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PREDICTION OF GLASS DURABILITY AS A FUNCTION OF ENVIRONMENTAL CONDITIONS

by

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PREDICTION OF GLASS DURABILITY AS A FUNCTION OF ENVIRONMENTAL CONDITIONS

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ABSTRACT

A thermodynamic model of glass durability has been applied to natural, ancient, and nuclear waste glasses. The durabilities of over 150 different natural and man-made glasses, including actual ancient Roman and Islamic glasses (Jalame ca. 350 A. D., Nishapur 10-11th century A. D., and Gorgon 9-11th century A.D.), have been compared. Glass durability has been shown to be a function of the thermodynamic hydration free energy, ΔG_{hyd}, which can be calculated from glass composition and solution pH. Using this approach, the durability of the most durable nuclear waste glasses examined was $\sim 10^6$ years by comparison with the durability of the natural basalts of $\sim 10^6$ years. The least durable waste glass formulations were comparable in durability to the most durable simulated medieval window glasses of $\sim 10^3$ years. In this manner, the durability of nuclear waste glasses has been interpolated to be $\sim 10^6$ years and no less than 10^3 years.

Hydration thermodynamics have been shown to be applicable to the dissolution of glass in various natural environments. Groundwater-glass interactions relative to geologic disposal of nuclear waste, hydration rind dating of obsidians, and/or other archeological studies can be modeled, e.g. the relative durabilities of six simulated medieval window glasses have been correctly predicted for both laboratory (one month) and burial (5 year) experiments.

The effects of solution pH on glass dissolution has been determined experimentally for the 150 different glasses and can be predicted theoretically by hydration thermodynamics. The effects of solution redox (oxidation potential expressed as Eh) on dissolution of glass matrix elements such as Si and B have been shown to be minimal. The combined effects of solution pH and Eh have been described and unified by construction of thermodynamically calculated Pourbaix (pH-Eh) diagrams for glass dissolution. The Pourbaix diagrams have been quantified to describe glass dissolution as a function of environmental conditions by use of the data derived from hydration thermodynamics.

INTRODUCTION

The durability of a glass is a function of both 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. A logarithmic relationship was found between a hydration free energy, which was calculated from glass composition, and such measures of reaction progress as K_2O released from the glass and "loss of thickness" of the glass measured in mm/century.

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 [24-25] 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. Jantzen's construction of Pourbaix diagrams for glass dissolution has conceptually and quantatively unified the dissolution behavior of all glasses as a function of the pH-Eh conditions imposed in natural environments. The results of these studies will be reviewed.

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

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

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 verses 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

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

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.

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 [27,28] 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 [29,30]. Newton [31] 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 [27,28] 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 [32].

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 [33] 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 [22,34] 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.

EXPERIMENTAL

Parameterization of the Factors Affecting Glass Durability

During laboratory experimentation, the following parameters are known [1] to affect glass durability:

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

Experimental Details

Initially, parameters 1-4 were kept constant and only the glass composition was varied. Over 150 different glasses of widely varying compositon were examined. 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 [35]. In this manner, the SA/V ratio was always kept constant. The durability test was performed at 90°C for 28 days duration. 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 time durations. Crushed glasses weighing 1.5 grams were immersed in 40 cm^3 of high-purity water (ASTM Type I) according to the MCC-3 leach test protocol [34]. The SA/V ratio was varied by testing glasses crushed to various mesh sizes. 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 [34]. 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

$$NL_i = \frac{C_i}{F_i \bullet (SA/V)} \qquad (4)$$

where
NL_i = normalized elemental mass loss (g_{glass}/m^2)
C_i = concentration of element "i" in the solution (g_i/m^3)
F_i = fraction of element "i" in the glass (g_i/g_{glass})
SA = specimen surface area (m^2)
V = 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. For simulated groundwater leachants, the measured pH was found to be controlled by the groundwater chemistry for even the most alkali-rich (poorly durable) glasses [26].

RESULTS AND DISCUSSION

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 Scienc 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 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 (Figure 2a), similar to the slope obtained for K_2O release. Bibler and Jantzen [36] 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 [37,38] also correlated with the ΔG_{hyd} [39]. 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 [38] and a slope of -0.421 (Figure 2b) 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 (Figure 2c).

