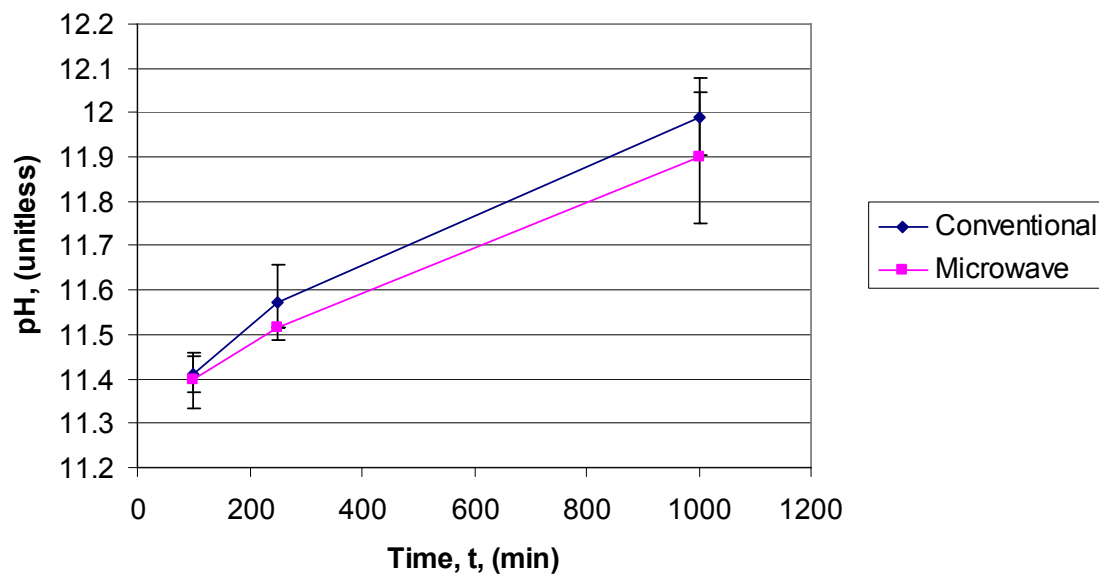


Figure 63: Average pH of solutions after bulk testing.

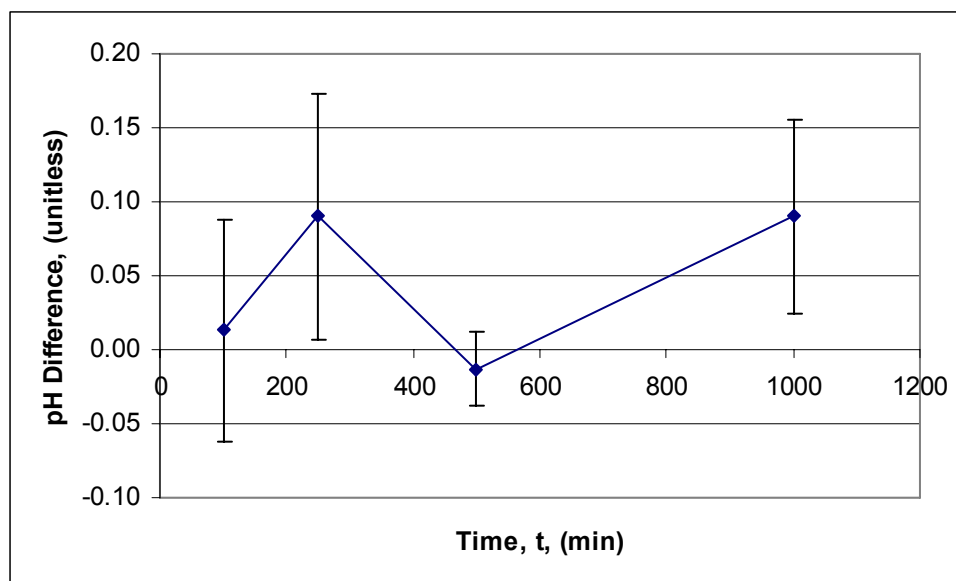


Figure 64: Average difference in individual pH measurements (conventional pH-microwave pH).

average *difference* of pH measurements for each individual test was considered (e.g. for any individual trial, the pH of the microwave-heated solution was subtracted from the pH of the conventionally-heated solution), the pH of the conventional solutions tended to be higher on average (Figure 64).

The pH of both microwave- and conventionally-heated solutions increased as corrosion time increased. This behavior was expected for a static solution and both types of heating caused the expected response.

An initial comparison of the solution data shows few differences between the microwave- and conventionally-heated samples except at short and long times (100 and 1000 min). The processes of corrosion, therefore, were essentially similar under conditions of conventional and microwave heating. No fundamental alterations in the mechanisms were experienced due to microwave processing. If a microwave effect were present, it was in the form of minor alterations in corrosion mechanisms and not major alterations.

In order to shed light on the differences which were present, conventional tests were performed at 91 and 92°C for 250 min and at 91°C for 1000 min. As the temperature increased, α decreased at 250 min but increased at 1000 min (Figure 62). At first glance, this data may appear to explain any difference in α between the microwave and conventional samples as purely thermal, i.e. the microwave bath was in actuality 1 to

2°C warmer than the conventional bath. However, Figures 60 and 61 showed that as the temperature increased, the release of Li^+ and Si did as well. This increase caused the conventionally-heated samples to release Li^+ and Si at levels greater than the microwave-heated samples. While this result does not prove a microwave effect, it does leave open the possibility that microwaves were responsible for the slightly different α -value because the levels of Li^+ and Si released into solution did not match those of the conventional temperatures required to match the value of α .

FTIR

For further characterization, the FTIR reflectance spectra from the top faces of the samples are given in Figures 65-68. At the shortest time, 100 min (Figure 65), the peak in the region of 900-1000 cm^{-1} was shifted further to the right for the samples heated with microwave energy than for those heated conventionally. As discussed previously, the position of this peak may be used to determine relative degree of corrosion. The differences in the other spectra are only slight for the longer times.

The shift at 100 min is indicative of possible increased corrosion at short times (dominated by leaching and shown by the trends of the conventional temperature series). The FTIR data supports the value of α derived from solution data for 100 min (Figure 62); it suggests increased or accelerated leaching, possibly due to microwave heating, at short times.

There appeared to be no significant differences between the spectra of the top faces of the conventional and microwave samples at 250 and 500 min because the scatter of the spectra was too great to distinguish one group from the other. This conclusion is supported by the similarity of, and lack of significant difference between, α -values in Figure 62.

The peak between 900 and 1000 cm^{-1} did appear to be shifted slightly further right for the conventional samples corroded for 1000 min. This shift implies slightly less leaching in the microwave samples, supported by the higher value of α in Figure 62. The FTIR results from the top faces indicate a possible effect of microwaves at both short and long times.

These conclusions corroborated the solution data. At short times (100 min), microwaves may have accelerated leaching and enhanced the development of a surface

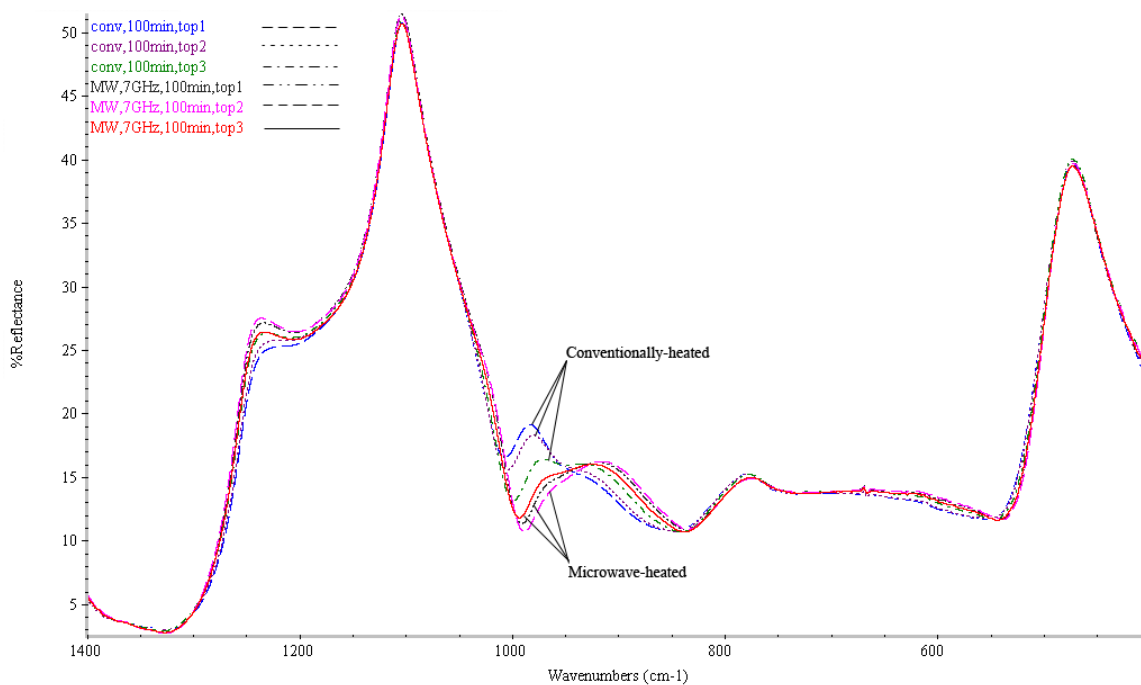


Figure 65: FTIR spectra of top faces of samples corroded for 100 min at 90°C.

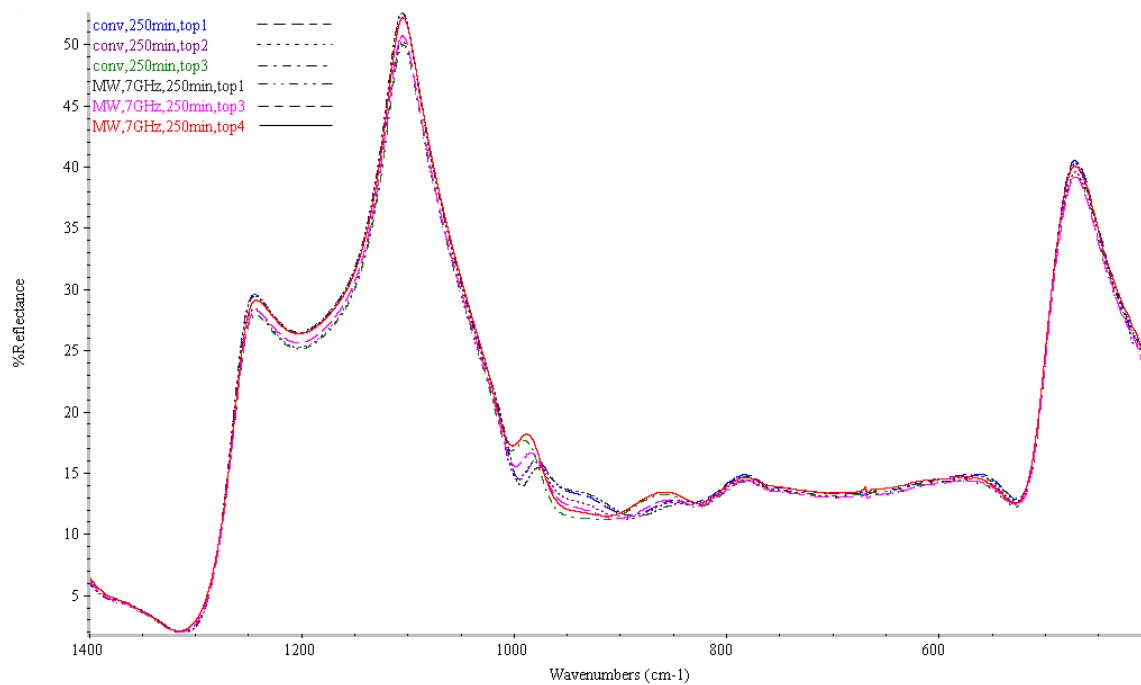


Figure 66: FTIR spectra of top faces of samples corroded for 250 min at 90°C.

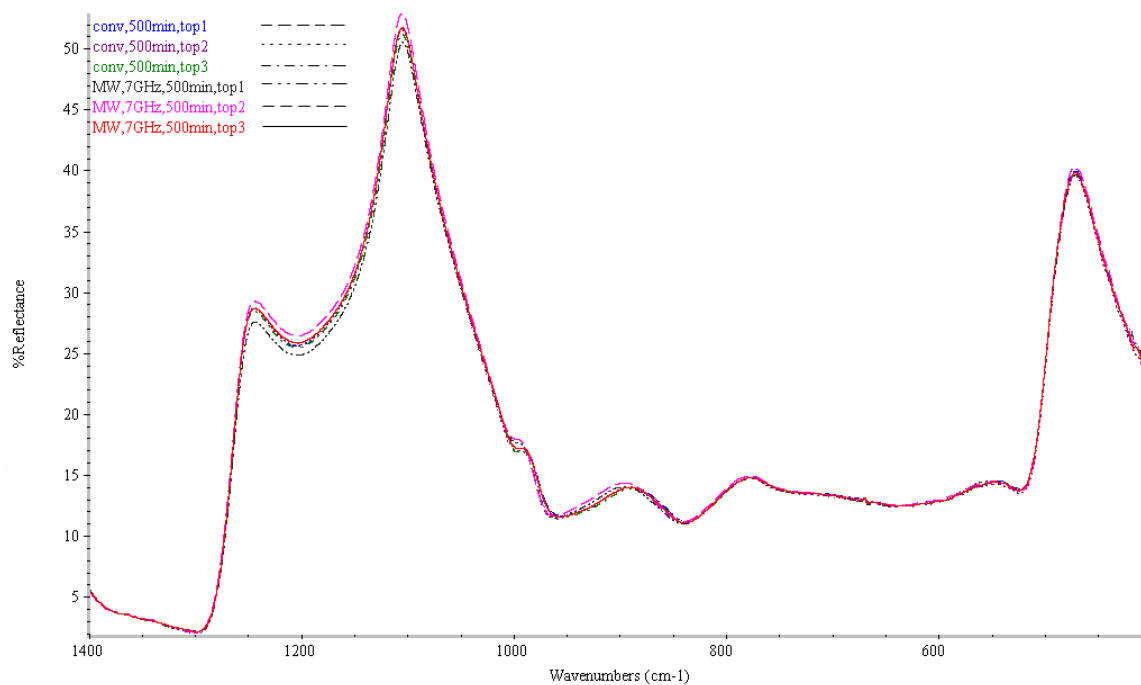


Figure 67: FTIR spectra of top faces of samples corroded for 500 min at 90°C.

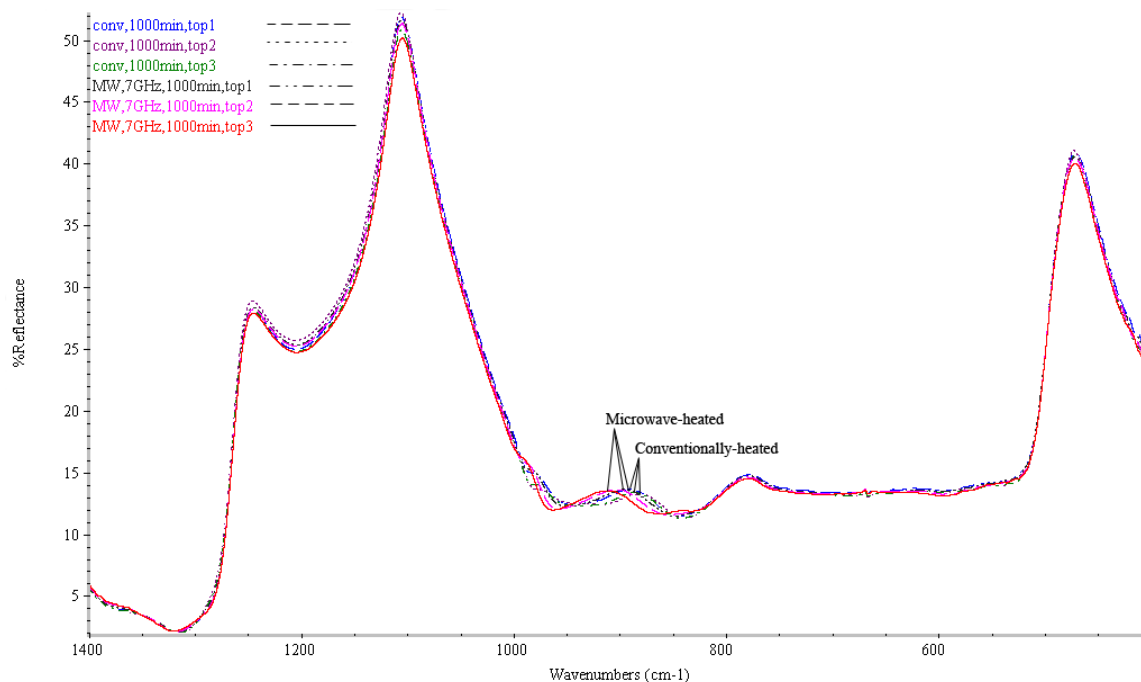


Figure 68: FTIR spectra of top faces of samples corroded for 1000 min at 90°C.

silica layer. As corrosion time progressed, the leaching leveled out and network dissolution began to dominate. At long times (1000 min), microwave radiation may have caused an acceleration of network dissolution.

The FTIR spectra of the bottom faces of the samples yielded slightly different results (Figures 69-72). As shown, the microwave samples' bottom-face spectra are shifted much more relative to those of the conventional samples. This shift may have been the result either of a local thermal gradient or increased exposure to microwaves.

The second possibility, increased exposure to microwaves, would have been brought on by the experimental setup in which the bottom faces rest directly on the PFA jar. Since the bottom faces of the samples rested on the bottom of the jar, there was very little water between the bottom face of the sample and the jar. This water layer would have been much thinner than the water that covered the top face of the sample. Therefore, with such a thin layer, any microwaves coming from the below the jar would have much less water to penetrate in order to get to the interface between the glass and water. This geometry would provide the bottom of the sample with more exposure to microwaves than the top face of the sample and, if a microwave effect did exist, it would be reasonable to expect it to be more apparent on the bottom of the sample.

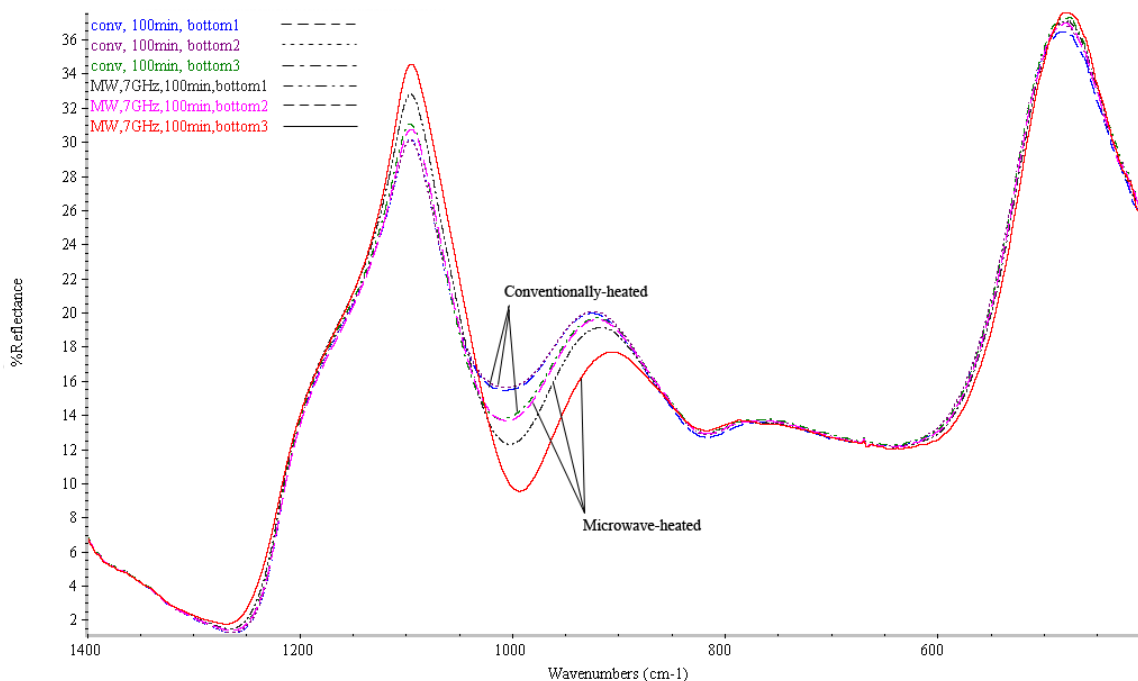


Figure 69: FTIR spectra of the bottom faces of samples corroded for 100 min at 90°C.

