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PREDICTION OF GLASS DURABILITY AS A FUNCTION OF GLASS COMPOSITION AND TEST CONDITIONS: THERMODYNAMICS AND KINETICS

by

C. M. Jantzen
E. I. du Pont de Nemours & Co.
Savannah River Laboratory
Aiken, SC 29808

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C. M. JANTZEN
E. I. du Pont de Nemours & Co.
Savannah River Laboratory
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ABSTRACT

The long-term durability of nuclear waste glasses can be predicted by comparing their performance to natural and ancient glasses. Glass durability is a function of the kinetic and thermodynamic stability of glass in solution. The relationship between the kinetic and thermodynamic aspects of glass durability can be understood when the relative contributions of glass composition and imposed test conditions are delineated. Glass durability has been shown to be a function of the thermodynamic hydration free energy which can be calculated from the glass composition. Hydration thermodynamics also furnishes a quantitative frame of reference to understand how various test parameters affect glass durability.

Linear relationships have been determined between the logarithmic extent of hydration and the calculated hydration free energy for several different test geometries. Different test conditions result in different kinetic reactivity parameters such as the exposed glass surface area (SA), the leachant solution volume (V), and the length of time that the glass is in the leachant (t). Leachate concentrations are known to be a function of the kinetic test parameter $(SA/V)t$. The relative durabilities of glasses including pure silica, obsidians, nuclear waste glasses, medieval window glasses, and frit glasses define a plane in three dimensional ΔG_{hyd}-concentration-$(SA/V)t$ space. At constant kinetic conditions, e.g. test geometry and test duration, the three dimensional plane is intersected at constant $(SA/V)t$ and the ΔG_{hyd}-concentration plots have similar slopes. The slope represents the natural logarithm of the theoretical slope, $(1/2.303\,RT)$, for the rate of glass dissolution.

INTRODUCTION

The durability of a glass is a function of both its kinetic and thermodynamic stability in an aqueous environment [1,2]. Kinetic models have been applied to the time dependent corrosion of glasses [3-6], waste glasses [7,8], and crystalline silicates [5,9]. These models mathematically describe ion exchange, diffusion, and protective layer formation in the form of time dependent master equations. Kinetic models describe the leaching behavior of a given glass but they do not predict which of a given group of glasses will be most durable.

Chemical thermodynamics has also been used to predict the stability of vitreous [1-2,10-11] and crystalline silicates [11-14] in aqueous environments. Application of chemical thermodynamics does not require determination of the time dependent kinetics of the leaching processes, but does compare the thermodynamic stability of the reactants (glass or crystalline silicates in solution) to the product species formed during leaching or weathering, e.g. silicic acid, cations or complexes in solution, precipitates, and /or solids. Such an ontological approach to glass durability was formulated by Newton and Paul [15] and applied to (1) the weathering of medieval window glasses and (2) to a comparison of the relative stabilities of these glasses to Roman window glass, modern container glass, Pyrex laboratory ware, and natural flint glass.

Determination of glass durability as a function of glass composition [15] is significant to the development of durable commercial glasses to be used as containers for corrosive liquids, to the understanding of the effects of dishwasher detergents on glass durability, to the understanding of the weathering of medieval and modern window glasses, and to the development of durable glasses for nuclear waste disposal. The long radioactive half-lives of fission products and actinides in high-level nuclear wastes require that they be isolated from the biosphere for 10^3 to 10^5 years. The isolation technique selected [16] for defense high-level waste produced at the Savannah River Plant is immobilization in borosilicate glass and subsequent emplacement in a geologic repository. The intrusion of groundwater into and passage through a repository, is the most likely mechanism by which radionuclides may be removed from the waste glass and carried to the biosphere. Thus, it is important that nuclear waste glasses be stable in the presence of groundwaters for very long periods of time.

It is impossible to directly demonstrate the long-term stability of any nuclear waste form. However, the existence of natural glasses, such as obsidians, basalts, or tektites, which are millions of years old, demonstrates that glasses can be formulated which will survive geologic environments. Similarly, synthetic glasses of known longevity or performance, such as medieval window glasses, can also demonstrate the potential long-range performance of nuclear waste glass. The concept of using natural glasses as analogues for waste glass durability was first proposed by Ewing [17]. Subsequent laboratory comparisons of the durability of rhyolite glasses [18] and basaltic glasses [19] to French, United Kingdom, and German nuclear waste glasses demonstrated that waste glasses can be fabricated to be as durable as some natural glasses. These mechanistic studies did not, however, provide a basis for predicting the glass compositions for which this would be true.

To quantify the relative durabilities of nuclear waste glasses, their performance relative to natural and ancient glasses (whose long-term performance is known) was investigated [20-25]. The thermodynamic approach of Newton and Paul [15] was applied to over 300 experimental laboratory results. Although equilibrium is rarely achieved in short term laboratory tests, the use of equilibrium thermodynamics furnishes a quantitative frame of reference for the relationship between any solid species and aqueous environments on historic and geologic time scales. During these studies, the thermodynamic approach of Newton and Paul [15] was expanded and shown to be applicable to a wide variety of glasses [20-25] in various environmental conditions [26].

Jantzen [24-26] combined the thermodynamic approach for glass durability with the thermodynamic approach used by Pourbaix [11] and Garrels [12] to describe the effects of natural aqueous environments on metallurgical and mineralogic species. The construction of Pourbaix diagrams for glass dissolution was shown to conceptually and quantatively unify the dissolution behavior of glasses in natural environments.

In this study, the relative role of kinetics and thermodynamics in predicting the long term durability of glasses will be examined. The relationship between the kinetic and thermodynamic aspects of glass durability can be understood when the relative contributions of glass composition and imposed test conditions are delineated. The kinetic contribution is primarily a function of the test geometry. In particular, test parameters such as exposed glass surface area (SA), the solution volume (V), the test duration (t), and the test temperature (T) alter the kinetic contribution. The thermodynamic contribution represents the long term glass stability as a function of the glass composition and structure (bonding).

THEORETICAL

Glass Durability: A Function of Glass Composition

The thermodynamic approach of Newton and Paul [15] assumes that the glass is a mechanical mixture of orthosilicate and oxide components. The overall free energy of hydration of a glass is assumed to be an additive function of the free energies of the hydration reactions of the individual silicate and oxide components. The formalism is

$$\Delta G_{hyd} = \Sigma \, x_i \cdot (\Delta G_{hyd})_i \qquad (1)$$

where $(\Delta G_{hyd})_i$ is the free energy change of the thermodynamically most stable hydration reaction of component i at mole fraction x_i.

Newton and Paul [15] did not apply their approach to borosilicate glasses. In order to evaluate borosilicate-based nuclear waste glasses, Plodinec and Jantzen [20,21] chose a consistent set of hydration reactions which included a reaction for boric oxide hydrating to boric acid. The thermodynamic data base of Paul [2] and Garrels and Christ [12] was used as the thermodynamic input for the hydration reactions. If a stable hydration product was observed experimentally on a leached glass surface [the hydration reaction for this product usually had a higher free energy of formation than the theoretical $(\Delta G_{hyd})_i$], the free energy of formation for the observed hydration product, $(\Delta G_{hyd})_{obs}$, was preferentially used [23].