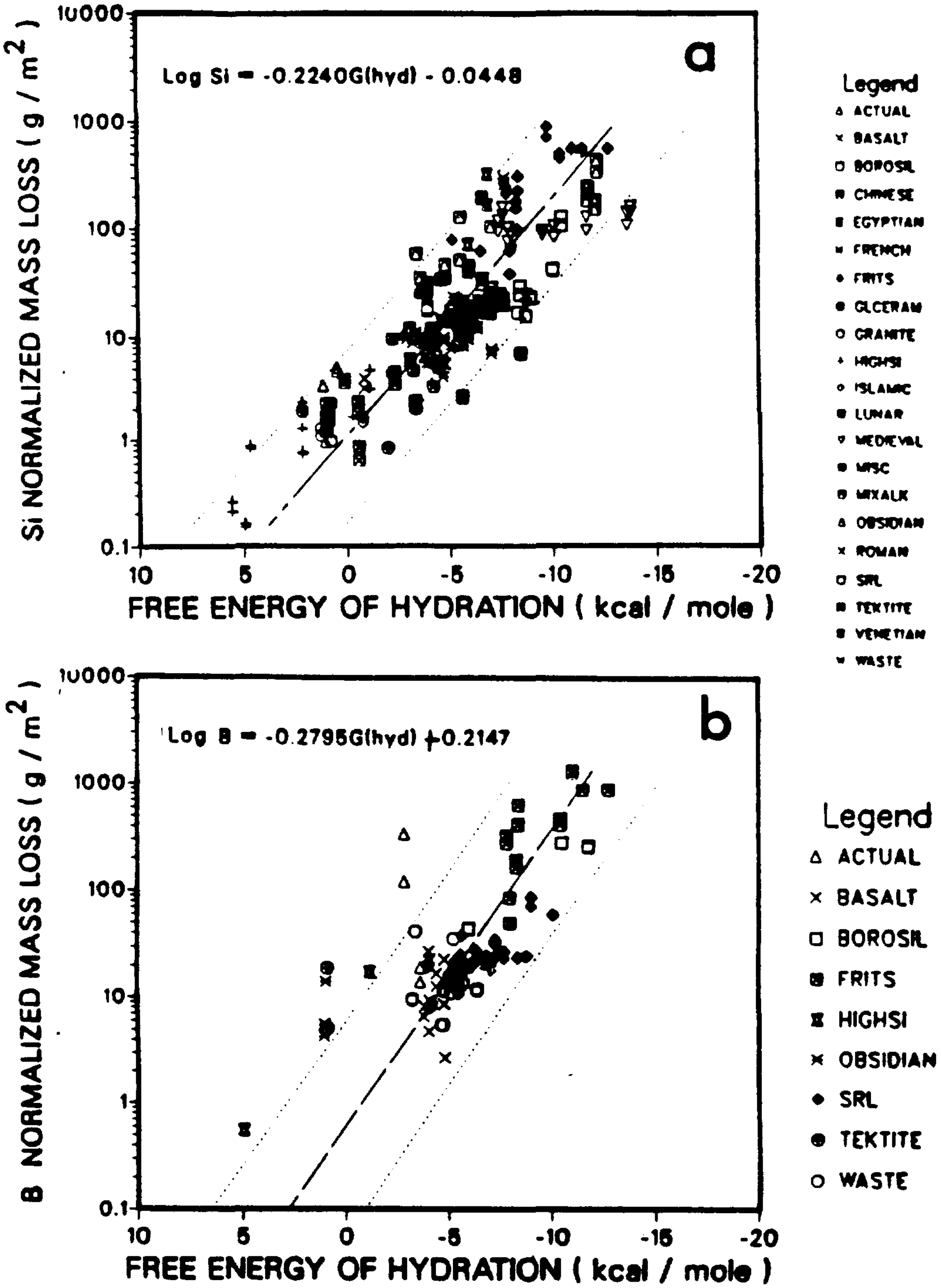


Figure 1a. Linear regression plot of over 300 experiments relating glass composition (ΔG_{hyd}) to glass durability (expressed as Si lost from the glass to the leachate solution in a 28 day laboratory experiment).