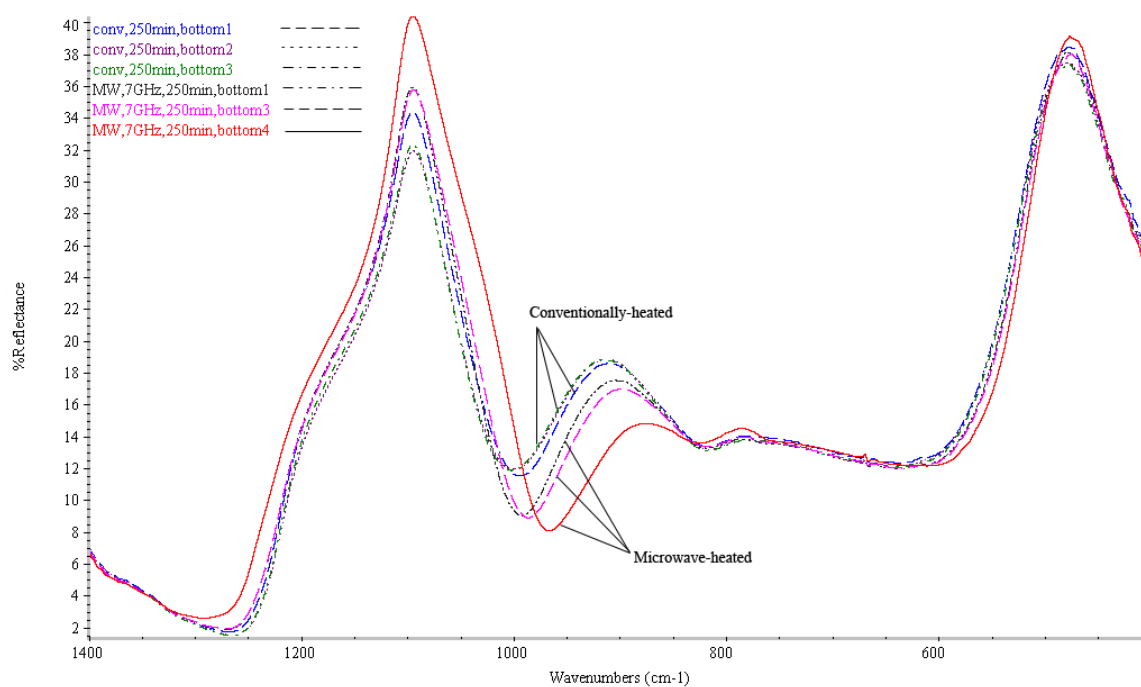


Figure 70: FTIR spectra of the bottom faces of samples corroded for 250 min at 90°C.

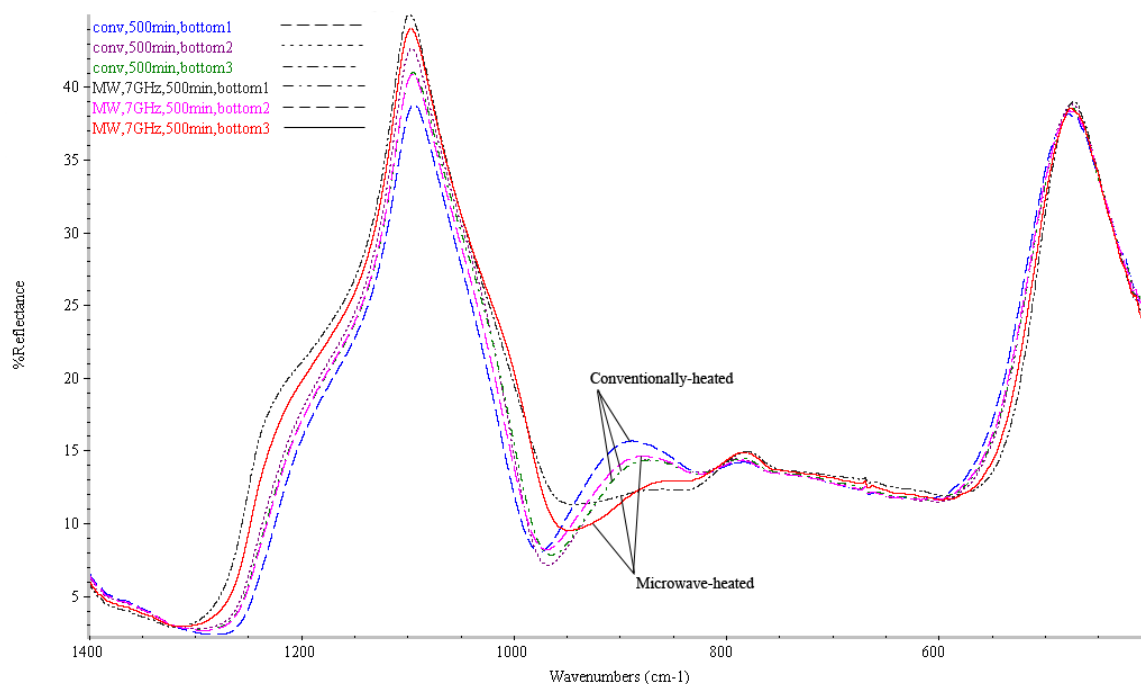


Figure 71: FTIR spectra of the bottom faces of samples corroded for 500 min at 90°C.

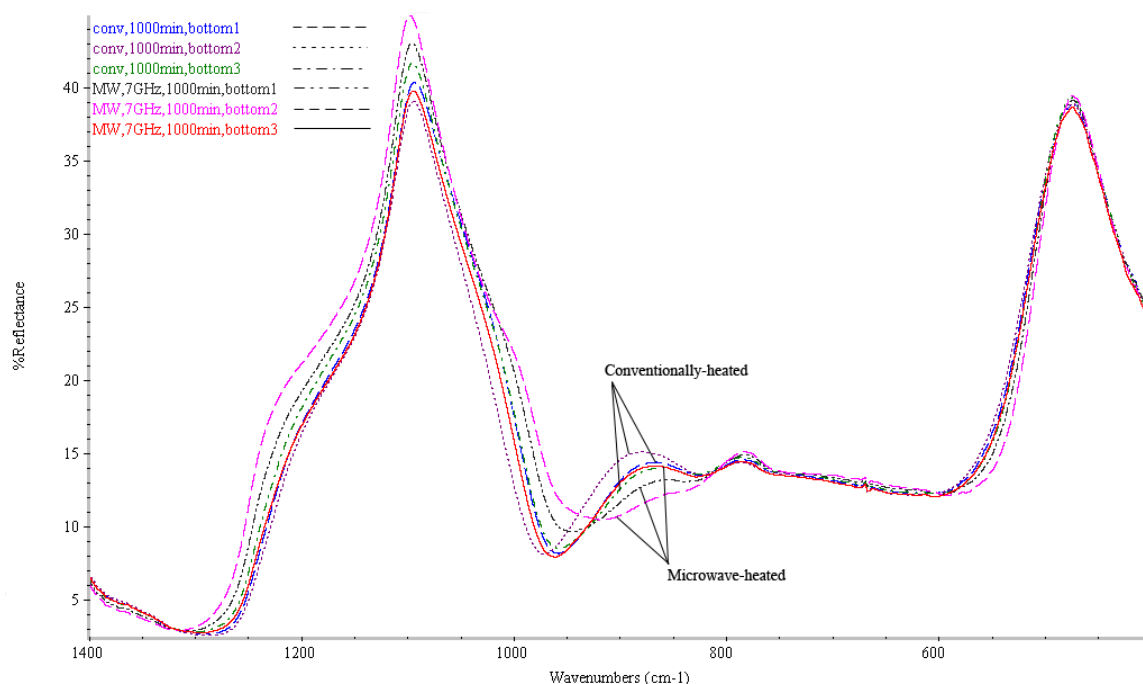


Figure 72: FTIR spectra of the bottom faces of samples corroded for 1000 min at 90°C.

Alternatively, it may have been that the bottom of the microwave samples was simply slightly hotter than expected. This phenomenon, known as a “hotspot,” is not unusual in a microwave oven. The differences apparent between the conventional and microwave samples may have been a real microwave effect but more corroborating evidence is required to conclude accurately.

SEM

SEM micrographs of the top faces of samples corroded for 100, 250, and 1000 min are shown in Figure 73 and the bottom faces of 100-min samples are shown in Figure 74. The micrographs of the conventionally-heated samples were presented previously (Figures 53-55) but are shown again with the micrographs of microwave-heated samples for side-by-side comparison.

The morphology of the microwave-heated samples exhibits the same general behavior as the conventionally-heated samples’ morphology (see Figures 52-55 for explanation of the features labeled I and II). The top faces of both sets of samples showed the retained sharp features of polishing tracks after 100 min, the significant rounding of the previously sharp features after 250 min, and the severe rounding and flattening of those tracks after 1000 min. The bottom faces also showed significant

rounding of tracks with some sharp features still retained. The overall behavior of the bottom faces appeared to be similar to that observed on the top faces, but with slightly more rounding having occurred.

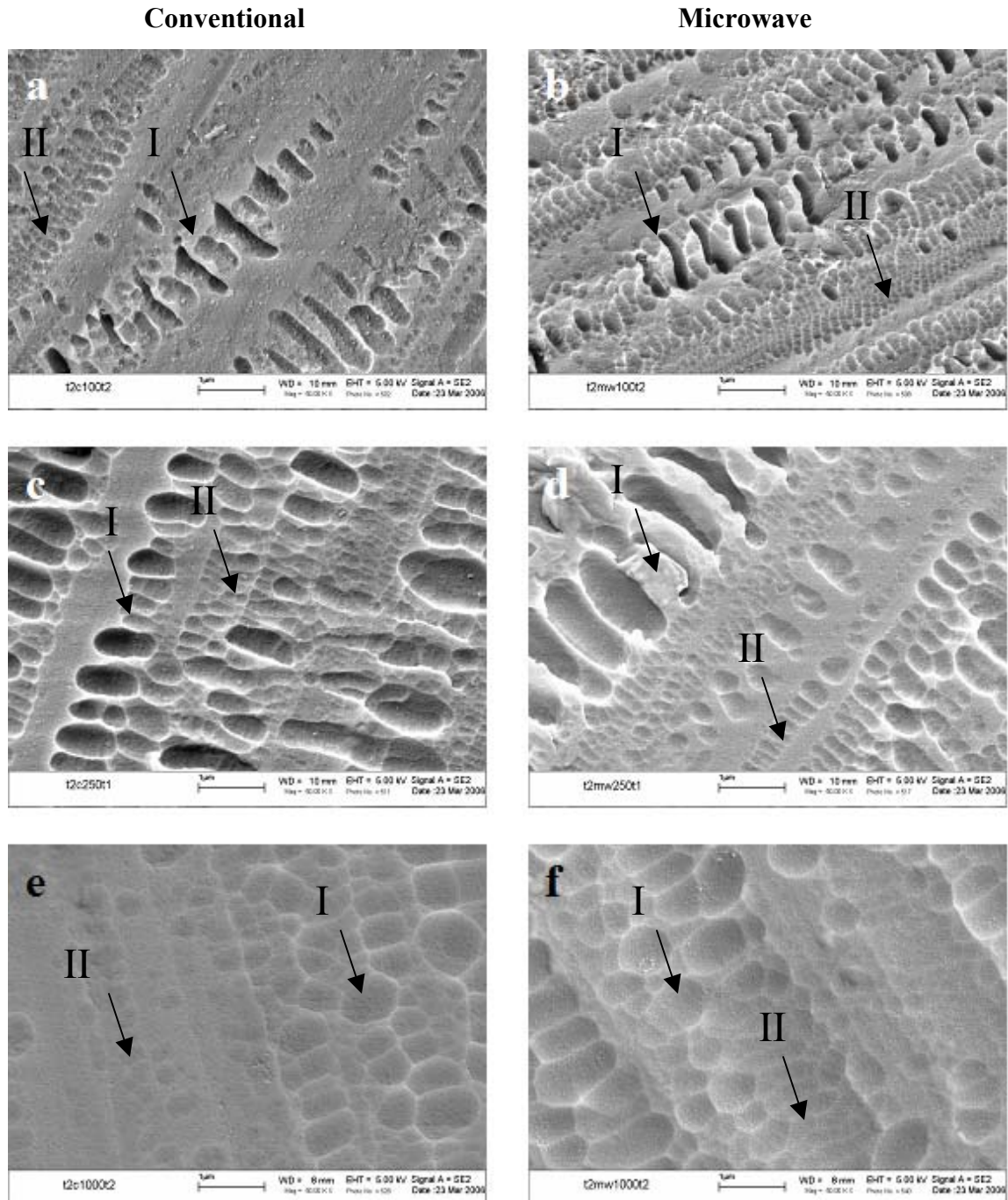


Figure 73: SEM micrographs of the top faces of samples in systematic bulk testing: a) conventional, 100 min; b) microwave, 100 min.; c) conventional, 250 min; d) microwave, 250 min; e) conventional, 1000 min; f) microwave, 1000 min.

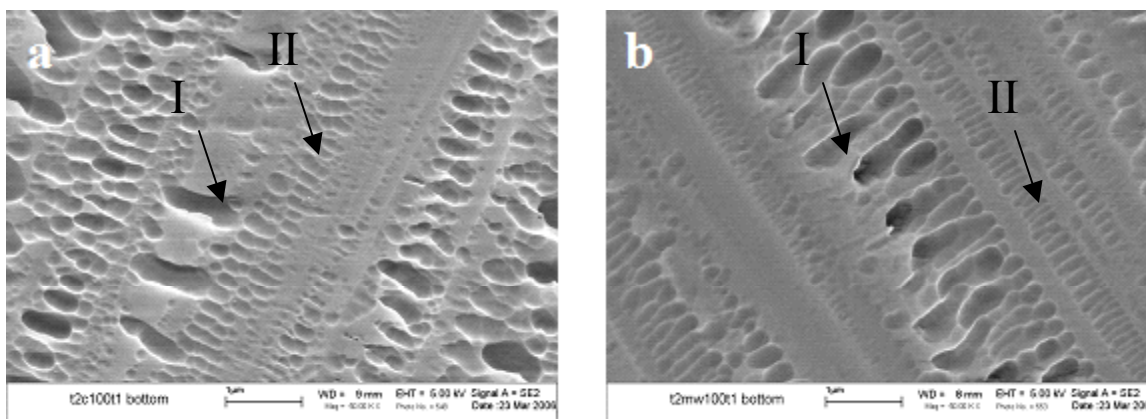


Figure 74: SEM micrographs of bottom faces of systematic bulk samples: a) conventional, 100 min; b) microwave, 100 min.

Rounding, as discussed previously, is characteristic of network dissolution. As expected for samples in static solution with high SA/V, the trends in morphology show that network dissolution occurred on both the top and bottom of all samples and increased in severity with corrosion time. Because the bottom faces at 100 min appeared to be slightly more rounded than the top faces, it is likely they tended more towards network dissolution than the top faces. This is reasonable considering that the SA/V ratio of the solution between the bottom face of a sample and jar is locally very high.

There were no significant, noticeable differences between the top faces of conventionally- and microwave-heated samples, as evidenced by the apparent morphological similarities. This conclusion supports the similarity observed between some of the FTIR spectra (Figures 66 and 68). The apparent difference in the top face of the 100-min samples (Figure 65) was not confirmed by SEM. Inspection of the bottom faces was not performed to a degree sufficient to draw conclusions about the apparent differences observed by FTIR (Figures 69-72).

SIMS

The concentration profiles from SIMS analysis are given in Figure 57 for a sample corroded using conventional heating at 90°C for 43.5 min and in Figures 75 and 76 for samples corroded for 43.5 min by conventional heating at 92°C and by microwave heating at 90°C, respectively. The FTIR spectra for the top and bottom faces of the three samples are presented in Figures 77 and 78. The ICP solution analysis is given in Table 4.

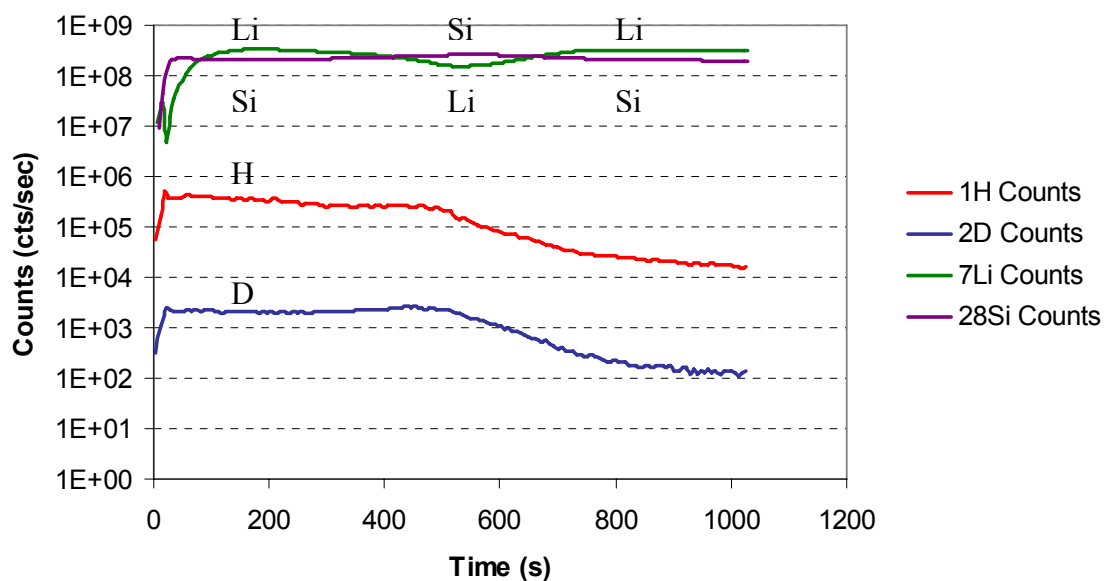


Figure 75: SIMS concentration profile for $\text{Li}_2\text{O}-2\text{SiO}_2$ glass sample corroded in conventionally-heated solution at 92°C .

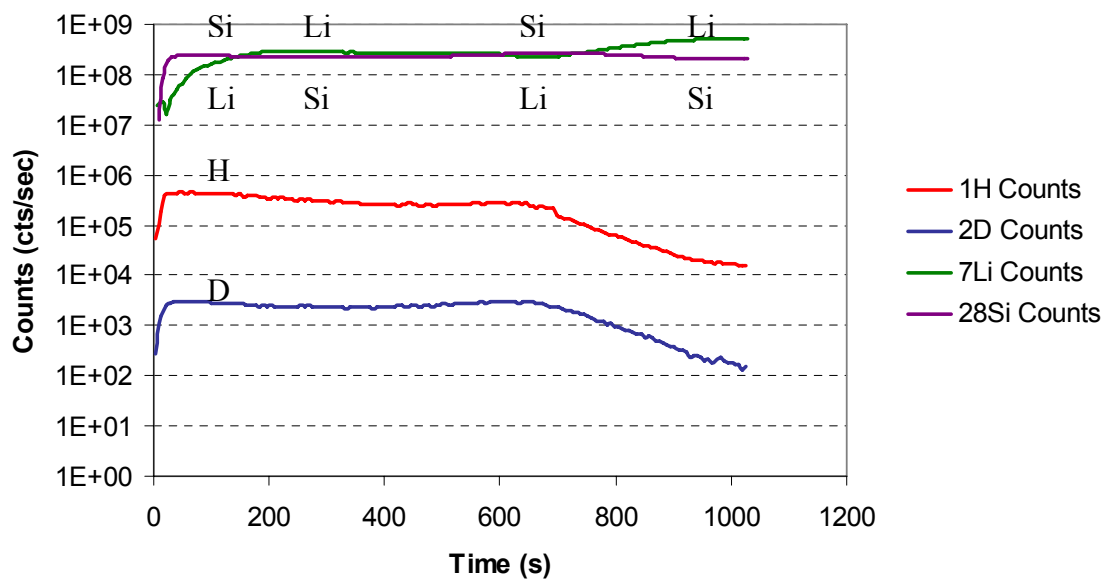


Figure 76: SIMS profile from $\text{Li}_2\text{O}-2\text{SiO}_2$ glass corroded using microwave heating for 43.5 min in a preheated 90°C static solution of D_2O .

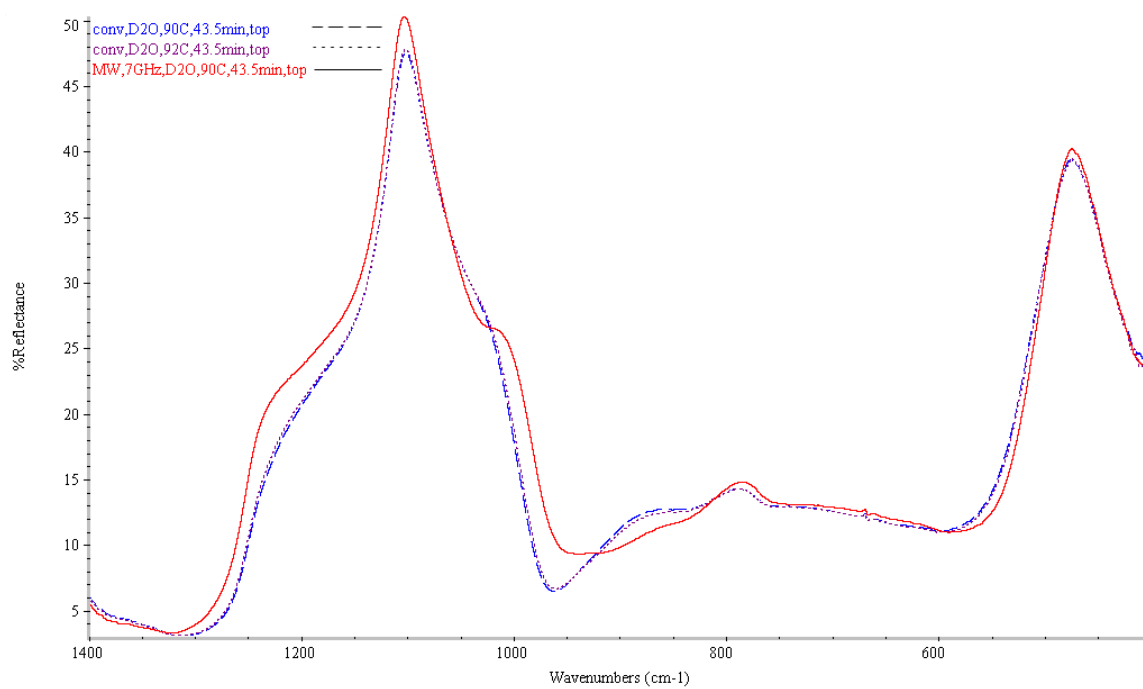


Figure 77: FTIR spectra of top faces of samples corroded in D₂O.