Linear relationships were determined between the logarithmic extent of hydration (log NL_{Si} released from the glass in grams of glass per square meter of glass surface area) and the calculated ΔG_{hyd} for over 300 glass dissolution experiments in deionized water [23]. The thermodynamic approach [15, 20-21], assumed that the silicate and borate components of a glass hydrated to silicic acid and boric acid respectively. For poorly durable glasses where the alkali released from the glass drove the solution pH to greater than 9.5, the logarithmic function of reaction progress versus ΔG_{hyd} was not accurate [22-23]. At pH values of >9.5, the solubility of silica and borate increases rapidly due to dissociation of silicic acid. Jantzen [22-23] demonstrated that an additional contribution to the hydration free energy based on the dissociation constants of silicic and boric acid at high pH was necessary. To account for the dissociation of silicic and boric acid at high pH, the equations below are calculated as additional contributions to ΔG_{hyd}:

for H_2SiO_3

$$\Delta(\Delta G_{hyd}) = 1.364 \left[- \log \left(1 + \frac{10^{-10}}{10^{-pH}} + \frac{10^{-21.994}}{10^{-2pH}} \right) \right] \qquad (2)$$

for H_2BO_3

$$\Delta(\Delta G_{hyd}) = 1.364 \left[-\log \left(1 + \frac{10^{-9.18}}{10^{-pH}} + \frac{10^{-21.89}}{10^{-2pH}} + \frac{10^{-35.69}}{10^{-3pH}}\right) \right] \quad (3)$$

The adjusted free energy term was statistically shown to be more highly correlated with glass durability than the uncorrected hydration free energy for over 150 glasses tested [23]. The pH-adjusted ΔG_{hyd} term is, therefore, preferentially used and glass durability can be calculated from glass composition alone or, more accurately, from glass composition and the pH of the environment.

The thermodynamic approach assumes that (1) the glass behaves as a mechanical solid solution of orthosilicate and oxide components, and that (2) the overall free energy of hydration is an additive function of the hydration reactions of the end member components. The use of additive functions of glass components, based on the solution behavior of glass, is not restricted to glass durability studies. Similar approaches have been used to calculate viscosity [27], heat capactiy [28], and the thermal expansion of glasses [29] as additive functions of composition.

The contribution of the glass compositon to the surface layer formation is fundamentally accounted for in the calculation of the hydration free energy from glass composition because (1) all glasses have some type of surface layer formation [30], (2) the type of surface layer formation is a function of the glass composition [30], and (3) the types of surface layers correlate with hydration free energy [22]. Because of the relationship of the free energy to the activities of all the species in a glass, the hydration free energy calculates the relative roles of amorphous silica dissolution as modified by surface layer formation. The data support the hypothesis of Grambow [31,32] that the dissolution of all silicate-based glasses can be described by the activity diagrams for the dissolution of amorphous silica.

Glass Durability: A Function of Glass Structure

Although the thermodynamic approach of Newton and Paul [15] assumes that a glass is composed of orthosilicate and oxide components, no correlation between glass composition and glass structure was made. The relationship between bonding, composition, and durability of crystalline and vitreous solids has been examined for over 40 years. Glass scientists such as Stevels [33,34] have attempted to relate the proportion of non-bridging oxygen atoms (NBO) in a glass network to durability. Similarily, geologists have tried to classify the relative durability (weathering classification) of silicate mineral species on the basis of structural silica-tetrahedra linkages [35,36]. Newton [37] attempted a glass durability classification based on network-building versus network-breaking and network modifying (RO) speciation.

Recent studies have demonstrated that the rate-limiting step in silica-water reactions is breakage of the structural Si-O bonds [5]. Since the reaction mechanism is directly related to the composition of the solid [13], and hence to the number of NBO bonds [33,34] and their strength [5], it is not suprising that the dynamic exchange reactions at the glass-solution interface can be described in terms of the thermodynamic equilibria [6]. This implies that the thermodynamic parameters are representations of the structural energetics of the hydration process and that the relation between the glass structure and durability is a function of the glass lattice energy. The bond strength is a component of the lattice free energy and an exact expression for the free energy of a glass has been derived and shown to be dependent only upon the concentration and energy of the bonds present in the structure [38].

Jantzen and Plodinec [22] demonstrated that the thermodynamic free energies of hydration of the orthosilicate and oxide glass components correlated with both the ionic potential (Z/r) and the ionic field strength $(F = Z/r^2)$ of these species. The relative hydration potential of the species based on $(\Delta G_{hyd})_i$, or on the ionic field strength, groups the species into network-formers, -breakers, and -modifiers. Recent investigations [39] of glass structure have hypothesized that glasses are, indeed, mixtures of silicate and oxide component clusters (the strained mixed cluster model).

The correlation of the ionic potential and the ionic field strength with the $(\Delta G_{hyd})_i$ supports the conclusion that the calculated hydration equations are the thermodynamic representations of the structural energetics of the hydration process [22]. The ΔG_{hyd} for over 150 glasses was shown [22,40] to highly correlate with the number of non-bridging oxygen bonds calculated from the glass composition, reinforcing this conclusion. Since the hydration thermodynamic approach assumes that glass structure is a primary function of glass composition, glass structure is not considered as an additional parameter affecting glass durability.

Glass Durability: A Function of Test Parameters

During laboratory experimentation, the following parameters have been shown [1] to affect glass durability:

(1) frequency of replenishing/changing the solution,
  e.g. time duration (t) of the experiment
(2) exposed surface area (SA) of the solid
(3) volume (V) of the leaching solution
(4) temperature (T) of leaching in °C
(5) type of leaching solution
(6) glass composition

The dissolution rate of species i in a glass follows a parabolic curve as a function of leaching time. The overall dissolution of the glass, expressed as the concentration dependent release of species i as a function of time, can be expressed [9] as

$$\frac{dc_i}{dt} = \frac{SA}{V}\, k_i \qquad (4)$$

where
$\quad c_i$ = concentration of the amount leached
$\quad t$ = time
$\quad SA$ = exposed surface area of the solid
$\quad V$ = volume of the leaching solution
$\quad k_i$ = rate of dissolution of species i in solution

The value of k_i can depend on solution pH, temperature, c_i, and the concentration of other species in solution. If the dissolution of glass is treated as congruent [9], then

$$\frac{dc_i}{dt} = SA\,(f_i)(k) \qquad (5)$$

where f_i = stoichiometric content of i in the glass
k = overall dissolution rate of the glass

In turn k, the dissolution rate of the glass, is affected by the test temperature. The temperature dependence of k follows an Arrhenius equation up to temperatures of $\sim 120^{\circ}C$ [41] and can be expressed [9] as

$$k = A\,e^{-E_o/RT} \tag{6}$$

where E_o = activation energy
T = test temperature
R = gas constant
A = constant.

If the solutions are undersaturated, and k is dependent primarily on the pH and the test temperature rather than on the concentrations of other components in solution, then the foward rate of dissolution can be expressed [9] as

$$\frac{dc_i}{dt} = \frac{SA}{V} f_i\,k^{+}\,(a_{H^+})^n \tag{7}$$

where k^{+} = foward rate of dissolution $k^{+} = A^{+}\,e^{-E^+/RT}$
n = effect of pH on the rate constant k (a value of ~ 1 in acid regimes and a value of 0.2-0.4 in alkaline regimes)

Static or slow flow leach tests at large SA/V ratio and long time durations permit the accumulation of glass dissolution products in the leachant to become significant, e.g. steady-state and or equilibrium saturation. As the solution concentration, c_i, approaches equilibrium with the concentration species i in the glass (f_i), precipitation of c_i from solution can occur. In mineral dissolution, a second term is added to equation 7 to represent the precipitation rate law. This term is negative since it is assumed to represent the reverse mechanism of mineral dissolution [9]. This leads to the equation

$$\frac{dc_i}{dt} = \underbrace{\frac{SA}{V} f_i\,k^{+}\,(a_{H^+})^n}_{\text{FORWARD RATE}} - \underbrace{\frac{SA}{V} f_i\,\frac{Q^m}{K_{eq}^{m}}\,k^{+}\,(a_{H^+})^n}_{\text{PRECIPITATION RATE}} \tag{8}$$

where Q = reaction activity quotient for the precipitating species
m = deviation from equilibrium determined experimentally from rate data near equilibrium

Because

$$\Delta G_r = \Delta G^{\circ}_r + RT \ln Q = RT \ln \frac{Q}{K_{eq}} \tag{9}$$

Equation 8 can be rewritten as

$$\frac{dc_i}{dt} = \frac{SA}{V} f_i\,k^{+}\,(a_{H^+})^n\,(1-e^{\,m\Delta G_r/RT}) \tag{10}$$

The general rate law expressed as equations 8 and 10 enables the extension of laboratory dissolution data and thermodynamic data to a general rate law which is applicable up to and including equilibrium. Equation 10 is analogous to expressions derived for mineral dissolution utilizing the progress variable approach and transition state theory [42]. In this latter approach, the ΔG_r is replaced by the affinity of the reaction , A, which is a measure of the steady state equilibrium achieved. The affinity of the reaction is equal to the ΔG_r divided by the reaction progress [43]. This is because the precipitation rate law depends on the solution composition [9] and in particular on the ion activity product (IAP) and the solubility product (K_L) of the precipitating species.

