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THERMODYNAMIC MODEL OF NATURAL, MEDIEVAL AND NUCLEAR WASTE GLASS DURABILITY

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ABSTRACT

A thermodynamic model of glass durability based on hydration of "structural units" has been applied to natural glass, medieval window glasses, and glasses containing nuclear waste. The relative durability predicted from the calculated thermodynamics correlates directly with the experimentally observed release of structural silicon in the leaching solution in short-term laboratory tests. By choosing natural glasses and ancient glasses whose long-term performance is known, and which bracket the durability of waste glasses, the long-term stability of nuclear waste glasses can be interpolated among these materials. The current Savannah River defense waste glass formulation is as durable as natural basalt from the Hanford Reservation (10^6 years old). The thermodynamic hydration energy is shown to be related to the bond energetics of the glass.

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INTRODUCTION

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[1] for defense high level waste produced at the Savannah River Plant is immobilization in borosilicate glass and subsequent emplacement in a geologic repository for long-term storage. The intrusion of groundwater into, and its movement through, a repository is the most likely potential 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 toward groundwaters for very long periods of time.

Unfortunately, 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 in 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.[2] Subsequent laboratory comparison of the durability of rhyolite glasses (5 X 10^2 to 6.7 X 10^5 years) to French and United Kingdom borosilicate waste glasses and a German waste glass ceramic demonstrated that the natural glasses tested were more stable* than the waste glasses due to their higher silica content.[3] On the other hand, Malow[4] recently demonstrated that, even in elevated temperature testing (approximately 200°C), a German borosilicate waste glass was as durable as basaltic glass. These studies demonstrate that waste glasses can be as durable as some natural glasses but these studies do not provide a basis for predicting for which glasses this will be true. In order to quantify the relative durabilities of the various materials, a theoretical basis for the comparison is necessary.

The durability of a glass is a function of both kinetic and thermodynamic stability in an aqueous environment.[5] Kinetic models can and have been applied to the time dependent corrosion of

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*Stability was based on the relative weight loss of each sample after leaching.

glasses,[6-9] waste glasses[10-11] and crystalline silicate[8,12] species. Chemical thermodynamics has previously been evoked to predict vitreous[5,13] and crystalline silicate[14,16] stability in aqueous environments and is here correlated with the measured elemental release rates for a wide compositional range of natural, medieval, and nuclear waste glasses and glass-ceramics. Although equilibrium is rarely achieved in short-term laboratory tests, the use of equilibrium thermodynamics furnishes a quantitative frame of reference for the relationship of any solid species with an aqueous environment on geologic time scales.

THERMODYNAMIC AND STRUCTURAL BASIS OF GLASS HYDRATION

The reactions at the glass surface-solution interface have been described in terms of two chemical reactions.[6,9]

A. Alkalis are released into solution as a result of ion exchange with protons from the solution.

$$\equiv \mathrm{Si{-}OR} + \mathrm{H_2O} \rightleftarrows \mathrm{Si{-}OH} + \mathrm{R^+} + \mathrm{OH^-} \qquad (1)$$

B. Silica is released into solution as the siloxane bonds in the glass are attacked by the hydroxyl ions from the solution.

$$\equiv \mathrm{Si{-}O{-}Si} \equiv \quad \mathrm{OH^-} \rightleftarrows \equiv \mathrm{Si{-}OH} + \equiv \mathrm{Si^-O^-} \qquad (2a)$$

$$\equiv \mathrm{Si{-}O^-} + \mathrm{H_2O} \rightleftarrows \mathrm{Si{-}OH} + \mathrm{OH^-} \qquad (2b)$$

A non-bridging oxygen is formed in reaction 2a which can interact with molecular water to form additional silanol bonds on the glass surface and release a hydroxyl ion which can serve as the source of hydroxyl for further breaking of siloxane bonds on the glass surface (reaction 2b). An increase in the activity of the hydroxyl ion in the solution will , therefore, favor increased removal of silica and suppression of reaction 1 as the activity of the hydrogen ion concentration is decreased.[9]