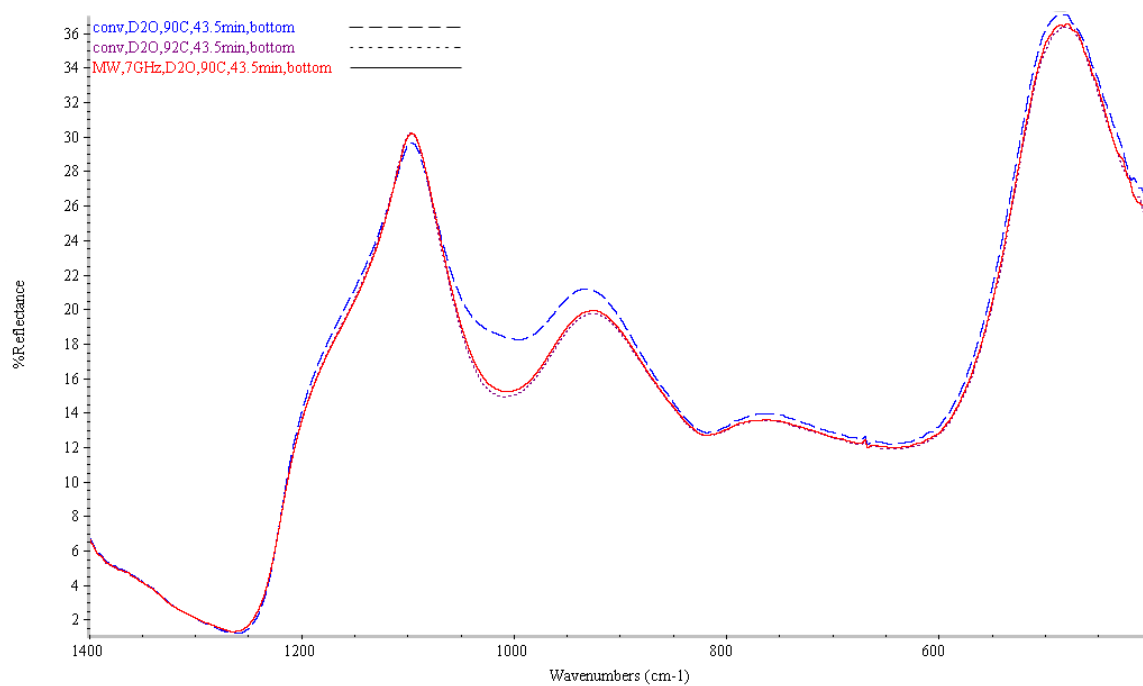


Figure 78: FTIR spectra of bottom faces of samples corroded in D₂O.

Table 4: ICP solution data from D₂O corrosion of SIMS samples.

	[Li] (mol/L)	[Si] (mol/L)	α ([Si]/[Li])
Conventional, 90°C	0.000757	0.000031	0.041
Conventional, 92°C	0.000804	0.000025	0.032
Microwave	0.001077	0.000040	0.037

The two samples corroded conventionally had very similar concentration profiles (Figures 57 and 75). In each plot, the Li concentration starts high, dips, and increases again in the S-shaped curved that is expected for glass corrosion^{*}. The opposite behavior is seen for Si. The SIMS profile for the microwave-heated sample (Figure 76) showed similar behavior but more time elapsed before the Li concentration rose to its full value. Assuming a constant rate of etching, a greater time to reach the full concentration of Li indicates a thicker leached layer.

The FTIR spectra of the top and bottom face of all the samples (Figures 77 and 78) show some slight differences. The top face of the microwave-heated sample appeared to be slightly more corroded, with greater intensity of the primary Si-O-Si bridging peak, more development of that peak's shoulders, and disappearance of the nonbridging oxygen peak (in the presence of Li⁺). The bottom face of the microwave-heated sample has an almost identical spectrum to the conventionally-heated sample at 92°C, while the sample heated at 90°C showed significantly less decoupling between the bridging and nonbridging peak, indicating that it experienced less corrosion. The conclusion is that the microwave-heated sample was more corroded on both the top and bottom face.

This conclusion is supported by the SIMS concentration profile. As noted, the sputtering time to reach the full Li⁺ concentration was greater for the microwave-heated sample. For a glass sample in the beginning stage of corrosion, as expected from a treatment of only 43.5 min at 90°C, a surface with a more-developed FTIR spectrum would have leached to a greater extent and would have a thicker leached layer. From the

^{*} This behavior was attributed to surface roughness, as described previously.

SIMS data, the microwave-heated sample, with a more developed FTIR spectrum, appeared to have a thicker leached layer.

Assuming a constant etch rate with time, this confirms the FTIR spectrum in Figure 77, which showed the top face to be slightly more corroded than the conventional samples. However, it is uncertain that the etch rate was constant with time.

Surface roughness profiles are shown in Figures 58, 79, and 80. All samples showed a region of uniform sputtering and a region of high-roughness and minimal sputtering. The microwave-heated sample was sputtered much deeper than the conventional samples (3μ versus 1.5μ), which may indicate that Li is depleted further into the glass than would be suggested simply on the basis of sputtering time alone.

Therefore, the microwave sample may have a thicker leached layer than concluded on the basis of sputtering time alone, separating it further from the conventional sample. This analysis confirms the validity of FTIR measurement for assessing degree of corrosion and comparing between samples, at least at short times.

The results of ICP solution analysis (Table 4) also show some differences. The sample corroded using microwave heating released more Li and Si than either conventional sample but had a value of α intermediate between the two. Due to the lack of repetitions and slight uncertainty in temperature, it is unclear whether these differences are significant or are the result of experimental error.

Conclusion

After considering solution, FTIR, SEM, and SIMS data, the totality of the information from systematic bulk testing using 7.00 GHz microwave radiation suggests only minor changes in glass corrosion mechanisms, if any, due to exposure to microwave energy. The systematic bulk test was a carefully-controlled time-study that provided a picture of the early stages of static corrosion of $\text{Li}_2\text{O}-2\text{SiO}_2$ glass in a static solution at 90°C . The basic processes, as observed by ICP, pH, FTIR, SEM, and SIMS, were essentially the same in the solutions heated by microwave radiation and those heated conventionally. The differences that were present were small and potentially caused by either experimental error or a true microwave effect. Testing under different circumstances is required to probe further the possibility of a microwave effect.

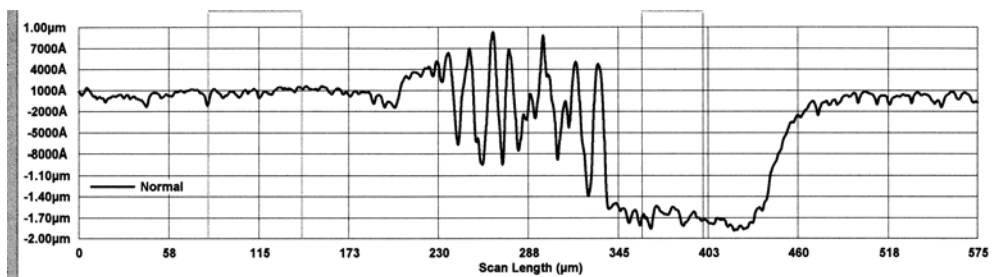


Figure 79: Profile of sputtered region of conventionally-heated sample (92°C) surface.

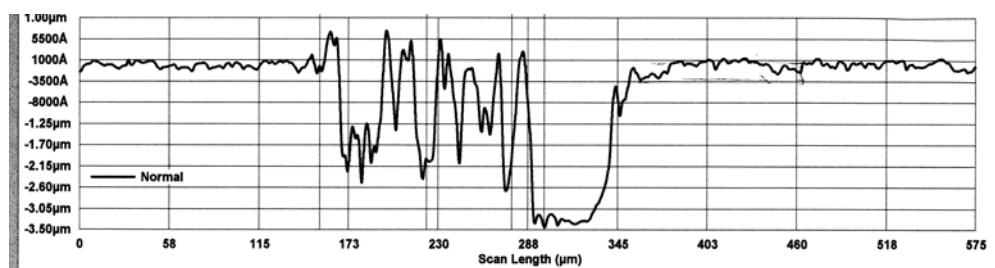


Figure 80: Profile of sputtered region of microwave-heated sample (90°C).

Effect of Frequency

Water may have inhibited 7.00 GHz microwave radiation from reaching the glass-water interface as effectively as possible despite depth of penetration calculations and careful control of the water level. To determine if any increased effect was present at a lower frequency, a MicroCure[®] variable frequency microwave oven at 5.86 GHz was used for testing. Furthermore, a different microwave cavity provided a different distribution of electric field, which may have caused more microwave radiation to reach the glass-water interface.

The FTIR spectra from microwave and conventional samples are given in Figures 81-86. The tops of the samples corroded by microwave heating appeared to be slightly more corroded at both 100 min and 250 min (Figures 81 and 82) and to have no difference at 1000 min (Figure 83). The bottoms of the samples heated by microwave energy appeared to be substantially more corroded for each time (Figures 84-86). The differences in the bottom faces are consistent with what was seen using 7.00 GHz microwave radiation (Figures 69-72), only more pronounced. The differences in the top

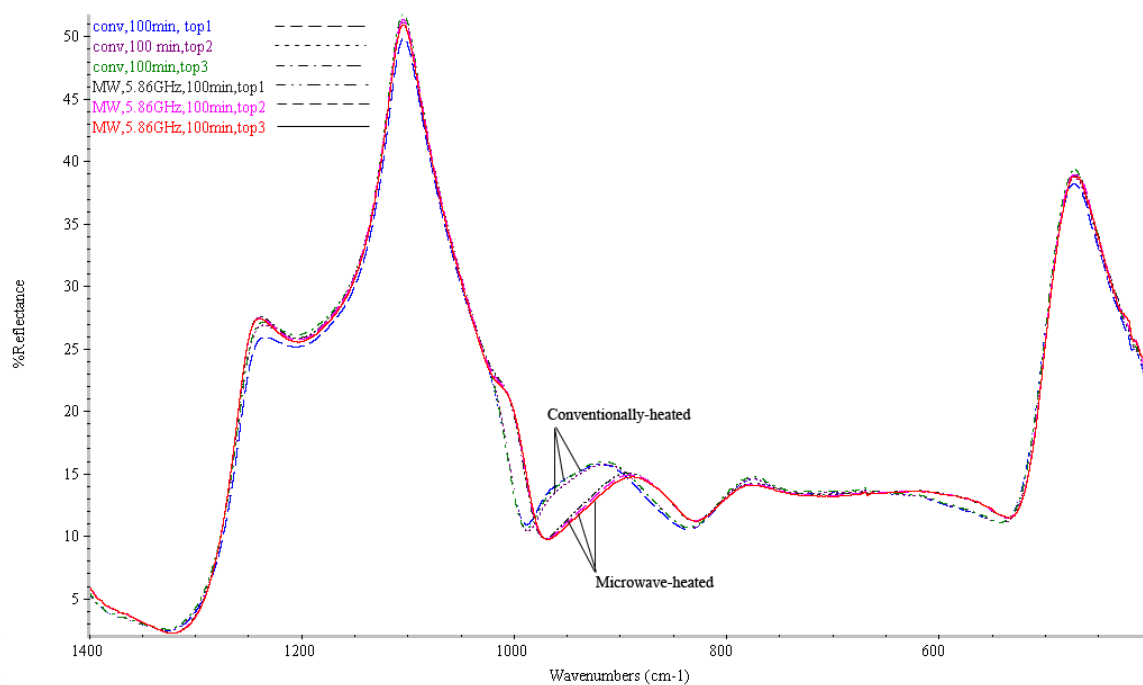


Figure 81: FTIR spectra of the top faces of samples corroded for 100 min at 90°C. Microwave heating performed at 5.86 GHz.

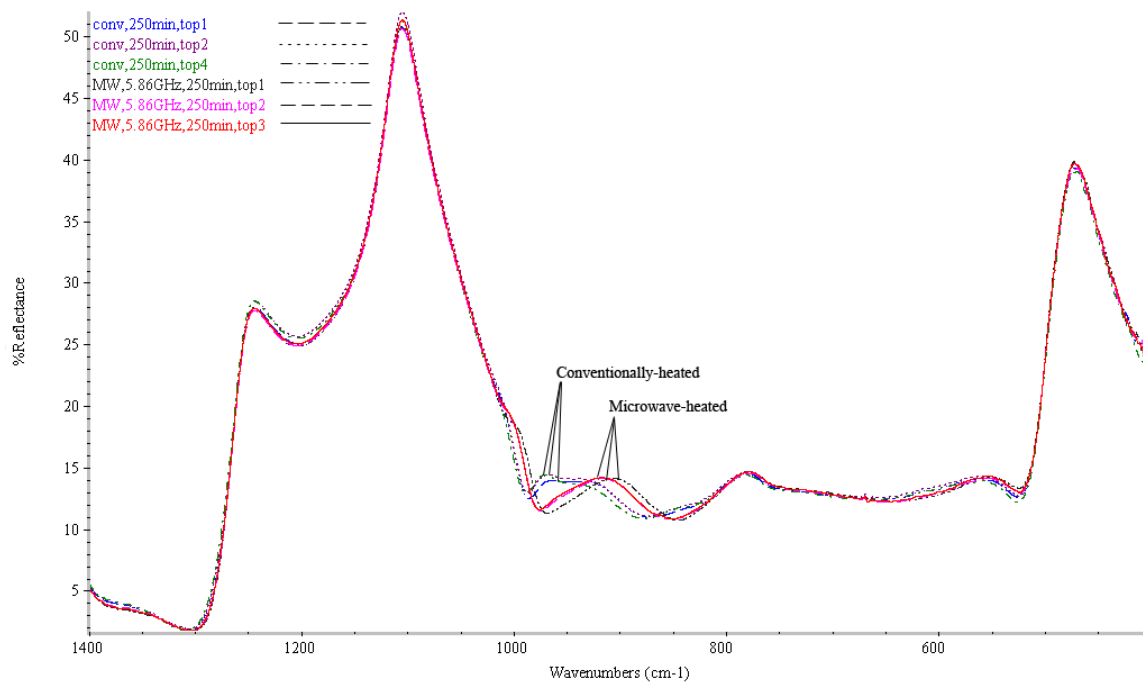


Figure 82: FTIR spectra of the top faces of samples corroded for 250 min at 90°C. Microwave heating performed at 5.86 GHz.

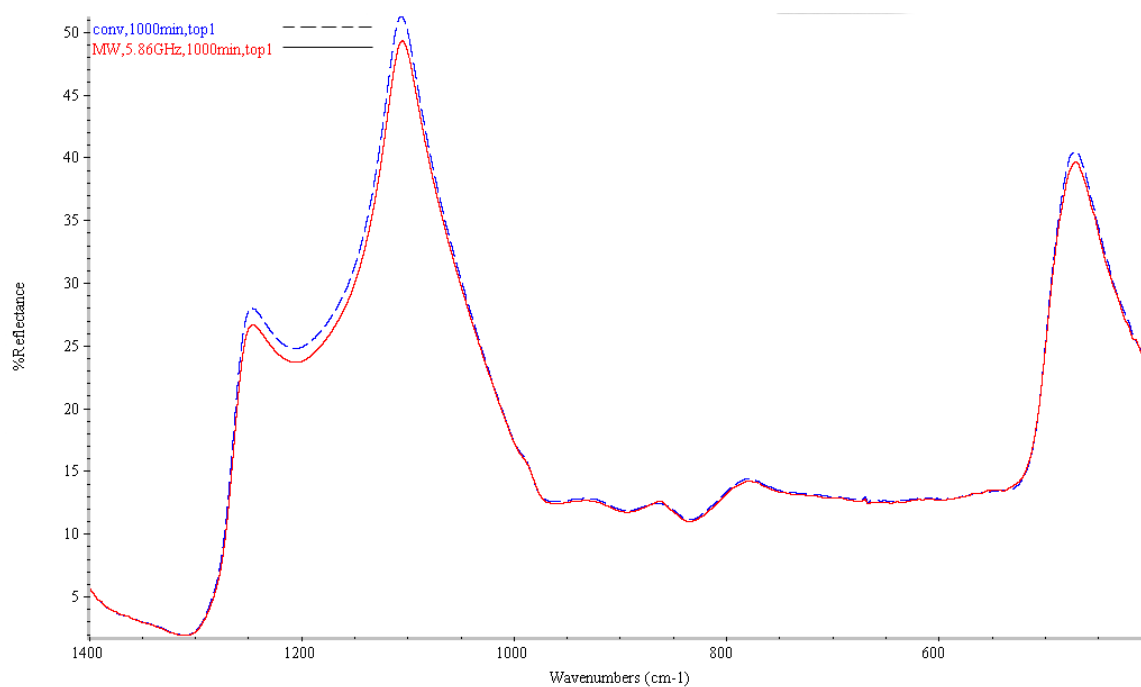


Figure 83: FTIR spectra of the top faces of samples corroded for 1000 min at 90°C. Microwave heating performed at 5.86 GHz.

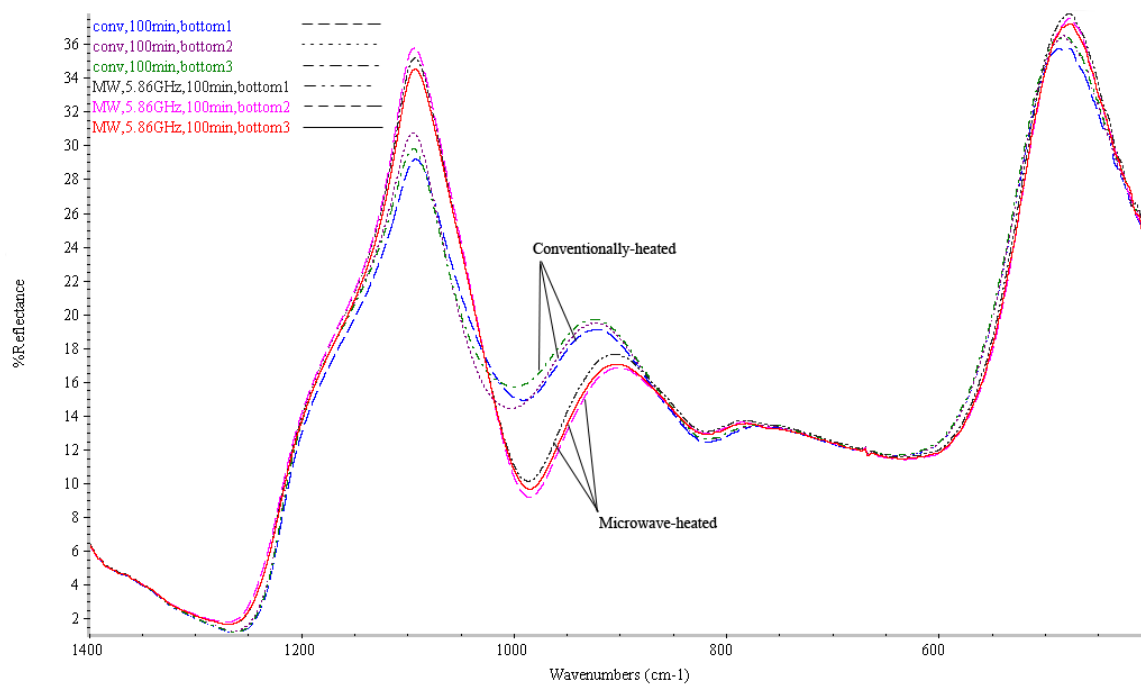


Figure 84: FTIR spectra of the bottom faces of samples corroded for 100 min at 90°C. Microwave heating performed at 5.86 GHz.