A detailed mathematical treatment where the effects of the solution composition are considered is given by Grambow [43]. The saturation index of the solution (IAP/K_L) is used to approximate the deviation of the solution from equilibrium, e.g. the steady state equilibrium achieved for a given experimental situation. The affinity of the rate limiting reaction (the measure of deviation from equilibrium) is proportional to the IAP/K_{eq} where K_{eq} is the equilibrium constant for the rate limiting reaction.

In Grambow 's [43] approach, the affinity of the rate limiting reaction , A*, describes the effects of solution saturation on glass dissolution, while the activation energy term describes the influence of temperature. By using simplifying assumptions and integrating the general rate equation (of the type given in equation 10) a first order rate equation of the type shown below can be derived:

$$c_i \quad = \quad c_s + (c_o - c_s) \; e^{-k+(SA/V)t} \tag{11}$$

where
c_s =   saturation concentration of c_i
c_o =   initial concentration of ci
k^+ =   foward rate of dissolution $k^+ = A^+ e^{-E+/RT}$

The overall rate of dissolution of the glass, k, is proportional to $(SA/V)(t)(\Sigma \, a_i)(k^+/K_{eq})$ where a_i is the activitiy of the species taking place in the reaction. Experimentally, the time-dependent release of an element from a given glass to the leachate was found to be a smooth function of the $(SA/V)t$ parameter [44,45].

In Grambow's approach [43] the influence of glass composition and solution pH are considered to be expressed in the Gibb's free energy term which is related to the affinity and to the saturation concentrations through the activities of the species in solution. In Lasaga's approach [9] the pH is considered to be a constant because of the buffering capacity of most natural environments (groundwaters). Alternatively, Lasaga considers the activities of the species to be constant at steady state. Since the activity-pH diagrams provide the fundamental correlation between minimum solubility of a species in solution and the free energy [12, 24, 46], these approaches are reasonable. The rate equations simplify to the type given in equation 11.

EXPERIMENTAL

The durability of 55 nuclear waste glasses were compared to 100 natural and man-made glasses in standard laboratory tests. Initially, all parameters except the glass composition was kept constant. Glass monoliths with a geometrically measured surface area of 4 cm^2 were immersed in 40 cm^3 of high-purity water (ASTM Type I) according to the MCC-1 leach test protocol [47]. In this manner, the SA/V ratio was always kept constant. The durability test was performed at 90°C for 28 days. All the durability tests were run in duplicate.

In later studies, the glass composition was kept constant by choosing a representative "reference set" of about 10 glasses. The test temperature was kept constant at 90°C, but the test duration was varied. Glass monoliths and crushed glasses were tested at various test durations. Crushed glasses weighing 1.5 grams (same weight of glass used in the glass monolith tests) were immersed in 40 cm^3 of high-purity water (ASTM Type I) according to the MCC-3 leach test protocol [47]. The SA/V ratio was varied by testing glasses crushed to various mesh sizes. The solutions were not filtered and the fines were not removed from the crushed glass by an alcohol wash. This is thought to contribute to some of the observed variability in the data. The details are given elsewhere [23].

Elemental concentrations in solution were measured by inductively coupled plasma (ICP) and by atomic adsorption (AA) spectroscopy. The concentrations are reported as normalized elemental mass losses, e. g. NL_i, released from the glass in grams of glass per square meter of glass surface area) according to the MCC protocols [47]. This has the advantage that the release concentrations in parts per million are normalized by the weight fraction of that element present in the glass by the formalism

$$NL_i = \frac{C_i}{F_i \cdot (SA/V)} \tag{12}$$

where

$$NL_i = \text{normalized elemental mass loss } (g_{glass}/m^2)$$
$$C_i = \text{concentration of element "i" in the solution } (g_i/m^3)$$
$$F_i = \text{fraction of element "i" in the glass } (g_i/g_{glass})$$
$$SA = \text{specimen surface area } (m^2)$$
$$V = \text{solution volume } (m^3)$$

The pH of the leachates was measured: for experiments in high-purity water, the pH excursions were considered to be controlled by the glass composition as discussed above.

Elemental compositions of all the glasses were determined by dissolution in HCl/HF or Na_2O_2 followed by ICP and AA solution analyses. All compositions were determined as weight percent oxides. All the compositions summed to 100 ± 5 wt%.

RESULTS

Glass Durability: A Function of Glass Composition

Over 150 different glasses were leached in duplicate by the MCC-1 test protocol. These included natural obsidians, tektites, basalts, pure SiO_2, Pyrex, modern window glass, and simulated medieval window glasses from the European Science Foundation (ESF). Four actual ancient Roman and Islamic glasses (Jalame ca. 350 A. D., Nishapur 10-11th century A. D., and Gorgon 9-11th century A.D.) obtained from the Corning Museum of Glass were also included in this study. The ΔG_{hyd} was calculated from the analyzed glass compositions and the solution pH. Statistically determined regression equations and the 95% upper and lower confidence limits were determined [23-24] for binary combinations of the following variables: ΔG_{hyd}, log(NL_{Si}), log(NL_B), and -log(H^+) or pH. Logarithmic concentrations were used throughout the statistical analysis because the ion concentrations are assumed to be proportional to the ideal ion activities in the thermodynamic treatment [24].

A simple linear regression of the ΔG_{hyd} and $\log(NL_{Si})$ data demonstrated that glass durability could be determined from glass composition for the 304 experimental data points (Figure 1a). The more negative the ΔG_{hyd} term, the less durable the glass and the more Si is released to solution. Using this approach, the durability of the most durable nuclear waste glasses is ~10^6 years by comparison with the durability of basalts of ~10^6 years [22]. These waste glasses are slightly less durable than the high-temperature tektite and obsidian glasses. The least durable waste glasses are comparable to the most durable simulated medieval window glasses of ~10^3 years. In this manner, the durability of nuclear glasses can be interpolated to be >10^3 years and $\leq 10^6$ years.

The computer generated equation of best fit relating glass composition to silicon released from the glass is plotted in Figure 1 and the mathematically determined slope is -0.2240. The computer-calculated 95% confidence interval is shown by the dotted lines. The statistical analysis also revealed that the primary contribution to the 95% confidence interval was from the ΔG_{hyd} term: errors in glass analysis are more significant than errors in leachate analyses [23].

Since many natural and man-made glasses do not contain boron, only 140 experimental observations (70 glasses) could be statistically fit (Figure 1b). Boron release follows a pattern similar to that of silicon: the more negative the ΔG_{hyd} term, the less durable the glass and the more boron is released to solution. The relative positions of the obsidian, tektite, nuclear waste glasses, and the medieval window glasses remains the same.

The slope relating ΔG_{hyd} and $\log(NL_B)$ is -0.2795. This is similar to the -0.2240 slope calculated for the relation between ΔG_{hyd} and $\log(NL_{Si})$. The high silica glasses, including the tektites and obsidians, contain very little boron and, hence, the positive free energy portion of the curve has a poorer statistical fit than the negative portion, which alters the slope somewhat. Since the slopes relating ΔG_{hyd} to $\log(NL_{Si})$ and to $\log(NL_B)$ are similar, it is not suprising that a plot of $\log(NL_{Si})$ and $\log(NL_B)$ has a slope of ~1 [23,24]. This is anticipated for glasses which undergo congruent dissolution. Although, the regression equations have similar slopes, the absolute value of $\log(NL_B)$ is greater than $\log(NL_{Si})$ for a given glass as predicted from the relative ion activities of these solution species.