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

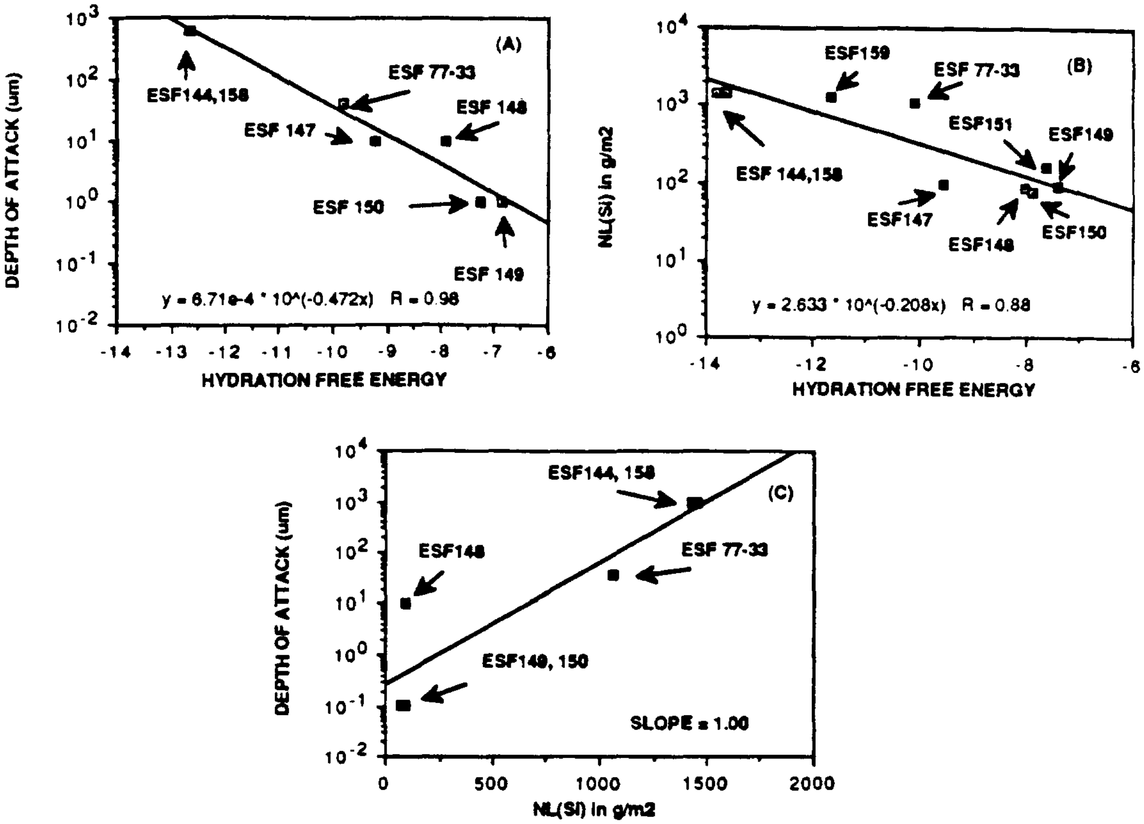


Figure 2a. Application of Hydration thermodynamics to MCC-1 laboratory test data for European Science Foundation medieval window glasses.
2b. Application of hydration thermodynamics to "depth of attack" of the glass surface after burial in the United Kingdom for 5 years.
2c. Comparison of the laboratory and in-situ data from 2a and 2b.

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].

Glass Durability: A Function of Glass and Groundwater (Solution) Composition

Many groundwaters are silica saturated from interactions with silica-rich rocks such as tuff, basalt, granite and/or silica-rich soils. Leaching of nuclear waste glasses in silicate saturated groundwaters has been found to minimize the dissolution of the glass [40]. Automatic dishwasher powders are laced with silica to saturate the washing solution and minimize attack on modern glassware. These empirical observations are supported by the data of Grambow [41,42], which suggests that dissolution of silicate and borosilicate glasses can be described by the activity diagrams for the dissolution of amorphous silica. The activity-pH diagrams provide the fundamental correlation between minimum solubility of a species in solution and the free energy [12, 24, 43].

In the initial studies of glass durability as a function of glass composition [20-25], leachants of high-purity water were used. In order to quantify the effects of groundwater (solution) chemistry on glass durability, a "reference set" of $\sim$10 glasses were chosen for study with the thermodynamic hydration approach. The glass compositions included pure SiO_2, tektites, basalts, waste glasses, two ESF glasses, and a poorly durable frit glass. The test temperature, test duration (28 days) , and SA/V ratio were kept the same as the studies in high-purity water.

The silica-saturated groundwaters were found to minimize the amount of silica released to solution as found in previous experiments [44]. The chemistry of the groundwater buffered the leachate pH: even the poorest glass, the frit glass, did not cause leachate pH excursions.

Since the ΔG_{hyd} defined in the high-purity water experiments is calculated from the glass composition and the solution pH, the linear equation determined is an expression of the response of both glass and solution pH (Figure 1a). In the buffered groundwater experiments, the constant pH altered the calculated ΔG_{hyd} term, but the buffering capacity of the groundwater also lowered the Si released from the glass. The data from the groundwater leachates, therefore, superimposes on the linear equation defined by the high-purity water experiments (Figure 3)[26]. When the groundwater pH and the glass composition are known, the performance of a given glass in nature can be predicted by hydration thermodynamic theory. If the groundwater pH is constant, then only the glass composition need be known in order to determine "relative" glass durabilities in a given environment.

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 [44]. 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 [40], similar to the slopes given for the elemental release concentrations in the high-purity water experiments and the ESF glass depths of attack.