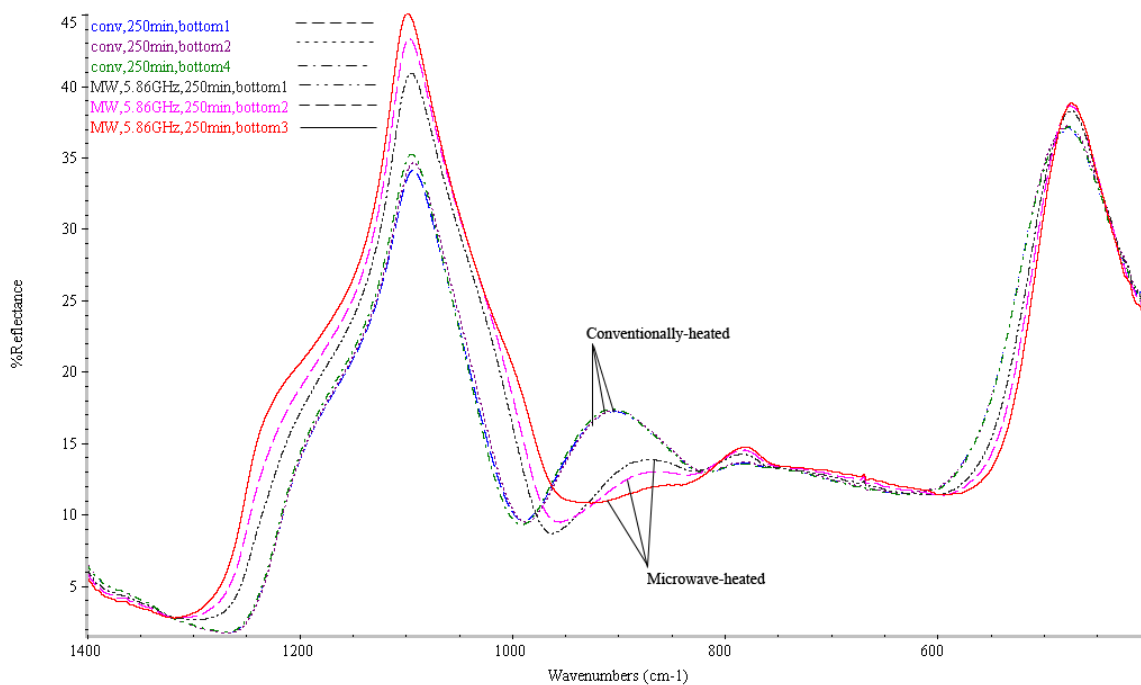


Figure 85: FTIR spectra of the bottom faces of samples corroded for 250 min at 90°C. Microwave heating performed at 5.86 GHz.

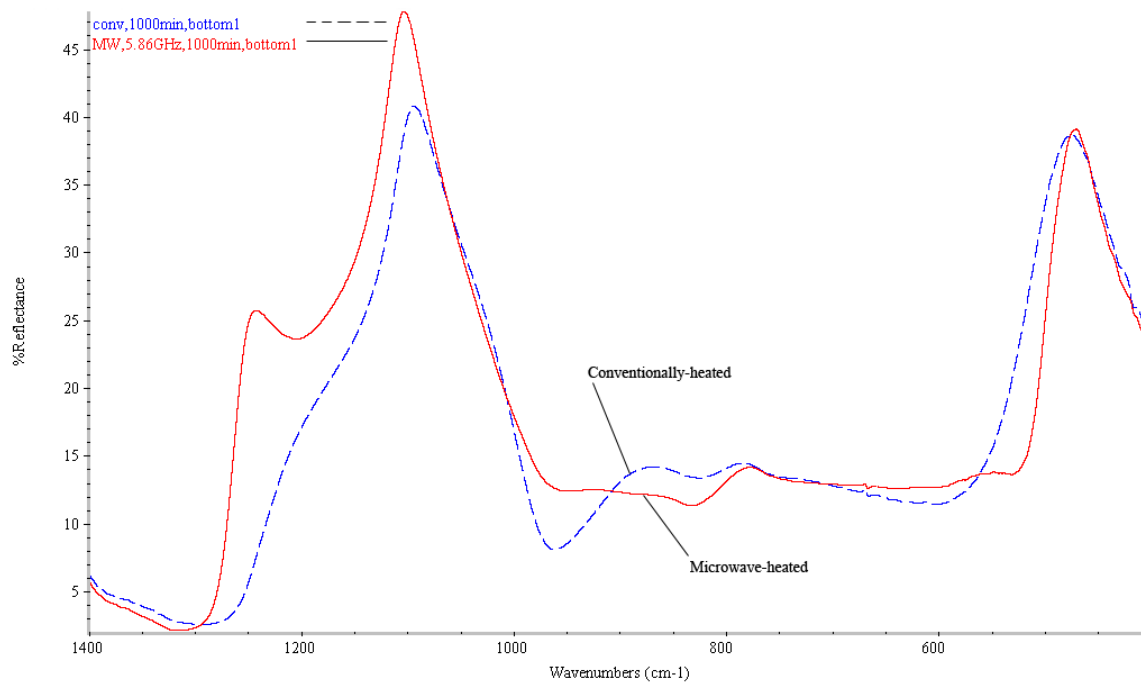


Figure 86: FTIR spectra of the bottom faces of samples corroded for 1000 min at 90°C. Microwave heating performed at 5.86 GHz.

faces were new, as the only previous significant difference in the top-face spectra was small and occurred for 100 min only (Figure 65). The differences in the spectra imply enhanced corrosion of those which were microwave-heated.

Analysis of the resulting solutions is given in Figures 87-89. Since three trials each were performed for both 100 min and 250 min and only 1 trial was performed for 1000 min, this fact is reflected by the error bars on 100- and 250-min data points and no error bars for the 1000-min points.

Much more Li^+ and Si were released by the samples heated using microwave energy (Figures 87 and 88, respectively). The samples heated by microwave energy released an average of 41% more Si and 25% more Li^+ into solution than those heated conventionally. Where multiple trials were performed (100 and 250 min), these differences were all significant at >98% confidence by ANOVA. Furthermore, the difference appears very large when 1 trial was performed (1000 min).

The α parameter for microwave and conventional heating were close together, with α being larger in all cases for microwave heating. The values of α were not significantly different at 100 min and were significant at a confidence of only >94% at 250 min.

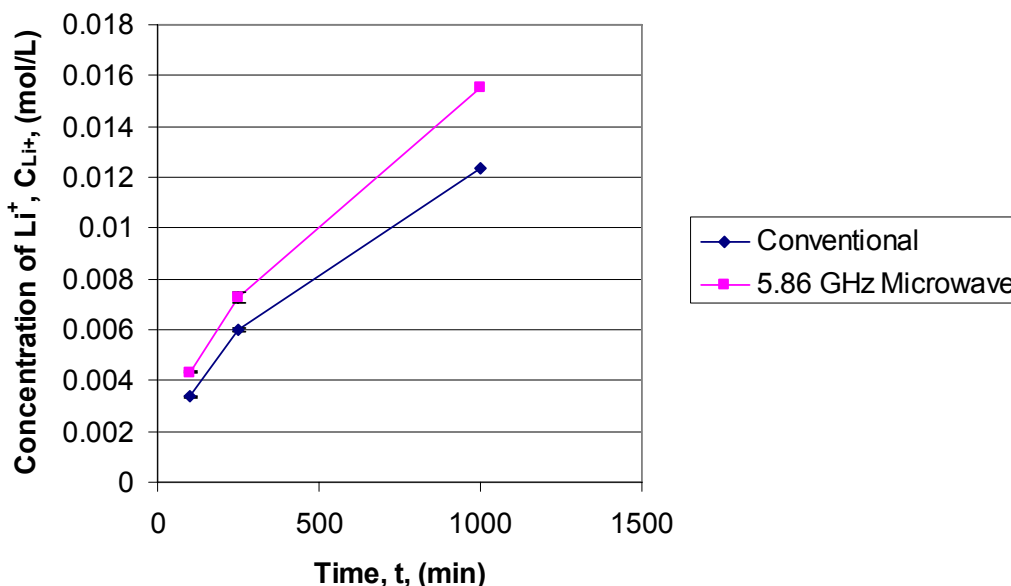


Figure 87: Li^+ released into solution during low-frequency (5.86 GHz) bulk testing.

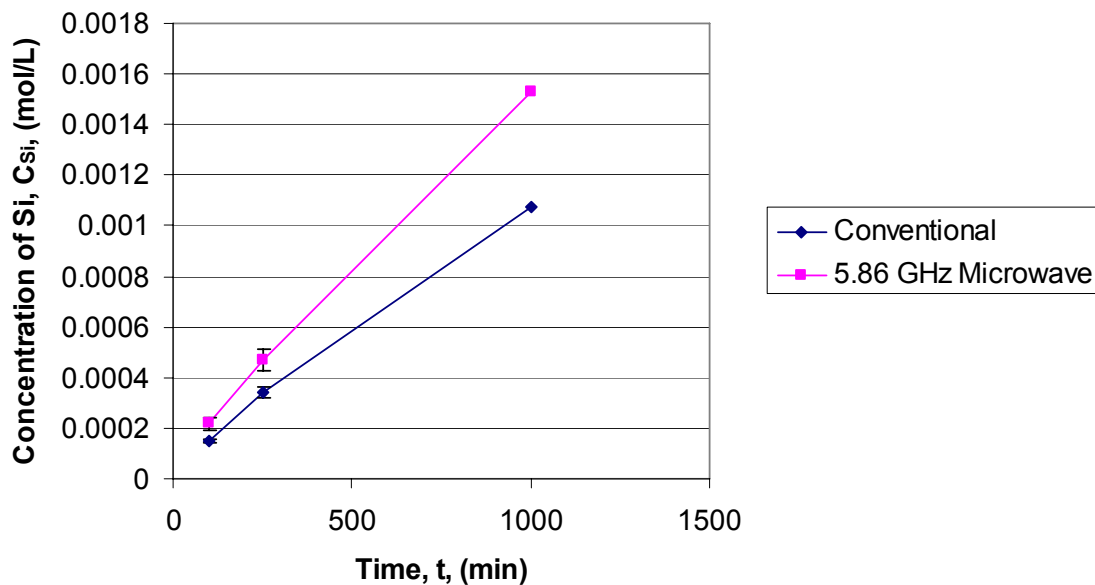


Figure 88: Si released into solution during low-frequency (5.86 GHz) bulk testing.

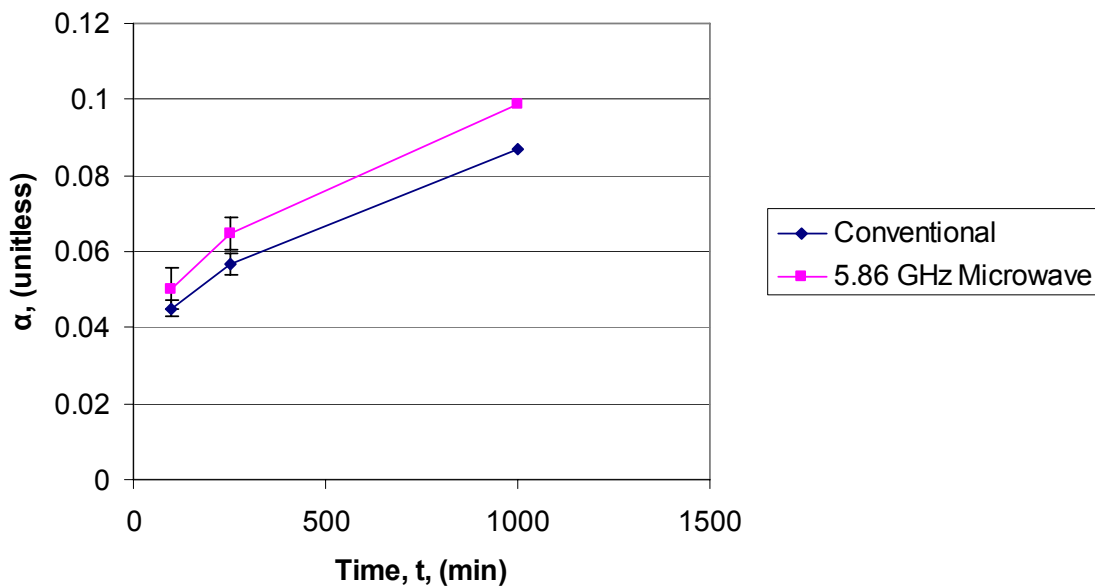


Figure 89: Kinetic parameter α calculated from solution data resulting from low-frequency (5.86 GHz) bulk testing.

Microwave heating caused greater release of both Li^+ and Si, accompanied by a larger value of α . The greater value of α for the microwave-heated samples is indicative of more network dissolution and so it caused the balance to shift slightly towards network dissolution as compared to conventional heating. The greater release of Li^+ and Si by the samples heated using microwaves was also reflected in the FTIR data. The region between 800 and 1000 cm^{-1} consistently showed the microwave-heated samples to be more corroded than the conventionally-heated samples.

The differences between microwave and conventional heating seen using 5.86 GHz were much more significant than those using 7.00 GHz. These differences were either due to a bona fide microwave effect or slight differences in calibration or experimental setup. If this difference in calibration were the case, it is possible that the thermocouple was not as close to the temperature probe as it was in the 7.00 GHz case.

However, as will be discussed in the next section, the calibration in this case was slightly more conservative than previous calibrations. If anything, the actual temperature of the corrosion solution in the conventional oven was slightly higher than in the microwave oven. Therefore, it is unlikely that calibration error caused the apparent increase in corrosion in the microwave-heated solution.

Calibration

In order to adequately study the effect of microwave heating versus conventional heating, it was necessary to ensure that the temperature of the baths were as close together as possible. In this manner, once effects due to slight differences in temperature had been removed, the microwave effects (if any) would be apparent.

The approach was to adjust the calibration screw of the thermocouple monitor to make the digital temperature reading match that given by the optical probe of the microwave oven. The method for doing so is described in the previous chapter.

Figures 90 and 91 are representative calibration curves. Figure 90 shows the entire curve from start to finish and Figure 91 shows the portion of that curve after the final adjustment had been made to the thermocouple. Other calibration curves and the specifications of the data with which they correspond are given in Appendix D.

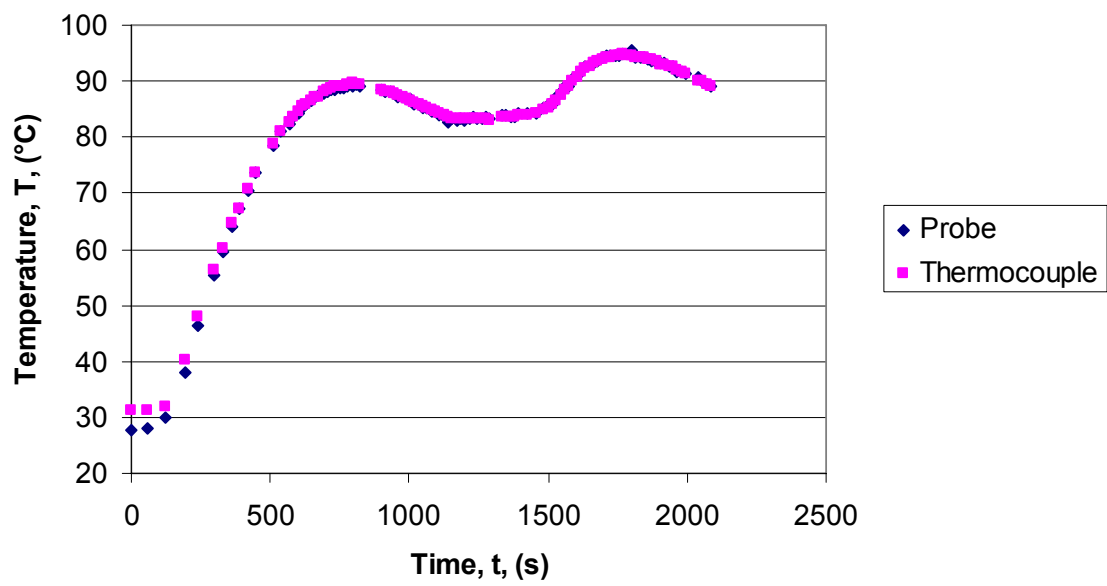


Figure 90: Representative thermocouple calibration curve.

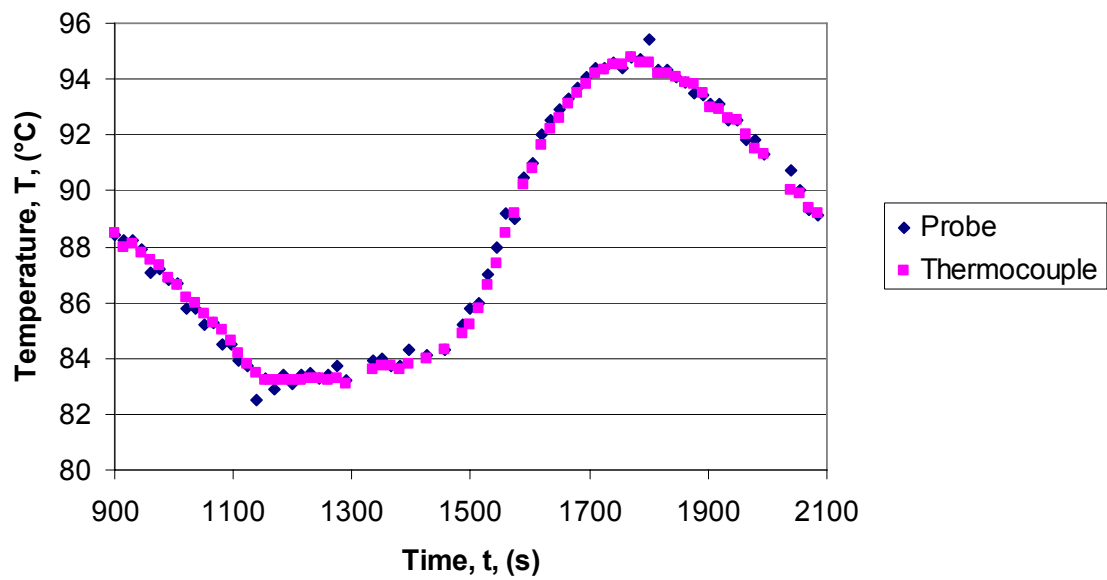


Figure 91: Calibration curve after final thermocouple adjustment.

As the temperature was increased up to 90°C, the thermocouple reading typically lagged several seconds behind the optical probe. The heat was shut off when the temperature reading reached approximately 90° and the temperature readings peaked: the readings became closer together, met one another, and then the optical probe's reading began to decrease followed by the thermocouple's reading. Ideally, when the temperature was increasing, the thermocouple's reading would be a few tenths of 1°C less than the optical probe's reading, when the temperature was decreasing it would be a few tenths greater than the probe's reading, and when the temperature reached a maximum or a minimum value, the reading would be the same. When this was the case, the average difference between the two readings would be near 0, and the absolute value of the difference when the temperature was increasing or decreasing would be slightly more than the average.

In Figure 91, after the thermocouple readout had been fully adjusted, the average difference (optical probe's reading minus thermocouple's reading) was 0.08°C, the difference when the temperature was ascending was 0.18°C, and the difference when descending was -0.05°C.

Several different calibrations were required to complete the experiments in this chapter. For all of the calibrations, the maximum average difference was 0.21°C, the maximum difference when ascending was 0.60°, and the minimum difference when descending was -0.15°C. Appendix D shows all of the calibration curves in question and details which calibration corresponds with which data in this chapter.

Calibration made a difference in the apparent relation of conventional heating to microwave heating and was a critical element of this work. Before calibration, both the microwave oven and the conventional oven were set to hold the corrosion bath at "90°C." However, the actual temperature of the solution in the microwave oven was 3-4°C cooler than in the conventional oven. After the thermocouple's nominal 90°C reading was adjusted to match the optical probe's nominal reading, the temperatures were much closer together.

Figure 92 gives the FTIR spectra of two samples after a preliminary test. This test was performed without the benefit of thermocouple calibration and the difference between the two spectra is primarily associated with the 3-4°C difference in temperature.

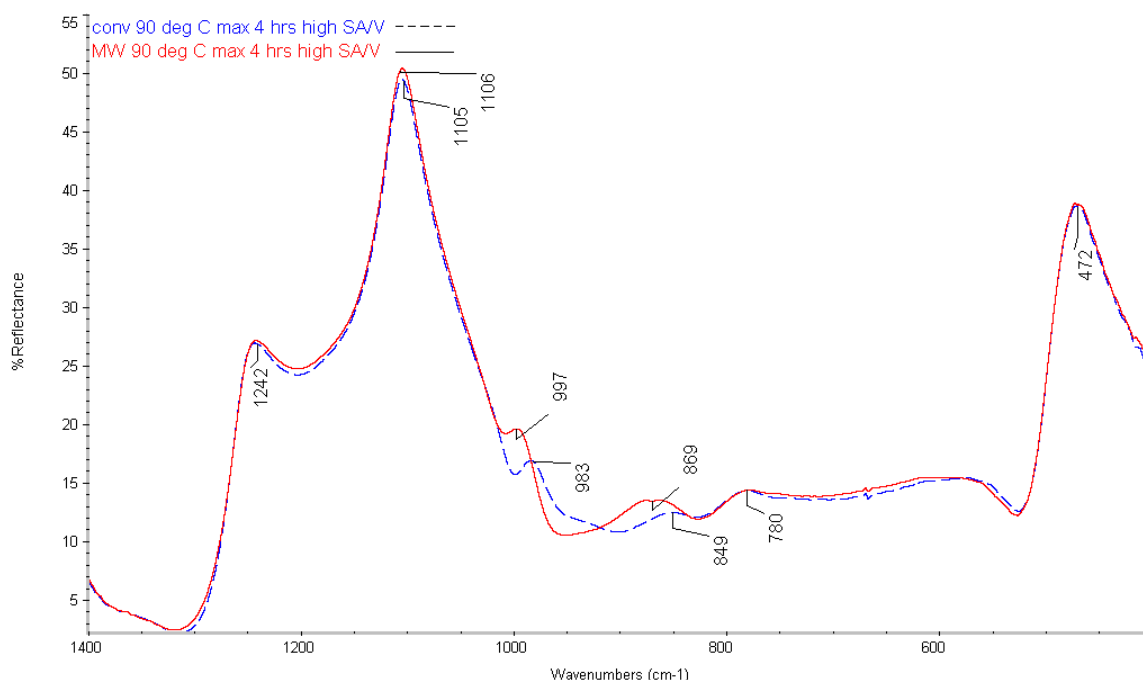


Figure 92: Sample FTIR spectra resulting from a preliminary test before thermocouple calibration.