Newton and Paul [15] leached ground ESF medieval window glasses in water at 25°C. The glass contacted the solution for only 24 hours and the amount of K_2O extracted was measured. A plot of the calculated ΔG_{hyd} and log K_2O in ppm gave a slope of -0.212 [2]. The same ESF medieval window glassses were leached by the MCC-1 procedure and are included in Figure 1a. Since they do not contain boron, they do not appear in Figure 1b. A ΔG_{hyd}-$\log(NL_{Si})$ plot for the nine ESF glasses studied yields a slope of -0.208, similar to the slope obtained by Newton and Paul for K_2O release. Bibler and Jantzen [48] have shown that Si, B, Na, and K released to solution during MCC-3 type crushed glass tests all correlate well with ΔG_{hyd}. The hydration thermodynamic model is, therefore, sufficiently sensitive to reaction progress measured as release concentrations.

Newton and Paul [15] also demonstrated that the free energy of hydration appeared to correlate with the logarithm of the loss of thickness of various glasses measured in mm/century. The effects of long-term weathering were simulated by immersing the glasses in water of pH 7 at 25°C. This correlation gave a slope of about -0.289, in agreement with the data shown for the response of ΔG_{hyd} with K_2O in the leachate solutions of crushed glass tests [15] and with $\log(NL_{Si})$. Analysis of ten of these simulated ESF glasses which were buried in a limestone mound in Ballidon, UK (pH~9.5) for 5 years [49,50] also correlated with the ΔG_{hyd} [26,51]. Since the pH of the environment was kept constant, the ΔG_{hyd} could be calculated from the glass composition alone or from composition and groundwater pH. The depths of attack were not measured very accurately [50] and a slope of -0.421 was obtained. When the laboratory release rate, NL_{Si}, was plotted against the in-situ depth of attack for these same glasses, a correlation with a slope of ~1 was obtained.

The relative durabilities of the ESF medieval window glasses predicted from ΔG_{hyd} are the same when plotted against

(1) K_2O released to solution in a 24 hour laboratory experiment
(2)   Si released to solution in a 28 day laboratory experiment
(3)   loss of thickness observed in "long-term" laboratory experiments
(3)   depth of attack observed in 5 year in-situ burial experiments

More importantly, the relative durabilities of the medieval window glasses predicted by hydration thermodynamics are the ones observed to occur in nature during weathering [15].

The hydration thermodynamic model was also applied to in-situ measured depth of attack for waste glasses which had been exposed to silica saturated groundwaters for two years [[52]. The waste glasses had been buried in a granitic mine in Stripa, Sweden to simulate burial of waste glass in a granitic repository. The glass monoliths were emplaced in boreholes in the mine which were allowed to fill with the natural silicate groundwater. The glass-groundwater environment in the borehole was kept at 90°C to simulate the heat of radioactive decay. After 2 years burial, the depth of attack was measured accurately by secondary ion mass spectroscopy (SIMS) analysis. The slope of in-situ depth of attack and ΔG_{hyd} for the waste glasses buried in Stripa was -0.270 [52], similar to the slopes given for the elemental release concentrations in the high-purity water experiments and the ESF glass depths of attack.

Glass Durability: A Function of the Kinetic (SA/V)t Parameters

The glass composition was held constant by examining a "reference set" of glasses at different (SA/V)t test conditions. The glass durabilities at high (SA/V)t followed the same linear trend as the glass monolith tests [low (SA/V)t] when plotted as a function of ΔG_{hyd} (Figure 2a). The amount of silicon released to the solution is a function of the mass fraction of that element in the glass and of the SA/V parameter (Equation 12). The SA/V term in the denominator of Equation 12 dominates the calculation of NL_i and hence the results of the crushed glass leach tests cluster regardless of the length of time of the test. Moreover, the crushed glasses appear to be releasing less silicon to solution than the monolithic samples. When the silicon content is plotted in ppm, the increased dissolution of the crushed glasses is readily observed (Figure 2b).

The results of the crushed glass tests can be more easily interpreted if the silicon release is plotted against the (SA/V)t parameter as previously suggested [44,45]. The sequence of parabolic curves is plotted against ppm silicon released to solution in Figure 3. The silicon relased to solution increases in the relative order predicted by the calculated ΔG_{hyd} for these glasses. The same durability sequence of the glasses, at any (SA/V)t can also be observed in Figure 2a.

The range of saturation values known [53] for amorphous silica at 90°C are overlain on Figure 3. Glasses with $\Delta Ghyd > -9$ kcal/mole require longer residence times or smaller particles sizes (larger SA) in order to approach stready state saturation with respect to silica, e.g. for the solution concentrations to be close to the saturation values for amorphous silica . For glasses which are poorly durable the alkali is quickly released to solution and drives the pH to extreme alkaline conditions. These extreme conditions accelerate glass matrix dissolution and hence, the silicon release to solution surpasses the reference saturation level even at small (SA/V)t.

The slopes of $\log(NL_{Si})$-ΔG_{hyd} for monolithic tests [low (SA/V)t] and crushed glass tests [high (SA/V)t] were the same [23]. This occurs because the test geometry alters only the kinetic reactivity parameters, e.g. surface area (SA), leachant volume (V), and the length of time that the glass has contacted the leachant (t). The kinetic reactivity parameters alter the rate at which the

saturation ion concentrations are approached. The slope represents the natural logarithm of the theoretical slope, (1/2.303 RT), for the rate of glass dissolution [43].

Measures of reaction progress such as $\log(NL_{Si})$ in g/m^2 or $\log(Si)$ in ppm have been shown (Figure 3) to be a function of $(SA/V)t$ for the sequence of "reference glasses" discussed above. The $\log(NL_{Si})$ versus $(SA/V)t$ curves for the various glasses increase in the order predicted by their relative ΔG_{hyd} values. Since $\log(NL_{Si})$ is a function of both $(SA/V)t$ and ΔG_{hyd}, a plot of over 120 data points collected on the "reference set" of glasses was plotted in three dimensional $\log(NL_{Si})$-$(SA/V)t$-ΔG_{hyd} space. A scatter plot of the data is shown in Figure 4a). The $(SA/V)t$ axis increases from left to right so that the parabolic curves represented by each glass appear reversed as shown in the inset. A statistically interpolated spline function was fit to the data and the data was found to form a plane in three-dimensional $\log(NL_{Si})$-$(SA/V)t$-ΔG_{hyd} space (Figure 4b). The surface shown in Figure 4b was derived from the data in Figure 4a with the same axial reprentations. The plane is fairly flat with the most curvature at the low $(SA/V)t$ values which represent the steep portions of the parabolic curves. The slopes of the ΔG_{hyd}-$\log(NL_{Si})$ plots for monolithic tests [low $(SA/V)t$] and for crushed glass tests [high $(SA/V)t$] are similar because they intersect the three-dimensional plane at constant $(SA/V)t$.

DISCUSSION AND CONCLUSIONS

The durability of a glass is a function of its kinetic and thermodynamic stability in solution. The relationship between the kinetic and thermodynamic aspects of glass durability can be understood when the relative contributions of glass composition and imposed test conditions are delineated. Glass durability has been shown to be a function of the thermodynamic hydration free energy which can be calculated from the glass composition. Hydration thermodynamics also furnishes a quantitative frame of reference to understand how the various test parameters given below affect glass durability:

(1) frequency of replenishing/changing the solution,
    e.g. time (t) of the experiment
(2) exposed surface area (SA) of the solid
(3) volume (V) of the leaching solution
(4) temperature (T) of leaching in °C
(5) type of leaching solution
(6) glass composition

By varying glass composition and holding the other parameters constant, the thermodynamic role of glass composition and surface layer formation can be evaluated. Once this is determined, the same glass compositions can be used to evaluate the effects of the other parameters which are the test variables. The test variable $(SA/V)t$ varies the rate at which the solution approaches saturation and hence varies the saturation index (and the afffinity of the solution). In the kinetic approach of Grambow [43], the saturation index and the affinity of a solution are used as approximations of the deviation of the solution from equilibrium. The influence of the type of leaching solution is also accounted for in the saturation index which is determined from the IAP (ion activity product) and the K_L (the solubility product of a species precipitating from the solution once saturation has been exceeded). The activation energy term in the kinetic treatment is a function of the test temperature. These five parameters essentially determine the steady state equilibrium achieved by a given experimental geometry, test duration, and test temperature. The role of glass composition and solution pH are considered to be expressed in the thermodynamic Gibb's free energy term which is proportional to the affinity and to the saturation concentrations through the activities of the species in solution [43].