The simplest case, the hydration of vitreous silica as expressed by the overall reaction

$$SiO_2 + H_2O \rightleftarrows H_2SiO_3 \qquad (3a)$$

has been described[6-8] in terms of a forward dissolution reaction an a reverse condensation reaction which are responsible for the formation of silica in the solution and in the leached layer, respectively. This hydration reaction has been quantitatively described[8] as a reversible first order dissolution reaction which has an associated equilibrium thermodynamic free energy. These thermodynamic equilibria can be used to describe the dynamic exchange equilibria at the interface of the leached layer with the aqueous solution.[9]

For the reaction of vitreous silica with water, the equilibrium constant, K, is

$$K = \frac{(a_{H_2SiO_3})}{(a_{SiO_2})(aH_2O)} \qquad (3b)$$

Since silica and water are assumed to be in their standard state at 25°C, then $a_{SiO_2} = 1$ and $a_{H_2O} = 1$ and the equilibrium constant constant is equal to $a_{H_2SiO_3}$. The relationship between the constant and the free energy of the exchange reaction when the reactants and the products are in the standard state is

$$\Delta G^\circ = -RT\ln K \tag{4}$$

ΔG° = standard state free energy of change (cal)

where R = gas constant (cal deg^{-1} $mole^{-1}$)

T = absolute temperature (°K)

The relationship between bonding, a function of composition, and durability for crystalline and vitreous solids has been examined for almost 35 years. Geologists[18,19] have tried to classify mineral species on the basis of the linkage of the silica tetrahedra, and then to relate the relative durability (weathering classification) to the mineralogic structure. Glass scientists such as Stevels[20,21] related the proportion of non-bridging oxygen (NBO) in the glass network to durability as early as 1948[20] while Newton[22] attempted a durability classification based on the network-building vs. RO and R_2O triangular scheme. Most recently, the rate-limiting step of silica-water reactions was found to be controlled by the breaking of the structural Si-O bonds.[8]

In 1977 Paul[23] predicted the durability of glasses from the thermodynamic aspects of chemical composition by assuming that the glass/water reactions could be described in terms of the summation of the free energies for hydration reactions of the individual structural components, e. g. component silicate or oxide groups, in a glass. This thermodynamic parameter, the free energy of hydration, was correlated to alkali release for a series of medieval glasses[24] but no correlation was made between the thermodynamic parameter and the glass structure. However, assuming the following criteria about the reaction mechanism

(1) The reaction mechanism is directly related to the stiochiometry of the solid.[16]

(2) The amount of silica extracted from a glass is a function of the molecular percentage of silica in the glass.[9,17]

(3) The release of silica into the solution is a function of (1) and (2) and hence a function of the number of non-bridging oxygen bonds[20,21] or of the strength of the bonds.[8]

(4) The dynamic exchange reactions at the glass-solution interface can be described in terms of the thermodynamic equilibria.[9]

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 free energy.

EXPERIMENTAL

Measured Release Rates

In any laboratory dissolution experiment the following parameters will affect the relative elemental release rates from the solid:

(1) exposed surface area of the solid

(2) volume of the leaching solution

(3) frequency of replenishing/changing the solution

(4) temperature of leaching

(5) glass composition.

For all the glasses and glass ceramics examined in this study monoliths with a surface area of 4 cm^2 were cut on a low speed diamond saw. Geometric surface areas were measured and the sample immersed in 40 cm^3 of deionized water so that the surface area to volume ratio was always 0.1 cm^{-1}. Teflon® (Du Pont) leach vessels were used and Materials Characterization Center MCC-1 test procedure[25] which has been used as a scoping test for durability of a variety of radioactive waste forms. This experimental procedure controls all of the variables listed above except glass composition. Therefore, a wide variety of glass compositions could be examined. Excursions in pH were considered to be controlled by the glass composition. Elemental concentrations in solution were measured by inductively coupled plasma (ICP) and atomic absorption (AA).