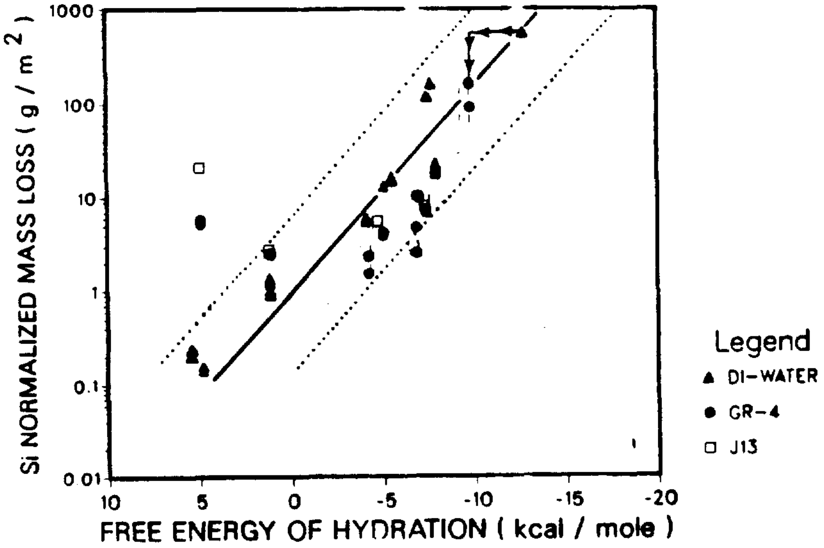


Figure 3. Comparison of the hydration thermodynamic data for a "reference set" of glasses tested by the MCC-1 test protocol. The equation of best fit and the 95% confidence limits were defined by the MCC-1 data in deionized water. The data for silica-saturated tuff groundwater (J-13) and basaltic groundwater (GR-4) are shown to revert to the same regression equation.

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

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 [45-46]. Crushed glass tests are glass dominated, e.g. the leachate chemistry is dominated by the large amount of glass surface area, which makes the response of these tests very senstive to glass composition. The hydration thermodynamic theory was, therefore, applied to crushed glass experiments (MCC-3 leaching test protocol) in high-purity water [23, 47]. It was noted [23] that 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. 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 [48].

Measures of reaction progress such as $\log(NL_{Si})$ or log(Si) in ppm have been shown to be a function of (SA/V)•t [23] 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 [23]. 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 glass was plotted in three dimensional $\log(NL_{Si})$-(SA/V)•t-ΔG_{hyd} space. The data formed a plane which could be fitted statistically with a spline function (Figure 4) [49]. 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.

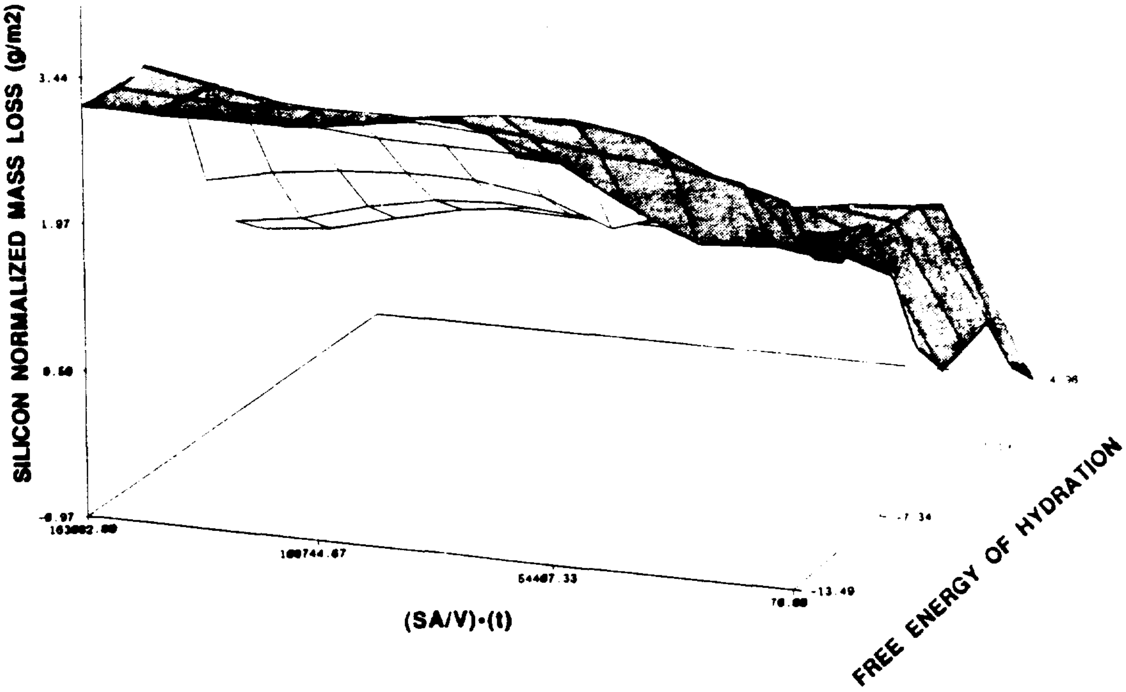


Figure 4. Computer-generated spline funciton for 122 durability experiments at low (SA/V)•t [MCC-1 test protocol for monoliths of glass] and at high (SA/V)•t [MCC-3 test protocol for crushed glass]. The data form a plane in ΔG_{hyd}-(SA/V)•t-$\log(NL_{Si})$ space. The ΔG_{hyd}-$\log(NL_{Si})$ plots from the different experimental test geometries exhibit similar slopes because they are slices through ΔG_{hyd}-(SA/V)•t-$\log(NL_{Si})$ space at constant (SA/V)•t.