The combined kinetic and thermodynamic contributions to glass durability have been verified experimentally by defining the plane in three dimesional ΔG_{hyd}-concentration-(SA/V)t space at constant temperature. At constant kinetic conditions, e.g. test geometry (SA/V), temperature, and test duration , the three dimensional plane is intersected at constant (SA/V)t and the ΔG_{hyd}-concentration plots for glass as a function of glass composition have similar slopes. The slope represents the natural logarithm of the theroetical slope, (1/2.303 RT), for the rate of glass dissolution.

Hydration thermodynamics has wide applicability to the prediction of the durability of natural, ancient, modern, and nuclear waste glass. The predicted durabilities correlate with those observed in nature and give a means for interpolation of the long-term durability of nuclear waste, commercial, and archeological glasses. Combined with the thermodynamic concepts of Pourbaix diagram construction, the hydration thermodynamic approach can predict the response of glass to environmental conditions, e.g. solution pH and oxidation potential as well.

ACKNOWLEDGEMENTS

REFERENCES

1.   A. Paul, Chemistry of Glasses, Chapman and Hall, NY (1982).
2.   A. Paul, J. Mat. Sci., 12, 2246 (1977).
3.   R. J. Charles, J. Appl. Phys., 29, 1549 (1958).
4.   R.K. Iler, Colloid Chemistry of Silica and Silicates, Cornell Univ. Press, Ithaca, NY (1955).
5.   J. D. Rimstidt and H. Z. Barnes, Geochem. Cosmochem. Acta, 44, 1683 (1980).
6.   R. W. Douglas and T. M. M. El-Shamy, J. Am. Ceram. Soc., 50, 1 (1967).
7.   B. Grambow, Glastechnische Berichte, 56, 566 (1983).
8.   R. M. Wallace and G. G. Wicks, Scientific Basis for Nuclear Waste Management, VI, D. G. Brookins (Ed.) 23 (1983).
9.   A. C. Lasaga, "Chemical Kinetics of Water-Rock Interactions", J. Geophys. Res., 89, 4009 (1984).
10.   J. A. Kittrick, ACS Symposium Series 93, 401 (1979).
11.   M. Pourbaix, "Atlas of Electrochemical Equilibria in Aqueous Solutions", Eng.Trans. by J.A.Franklin, NACE,Houston, TX,644p (1974).
12.   R. M. Garrels and C. L. Christ, Solutions, Minerals, and Equilibria, Harper and Row, NY 435p. (1965).
13.   H. C. Helgeson and F. T. Mackenzie, Deep Sea Res., 17, 877 (1970).
14.   J. D. Rimstidt, The Kinetics of Silica-Water Reactions, Unpublished PhD Thesis, The Pennsylvania State University, 135p (1979).
15.   R. G. Newton and A. Paul, Glass Technology, 21, 307 (1980).
16.   US Dept. of Energy, Waste Form Selection for SRP High-Level Waste, Report No. DOE/EA-0179 (1982).
17.   R. C. Ewing, Sci. Basis for Nuclear Waste Mgt., I, G. J. McCarthy (Ed.), Plenum Press, NY, 57 (1979).
18.   G. Malow and R. C. Ewing , Sci. Basis for Nuclear Waste Mgt., III, J. G. Moore (Ed.), Plenum Press, NY, 315 (1981).

19. G. Malow, W. Lutze and R. C. Ewing, J. Non-Cryst. Solids, 67, 305 (1984).

20. M. J. Plodinec, C. M. Jantzen, and G. G. Wicks, Adv. in Ceramics, V.8, G. G. Wicks and W. A. Ross (Eds.), Am. Ceram.Soc., Columbus, OH, 491 (1984).

21. M. J. Plodinec, C. M. Jantzen and G. G. Wicks, Sci. Basis for Nuclear Waste Mgt., VII, G. L. McVay (Ed.), North-Holland, NY,755(1984).

22. C. M. Jantzen and M. J. Plodinec, J. Non-Cryst. Solids, 67, 207 (1984).

23. C. M. Jantzen, Adv. in Ceramics, V.20, D. E. Clarke, et. al. (Eds.) Am. Ceram. Soc., Columbus, OH, 703 (1986).

24. C. M. Jantzen, Nuclear Waste Glass Durability: I. Predicting Environmental Response from Thermodynamic (Pourbaix) Diagrams, DP-MS-87-2, J. Am. Ceram. Soc. (in press).

25. C. M. Jantzen, Pourbaix Diagram for the Prediction of Waste Glass Durability in Geologic Environments, Sci. Basis for Nuclear Waste Mgt., XI, M. J. Apted and R.E. Westerman (Eds.), Materials Research Society, Pittsburgh, PA, DP-MS-87-77 (in press).

26. C. M. Jantzen, Prediction of Glass Durability as a Function of Environmental Conditions, Materials Research Symposium on Materials Stability and Environmental Degredation, A. Barkatt et al (Eds), Mateials Research Society, Pittsburgh, PA, DP-MS-87-157 (in press).

27. Y. Bottinga and D. F. Weill, Am. J. Sci., 272, 438 (1972).

28. P. Richert and Y. Bottinga, C.R. Acad. Sci. Paris, 295, 1121 (1982).

29. J. Hormadaly, J. Non-Cryst. Solids, 79, 311 (1986).

30. L.L. Hench and D.E. Clark, J. Non-Cryst. Solids, 28, 83 (1978).

31. B. Grambow, Adv. in Ceramics, V. 8, G. G. Wicks and W. A. Ross (Eds.), The American Ceramic Society, Columbus, OH, 474 (1984).

32. B. Grambow and D. M. Strachan, Sci. Basis for Nuclear Waste Mgt., VII, G. L. McVay (Ed.), North-Holland, New York, 623 (1984).

33. J. M. Stevels, Progress in the Theory of the Physical Properties of Glass, Elsevier, NY (1948).

34. J. M. Stevels, Phillips Tech. Rev., 22, 300 (1960/61).

35. F. J. Pettijohn, J. Geology, 49, 610 (1941).

36. F. C. Loughnan, Chemical Weathering of the Silicate Minerals, Elsevier, NY 141p. (1969).

37. R. G. Newton, J. Glass Studies, 17, 161 (1975).

38. D. G. Howitt, Phys. Chem. Glasses, 22, 29 (1981).

39. C. H. L. Goodman, Glass Technology, 28 [1]. 19 (1987).

40. C. M. Jantzen, Nuclear Waste Glass Durability: II. Structural Considerations, J. Am. Ceram. Soc. (in prep).

41. G. G. Wicks, W.C. Mosley, P.G. Whitkop, and K. A. Saturday, J. Non-Cryst. Solids, 49, 413 (1982).

42. P. Aagaard and H.C. Helgeson, Am. J. Sci., 281, 237 (1982).

43. B. Grambow, Sci. Basis for Nuclear Waste Mgt., VIII, C.M. Jantzen, J. A. Stone, and R. C. Ewing (Eds), Materials Research Society, Pittsburgh, PA, 15 (1985).

44. V. M. Oversby, Leach Testing of Waste Forms: Interrelationship of ISO and MCC Type Tests, in Workshop on Leaching Mechanisms of Nuclear Waste Forms, PNL-4382, Richland, WA, 97-129 (1982).

45. L. R. Pederson, C. Q. Buckwalter, G. L. McVay and B. L. Riddle, Sci. Basis for Nuclear Waste Mgt., VII, D. G. Brookins (Ed.), North Holland , New York, 47 (1983).