Glass monoliths were dried for 1 hour at 90°C and the surfaces analyzed by x-ray diffraction. Elemental compositions of natural glasses and glass-ceramics were determined by dissolution in HCl/HF or Na_2O_2 followed by ICP and AA solution analysis.

Application of Paul's Thermodynamic Theory

The thermodynamic basis of glass hydration has been fully described elsewhere[5,23,26,27] and will only be summarized briefly. The glass is treated as a homogeneous mixture of structural species or units such as Na_2SiO_3, SiO_2, Fe_2O_3, or $FeSiO_3$. The reaction of each species with water allows calculation of a hydration free energy or a known thermodynamic stability toward aqueous attack (Table I). The stability of the glass is then assumed to be the sum of these component hydration stabilities ($\Delta G°$ values), weighted by the mole fraction of that component in the glass. More positive free energies represent more durable species. The calculations are simple as given in Appendix I.

The calculated free energy is the standard free energy of hydration. The use of thermodynamics in this simple approach assumes that these hydration reactions are the predominant overall reactions taking place during glass leaching. For example it assumes that silicate structural groups hydrate to form silicic acid, and Fe_3O_3 and Al_2O_3 hydrate to form iron and aluminum hydroxides. Thus, the $\Delta G°$ values in Table I may not apply at extreme pH values or extreme temperatures where other reactions may contribute additional thermodynamic terms.

Calculation of Non-Bridging Oxygen Bonds

A modification of White and Misner's[28] formula for deriving the number of non-bridging oxygen atoms for natural glasses such as tektites and obsidians from compositional data was used:

$$\mathrm{NBO} = 2(\mathrm{BaO} + \mathrm{CaO} + \mathrm{Cs_2O} + \mathrm{FeO} + \mathrm{K_2O} + \mathrm{Li_2O} + \mathrm{MgO} + \mathrm{MnO} + \mathrm{Na_2O} + \mathrm{NiO} + \mathrm{SrO} - \mathrm{Fe_2O_3} - \mathrm{Al_2O_3}) + 4\,(\mathrm{TiO_2} + \mathrm{ZrO_2} + \mathrm{UO_2}) \;/\; \text{oxide mole sum} \qquad (5)$$

This formula assumes that every mole of mono- and di-valent oxide components contributes two non-bridging oxygen atoms while every Fe_2O_3 and Al_2O_3 component create two bridging oxygen atoms. Tetravalent ions such as Ti, Zr, and U are assumed to create four non-bridging oxygen atoms.

Partitioning of Al^{+3} and Fe^{+3} between the structural components of a melt and the different structural roles of Fe^{+3} and Fe^{+2} is especially critical to the calculation of the non-bridging oxygen atoms and the hydration free energy. The structural role of iron is controlled by an involved relationship between degree of polymerization of the melt, types of cations present, amount of iron present and its oxidation state.[29] Al^{+3} is considered an intermediate[30] or conditional[31] glass forming ion. In silicate melts, the addition of Al^{+3} increases the degree of polymerization of the melt by creating more network forming complexes and by transferring a divalent cation from a network breaking position to a charge balancing position within the aluminosilicate network.[32] The monovalent alkali metals are more efficient at charge balancing within an alumino-silicate network.[31,32] In iron silicate melts the alkalis stabilize Fe^{3+} in tetrahedral coordination as a network former. If the M^{+}/M^{++} ratio is less than that required to form tetrahedral Fe^{3+} then mixed coordination of Fe^{3+} is found. Secondly, if only M^{+} cations are available and $M^{+} = Fe^{3+} = Al^{3+}$ then Al is tetrahedral and Fe^{3+} acts as a network modifier. Thirdly, if M^{+} is sufficient to stabilize either Fe^{3+} or Al^{3+} as a network former, but additional M^{2+} cations are available, then tetrahedral iron is preferentially charge balanced by alkai while tetrahedral alumina is preferentially charge balanced by divalent cations. The alkali-ferric iron associations are more stable than the alkali-alumina associations.[33] This explains the early empirical observations of Paul and Douglas[34] that Al_2O_3 in glass melts can disturb the ferrous-ferric equilibria and that melt equilibria shifts toward the more oxidized state when the glass is more alkali-rich.[35]

In summary, in iron-free silica glasses, Al^{3+} would be expected to occur as a tetrahedrally coordinated cation provided that either monovalent or divalent cations are present for charge balance complexing. When iron is present, the Fe^{3+} associations require cations with lower Z/r^2 ratios than the Al^{3+}. Therefore, in multicomponent melts, the relative stabilities of the Al^{3+} and Fe^{3+} associations, as well as, the redox equilibria, will be of importance to determining the number of non-bridging oxygen bonds.