Glass Durability: A Function of Solution pH and Oxidation Potential (Eh)

Equilibrium pH-electrochemical potential (E or Eh) diagrams were developed by Pourbaix [11] to describe the effects of aqueous environments on corrosion of metals. Pourbaix diagrams, referred to as pH-Eh diagrams, have been developed by geochemists to depict the stability relations among solid phases [50,51] and to assess mineral (rock) stability during weathering [12]. The thermodynamic approach of Pourbaix which is dependent on thermodynamically calculated phase stability boundaries can be combined with the hydration thermodynamic approach to derive a generic Pourbaix diagram for glass dissolution.

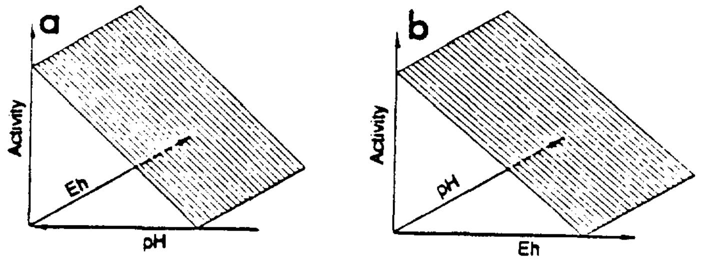
The statistically-determined relationships between pH-ΔG_{hyd}, pH-log(NL_{Si}), and pH-log(NL_B) based on response of the 150 glasses during the MCC-1 durabillity tests can be used to quantifiy the generic Pourbaix diagram for glass dissolution [24,25]. This is supported by the data of Grambow [41,42] which suggests that the dissolution of all silicate and borosilicate glasses can be described by the activity diagram for the dissolution of amorphous silica. The known effects of solution pH and Eh on nuclear waste glass dissolution and surface layer formation can then be used to thermodynamically calculate the pertinent phase stability fields for dissolution of this type of glass. This type of approach conceptually unifies all glass dissolution as a function of solution pH and Eh.

Activity-pH (or activity-Eh) diagrams provide the fundamental correlation between ion concentrations in solution and the free energy of a hydration reaction. Although solubility concentrations differ from the activities by a factor, γ, known as the activity coefficient [12]. If γ is approximately equal to one, then the ion activity approximately equals the ion concentration. The factor γ is dependent on the ionic strength of the solution and is a function of the multiple hydration, ionization, and complexation reactions that the ion participates in. However, the activity-pH diagrams provide the fundamental correlation between minimum solubility of an ion in solution and the free energy [12,43]. In this manner, a three dimensional Pourbaix diagram can be constructed. The three dimensional representation of activity (concentration), pH, and Eh is shown schematically [51] in Figure 5 for species which are

- independent of Eh
- independent of pH
- independent of both Eh and pH
- dependent on both Eh and pH.

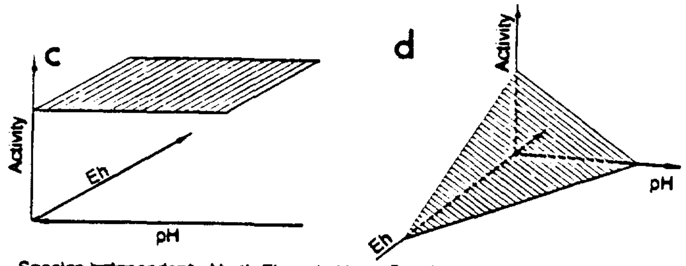
Glass components which respond to solution Eh are generally multivalent redox sensitive species. Species such as B and Si are more sensitive to changes in pH than Eh [24].

The influence of pH on the activity of vitreous silica can be thermodynamically calculated from the equilibrium constants for the hydration of SiO_2 to silicic acid and the equilibrium constants for silicic acid dissociation [2,11]. Likewise, the activity-pH relations for vitreous B_2O_3 hydration can be calculated from the equilibrium constants for the hydration of vitreous B_2O_3 to boric acid and the equilibrium constants for boric acid dissociation [24]. The hydration of vitreous silica (or vitreous boric oxide) is independent of Eh, and hence the activity-pH diagrams provide the fundamental correlation between silica (or boron) concentration in solution and the free energy. Silicon and boron concentration-dependent contours would, therefore, parallel the Eh axis as shown in Figure 5a [24,11].