46. D. Cooke and A. Paul, J. Br. Ceram. Soc., 77, 104 (1978).

47. J.E. Mendel (compiler), U.S. DOE Report DOE/TIC-11400 (1981).

48. N. E. Bibler and C. M. Jantzen, A Product Consistency Durability Test for SRP Nuclear Waste Glass, DP-MS-87-174 (1988).

49. R. G. Newton, Glass Technology, 26[6], 293 (1985).

50. R. G. Newton, More Results from the Ballidon Glass Burial Experiment, Glass Technology (in press).

51. C. M. Jantzen and R. G. Newton, Application of Hydration Thermodynamics to the Durability of Medieval Window Glasses (in preparation).

52. M. J. Plodinec, MRS Bulletin, XII [5], 61 (1987).

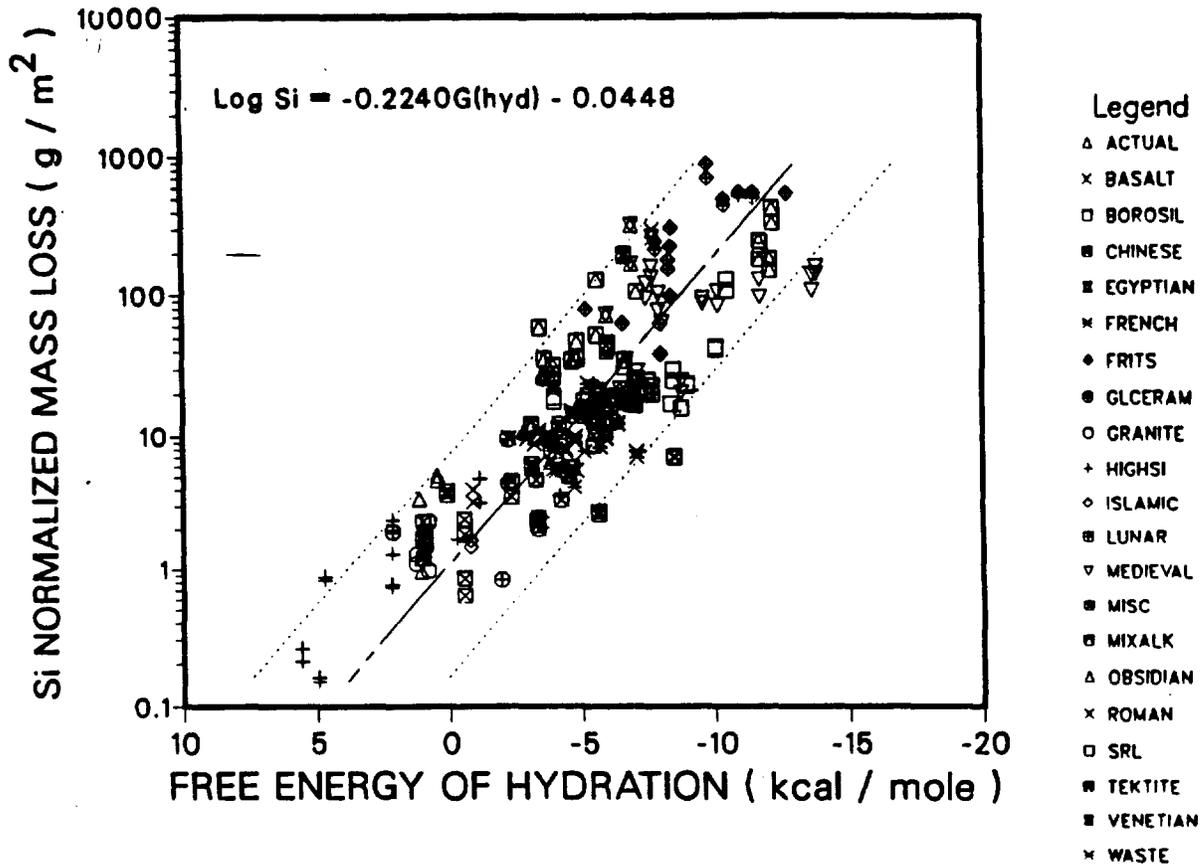53. G.W. Morey, R.O. Fournier and J.J. Rowe, J. Geophys. Res., 69, 1995 (1964).

Figure 1a   Linear regression plot of over 300 experiments relating glass composition (ΔG_{hyd}) to glass durability (expressed as Si lost from the glass to the leachate solution in a 28 day laboratory experiment).
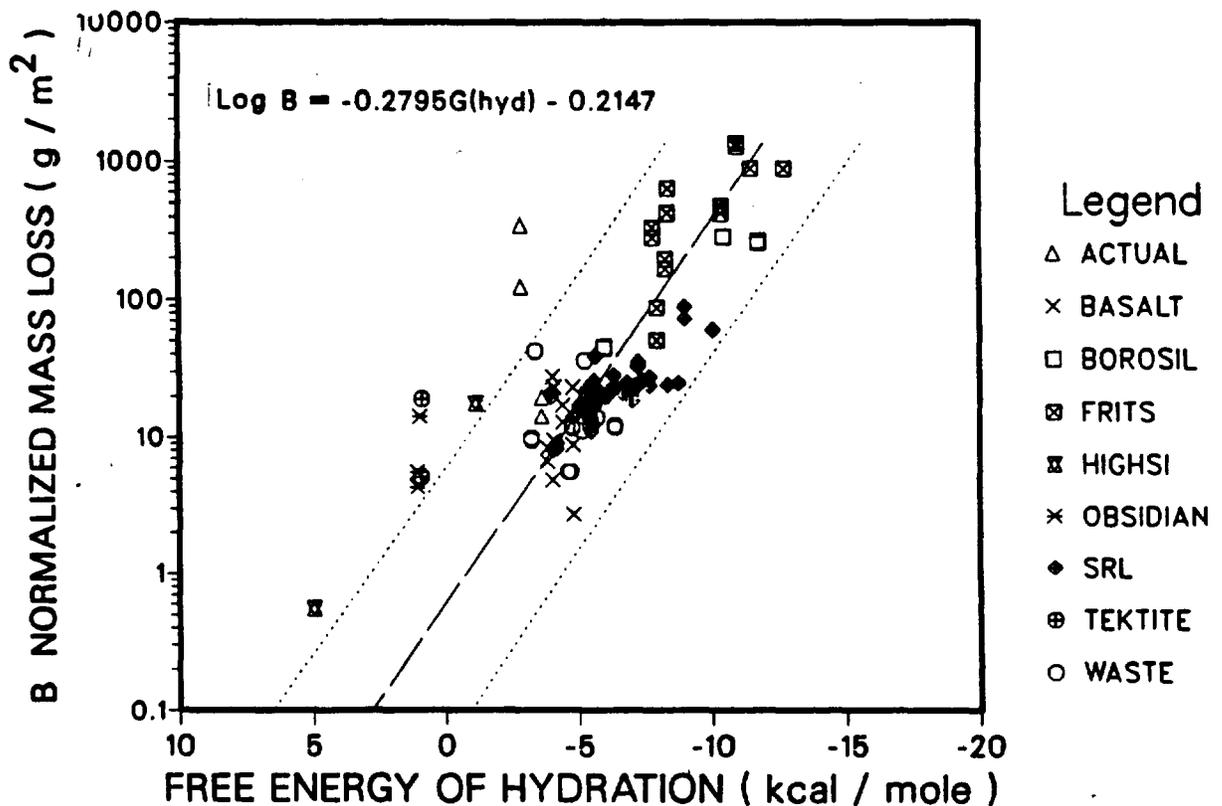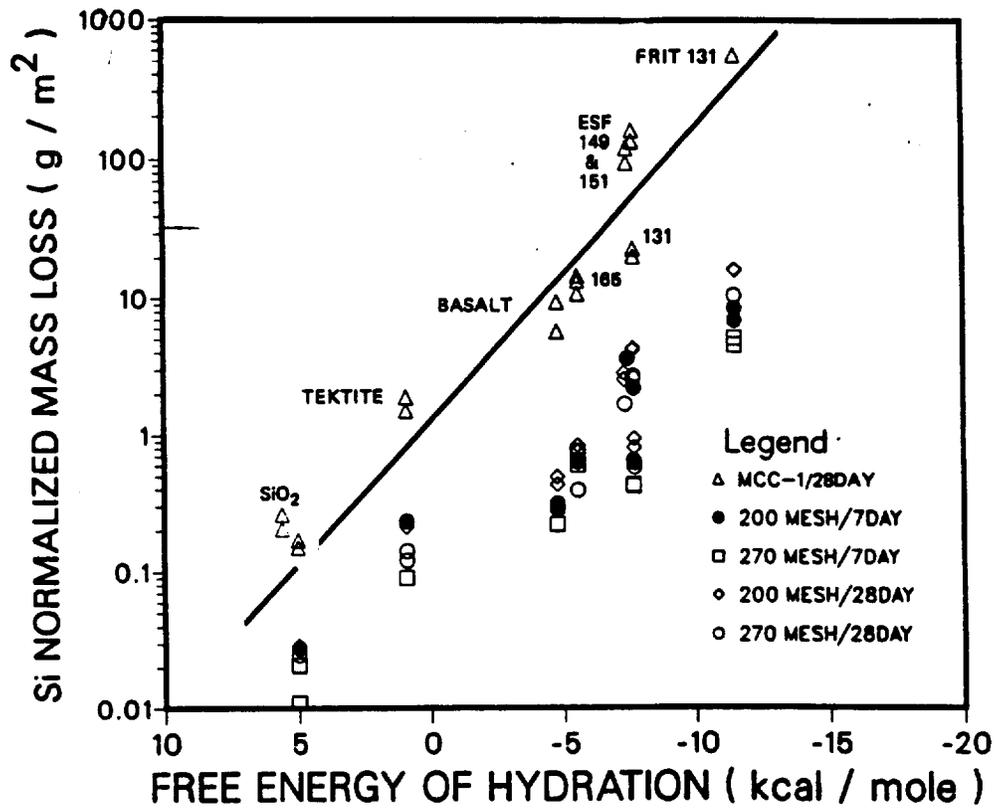