It is not likely that microwaves affected these spectra more than in Figures 66-68 because the microwave frequency used in this test was 11.00 GHz, which has a very small depth of penetration, and so it is unlikely that a microwave field as strong as that resulting from 7.00 GHz testing reached the sample. The fact that the microwave sample's spectrum lagged behind the conventional sample's spectrum indicates that the conventionally heated solution was just slightly warmer and therefore caused slightly more corrosion to occur.

These spectra may be compared to Figures 66-68. In these figures, the spectra of the top faces are much closer together than in Figure 92. The closeness occurred even though 7.00 GHz microwave radiation was used and the thickness of the water layer on top of the sample was less, thus allowing microwave radiation to better reach the glass-water interface.

Two conclusions may be drawn from these data. First, the calibration was effective in rendering the actual temperatures measured by the thermocouple and optical probe very similar to one another. Second, the differences that do appear in the testing are likely due to the effects of microwave heating or other experimental error (i.e. not related to disparity in measurement of absolute temperature).

Commercial Soda-Lime Experiments

Energy dispersive spectrometry (EDS) was used to determine the approximate composition of the commercial soda-lime glass bowls described in the previous chapter. One bowl was placed inside a plastic trash bag and hit with a hammer until it broke. The fracture surfaces of 2 small shards were examined. The spectrometer was not capable of detecting B and was not capable of detecting components present at less than 0.1-0.5 at% [98]. Since EDS is a semi-quantitative technique, the measurements had a large degree of error and were used only as a coarse estimate of the composition.

On each of the 2 samples, 3 areas were measured. After averaging the 6 measurements of at% for Na, Ca, Al, and Si and adjusting for stoichiometry, the average composition was found to be approximately 0.08 Na₂O - 0.10 CaO - 0.01 Al₂O₃ - 0.81 SiO₂. Tables 5 and 6 show the data and the calculations.

Table 5: EDS data for commercial soda-lime glass fracture surface.

Measurement	Element (at%)					
	O	Na	Al	Si	Ca	Total
1	53.484	6.336	1.018	34.822	4.340	100.0
2	53.190	6.685	1.015	34.821	4.289	100.0
3	53.300	6.544	0.977	34.911	4.269	100.0
4	56.512	6.995	0.992	31.899	3.602	100.0
5	56.544	7.004	0.930	31.833	3.679	100.0
6	55.952	6.686	0.963	32.543	3.857	100.0
Average at%	0.548	0.067	0.010	0.335	0.040	1.000

Table 6: Calculated stoichiometry for commercial soda-lime glass.

Element	Na	Ca	Al	Si
Element fraction	0.067	0.040	0.010	0.335
Compound	Na ₂ O	CaO	Al ₂ O ₃	SiO ₂
Compound Fraction	0.034	0.040	0.005	0.335
Normalization to SiO ₂	0.10	0.12	0.01	1.00
Normalization to 1	0.08	0.10	0.01	0.81

For the corrosion experiments, two trials were performed using 30 mL of deionized water. The raw solution data is presented in Table 7 and a summary of the data is presented in Table 8. Typical FTIR measurements yielded a corroded surface which appeared like the bulk surface, showing no significant differences, and are not shown.

The data were very scattered, with some similarities in concentration occurring between the microwave and conventional samples resulting from corresponding trials. These similarities suggest variations from trial to trial may have substantially influenced the solution data. No substantial trends were discovered when considering each trial individually.

Nevertheless, the raw data was averaged and shown in Table 8. When the concentration of a specific species was less than the detectable limit, it was assumed to be 0 for the purposes of calculating a mean. When comparing the means, there were no real differences between microwave-heated and conventionally-heated solutions apparent for Al, B, or Ca. However, the microwave-heated bath contained much more Na and Si. The molar ratio of released Na to Si was 1.51 in the conventionally-heated solution and 1.10 in the microwave-heated solution. Possible explanations for the increased corrosion rate in the microwave-heated solution versus the conventionally-heated solution included a real microwave effect (which accelerated corrosion and slightly altered the mechanism) or experimental error.

This error could have been introduced by the large amount of condensation occurring during microwave heating. This condensation was likely caused by water vapor from the microwave-heated water meeting the relatively cool plastic wrap or glass not covered by water. These were cool because they were not targeted by microwaves and not heated by convection, as in the conventional oven.

Contaminants may have been introduced by the plastic wrap or by leaching on the sides of the glass container which occurred when vapor condensed. To test each of these possibilities, additional experiments were performed.

First, a strip of plastic wrap was cut and immersed in 18 mL of deionized water in a PFA jar. This solution was heated to 90°C and held for several hours. A blank sample, with 18 mL of deionized water by itself, was also heated at the same time. The results in Table 9 indicate that some traces of Ca, Na, and Si may have been introduced to a

solution when in contact with the plastic wrap. For the microwave-heated samples, the large amount of condensation on the plastic wrap may have been sufficient to artificially increase the concentration of Ca, Na, and Si shown in Table 8.

Table 7: Raw solution data from 30-mL bowl test.

Conventional	Al (ppm)	B (ppm)	Ca (ppm)	Na (ppm)	Si (ppm)
Trial 1	0.0075	0.0108	0.1218	2.2562	2.029
Trial 2	<0.001	0.0201	0.1019	1.6059	1.0873
Microwave					
Trial 1	0.0264	0.0174	0.423	5.0808	5.8945
Trial 2	0.0048	0.0067	0.3217	3.3816	3.5395

Table 8: Solution analysis for 30-mL bowl test.

		Al (ppm)	B (ppm)	Ca (ppm)	Na (ppm)	Si (ppm)
Conventional	mean	0.004	0.015	0.112	1.931	1.558
	standard deviation	0.005	0.007	0.014	0.460	0.666
Microwave	mean	0.016	0.012	0.372	4.231	4.717
	standard deviation	0.015	0.008	0.072	1.202	1.665

Table 9: Solution data for plastic wrap test.

	Al (ppm)	B (ppm)	Ca (ppm)	Na (ppm)	Si (ppm)
with plastic	0.000	0.010	0.094	0.230	0.012
without plastic	0.000	0.008	0.000	0.045	0.000

The concentrations of Ca, Na, and Si were 3.33, 2.19, and 3.03 times higher in Table 8, respectively, in the microwave-heated solution than in the conventionally-heated solution. Since they increased by similar ratios, it is possible the increase was due to release by the plastic wrap.

To eliminate the possibility that condensation on the sides of the bowl may have drawn out migrants from areas which were not supposed to be exposed to solution, the bowl was filled nearly to capacity with 250 mL of deionized water. This ensured that very little surface area inside the bowl was unexposed to the bulk solution and therefore was not susceptible to condensation. Three trials were performed and the results are shown in Tables 10 and 11. The concentrations of migrants are smaller in this test due to a lower SA/V. Again, there were similarities between microwave and conventional samples in corresponding trials.

Table 10: Raw solution data from 250-mL bowl test.

Conventional	Al (ppm)	B (ppm)	Ca (ppm)	Na (ppm)	Si (ppm)
Trial 1	<0.001	0.0067	<0.002	0.5927	0.0599
Trial 2	<0.001	0.0092	0.0214	0.3876	0.3641
Trial 3	<0.001	0.0113	0.0031	0.3668	0.1488
Microwave					
Trial 1	<0.001	0.0105	<0.002	0.4100	0.1477
Trial 2	<0.001	0.0072	0.0264	0.4275	0.4268
Trial 3	<0.001	0.0071	0.0082	0.2889	0.3079

Table 11: Solution analysis for 250-mL bowl test.

		Al (ppm)	B (ppm)	Ca (ppm)	Na (ppm)	Si (ppm)
Conventional	mean	0.000	0.009	0.008	0.449	0.191
	standard deviation	0.000	0.002	0.012	0.125	0.156
Microwave	mean	0.000	0.008	0.012	0.375	0.294
	standard deviation	0.000	0.002	0.014	0.075	0.140

Using the mean values, one key result was that the concentrations of Na and Si were much closer together. The microwave-heated solution, instead of having approximately 2-3 times higher concentrations of Ca, Na, and Si than the conventionally-heated solution actually had *less* Na in solution and only approximately 1.5 times more Ca and Si.

The molar ratio of Na to Si was 3.39 for the microwave-heated solution and 2.87 for the conventionally heated solution. Both of these ratios, much higher than in the 30-mL test, actually represent the opposite behavior as seen previously. The conventionally-heated solution had a higher Na to Si ratio in the 30-mL test.

These tests represent a quick look at the corrosion of consumer soda-lime glass in a representative environment. There was much error in the measurements, as shown by the standard deviation values in Tables 8 and 11, and so caution should be exercised in interpreting too much from the data. It is demonstrated by the 250-mL test that the differences between microwave and conventional heating are not as great as suggested by the 30-mL test. Any remaining differences are not clearly statistically significant and may be the result of a contribution from the plastic wrap. Therefore, it is unclear if the small differences are because microwaves do indeed have some effect. Nevertheless, there are differences between microwave-heated and conventionally-heated samples. The source of the differences is important and may not be due to changes in fundamental corrosion mechanisms, but differences do indeed exist.

Chapter V: Summary

The hypothesis was that microwaves cause accelerated aqueous corrosion of glass by enhancing one or more of the responsible mechanisms. The objective of this work was to test the hypothesis by performing corrosion studies on glass using conventional heating as well as heating by microwaves. The primary motivation was to investigate possible enhanced corrosion of glass containers for food and beverages when exposed to microwave energy.

This work compared the aqueous corrosion of $\text{Li}_2\text{O}-2\text{SiO}_2$ glass and a commercial soda-lime glass caused by both microwave and conventional heating of static solutions. Methods of characterization included those analyzing the solution (ICP and pH) and those analyzing the corroded surface of the glass (FTIR, SEM, and SIMS). The bulk of the evidence generated did not clearly support the hypothesis by indicating a substantial difference between the two types of heating, but there is some evidence that is ambiguous and inconclusive and deserves future scientific study.

In most instances, microwave heating caused the corrosion experienced by $\text{Li}_2\text{O}-2\text{SiO}_2$ glass to match that experienced due to conventional heating. Experiments using 7.00 GHz microwave radiation versus conventional heating caused samples to develop surfaces with similar microstructures and FTIR reflectance spectra. Similar amounts and types of corrosion products were also released into solution in both cases.

Chapter II reviewed relevant mechanisms of glass corrosion. The data collected from experiments for both conventional and microwave heating was consistent with preferential leaching of Li^+ from the $\text{Li}_2\text{O}-2\text{SiO}_2$ glass. Network dissolution increased in relative prominence with time, as expected for a static solution. This behavior conformed to the behavior reported in the literature for conventional heating.

From this data, dramatic differences in glass corrosion mechanisms due to microwaves cannot be supported, at least for the narrow range of glasses and conditions studied. The differences that appeared in the data were mostly small and suggested only small alterations in the mechanisms, if these differences were in fact due to microwaves. Through the lack of major differences in the data as a whole, microwaves appeared to

have no clear, dramatic effects on the diffusion of H_2O or H_3O^+ through the leached layer or on the reactivity of H_2O or OH^- with silica under these conditions.

From a scientific perspective with an interest in fundamental mechanisms, there are a number of interesting questions to be resolved. Some of the differences observed between the two methods of heating make an emphatic statement against a microwave effect impossible for the conditions tested. These differences are intriguing and deserve a closer look.

Perhaps the most compelling piece of data is the fact that obvious differences were present in the tests using 5.86 GHz microwave radiation. These differences were the largest seen in any test and were present despite a more conservative calibration which would have favored greater release from the conventionally-heated samples. Of course, experimental error may have been to blame, but lower frequency and different distribution of the electric field may have also played the major role in separating the two sets of data. Similarly, differences on the bottom faces of samples, though possibly due to thermal hotspots, suggest that increasing exposure of the face to microwave radiation exaggerates any microwave effects that are present. Both of these cases suggest the possibility that major differences may be present at an even lower frequency such as 2.45 GHz, the frequency used for consumer microwave ovens. Taken together they lend credence to one another and suggest that future work, especially at 2.45 GHz, may be worthwhile.

Another difference was the lack of similarity at short and long times during testing at 7.00 GHz. Differences between the two, though possibly purely due to experimental setup or error, suggest there may be some minor alterations in mechanisms.

Also, the experiments with commercial soda-lime glass show that large differences may exist between conventionally-heated and microwave-heated systems under the same circumstances, whether they are brought on by the fundamental mechanisms of glass corrosion or by microwave-induced migration over a larger surface. This larger surface, as explained previously, was caused by increased condensation due to microwave heating. The condensation likely formed on the plastic wrap and portions of the glass bowl not covered with water because they remained cool and provided a surface for the much warmer water vapor resulting from locally heated water.

This phenomenon in itself may not represent a change in fundamental glass corrosion processes, but it is nonetheless a mechanism caused by microwave heating for releasing migrants. Currently, this effect is not taken into account by migration testing, because conventional heating is substituted for microwave heating in the existing standards [69]. Therefore, this result is significant as it reveals a source of microwave-enhanced migration and suggests that future study will be worthwhile; the differences were demonstrated here but not fully investigated.

Opportunities for future work abound. First are the areas mentioned above: the effect of lower frequencies, different electric field configurations due to cavity geometry, water layer thickness, and experimental setup. Also, the more detailed testing of commercial glass used for actual food or beverage containers to achieve more consistent and complete results. There are also other areas to investigate. As discussed in Chapter II, the pH of a corrosion solution has a large effect on the corrosion mechanisms and was not investigated in this work. To simulate high pH (and/or long times) glass grains or powder may be tested. To test at low pH, acetic acid could be used to simulate actual food or beverage chemistry.

The problem of ensuring similarity between microwave and conventional heating test setup is significant. Fundamentally, microwave heating is not the same as conventional heating. There are different mechanisms involved, different heating rates, and different temperature profiles. This issue has always been a part of microwave research and will likely always remain a concern.

There are certainly significant differences in glass corrosion between microwave and conventional heating when the test setup is not considered or not considered with adequate detail. These may result from hotspots in the microwave oven, different heating rates, different testing times, or different maximum temperatures. The disparity in these thermal parameters is already recognized by FDA regulations [69] and in this work it was attempted to keep them from occurring. Other, less tangible, differences like fundamental corrosion mechanisms or microwave-induced corrosion of incidentally-exposed areas (as shown in bowl testing) have historically not been given significant consideration because a side-by-side comparison is difficult to achieve. This type of comparison has been the primary technical challenge of this work.

The test setups here were designed to be as similar as possible between the microwave and conventional ovens and to mitigate external influences. Furthermore, accurate temperature measurement was achieved by close calibration. This similarity in setup and measurement is itself an accomplishment and made possible the type of detailed comparisons given. However, the inherent differences between microwave and conventional heating still existed on a small level during testing and will always somewhat hinder the direct comparison of microwave and conventional processes. This difficulty is part of the reason that the inconclusive pieces of evidence remain inconclusive: it is not possible to say definitively whether they were caused either by experimental setup or by the influence of microwaves.

Prior to this study, the conventional wisdom (based on studies of polymers) was that microwave heating does not significantly impact migration from glass. Good reason existed to believe that microwaves may accelerate or alter glass corrosion mechanisms. This work served as a systematic investigation to test that hypothesis with an emphasis on isolating and studying fundamental corrosion mechanisms with minimal interference from experimental setup. The results showed no dramatic differences immediately apparent at a high frequency (7 GHz), but suggest that differences may be present at a lower frequency (2.45 GHz).

Here is a list of the major accomplishments of this work:

- Discovery of the transient nature of the FTIR peak in the 800-1000 cm^{-1} region (attributed to Si-OH stretching). No literature exists which suggests the location of this peak changes radically or that the location may be a means of characterizing glass corrosion or water content.
- Calibration of a standard, type T thermocouple to the nominal measurement of an optical temperature sensor. This allowed fine temperature measurements and direct comparison of a conventionally-heated environment to a microwave-heated environment with minimal error. Differences in temperature measurement can easily obscure the results of microwave-conventional studies.
- Experimental setup that closely related the microwave and conventional heating processes and minimized external influences.

- Fundamental, systematic investigation of the corrosion behavior of $\text{Li}_2\text{O}-2\text{SiO}_2$ glass under microwave heating and equivalent conventional heating conditions. The study rigorously evaluated time and treated frequency to a limited extent. No literature exists in which such a careful study of glass corrosion during microwave heating is performed.
- Examination of the microwave effects on a real glass (commercial soda-lime) container, simulating actual use conditions.

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Appendix A: Solutions to Diffusion Equations

Solution to the Boltzmann's transformation of the Doremus interdiffusion equation

The following fills in the details of the mathematical argument given by Doremus.

The interdiffusion coefficient is:

$$\tilde{D} = \frac{D_H D_{Na}}{C_H D_H + (1 - C_H) D_{Na}} = \frac{1}{1 + b C_H} D_H \quad (A1)$$

where $b = \frac{D_H}{D_{Na}} - 1$ and the intrinsic diffusivities D_H and D_{Na} are assumed constant.

Adjusting the interdiffusion coefficient empirically, Equation 7 is derived:

$$\tilde{D}_T = \tilde{D}(1 + \alpha C_H) = \left(\frac{1 + \alpha C_H}{1 + b C_H} \right) D_H.$$

Starting with Fick's 2nd Law using the adjusted interdiffusion coefficient $\tilde{D}_T$ and calculating for the concentration of the hydrogen diffusant, C_H :

$$\frac{\partial C_H}{\partial t} = \frac{\partial}{\partial x} \left[\tilde{D}_T \frac{\partial C_H}{\partial x} \right] = \left(\frac{\partial \tilde{D}_T}{\partial x} \right) \left(\frac{\partial C_H}{\partial x} \right) + \tilde{D}_T \frac{\partial}{\partial x} \left(\frac{\partial C_H}{\partial x} \right) \quad (A2)$$

Now, using Boltzmann's transformation to convert the partial differential equation into a nonlinear ordinary differential equation. The transformation variable is $y = \frac{x}{\sqrt{4 D_H t}}$.

Now, Fick's 2nd Law can be transformed:

$$\begin{aligned} \bullet \frac{\partial y}{\partial t} &= \frac{\partial}{\partial t} \left(\frac{x}{\sqrt{4 D_H t}} t^{-1/2} \right) = -\frac{1}{2} \frac{x}{\sqrt{4 D_H t}} t^{-3/2} \\ \bullet \frac{\partial y}{\partial x} &= \frac{1}{\sqrt{4 D_H t}} \\ \bullet \frac{\partial C_H}{\partial t} &= \frac{\partial C_H}{\partial y} \frac{\partial y}{\partial t} = -\frac{1}{2} \frac{x}{\sqrt{4 D_H t}} t^{-3/2} \left(\frac{\partial C_H}{\partial y} \right) = -\frac{y}{2t} \left(\frac{\partial C_H}{\partial y} \right) \\ \bullet \frac{\partial C_H}{\partial x} &= \left(\frac{\partial C_H}{\partial y} \right) \left(\frac{\partial y}{\partial x} \right) = \frac{1}{\sqrt{4 D_H t}} \left(\frac{\partial C_H}{\partial y} \right) \\ \bullet \frac{\partial \tilde{D}_T}{\partial x} &= \frac{\partial}{\partial x} \left(D_H (1 + \alpha C_H) (1 + b C_H)^{-1} \right) = D_H \left((1 + b C_H)^{-1} \frac{\partial}{\partial x} (1 + \alpha C_H) + (1 + \alpha C_H) \frac{\partial}{\partial x} (1 + b C_H)^{-1} \right) \\ &= D_H \left[\left(\alpha \frac{\partial C_H}{\partial x} \right) (1 + b C_H)^{-1} + (1 + \alpha C_H) \left(- (1 + b C_H)^{-2} \left(b \frac{\partial C_H}{\partial x} \right) \right) \right] = \left(\frac{\alpha - b}{(1 + b C_H)^2} \right) \left(\frac{D_H}{\sqrt{4 D_H t}} \right) \left(\frac{\partial C_H}{\partial y} \right) \\ \bullet \frac{\partial^2 C_H}{\partial x^2} &= \frac{\partial}{\partial x} \left(\frac{\partial C_H}{\partial x} \right) = \frac{\partial}{\partial x} \left[\frac{1}{\sqrt{4 D_H t}} \left(\frac{\partial C_H}{\partial y} \right) \right] = \frac{\partial}{\partial x} \left(\frac{1}{\sqrt{4 D_H t}} \right) \cdot \left(\frac{\partial C_H}{\partial y} \right) + \left(\frac{1}{\sqrt{4 D_H t}} \right) \frac{\partial}{\partial x} \left(\frac{\partial C_H}{\partial y} \right) \end{aligned}$$

$$= \left(\frac{1}{\sqrt{4D_H t}} \right) \frac{\partial}{\partial x} \left(\frac{\partial C_H}{\partial y} \right) = \frac{1}{\sqrt{4D_H t}} \left(\frac{\partial}{\partial x} \left(\frac{\partial C_H}{\partial y} \right) \right) = \frac{1}{\sqrt{4D_H t}} \left(\frac{\partial}{\partial y} \left(\frac{\partial C_H}{\partial x} \right) \left(\frac{\partial y}{\partial x} \right) \right) = \frac{1}{4D_H t} \frac{\partial^2 C_H}{\partial y^2}$$

$$\frac{\partial}{\partial x} \left[\tilde{D}_T \frac{\partial C_H}{\partial x} \right] = \left(\frac{\partial \tilde{D}_T}{\partial x} \right) \left(\frac{\partial C_H}{\partial x} \right) + \tilde{D}_T \frac{\partial^2 C_H}{\partial x^2}$$

$$= \left(\left(\frac{\alpha - b}{(1 + bC_H)^2} \right) \left(\frac{D_H}{\sqrt{4D_H t}} \right) \left(\frac{\partial C_H}{\partial y} \right) \right) \left(\frac{1}{\sqrt{4D_H t}} \left(\frac{\partial C_H}{\partial y} \right) \right) + \left(\left(\frac{1 + \alpha C_H}{1 + bC_H} \right) D_H \right) \left(\frac{1}{4D_H t} \frac{\partial^2 C_H}{\partial y^2} \right)$$

$$= \left(\frac{\alpha - b}{(1 + bC_H)^2} \right) \left(\frac{\partial C_H}{\partial y} \right)^2 + \left(\frac{1 + \alpha C_H}{1 + bC_H} \right) \left(\frac{\partial^2 C_H}{\partial y^2} \right)$$

Putting both sides of the transform of Fick's 2nd Law together:

$$\frac{\partial C_H}{\partial t} = \frac{\partial}{\partial x} \left[\tilde{D}_T \frac{\partial C_H}{\partial x} \right] \Rightarrow -\frac{y}{2t} \left(\frac{dC_H}{dy} \right) = \left(\frac{\alpha - b}{(1 + bC_H)^2} \right) \left(\frac{dC_H}{dy} \right)^2 + \left(\frac{1 + \alpha C_H}{1 + bC_H} \right) \left(\frac{d^2 C_H}{dy^2} \right) \quad (A3)$$

Rearranging to derive Equation 8:

$$\left(\frac{d^2 C_H}{dy^2} \right) = -2y \left(\frac{1 + bC_H}{1 + \alpha C_H} \right) \left(\frac{dC_H}{dy} \right) + \left(\frac{b - \alpha}{1 + \alpha C_H} \right) \left(\frac{dC_H}{dy} \right)^2$$

This equation is in agreement with Doremus.