Species independent of Eh

Species independent of pH



Species independent of both Eh and pH

Species dependent on both Eh and pH

Figure 5. Three dimensional representation of the relations between the activity of a species with solution Eh and pH (after Krumbein and Garrels [51]). Note the different behavior of species which are dependent or independent of solution Eh and/or pH.

For the 300 individual glass durability tests, the regression equations were statistically calculated [24] for binary combinations of the following variables: ΔG_{hyd}, $\log(NL_{Si})$, $\log(NL_B)$, and pH. Several regressors were found to be nearly linear combinations of other regressors in the data base, e.g. colinear. The variables (n=4) were examined in n-1 combinations. Combinations of n-1 variables have three degrees of freedom. However, the three degrees of freedom are limited by the strong variable pair interactions between ΔG_{hyd}-pH, $\log(NL_{Si})$-pH, and $\log(NL_B)$-pH [24]. The variable pair interactions impart an additional restriction on any n-1 combination so that the degrees of freedom is reduced to n-2 or 2.

The colinearity between the regressors is caused by the fundamental thermodynamic relationships among ΔG_{hyd}, the solution pH, and the concentration of species in solution. The $\log(NL_{Si})$, ΔG_{hyd}, and the pH are highly colinear because the pH and ΔG_{hyd} are related through the Nernst equation [24]. In addition, $\log(NL_{Si})$ is related to the pH through the activity-pH relationship. The $\log(NL_{Si})$, $\log(NL_B)$, and the pH are highly colinear because of the restriction imposed by congruent dissolution [24]. Each of these solution species is colinear with pH because of the pH dependence of the saturation ion activities. The $\log(NL_{Si})$ and $\log(NL_B)$ are related to ΔG_{hyd} through the equilibrium constants for the hydration of SiO_2 and B_2O_3, and the equilibrium constants for silicic acid and boric acid dissociation. Therefore, combinations of the following n-1 variables can be defined by the slopes between any binary pair of variables:

- $\log(NL_{Si})$ - ΔG_{hyd} - pH
- $\log(NL_B)$ - ΔG_{hyd} - pH
- ΔG_{hyd} - $\log(NL_{Si})$ - $\log(NL_B)$
- pH - $\log(NL_{Si})$ - $\log(NL_B)$

Over the limited pH range (~5-13 pH) of the deionized water experiments, the statistically determined slopes between pH and the remaining three variables gave [24] the following:

$$\mathrm{pH} = -\,0.489\ \Delta G_{hyd} + 6.12 \tag{5}$$

$$\log(NL_{Si}) = +\,0.429\ \mathrm{pH} - 2.73 \tag{6}$$

$$\log(NL_{B}) = +\,0.416\ \mathrm{pH} - 2.31 \tag{7}$$

Because of the colinearity relationships between pH-log(NL_{Si}) and pH-log(NL_B), a three dimensional Eh-pH-concentration diagram similar to the schematic Eh-pH-activity diagram in Figure 5 can be constructed. The concentrations of Si and B in solution have been shown experimentally [52,53] to be almost completely independent of the solution Eh. The Eh independent equilibria will, therefore, parallel the Eh axis as shown schematically in Figure 5a. Isopleths of constant solution concentration can be contoured on the Eh-pH plane from the statistically determined slopes given in Equations 6 and 7. A quantitative Pourbaix diagram for glass dissolution can, therefore, be developed (Figure 6a and 6b).