For all the glasses considered Al^{3+} and Fe^{3+} are considered to be tetrahedral since the ratio NBO/T is a measure of the structural role of the network forming cations and has been found to vary with the Fe^{3+}/ Fe ratio.[36]

RESULTS AND DISCUSSION

The Thermodynamic Approach

Using the thermodynamic data derived from Paul's hydration thermodynamics (Table I) gives the free energy values plotted in Figure 1a. The ordinate is plotted as the normalized mass loss of elemental Si from the glass to the leachate. The elemental value of the silicon released is normalized to the mass fraction or silicon in the glass and is a function of the exposed surface area of the glass and the leachate volume[25] as given below:

$$NL_i = \frac{M_i}{F_i \cdot SA}, \qquad (6)$$

where

NL_i = normalized elemental mass loss ($g \cdot m^{-2}$),

M_i = mass of element "i" in the leachate (g),

F_i = fraction of element "i" in the unleached waste form (unitless),

SA = specimen surface area (m^2).

Silicon was chosen as the structural component common to all the glasses surveyed. The durable glasses made at high temperatures and the nuclear waste glasses follow a linear trend (Figure 1a).

with the most durable glass represented by pure vitreous SiO_2 (Corning 7740). Two different obsidian compositions, two tektites and two basalts were analyzed for reproducibility. The exact values of the compositions, $\Delta G°$ (hydration) and the normalized mass loss of silicon are given in Appendix II.

Glasses higher in silicon content, e.g. pyrex, obsidians, and the tektites, have lower release rates than the waste glasses in accord with the predictions of Douglas and ElShamy.[9] The waste glasses have lower silica contents since fabrication temperatures need to be as low as possible to minimize potential problems with volatile fission products such as cesium. The waste glasses cluster in one region due to the similarity of their compositions and release rates (Figure 1a).

The frit glasses were made from frit formulations melted without waste components added and the medieval window glass compositions are poorly durable European Science Foundation (ESF) simulated glasses. These glasses do not fit the linear extrapolation suggested by the more durable glasses in Figure 1a. This deviation is due to pH excursions and will be discussed in more detail below.

The Thermodynamic Role of Iron

The original thermodynamic approach of Paul[5,23] was applied to the prediction of the relative durability of medieval window glasses.[24] It was modified[26] to include large amounts of redox ions such as found in borosilicate glasses for defense nuclear waste. These glasses contain large amounts of iron and manganese. Experimentation has shown that glasses made under more oxidizing conditions are more durable than those made under reducing conditions.

In applying the data of Table I, the redox state of iron can be a crucial parameter, since Fe^{3+}(as Fe_2O_3) improves the calculated durability ($\Delta G_{hy}>0$) while Fe^{2+}(as $FeSiO_3$) reduces the durability ($\Delta G_{hy}<0$). In those cases where the approach has been applied to simulated waste glasses, the redox state of the glass is inferred from previous studies[37,38] or obtained by Fe^{2+}/Fe^{3+} analysis, e. g. SRL 165 had an analytic Fe^{2+}/Fe^{3+} of 0.48 while both tektites were analyzed as entirely Fe^{2+}.

The tektites were used to validate the use of $FeSiO_3$ as a ferrous iron structural component. One tektite was an Indochinite and one a Phillipino. The hydration free energies were 0.952 and 0.959 and the release rates were 1.65 and 1.69 g/m^2 Si, respectively.