Derivation of the Smets Diffusion Equation

The following fills in the details of the mathematical argument presented by Smets.

Modified form of Fick's 2nd Law to reflect the presence of mobile and immobilized water (Equation 10): $\frac{\partial c_m}{\partial t} + \frac{\partial c_{im}}{\partial t} = \frac{\partial}{\partial x} \left(D_m \frac{\partial c_m}{\partial x} \right)$.

Relating the concentration of the immobilized water to the mobile water using the

dissociation constant K' (Equation 11): $c_m = \frac{K' c_{im}}{c_A} = \frac{K' c_{im}}{1 - c_{im}}$

Computing the derivatives using the above relation:

$$\frac{\partial c_m}{\partial t} = \frac{\partial}{\partial t} \left(\frac{K' c_{im}}{1 - c_{im}} \right) = K' \frac{\partial}{\partial t} \left(c_{im} (1 - c_{im})^{-1} \right) = K' \left((1 - c_{im})^{-1} \frac{\partial c_{im}}{\partial t} - c_{im} (1 - c_{im})^{-2} \left(-\frac{\partial c_{im}}{\partial t} \right) \right)$$

$$= K' \left(\frac{(1 - c_{im})}{(1 - c_{im})^2} \frac{\partial c_{im}}{\partial t} + \frac{c_{im}}{(1 - c_{im})^2} \frac{\partial c_{im}}{\partial t} \right) = \frac{K'}{(1 - c_{im})^2} \frac{\partial c_{im}}{\partial t}$$

$$\frac{\partial c_m}{\partial x} = \frac{\partial}{\partial x} \left(\frac{K' c_{im}}{1 - c_{im}} \right) = K' \frac{\partial}{\partial x} \left(c_{im} (1 - c_{im})^{-1} \right) = K' \left((1 - c_{im})^{-1} \frac{\partial c_{im}}{\partial x} - c_{im} (1 - c_{im})^{-2} \left(-\frac{\partial c_{im}}{\partial x} \right) \right)$$

$$= K' \left(\frac{(1 - c_{im})}{(1 - c_{im})^2} \frac{\partial c_{im}}{\partial x} + \frac{c_{im}}{(1 - c_{im})^2} \frac{\partial c_{im}}{\partial x} \right) = \frac{K'}{(1 - c_{im})^2} \frac{\partial c_{im}}{\partial x}$$

The assumption that $c_{im} \gg c_m$ was made so that $\frac{\partial c_{im}}{\partial t} \gg \frac{\partial c_m}{\partial t}$. Therefore, the diffusion equation becomes $\frac{\partial c_m}{\partial t} + \frac{\partial c_{im}}{\partial t} = \frac{\partial}{\partial x} \left(D_m \frac{\partial c_m}{\partial x} \right) \approx \frac{\partial c_{im}}{\partial t}$. Plugging in the derivatives obtained above to derive Equation 12:

$$\frac{\partial c_{im}}{\partial t} = \frac{\partial}{\partial x} \left(D_m \frac{\partial c_m}{\partial x} \right) \Rightarrow \frac{\partial c_{im}}{\partial t} = \frac{\partial}{\partial x} \left(\frac{D_m K'}{(1 - c_{im})^2} \frac{\partial c_{im}}{\partial x} \right).$$

Using the Boltzmann transform $y = \frac{x}{\sqrt{4D_m K' t}}$ and the equation for $\frac{\partial c_{im}}{\partial t}$ derived above and finally making the substitution $c_A = 1 - c_{im}$, the same mathematics as shown previously may be followed to obtain a nonlinear ordinary differential equation solvable numerically using experimental data (solving again would be gratuitous) to obtain Equation 13:

$$\frac{d^2 c_A}{dy^2} = -2c_A^2 \frac{dc_A}{dy} + \frac{2}{c_A} \left(\frac{dc_A}{dy} \right)^2$$

This equation gives the concentration profile for the concentration of alkali, c_A .

Appendix B: Example Calculations for Depth of Penetration Values

Depth of Penetration Derivation

This derivation follows the one given in [92] for power attenuated to 1/e with the mathematical details filled in by the author. The derivation for power attenuation to 1/2 is the author's and follows similar logic to the first argument. The equation that describes the electric field within a dielectric material is given by the following equation:

$$E = E_{\max} e^{-\alpha z} e^{j(\omega t - \beta z)} \quad (\text{B1})$$

In this equation, α is the attenuation factor, z is the depth of interest in the material, ω is the angular frequency of the microwave radiation ($\omega = 2\pi f$ where f is the frequency of the radiation), t is time, and β is the phase factor. The first two terms are important in discussing attenuation as they describe the maximum strength of the electric field at a certain distance z into the material. Therefore, the term E_{peak} is defined to describe the maximum value of the electric field available at a distance z :

$$E_{\text{peak}} = E_{\max} e^{-\alpha z} \quad (\text{B2})$$

Now, the attenuation factor α may be defined, where μ_0 is the permeability of free space, μ' is the real permeability of the material (assumed to be equal to 1 for nonmagnetic materials such as water), ϵ_0 is the permittivity of free space, ϵ' is the relative dielectric constant of the material, and ϵ''_{eff} is the effective relative loss factor:

$$\alpha = \omega \left(\frac{\mu_0 \mu' \epsilon' \epsilon_0}{2} \right)^{1/2} \left[\left(1 + \left(\frac{\epsilon''_{\text{eff}}}{\epsilon'} \right)^2 \right)^{1/2} - 1 \right]^{1/2} \quad (\text{B3})$$

The power contained in the electromagnetic wave is proportional to the square of the electric field, thus:

$$P_{\text{peak}} \propto (E_{\text{peak}})^2 = (E_{\max})^2 e^{-2\alpha z} \quad (\text{B4})$$

Therefore, the power delivered to the material along z is proportional to the electric field also:

$$P_{\text{delivered}} \propto P_{\text{peak}} \propto e^{-2\alpha z} \quad (\text{B5})$$

When the power contained in the wave is attenuated to 1/e, $P_{\text{peak}} = (1/e)P_{\max}$. Thus,

$$P_{Dp\frac{1}{e}} = \frac{1}{e} P_{\max} = P_{\max} e^{-2\alpha z_c} \quad (\text{B6})$$

Solving for z_c , the depth of penetration results:

$$z_c = \frac{1}{2\alpha} = D_{p\frac{1}{e}} \quad (\text{B7})$$

Now, the electric field may be related to the depth of penetration,

$$E_{\text{peak}} \propto E_{\max} e^{-\alpha z} \\ E_{\text{peak}, Dp\frac{1}{e}} \propto E_{\max} e^{-\alpha\left(\frac{1}{2\alpha}\right)} = E_{\max} e^{-\frac{1}{2}} = \sqrt{\frac{1}{e}} E_{\max} \approx 0.607 E_{\max} \quad (\text{B8})$$

Thus, the electric field is attenuated to 60.7% of its original value when the power contained in the wave is attenuated to 1/e or 36.8% of its original value.

Similar logic is followed when the power is attenuated to 1/2 its original value:

$$P_{Dp\frac{1}{2}} = \frac{1}{2} P_{\max} = P_{\max} e^{-2\alpha z_c} \quad (\text{B9})$$

$$z_c = -\frac{1}{2\alpha} \ln\left(\frac{1}{2}\right) = \frac{1}{2\alpha} \ln(2) = \frac{\ln(2)}{2\alpha} = D_{p\frac{1}{2}}$$

$$E_{\text{peak}, Dp\frac{1}{2}} \propto E_{\max} e^{-\alpha\left(\frac{\ln(2)}{2\alpha}\right)} = E_{\max} e^{-\frac{\ln(2)}{2}} = \left(e^{\ln(2)}\right)^{-1/2} E_{\max} = (2)^{-1/2} E_{\max} = \sqrt{\frac{1}{2}} E_{\max} \approx 0.707 E_{\max} \quad (\text{B10})$$

Therefore, the electric field is attenuated to 70.7% of its original value when the power contained in the wave is attenuated to 50% of its original value.

Sample Calculations: Depth of Penetration

From [92], for pure water at 55°C with microwave radiation of 7 GHz incident upon it, $\epsilon' = 66$ and $\epsilon'' = 14$. Therefore, the following calculations can be performed:

Wavelength of the incident microwave radiation:

$$c = \lambda \nu \Rightarrow \lambda = \frac{c}{\nu} = \frac{3.00 \times 10^8 \text{ m/s}}{7.00 \times 10^9 / \text{s}} = 0.0429 \text{ m}$$

$$D_p = \frac{\lambda'_0}{2\pi(2\epsilon')^{1/2}} \left[\left(1 + \left(\frac{\epsilon''}{\epsilon'} \right)^2 \right)^{1/2} - 1 \right]^{-1/2} = \frac{0.0429 \text{ m}}{2\pi\sqrt{2 \cdot 66}} \left[\left(1 + \left(\frac{14}{66} \right)^2 \right)^{1/2} - 1 \right]^{-1/2} \\ = (5.94 \times 10^{-4} \text{ m}) [6.70] = 0.00398 \text{ m} = 3.98 \text{ mm} \quad (\text{B11})$$

Appendix C: Preliminary and Intermediate Testing

Preliminary Experiments

Initial Microwave Tests: Procedure

To perform initial microwave tests, the temperature profiles from conventional tests were approximated in the Vari-Wave. The Vari-Wave was controlled by a program which allowed up to 13 consecutive temperatures to be maintained for specific periods of time. The conventional temperature profile was modeled by these 13 steps. An example of one program is shown in Figure 93, represented by horizontal lines and juxtaposed with the conventional profile. The actual performance of the program is shown in Figure 94. It is a good approximation to the conventional profile. The Vari-Wave's heating algorithm functioned by applying microwaves until it reached $+0.5^{\circ}\text{C}$ above the setpoint, then stopped applying the microwaves until the temperature decreased to 0.5°C under the setpoint, and then applied microwaves and brought the temperature to 0.5°C above the setpoint, sometimes even 1°C higher.

Several tests were run to observe if there were any obvious effects of the microwaves on corrosion before a systematic study was begun. All of these tests were performed using 11.00 GHz microwave radiation.

The first two tests used 125 ml of deionized water and a large glass surface area to solution volume ratio (SA/V). The first test was run for 3 hours and consisted of a ramp from room temperature to 90°C . The second test was run for 3 hours and consisted of a ramp from room temperature to 50°C . The results are shown in Figures 95 and 96.

The third and fourth tests used 25 ml deionized water and therefore had a much smaller SA/V ratio. The idea in reducing the amount of water was to enable the interface to experience a higher electric field. The first of these tests consisted of a ramp from room temperature to 90°C over the course of 4 hours. The second consisted of putting the glass sample in a preheated water bath and heating up to 90°C over 2 hours. The results of these tests are shown in Figures 97 and 98.

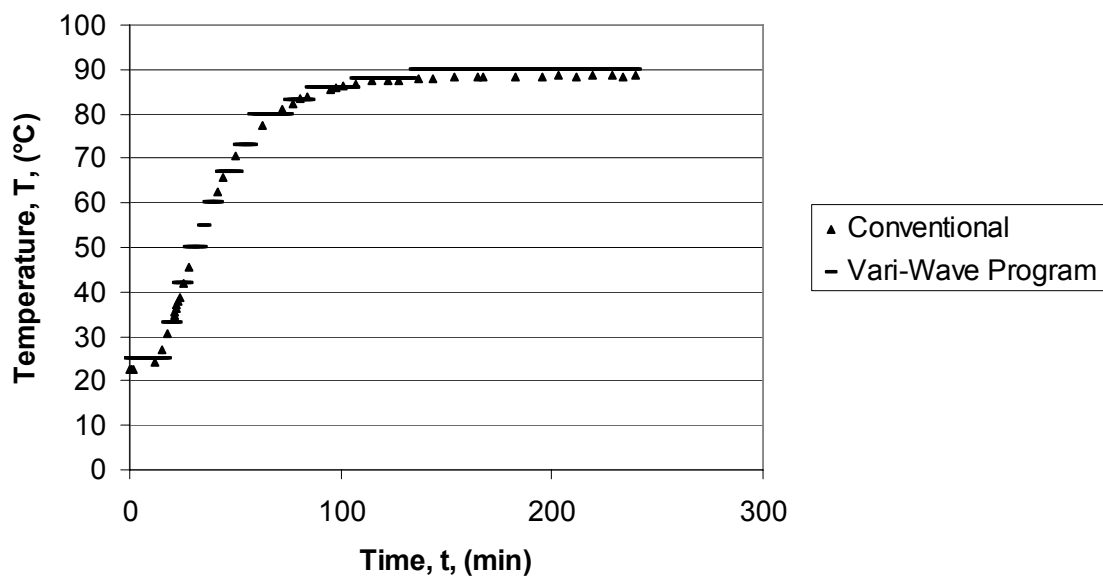


Figure 93: Planned Vari-Wave approximation to conventional temperature profile for a 90°C setpoint.

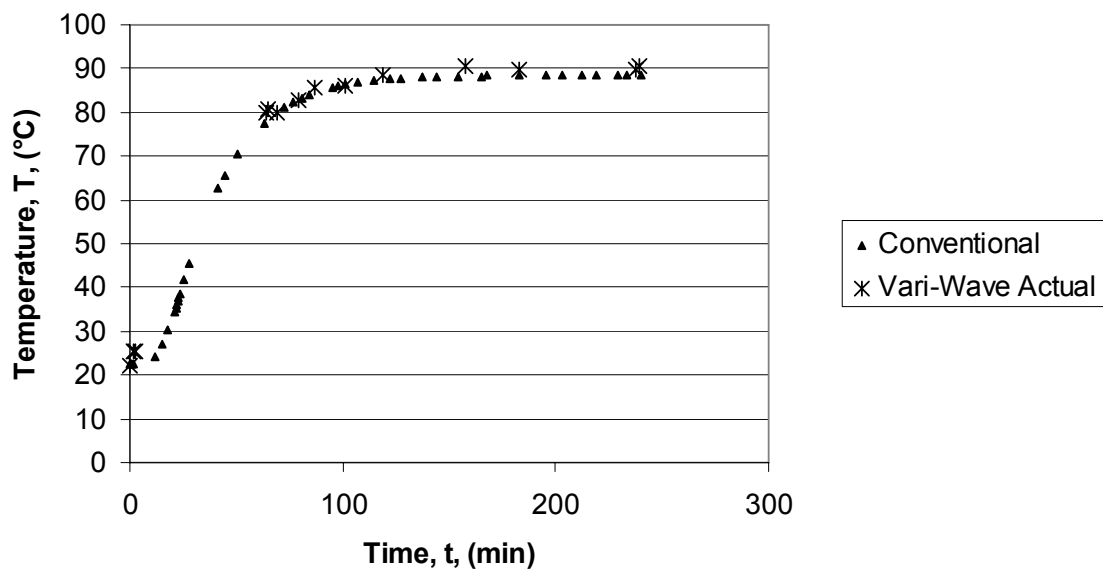


Figure 94: Actual Vari-Wave approximation to conventional temperature profile for a 90°C setpoint.

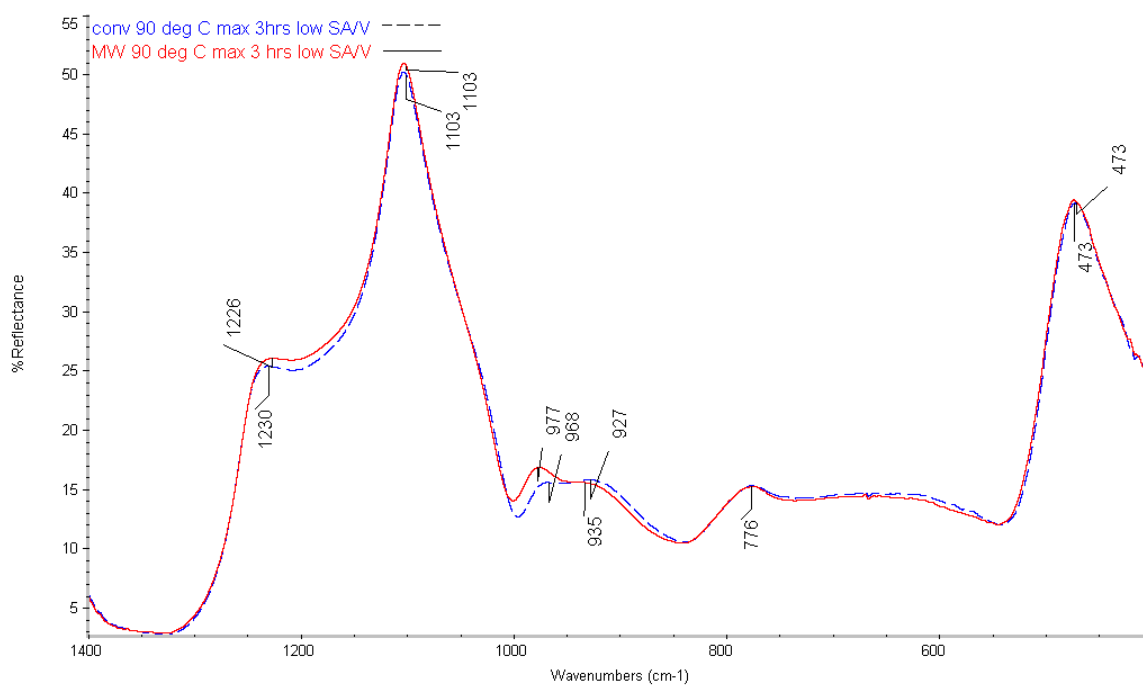


Figure 95: FTIR spectra for first preliminary comparison. Ramp to 90°C, 3 hrs, low SA/V ratio.

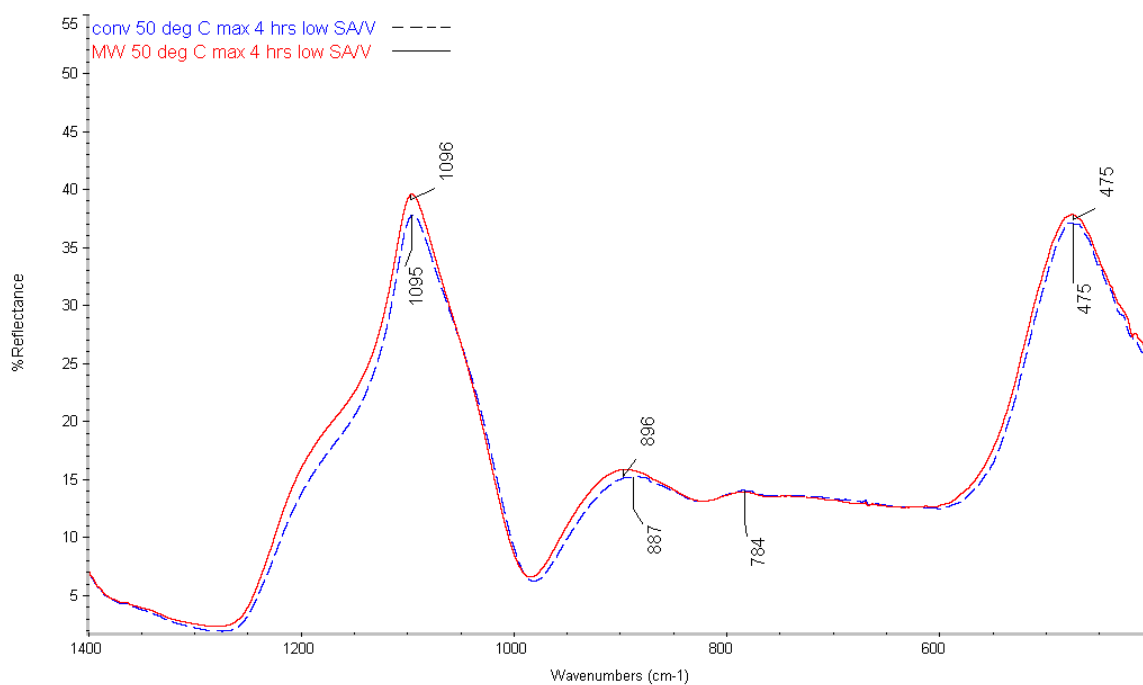


Figure 96: FTIR spectra for second preliminary comparison. Ramp to 50°C, 4 hrs, low SA/V ratio.