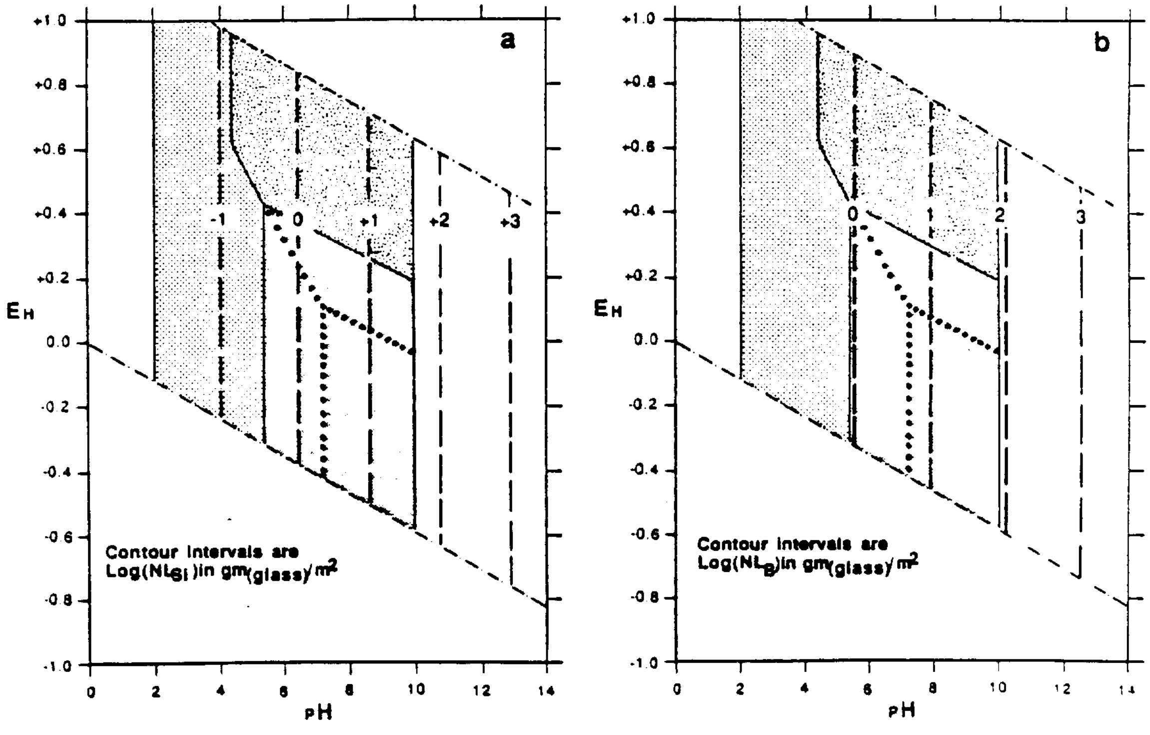


Figure 6a. Pourbaix diagram for glass dissolution based on Eh independent release of silicon to solution for over 300 glasses studied. Contour intervals were determined from the slope of Equation 6 in text.

6b. Pourbaix diagram for glass dissolution based on Eh independent release of boron to solution for over 140 glasses studied. Contour intervals were determined from the slope of Equation 7 in text.

Because of the relation of ΔG_{hyd} to Eh and pH through the Nernst equation [24] and the colinearity of ΔG_{hyd} (here ΔG_{hyd} is calculated only from the glass composition) to pH, a similar three dimensional Eh-pH-ΔG_{hyd} diagram can be derived. Since ΔG_{hyd} was theoretically shown [24] to be relatively insensitive to solution Eh, it can also be contoured parallel to the Eh axis on a Pourbaix diagram for glass (Figure 6c). The statistically determined ΔG_{hyd}-pH slope given in Equation 5 is used to determine the contour interval.

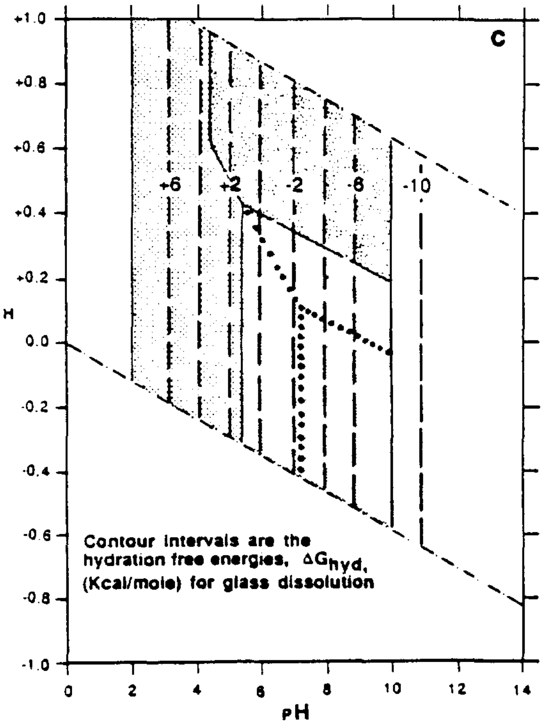


Figure 6c. Pourbaix diagram for glass dissolution based on Eh independent ΔG_{hyd} for over 300 glasses studied. The ΔG_{hyd} term was calculated from glass composition and environmental pH. Contour intervals were determined from the slope of Equation 5.

The shaded stability fields shown in Figures 6a-6c relate to the observed phase stability fields and surface layer formation observed for nuclear waste glass dissolution (Figure 7a). A similar stability field diagram is shown in Figure 7b for high silica glasses. The calculated stability fields will vary depending on glass type, but the quantification of the Pourbaix diagram is generic. The alkaline boundary of active corrosion is defined by the dissociation $H_2SiO_3/HSiO_3^-$ boundary and is calculated for $H_2SiO_3 = 10^{-4}$ M. Higher concentrations of $\sim 10^{-3}$ move the $H_2SiO_3/HSiO_3^-$ active corrosion boundary to higher pH values. In other words, Pourbaix diagrams provide the thermodynamic rationale of why glass dissolution at higher pH values can be minimal in silica saturated groundwaters. The active dissolution boundary shifts, depending on the concentration of silica present.