Additional verification for the role of ferrous iron in the hydration free energy calculation came from the data of Welch et al[39] from the interstitial glass composition of iron enriched basalts melted at 1550°C. It was assumed that the leaching in this glass ceramic was controlled by the intergranular glassy phase as reported by Jantzen et al.[40] Further, it was assumed that the iron was in the reduced state due to the high temperature of formation. The compositions and leaching data of

Welch et al[39] are plotted in Figure 1b. Data for both a coarse-grained (IEBCG) and a fine-grained (IEBFG) intergranular phase were plotted and fit near the linear slope delineated by other non-ferrous iron glasses. The greater deviation exhibited by the fine grained intergranular glass is attributed to analytic errors due to the fineness of the structure. Overall, the data on the glasses and glass ceramics with reduced iron validate the use of the redox structural components.

The Thermodynamic Role of Alumina

In the original application of Paul's model[26] the hydration reaction assumed that boehmite, AlOOH, was the hydration product of Al_2O_3 and water (Table I). Three Al_2O_3-SiO_2 glasses[41] were leached and the glass monoliths dried at 90°C for 1 hour. The glass surfaces were then analyzed by x-ray diffraction and the $Al(OH)_3$ polymorph, gibbsite, was found to be reprecipitated on the glass surface along with poorly crystallized pyrophyllite (a clay in the smectite-montmorillonite family of composition $Al_2Si_4O_{10}(OH)_2$). The free energy for the hydration of Al_2O_3 to gibbsite is -7.73 kcal/mole vs. +3.04 kcal/mole for hydration to boehmite. Also, if a certain mole percent of silica is consumed to hydrate to clay and an additional free energy contribution of -7.82 kcal/mole of Al_2O_3 is added. The residual moles of SiO_2 are assumed to hydrate to H_2SiO_3 as in Table I.

Assuming that half the amount of available alumina hydrates to gibbsite and half to pyrophyllite for glasses of the composition SiO_2 - 20, 25, 30 mole percent Al_2O_3 yielded the three alumina-glass points in Figure 1b. Deviations in the release rate for silicon could be in error for these glasses by as much as 20% due to difficulty in measurement of the surface areas of these roller quenched glass ribbons.

In these glasses Al^{3+} is structural and in tetrahedral coordination.[41] In glasses where Al^{3+} is known to be structural, or where surface layer analysis indicates the presence of gibbsite or clay, then the negative rather than the positive free energy of hydration for Al_2O_3 given in Table I should be used. In cases where the coordination of aluminum is not known or surface analyses are not obtained or are inconclusive then the positive free energy of hydration for Al_2O_3 should be applied.

The Thermodynamic Role of Silicic Acid Dissociation

Paul's model[5,23] assumes that each silicate glass structural component hydrates to silicic acid plus a cation in solution. However, in poorly durable glasses such as the frit glasses and medieval window glasses (Figure 1a) high pH values are obtained experimentally with concomittant increases in structural silicon. This is predicted by the matrix dissolution equations 2a and 2b. Moreover, at pH values greater than about 9.5 the solubility of silica increases rapidly since silicic acid is no longer stable and it dissociates into $HSiO_3^-$ and H^+[5]. Since the equilibrium constant and free energy of hydration are based on the activity of silicic acid, e.g. equations 3 and 4, an additional free energy of hydration must be calculated for the reaction

$$H_2SiO_3 \rightleftarrows HSiO_3^- + H^+ \qquad (7)$$

It can be shown[42] that the concentration of silicic acid can be calculated from the sum of Paul's thermodynamic hydration free energy of the silicate components only, e.g. the product of an effective k_1 equal to

$$\frac{\Delta G SiO_2}{1.364}$$

and an effective k_2 equal to

$$\frac{\Delta G \text{ silicate groups}}{1.364}$$

so that

$$k_1 k_2 = \frac{[Si]^2}{k_3} \cdot \frac{1}{[H^+]} \qquad (8)$$

where $[Si] = m/L = 1.666 \times 10^{-4}$ wt fract SiO_2 NLSi

$k_3 = 1 \times 10^{-10}$ for equation 7

$$\frac{1}{[H^+]} = 10^{+pH}$$

Equation (8) can be used to predict the Si concentration from the pH or vice versa if k_1k_2 is known or vice versa. The additional free energy of hydration term is then derived from equation 8 and the known pH. At pH 10, k_3 equals $1/[H^+]$ and so the equation is only applied at pH values greater than 10 as follows:

$$\Delta(\Delta G)\text{ hydration} = 1.364(\log k_1 k_2)(10-\text{pH}) \qquad (9)$$