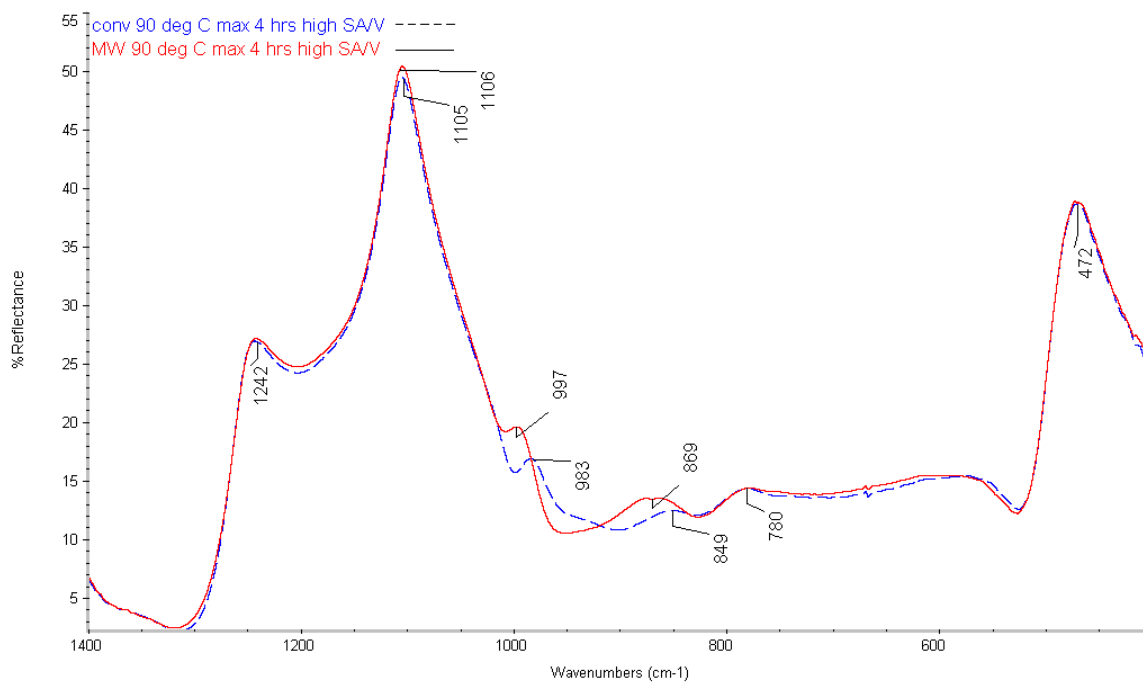


Figure 97: FTIR spectra for third preliminary comparison. Ramp to 90°C, 4 hr, high SA/V ratio.

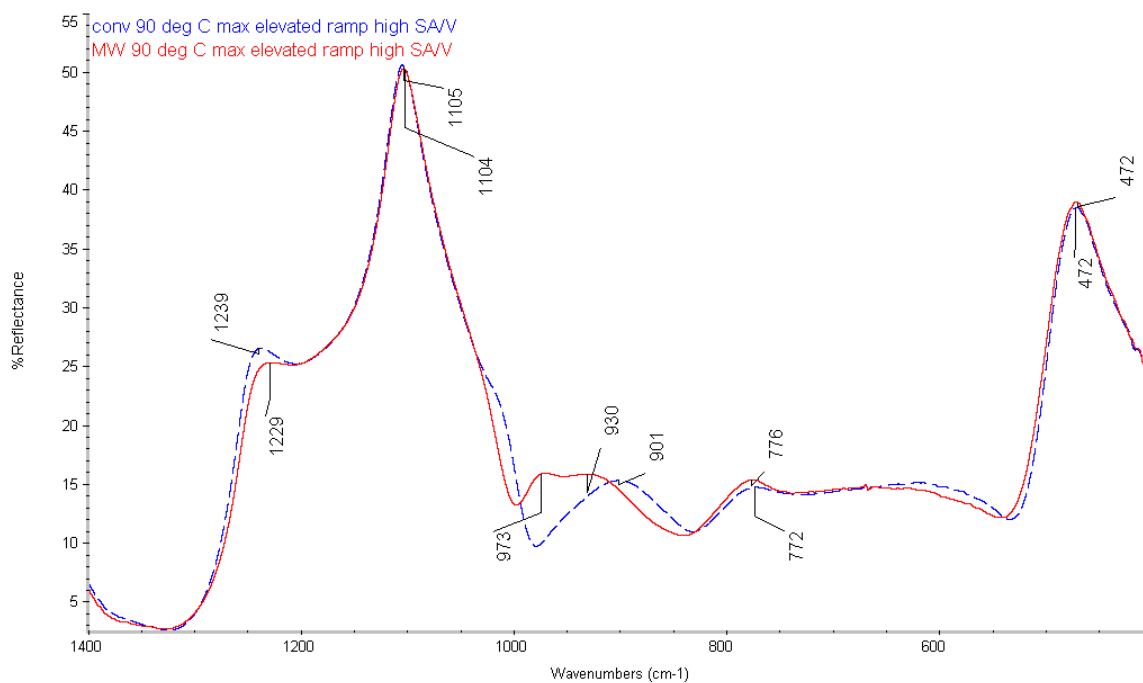


Figure 98: FTIR spectra for fourth preliminary comparison. Ramp to 90°C from elevated temperature, 2 hr, high SA/V ratio.

There was no radical difference between the sample spectra in any of the tests. In general, all of the major peaks for both the conventional and microwave samples had a similar height and position except those in the transient 800-1000 cm^{-1} region.

The shapes of the curves in this region bore striking similarity to those obtained from the conventional temperature series. Both of the curves in Figure 95 looked very similar to the curve obtained from the 75°C series test. This result was due to the fact that even though the bath was at a higher temperature, it was at that temperature for less time. Therefore, an approximately equal amount of corrosion occurred due to a time-temperature kinetic tradeoff. Because the peak in the 800-1000 cm^{-1} region was more prominent and at a higher wavenumber in the microwave sample, it appeared that it was not as far along in the corrosion process as the conventional sample.

The two samples in Figure 96 had spectra with very little difference. Their surfaces appear to have undergone the same degree of corrosion.

The samples in Figure 97 which were ramped to 90°C over 4 hours resembled the 85 and 90°C test in the conventional temperature series. The conventional sample appeared further in the corrosion process because it resembled the 90°C series sample, whereas the microwave sample resembled the 85°C series sample.

The samples in Figure 98 which were ramped to 90°C over 2 hours starting at an elevated temperature and resembled the 75 and 80°C curves from the temperature series. The conventional sample again appeared further along in the corrosion process.

The fact that the conventional sample appeared to have experienced more corrosion was probably due to a temperature difference in the two baths. As explained in the previous chapters, the optical probe was found to measure an average of 2.6°C higher than the shielded type K thermocouple when only the tips were used to measure bath temperature and without any attempt at calibration. Therefore, if two baths, one measured by the thermocouple and the other by the optical probe, were each held at the same nominal temperature, the bath measured by the optical probe would be approximately 2-3°C cooler than the other bath.

When the baths were each held at a nominal value, say 90°C, the bath in the microwave was probably near 87°C. This temperature difference could account for the increased corrosion seen in the conventional samples, which was sometimes, especially

in Figure 98, nearly equivalent to two samples separated by 5°C in the conventional temperature series. The effect was more severe at 90°C than at 50°C because, from the kinetic standpoint, several degrees causes a bigger difference in the corrosion driving force at a higher temperature than a lower temperature.

Under these particular circumstances, the corrosion processes detectible with infrared spectroscopy were similar between the samples heated conventionally and with microwave energy.

Assuming that microwaves did in fact affect corrosion, a possible explanation for the lack of any major observable microwave effect was the effects of depth of penetration. It is possible that the layer of water on top of the polished face of the glass specimen was too thick, causing attenuation of the microwave field long before it penetrated to the water-glass interface.

Temperature Measurement

Temperature was measured using an inconel-shielded type K thermocouple in the conventional oven and the optical probe in the microwave oven. In both cases, only the tips could be inserted into the water bath. To determine the comparability of the measurements from the two instruments, a side-by-side comparison was performed in which the two tips were placed in close proximity in a heated bath and the temperatures were measured. The shielded thermocouple was allowed to sit in the bath until its measurement stopped changing rapidly, indicating it had come to thermal equilibrium. Measurements were then taken as the bath cooled and the readings compared to one another.

When just the tips were submerged, there was an average difference of 2.6°C in the readings, with the optical probe reporting a higher temperature than thermocouple. The average value had a standard deviation of 0.40. When the instruments were substantially submerged, the average difference improved to 1.8°C, with a standard deviation of 0.82. Combining these two conditions, the average difference was 2.1°C with a standard deviation of 0.78.

To solve this problem, an unshielded type T thermocouple was used in all tests after the preliminary round.

Key Lessons from Preliminary Experiments

It was realized from these preliminary tests that better control should be maintained over temperature by using a type T thermocouple, adjusting zero point, and eliminating the ramp in favor of a pre-heated solution. Also, water layer thickness must be decreased and kept constant by developing a way to keep the sample positioning the same and limit evaporation. Consideration of depth of penetration was very important and could be exercised by using 7.00 GHz microwaves and decreasing water layer thickness.

Intermediate Experiments

Intermediate Experiments: Procedure

Experiments were carried out in the same PFA jars as described previously. Prior to use, each jar was cleaned with solutions of hydrofluoric and nitric acid to remove adsorbed contaminants, such as lithium and silica, should any have been present. Three PFA rings were used to keep the glass specimen from touching the bottom of the jar. The rings were cut from a threaded PFA tube and were 2 mm in diameter with a thickness of 1-2 mm.

A schematic drawing of the setup is shown in Figure 99. In this drawing, the thermocouple is inserted into the bath. The optical temperature measurement device used in the microwave oven was inserted in a similar manner.

To perform microwave tests, the temperature profiles of baths heated conventionally were approximated in the microwave oven. The actual performance of the program is shown in Figure 100.

A type T thermocouple (copper-constantan) with exposed tip was used for the experiments reported in detail here. It was calibrated to the measurement of the optical probe by boiling water so that the measurements provided in the microwave and in the conventional oven were nearly the same (approximately $\pm 0.5^{\circ}\text{C}$).

Six samples, all cut and polished on both sides to a thickness of approximately 6 cm, were divided so that three samples each were corroded conventionally or by microwaves in a bath of deionized water (18.2 M Ω -cm). The samples were corroded one at a time in 25 mL of deionized water during testing. The heating profile is shown in

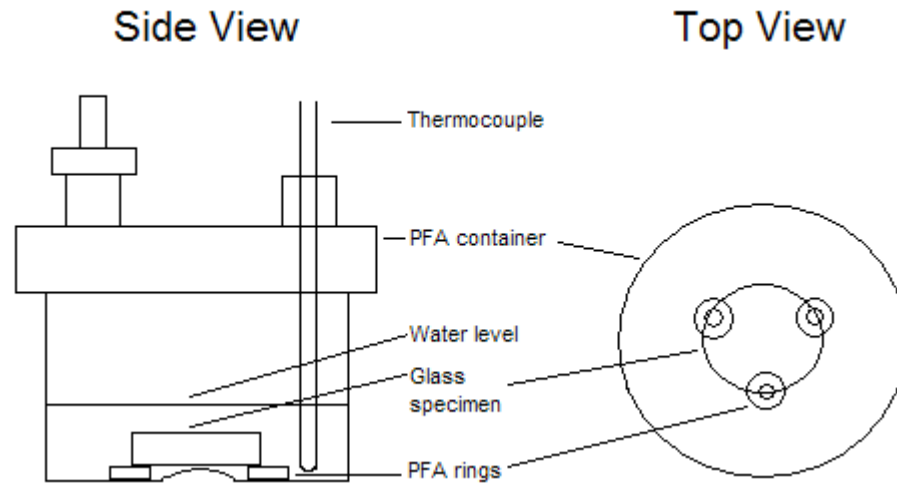


Figure 99: Schematic illustration of test setup for intermediate bulk testing.

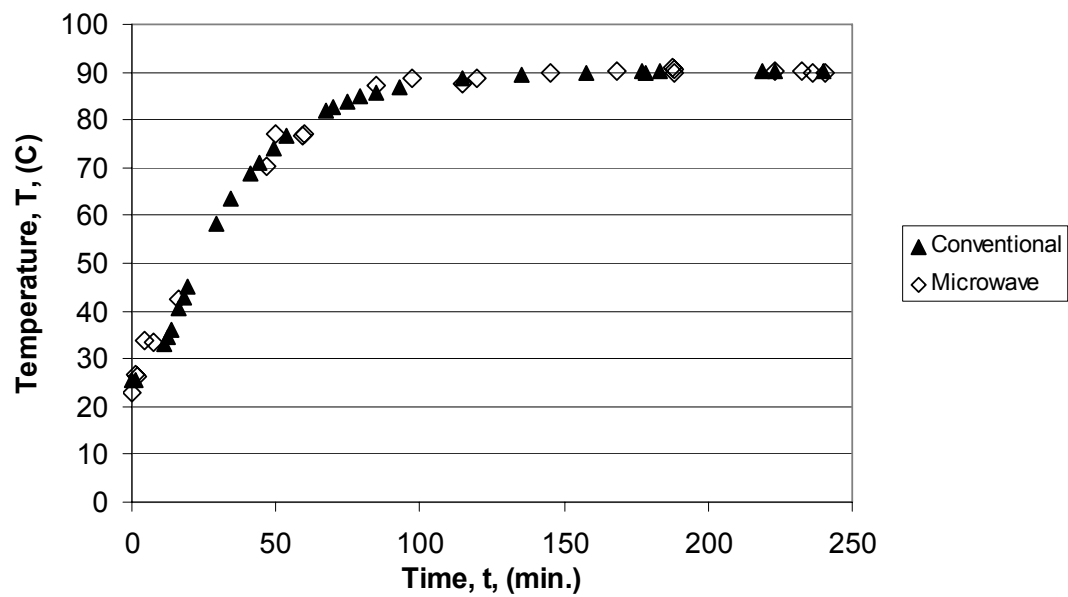


Figure 100: Temperature vs. time profile in the conventional and microwave ovens for intermediate bulk testing.

Figure 100 and involved a ramp from room temperature to 90°C. The total duration of the test was 240 min.

Intermediate Experiments: Results

Six samples were corroded as described. The resulting FTIR spectra of the top faces are shown in Figure 101.

There was relatively little difference between the spectra of the microwave samples and the conventional samples. It appeared that, if anything, the microwave samples showed fewer signs of corrosion on the top face.

Solution data is given for all six samples in Table 12. The concentration of leached Li^+ was higher (>95% confidence by ANOVA) for the samples heated by microwave energy and the concentration of Si was higher for the samples heated conventionally (>95% confidence). The pH of both sets of samples was not significantly different. The fact that the ratios of corrosion product released into solution was significantly different suggests a change in mechanism because if a difference in temperature was responsible, the ratio of leaching to network dissolution would be expected to be the same for both conventional and microwave samples.

The kinetic parameter α describes the degree of leaching versus the degree of network dissolution and is given by Equation 21 for $\text{Li}_2\text{O}-2\text{SiO}_2$ [31]. When $\alpha=0$, only leaching occurs (Equations 2 and 9). When $\alpha=1$, congruent dissolution dominates (Equations 3, 18, and 20). Values in between consist of mixed types.

For the conventional samples, the average value was $\alpha=0.05$. For the microwave samples, $\alpha=0.04$. This difference suggests that the microwave samples actually leached slightly more than the conventional samples but experienced less network dissolution.

This hypothesis is supported by the scanning electron micrographs in Figure 102 (See Figures 52-55 for an explanation of those features labeled I and II in the micrographs). After polishing with 1000-grit silicon carbide paper, the polishing tracks had sharp features (102a and b). These features appeared rounded and increased in size after corrosion in both environments. In general, the features appeared more rounded due to conventional heating (102c and d) than microwave heating (102e and f). Rounded, eroded features are characteristic of network dissolution (Equations 3, 18, and 20) and so it appeared that, in general, more network dissolution occurred in the conventional

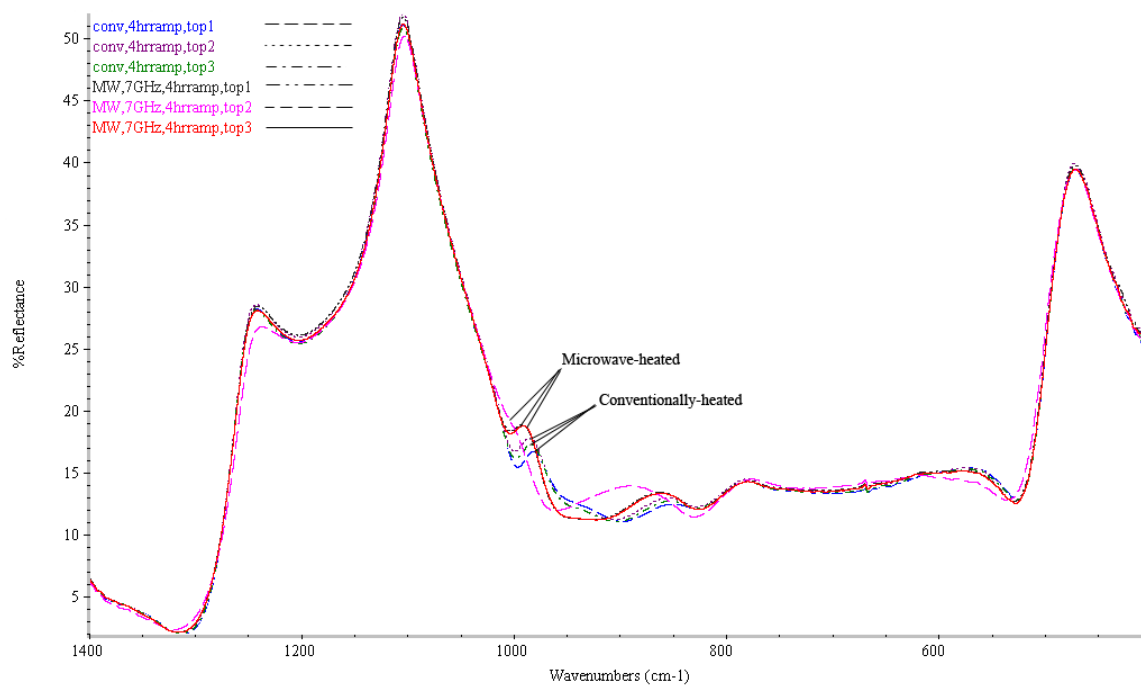


Figure 101: FTIR spectra of the six intermediate bulk samples.