The details of the stability field calculations are given elsewhere [24,25]. The pH dependence of the active corrosion fields is a function of the silica content of the glass [54,55]. However, 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 [56], (2) the type of surface layer formation is a function of the glass composition [56], 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 [41,42] that the dissolution of all silicate-based glasses can be described by the activity diagrams for the dissolution of amorphous silica.

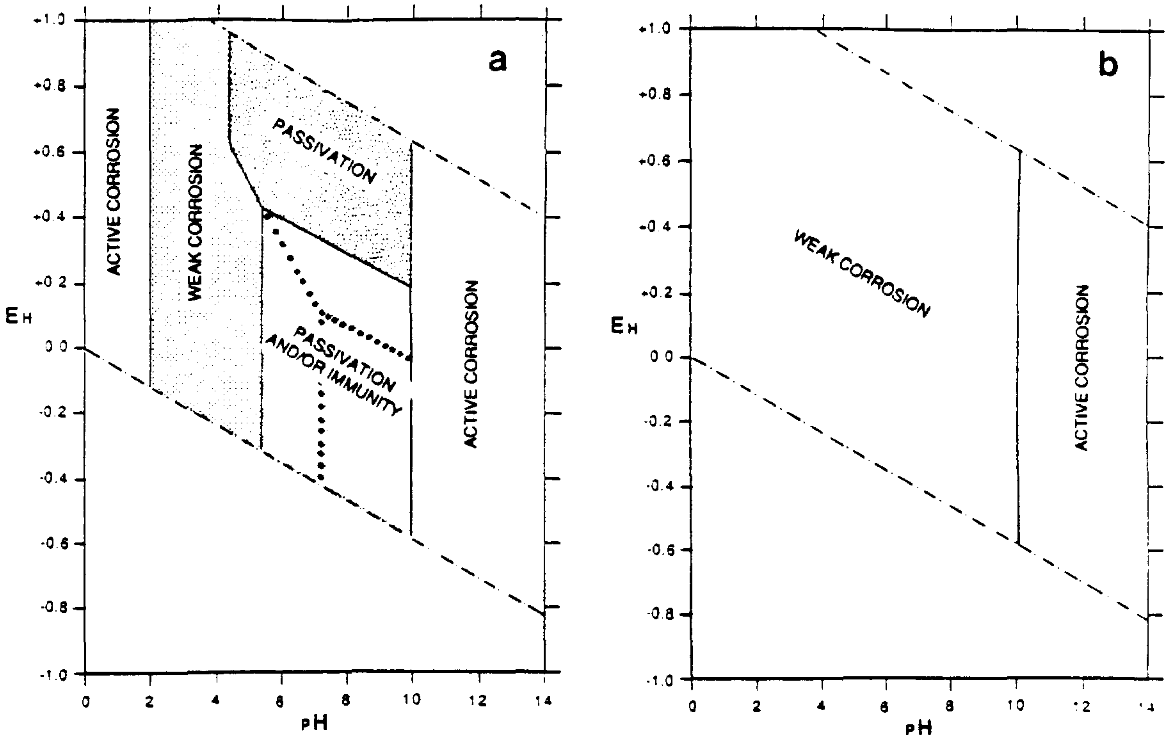


Figure 7a. The Pourbaix diagram for low silica and borosilicate glasses. Note this diagram can be quantatively used to predict glass dissolution by superimposing the contours of Figure 6 a, b, or c.

7b. Simplified Pourbaix diagram for high silica glasses. Note this diagram can also be quantatively used to predict glass dissolution as given above.

CONCLUSIONS

Application of hydration thermodynamics has wide applicability to the prediction of natural, ancient, modern, and nuclear waste glass durability. The predicted durabilities correlate with those observed in nature and give a means for interpolation of the long-term durability of nuclear waste glasses. Hydration thermodynamics can also be used to determine the relative durability of commercial glasses and for archeological applications. The hydration thermodynamic approach was shown to apply to such measures of reaction progress as Si, B, and K releases from solution in both short term and long term laboratory tests. The approach was also shown to apply to glass surface "depths of attack" from 2 year and 5 year in-situ burial tests in Sweden and in the United Kingdom.

Hydration thermodynamics furnishes a quantitative frame of reference to explain how the following parameters affect glass durability:

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

Combined with the thermodynamic concepts of Pourbaix diagram construction, the hydration thermodynamic approach has been shown to predict the response of glass to environmental conditions, e.g. solution pH and oxidation potential.

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