Figure 1b   Linear regression plot of 140 experiments on boron-containing glasses relating glass composition (ΔG_{hyd}) to glass duarbility (expressed as B lost from the glass to the leachate solution in a 28 day laboratory experiment).

Figure 2a   Free energy of hydration versus silicon release for a "reference set" of glass monoliths and crushed glasses. Note that the silicon release is given in g/m².
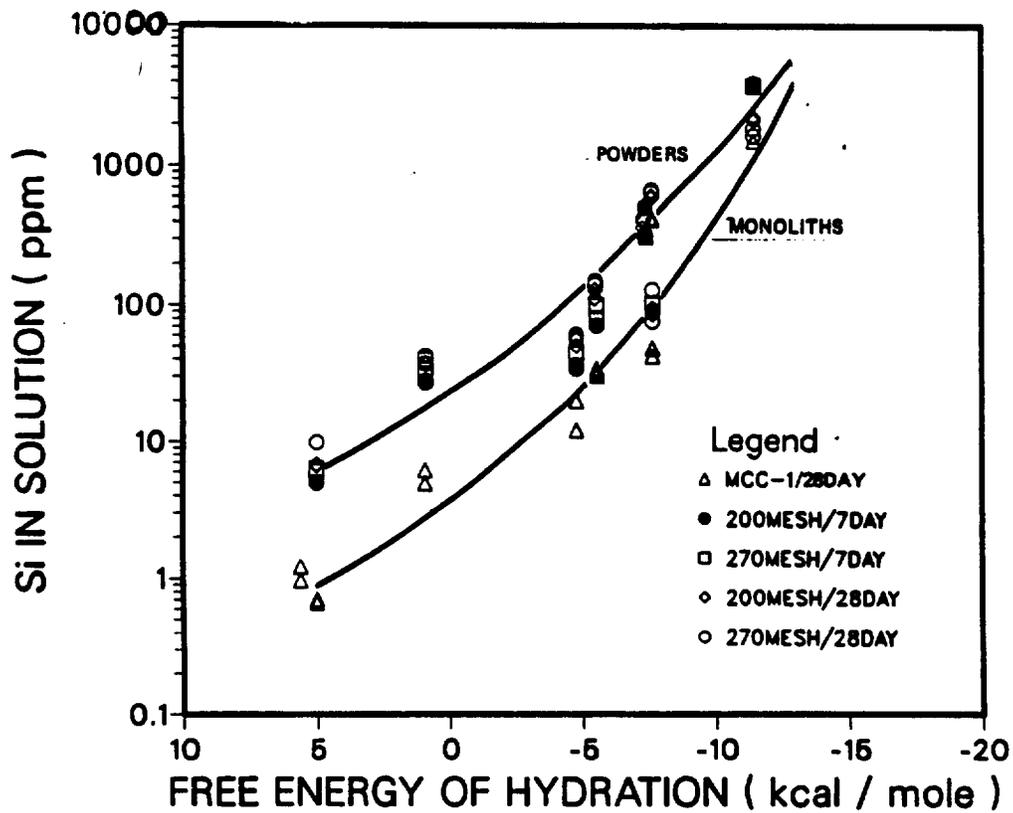