If the extra free energy of hydration for the dissociation of silicic acid into its component anionic derivatives is added to the hydration free energy of the poorly durable glasses then these glasses assume positions on the linear extrapolation of the free energy vs. silicon release plot as delineated by the more durable glasses (Figure 1b).

The one frit glass at a pH of 9.45 lies on the linear extrapolation and needs no $\Delta(\Delta G)_{\text{hydration}}$ addition. Equation 9 is very sensitive to the pH term and poor reproducibility of the pH measurements are largely responsible for the scatter in Figure 1b.

Validation of the Structural Basis of Hydration Thermodynamics

The hydration free energies calculated from Paul's hydration thermodynamics based on glass structural components are listed in Table I starting with the most negative free energies and ending with the most positive free energies. They fall into two natural groupings of network forming and network breaking ions as the free energy of hydration term becomes more positive. Correlation of the free energies of hydration with ionic potentials calculated from the ionic radii of Whittaker and Muntus[43] for the coordination numbers (CN) listed are also given in Table I. The trend for the network breaking ions is for a higher Z/r as the free energy becomes more positive.

The correlation of the free energy of hydration based on Paul's glass structural components with the ionic potential implies that the structural components are related to bond strengths in the glass. The ionic character of fused silicates is widely accepted[44] and the ionic field strength criterion should, therefore, apply. For this criterion to apply to glass structures the ions are considered to be rigid spheres and

$$F = Z/r^2 \tag{10}$$

where F = ionic field strength.

Values of F and the relative coordination numbers are also given in Table I. The same trends are observed but a more consistent relationship exists with Paul's thermodynamic hydration values. The bond strength criterion is a representation of the lattice free energy as demonstrated recently by Howitt[45] who derived an expression for the free energy of a glass which is dependent only upon the concentration and energy of the bonds present in the structure.

The correlation of Paul's hydration free energies with lattice energy for a glass may also explain why crystalline free energies of formation can be applied to the vitreous state. The free energy of a crystalline material is equal to

$$\Delta G = \Delta U + p \nabla V - T \nabla S$$

where U = internal energy

V = volume

S = entropy

p, T = pressure and temperature.

It is the internal energy term, U, which represents the lattice energy and is a function of the ionic and electronic charges and the interionic distances[46,47]. Therefore,

$$\Delta G_{cryst} - \Delta G_{glass} = - \Delta U_{cryst} + \Delta U_{glass} - p \Delta V_{cryst} + p \Delta V_{glass} + T \Delta S_{cryst} - T \Delta S_{glass}.$$

For any given silicate system the $p\Delta V$ term can be neglected and the T S term is usually much less than ΔU so that $\Delta G \approx \Delta U$. The (ΔU) term between a glass and a crystal is small[47] since both are dependent on the electronegativity, mean value of the cation charge and cation radius[49]. Since (ΔU) is small then (ΔG) is small and ΔG°cryst ΔG°glass.

Additional validation for the correlation of the lattice energy as represented by polymerization of the melt to Paul's free energy of hydration is indicated by the direct correlation of the calculated free energy of hydration term with the number of non-bridging oxygen (NBO) bonds predicted* for a given glass from its composition

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* Evaluation of NBO/BO bonds was attempted experimentally by ESCA. Several glasses were examined but the oxygen spectra was too broad for the relative contributions of bridging and non-bridging oxygen atoms to be resolved.