Table 12: Solution data for intermediate bulk testing

	Sample	[Li ⁺] (ppm)	[Si] (ppm)	pH	α
Conventional	C1	28.29	5.78	11.80	0.05
	C2	30.73	6.25	11.93	0.05
	C3	29.94	5.72	11.77	0.05
	average	29.65	5.92	11.83	0.05
Microwave	M1	32.08	5.21	11.79	0.04
	M2	31.59	5.30	11.72	0.04
	M3	31.72	4.75	11.74	0.04
	average	31.80	5.09	11.75	0.04

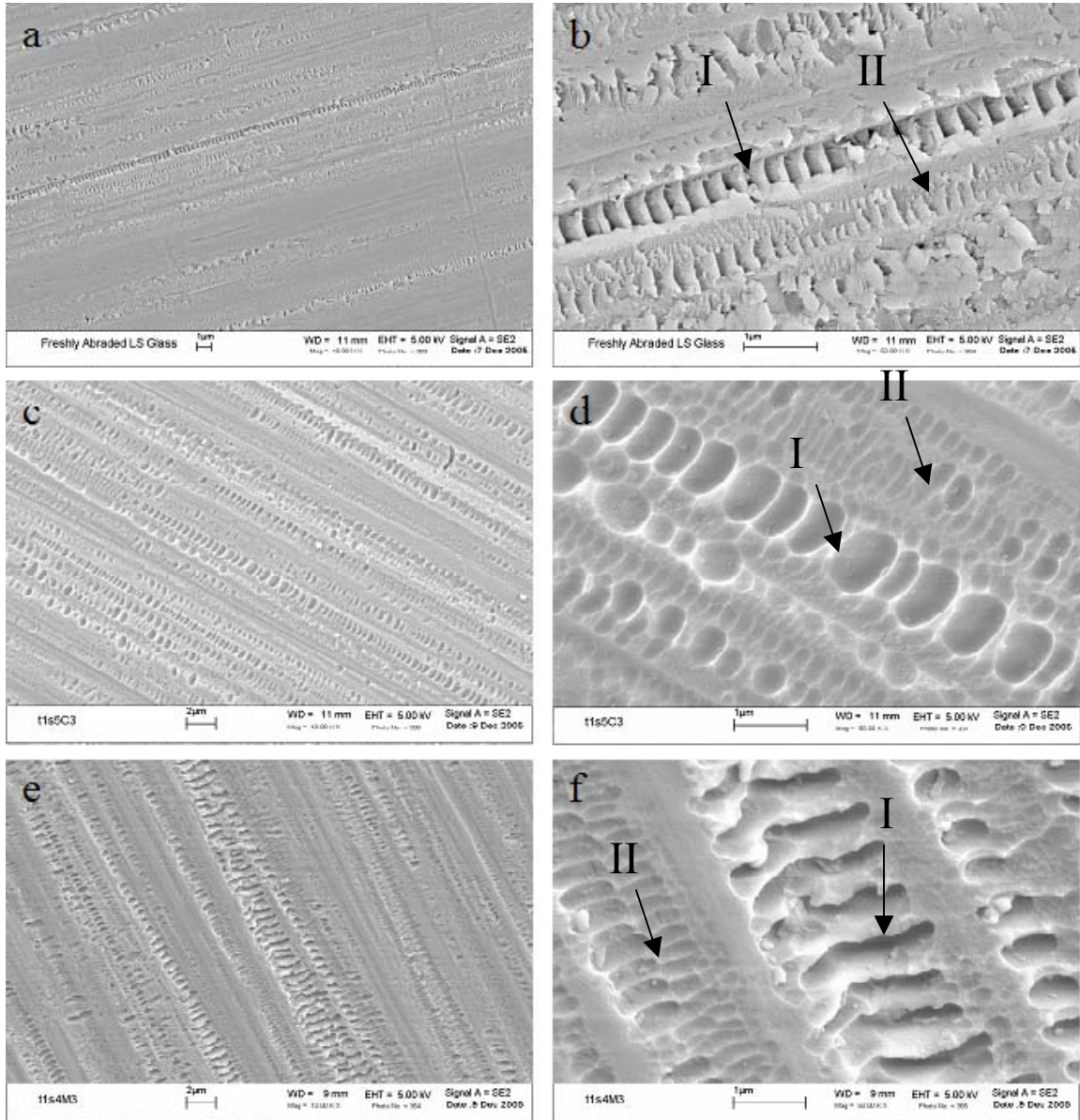


Figure 102: SEM micrographs of the top faces of specimens (the rough features are polishing abrasions): a and b) Freshly abraded glass; c and d) Glass corroded in conventionally heated bath; e) and f) Glass corroded in bath heated by microwaves.

samples. These micrographs were taken of the top faces of samples; the bottoms were not investigated.

The FTIR spectra, however, suggest that the top faces were slightly less corroded for the microwave samples than the conventional samples. It is possible that the lack of rounding of the microwave samples was the result of an accelerated leaching mechanism which preserved the silica network or some other cause.

A common objection to processes seemingly altered by microwave energy is to argue that differences in temperature were responsible for any observed microwave effect. However, in the case of glass corrosion it would be expected that a simple difference in temperature by several degrees would affect both the release of lithium and silicon in the same manner [31]. That is, if one mechanism's rate were enhanced, the other mechanism's rate should be similarly enhanced. A simple thermal effect cannot explain the increase of leaching and suppression of silica dissolution experienced by the sample heated with microwave energy.

Key Lessons from Intermediate Experiments

From these tests, several improvements to the experimental setup were developed. First, the PFA rings that supported the glass samples were eliminated in favor of resting the sample on the bottom of the jar. This eliminated a free surface but it also eliminated much of the experimental error and variability inherent to the PFA rings. Second, the direct insertion of the thermocouple into the test solution was eliminated. This was done because it was discovered from the literature that copper (entering solution perhaps from the copper-constantan thermocouple tip) can suppress leaching [99]. Finally, rotation of the test jars and boiling of water between trials were implemented in order to reduce interference with the solution data of Li^+ and Si adsorbed to the jar's side.

The subsequent data presented in Chapter IV did not support the differences observed between the conventionally-heated and microwave-heated samples to the degree to which they are suggested in this section. It is likely that the results in Chapter IV reflect the inclusion of less experimental error due to improved testing procedures.

Appendix D: Thermocouple Calibration

Shown are the curves from calibration of the thermocouple to the optical probe. The differences (optical probe reading minus thermocouple reading) are given.

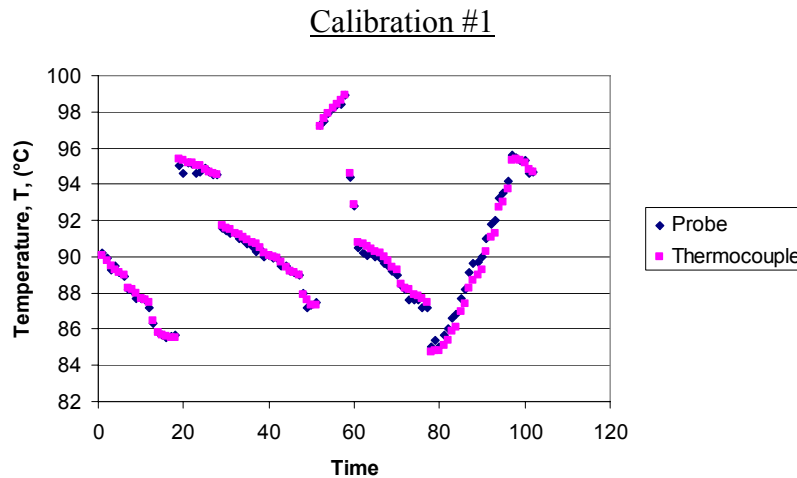


Figure 103: Calibration curves for entire calibration #1.

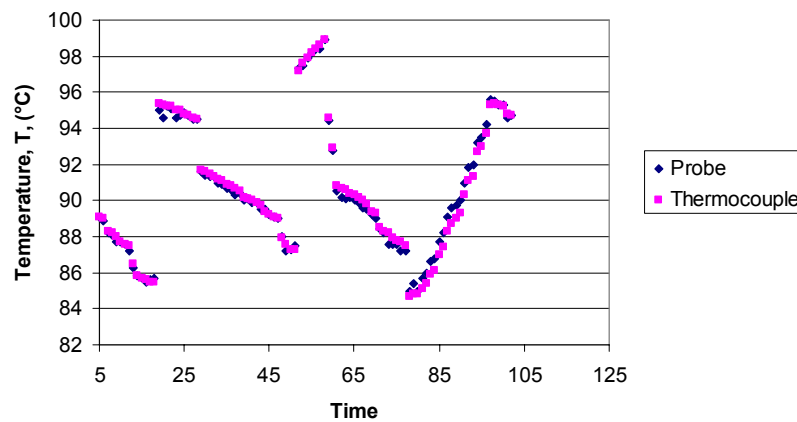


Figure 104: Calibration curves for calibration #1 after final adjustment.

Table 13: Average difference between the optical probe and thermocouple for calibration #1.

	Difference after final adjustment (°C)
Average	0.012
Ascending	0.6
Descending	-0.15

This calibration was used for all data in Figures 47-55 and 60-74, except for the 500-min data. The conventional oven was set at 85.7°C in order to match the optical probe's "90°C."

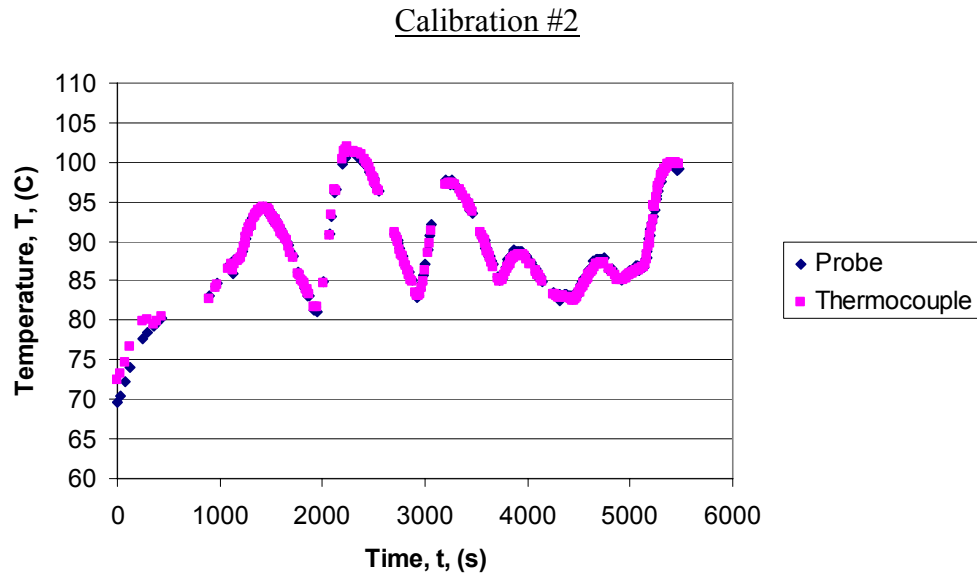


Figure 105: Calibration curves for entire calibration #2.

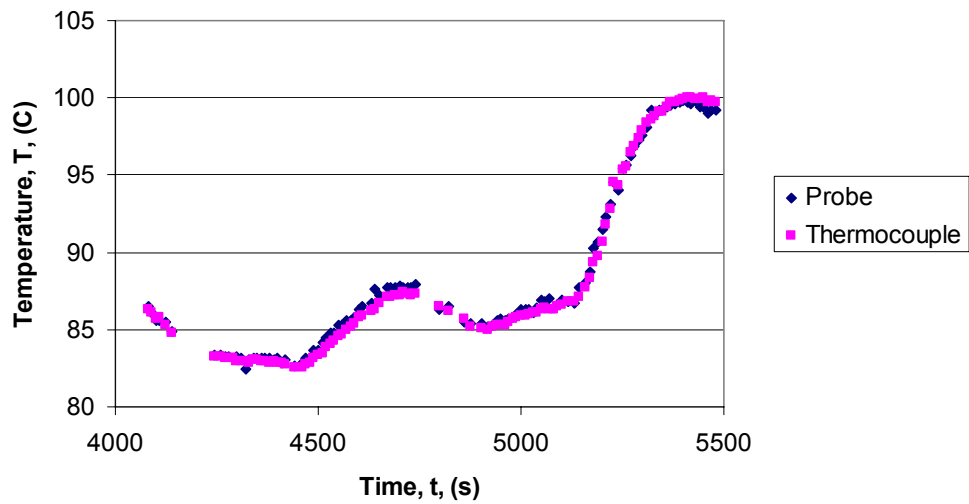


Figure 106: Calibration curves for calibration #2 after final adjustment.

Table 14: Average difference between the optical probe and thermocouple for calibration #2.

	Difference after final adjustment (°C)
Average	0.21
Ascending	0.30
Descending	0.07

This calibration was used to obtain all data in Figures 56-58, 75-80, and Tables 3-4. The conventional oven was set for 85.1°C in order to match the optical probe's “90°C.”

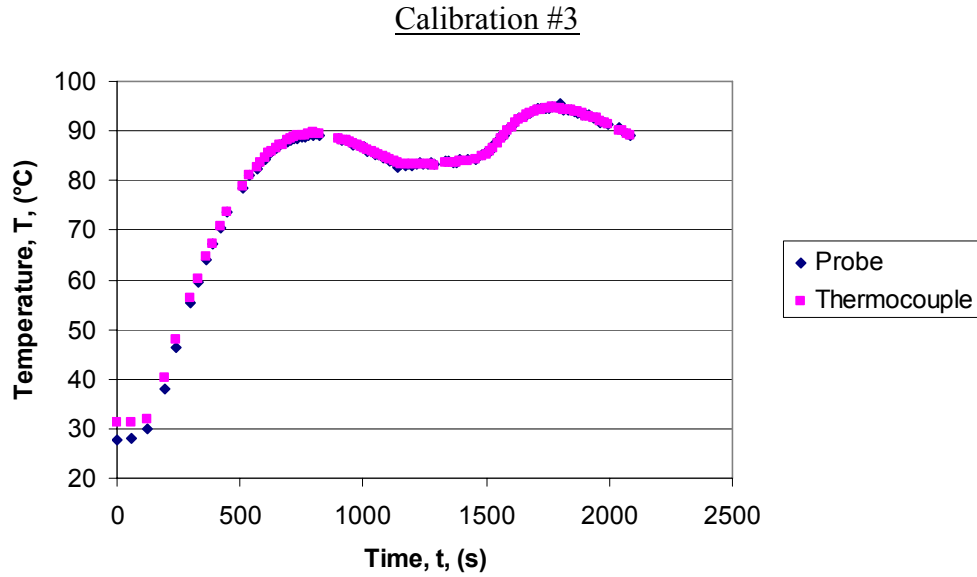


Figure 107: Calibration curves for entire calibration #3.

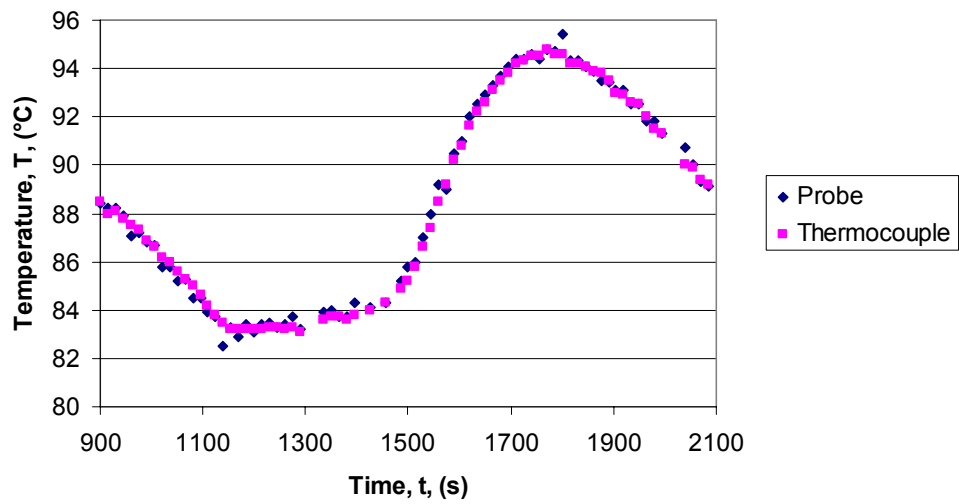


Figure 108: Calibration curves for calibration #3 after final adjustment.

Table 15: Average difference between the optical probe and thermocouple for calibration #3.

	Difference after final adjustment (°C)
Average	0.08
Ascending	0.18
Descending	-0.05

This calibration was used to obtain all 500-min data in Figures 47-55 and 60-74 as well as all data in Tables 7-11. The conventional oven was set to 84.1°C in order to match the optical probe’s “90°C.”

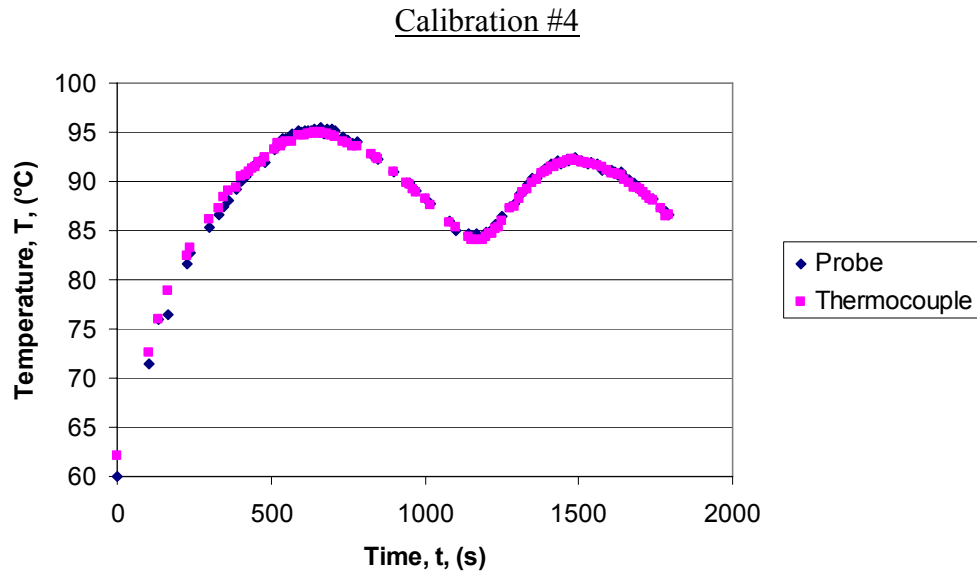


Figure 109: Calibration curves for entire calibration #4.

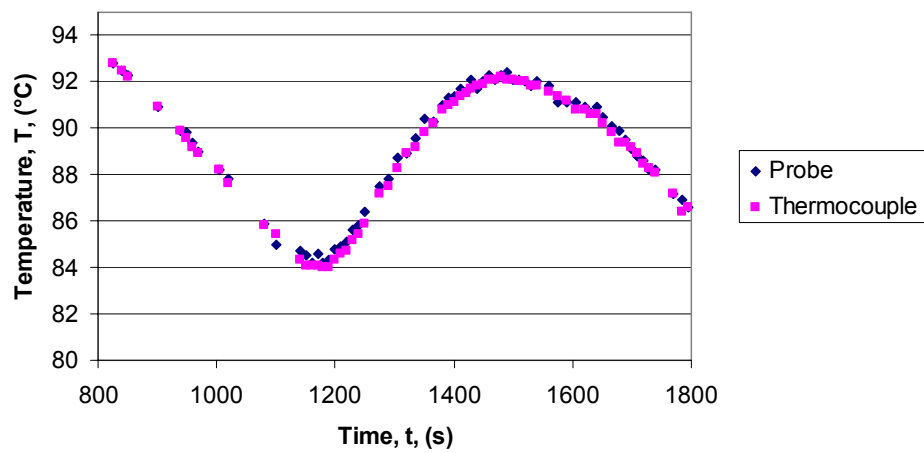


Figure 110: Calibration curves for calibration #4 after final adjustment.

Table 16: Average difference between the optical probe and thermocouple for calibration #4.

	Difference after final adjustment (°C)
Average	0.17
Ascending	0.25
Descending	0.12

This calibration was used to obtain all data in Figures 81-89. The conventional oven was set to 88.8°C in order to match the optical probe's "90°C."

Appendix E: Solutions to Equipment Issues

During the course of experimentation, the Vari-Wave oven developed a problem that inhibited testing. This section details the problem and the steps taken to fix it and proceed with experimentation.

Problems in Systematic Bulk Testing

After a short amount of time into a trial, usually 30 to 60 min, the hardware controlling the oven momentarily stopped acknowledging the signal from the temperature probe. The equipment interpreted this failure to read the temperature as a reading of 0°C and so it applied microwave energy. The failures were frequent, and so the corrosion solution quickly rose above 90°C until the test was invalidated. When the reading returned, the application of microwave power stopped. Unfortunately, this problem resulted in ever-increasing temperature resulting from the unnecessary application of power. Usually, when the problem occurred, the Vari-Wave had to be cooled down to room temperature before it would work properly again.

To fix the problem, the optical probe was replaced by a new, longer probe. This new probe, an STF probe with an SMA-style optical connector, was special-ordered from Luxtron Corporation in Santa Clara, CA. Initially, this new probe did not work until a connector wire inside the Vari-Wave was bypassed. To do this, the casing was removed from the Vari-Wave, the connector wire was unscrewed from the computer card that controlled temperature measurements, and the new probe was screwed directly into the card. To make sample readings, an exhaust hose was removed from the microwave cavity and the new probe was threaded through the exhaust port. A piece of mica (microwave-transparent) was placed over the exhaust port in order to keep steam and other gases from escaping the chamber and damaging the electronics of the Vari-Wave. A small hole was drilled into the mica to allow the probe to pass through. This new setup is the one shown in Figures 28 and 29.

The old probe did not have the length required for the new setup and so the new probe was used exclusively after the fix. Unfortunately, this new probe read temperatures several degrees higher than the old probe. Therefore, setting the Vari-Wave to hold at 90°C with the new probe actually meant that it was holding at 86 or 87° when

compared to the previous probe. Subsequent tests were performed at the new “90°C” and the conventional oven was calibrated appropriately to compensate.

One additional systematic bulk trial was performed with this new setup. The duration was 500 min and three repetitions were performed.

Problems in SIMS Sample Preparation

These trials were originally planned to last for 100 min. Unfortunately, the Vari-Wave problem occurred at around 40 min and the microwave program was terminated 43.5 min into the trial. The temperature had only risen to 91.8 °C, a temperature which was higher than what usually occurs in cycling but not uncommon, thus indicating that the problem had just started when the program was terminated. Trials in the conventional oven were restricted to 43.5 min to allow direct comparison of the resulting experimental data.

There was also a slight problem in loading the sample into the 92°C pre-heated solution. It was originally put in upside down and had to be righted. During this time, the pre-heated solution cooled. Due to the short duration of the test, it is not known for certain whether the conventional sample reached 92°C again for a significant portion of the test.

Vita

Matthew E. Lynch was born in Richmond, VA on March 15, 1983. He attended the Chesterfield County Mathematics and Science High School from which he graduated in 2001. He received his B.S. degree in Materials Science and Engineering and his B.S. degree in Mathematics from Virginia Tech in May 2005. As an undergraduate, he did research on high-temperature superconductors with Dr. David Clark's group. He was awarded a National Science Foundation Graduate Research Fellowship in April 2005 and will use the remainder of fellowship tenure pursuing a Ph.D. in Materials Science and Engineering at Georgia Tech. He was married in May 2006 to his wife, Lisa.