Figure 2b   Free energy of hydration versus silicon release for the "reference set" of glass monoliths and powders. Note that the silicon release is given in ppm for comparison with Figure 2a.
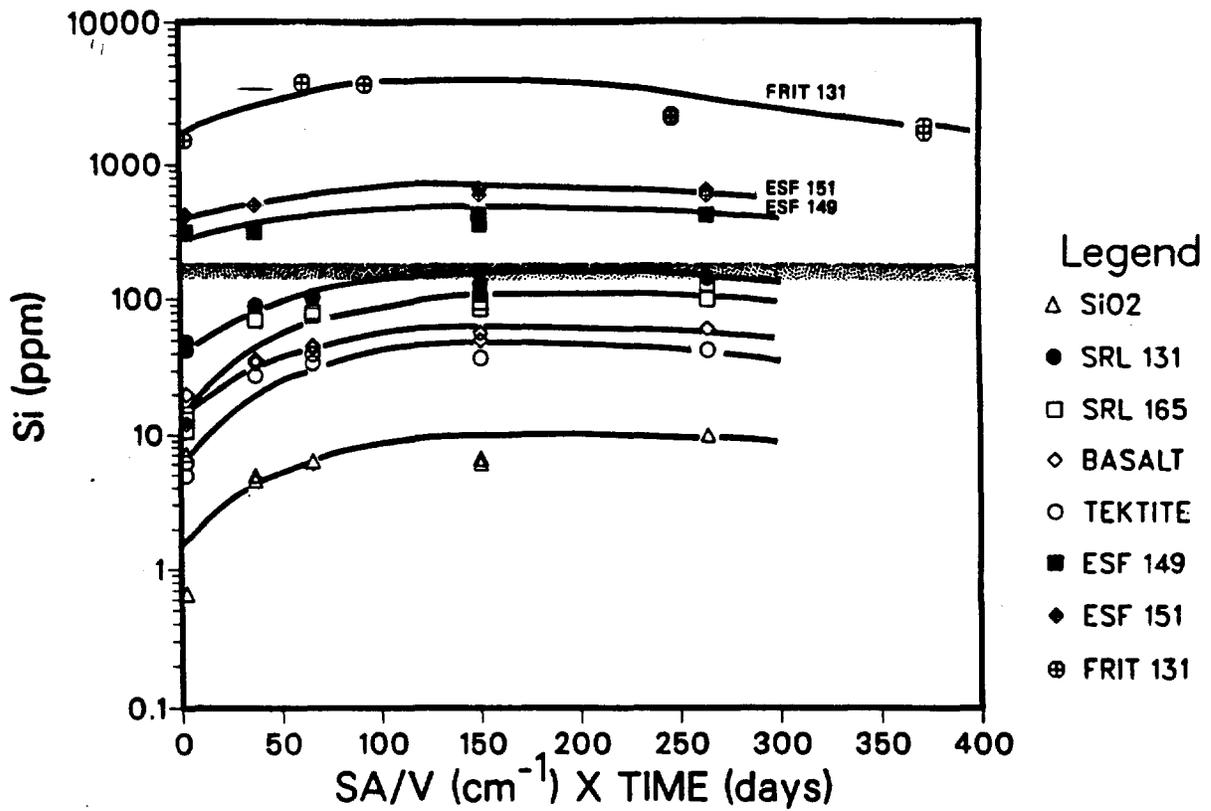
Figure 3   (SA/V)•t parameter plotted versus silicon release to solution in ppm for the "reference set" of glasses indicated. The shaded region is the reference silica saturation value at 90°C given in reference 53.
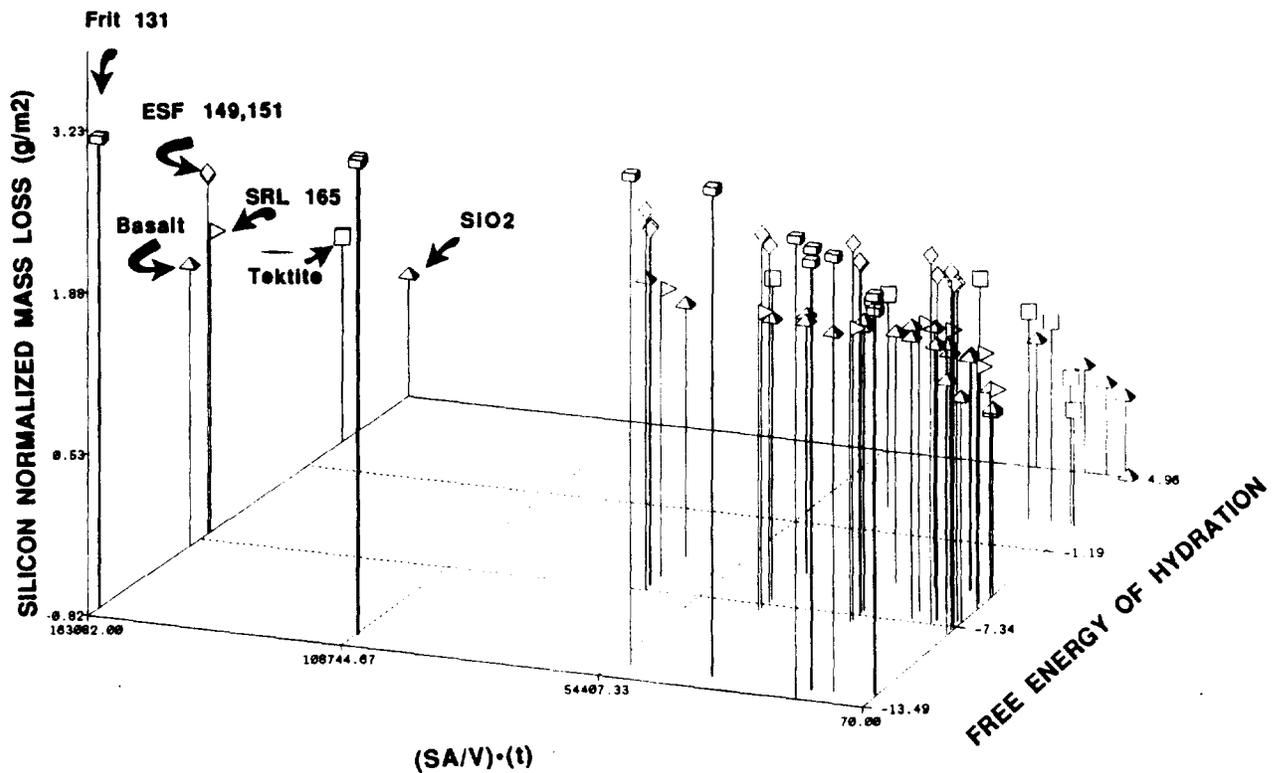
Figure 4a   Scatter plot of the data from Figure 3 plotted in log(NL_{Si})-(SA/V)•t-ΔG_{hyd} space. Note that the symbols for any one glass form a parabolic shape from left to right along the (SA/V)•t axis and that the glasses along the log(NL_{Si})-ΔG_{hyd} plane follow a linear trend as defined in Figure 1a.
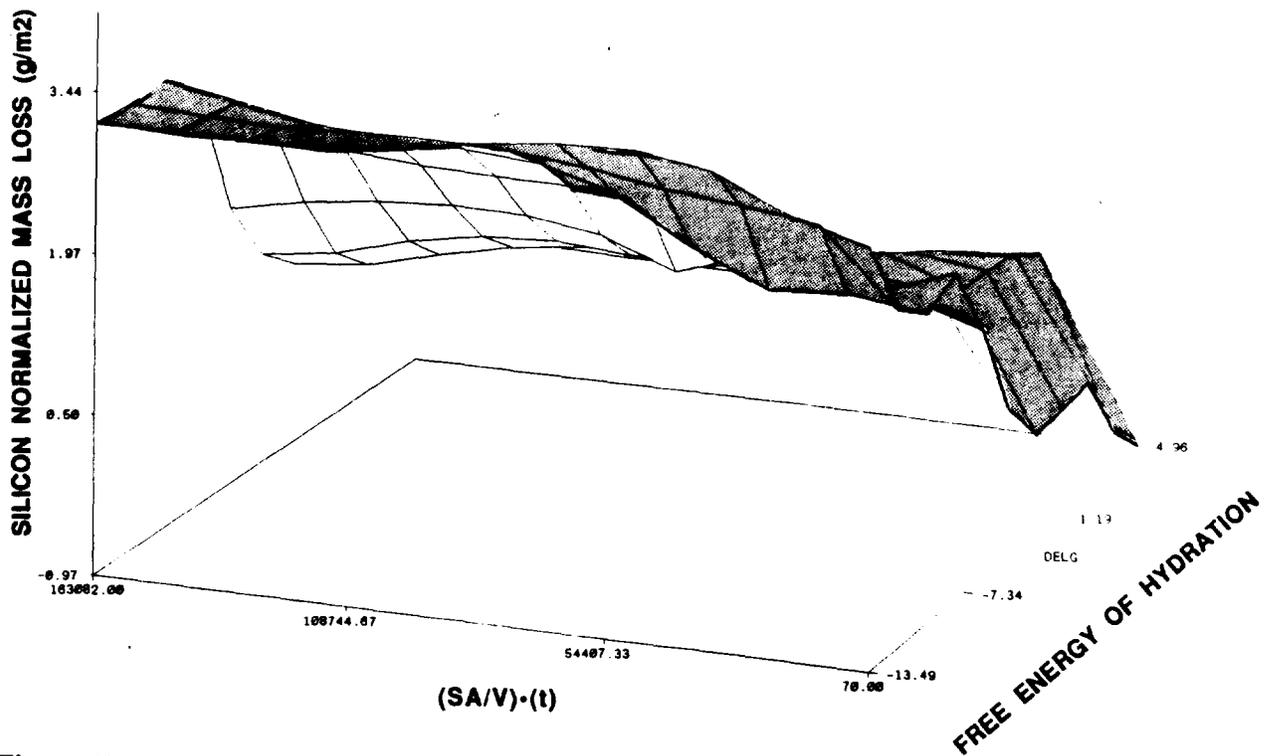

Figure 4b   A statistically interpolated spline function fit to the 122 data points of Figure 4a. The surface shows the greatest curvature at low (SA/V)•t in response to the parabolic trends delineated by each glass as a function of (SA/V)•t. The slopes of the log(NL_{Si})-ΔG_{hyd} are the same for glass monoliths (low SA/V•t) and for crushed glasses (high SA/V•t) because they intersect the three-dimensional plane at constant (SA/V)•t.