(Figure 2a). A similar correlation is observed when the NBO term is plotted verses the release of structural silicon (Figure 1b) providing validation that the relationship between glass durability and structure is the thermodynamic representation of the bond energetics. Since this correlation involves the glass only and not the solution no $\Delta(\Delta G)$ hydration is added to the free energy of hydration for poorly durable glasses.

Surface Layer Formation

Species may be leached from a glass surface by the two mechanisms represented by Equations 1 and 2 which can be thought of as dissolution. At high pH values the corrosion mechanism changes from one of primarily ion exchange to one of primarily matrix dissolution as attack on the Si-O bonds is accelerated by increase OH^- [9].

Glass surfaces have been categorized by Hench[50] into five groupings defined on the basis of surface composition profiles. These surface categories, labeled I to V, follow a natural progression along the linear relation between hydration free energy and silicon release in Figure 1b. For example, a Type I glass surface has less than a 50A surface layer and is exemplified by pure silica glass. A Type II glass has a silica rich layer depleted in alkali while a Type III glass has two layers,* one silica rich and one a

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* Douglas and ElShamy[9] consider two reaction zones: one at the leached layer solution interface where equilibrium is considered to be between the surface sites and the ions in solution and the second at or near the leached layer glass interface consisting of a counterion exchange. The authors also recognized that the relative size of the two zones in glasses exposed to identical conditions varies according to the type of glass. They note that highly durable glasses have thicker glass-leached layer zones and thinner leached layer-solution zones whereas the opposite was found for glasses having low durability.

protective surface layer composed of one of the elements such as aluminum or iron leached from the glass. A Type III glass is represented by the aluminosilicates.[50] Type IV glasses also have a silica rich film but the silica concentration is insufficien to protect the glass from rapid attack while the Type V glasses have no layer formation and alkali and silica are lost from the surface at the same rate. Nuclear waste glasses have been found to form Type II, III, and IV surfaces depending on the concentration of network formers.[51] Medieval glasses form Type IV surfaces as well.

The leached surface categorization is related to the number of Si-O-Si and the Si-O-M (where M is a modifying cation) bonds by IR studies.[52,53] Paul's theoretical thermodynamic theory has been demonstrated to relate the bond energy of glass to its hydration characteristics. The thermodynamic hydration term may therefore represent a quantative prediction of the type of surface layers expected for a glass as a function of its composition.

Higher valence ions concentrate within the silica rich gel layers formed on the glass surface so that Type III surface with protective films are formed.[51] Recently, it has been demonstrated that this occurs by adsorption of these ions as positively charged aqueous hydroxo-complexes which charge neutralize the negative surfaces of leached glass monoliths[54] and that the relative enrichment of the elements in the leached surface layers correlate with the Z/r of these elements[55] and hence with the Z/r^2 and with Paul's thermodynamic free energies of hydration (Table I).

For the glasses shown in Figure 1b the following have been found after drying of the monolith surface at 90°C for 1 hour:

- Ca_2SiO_3 H_2O on simulated medieval window glasses
- $Al(OH)_3$ on pure aluminosilicate glasses
- $Pb_3(CO_3)_3(OH)_2$ (hydrocerussite) on $PbSiO_3$ glasses.

In other studies the following has been found:

- Fe rich protective films on SRL 131 waste glasses[56]
- Si, Ti, Fe, Mg, and Ca enrichment in basaltic glass surfaces.[57]

CONCLUSIONS

Thermodynamics, Structure, and Durability

The thermodynamic approach to prediction of glass durability introduced by Paul[5,23] is a representation of the bond energetics of the glass during hydration. When the calculated free energy of hydration is plotted for a wide variety of glass compositions against the release of structural silicon into deionized water in a standardized test a linear relationship is found. The contributions from the redox state of iron or the structural site of alumina must also be considered. Glass compositions which cause pH excursions to values greater than 10 must have an additional free energy term added to account for the dissociation of silicic acid since Paul's model only determines the energetics of silicate structural components hydrating to silicic acid.

HISTORICAL CONTEXT FOR RADIOACTIVE WASTE GLASSES

Paul's thermodynamic approach can be used to accurately predict glass stability since it is a structural manifestation of the bond energetics of the glass. The theory works as well for basalt and LLNLS29 and SPODC (spodume) which are glass ceramics since leaching is controlled by the least durable phase,[40] the glass. More polymerized glasses are more durable and all the glasses exhibit some type of surface layer formation.

The radioactive waste glasses cluster in a region which is representative of glasses more durable than frit glasses and medieval window glass but somewhat less durable than high melting temperature, high silica-containing glasses. The waste glasses, therefore, are more durable than the medieval window glasses of 10^3 years old[58] while SRL glass 165, the current defense waste glass formulation, is as durable as the Hanford basalt of 30×10^6 years[59] but somewhat less durable than the tektites of $1\text{-}3 \times 10^6$ years[2] and the obsidian from Snake River of 30×10^6 years.[59] The quantitative use of thermodynamics predicts that SRL 165 defense waste glass will be as durable as one of the proposed repository host materials, basalt.

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TABLE 1

FREE ENERGIES OF HYDRATION FOR GLASS COMPONENTS

(Reactions assumed are $R_xO_y+H_2O$ hydrated species, pH≤10)

Glass Component	Hydrated Species	G°(kcal/mol)	$F = Z/r^2$	CN	Z/r	CN
Cs_2SiO_3	Cs^+,H_2SiO_3	-46.820	0.26	VI	0.56	VI
K_2SiO_3	K^+,H_2SiO_3	-41.735	0.35	VI	0.68	VI
$BaSiO_3$	Ba^{2+},H_2SiO_3	-30.570	0.88^t 0.71	VIII XII	1.32 1.19^t	VIII XII
Na_2SiO_3	Na^+,H_2SiO_3	-28.815	0.82^t	VI	0.91	VI
$SrSiO_3$	Sr^{2+},H_2SiO_3	-24.400	1.13^t 0.91	VIII XII	1.50 1.35^t	VIII XII
Li_2SiO_3	Li^+,H_2SiO_3	-22.740	1.49^t	VI	1.21	VI
$CaSiO_3$	Ca^{2+},H_2SiO_3	-16.116	1.39^t 0.97	VIII XII	1.67 1.40	VIII XII
$MnSiO_3$	Mn^{2+},H_2SiO_3	-14.871	3.75	VI_H	2.19	VI_H
$FeSiO_3$	Fe^{2+},H_2SiO_3	-14.609	2.70^t 4.2	VI_H VI_L	2.32^t_H 2.89	VI VI_L
$NiSiO_3$	Ni^{2+},H_2SiO_3	-14.347	4.88^t	VI	2.59	VI
$MgSiO_3$	Mg^{2+},H_2SiO_3	-13.888	4.59^t 3.12	IV VI	3.03 2.50^t	IV VI
B_2O_3	H_3BO_3	-9.930	75.00	IV	15.00	IV
Al_2O_3	AlO(OH)	+3.040	13.6^t	IV	6.38^t	IV
Al_2O_3	$Al(OH)_3$	-7.73	8.06	VI	4.92	VI
UO_3	$UO_2(OH)_2$ H_2O	-6.80	9.14	VI	6.25	VI
SiO_2	H_2SiO_3	+5.590*	34.60	IV	11.76	IV
Al_2O_3	$Al(OH)_3$					
Fe_2O_3	$Fe(OH)_3$	+15.500	9.23	IV_H	5.26	IV_H
TiO_2	$TiO(OH)_2$	+15.990	8.40	VI	5.79	VI
$ZrSiO_4$	$ZrO(OH)^+,HSiO_3^-$	+45.100	4.72	VI	5.0	VI

---

* G hydration for SiO_2 is given by Paul (1982) ref. 5 as +5.59°Kcal/mol. However, a more realistic value of +3.7 Kcal/mole (Morey, Fournier, and Rowe, ref. 60) or +3.76 or (Rimstidt, ref. 16) may apply for vitreous silica.

** Where H and L refer to ions in high spin or low spin states.

t Preferred value of F or Z/R.

#6

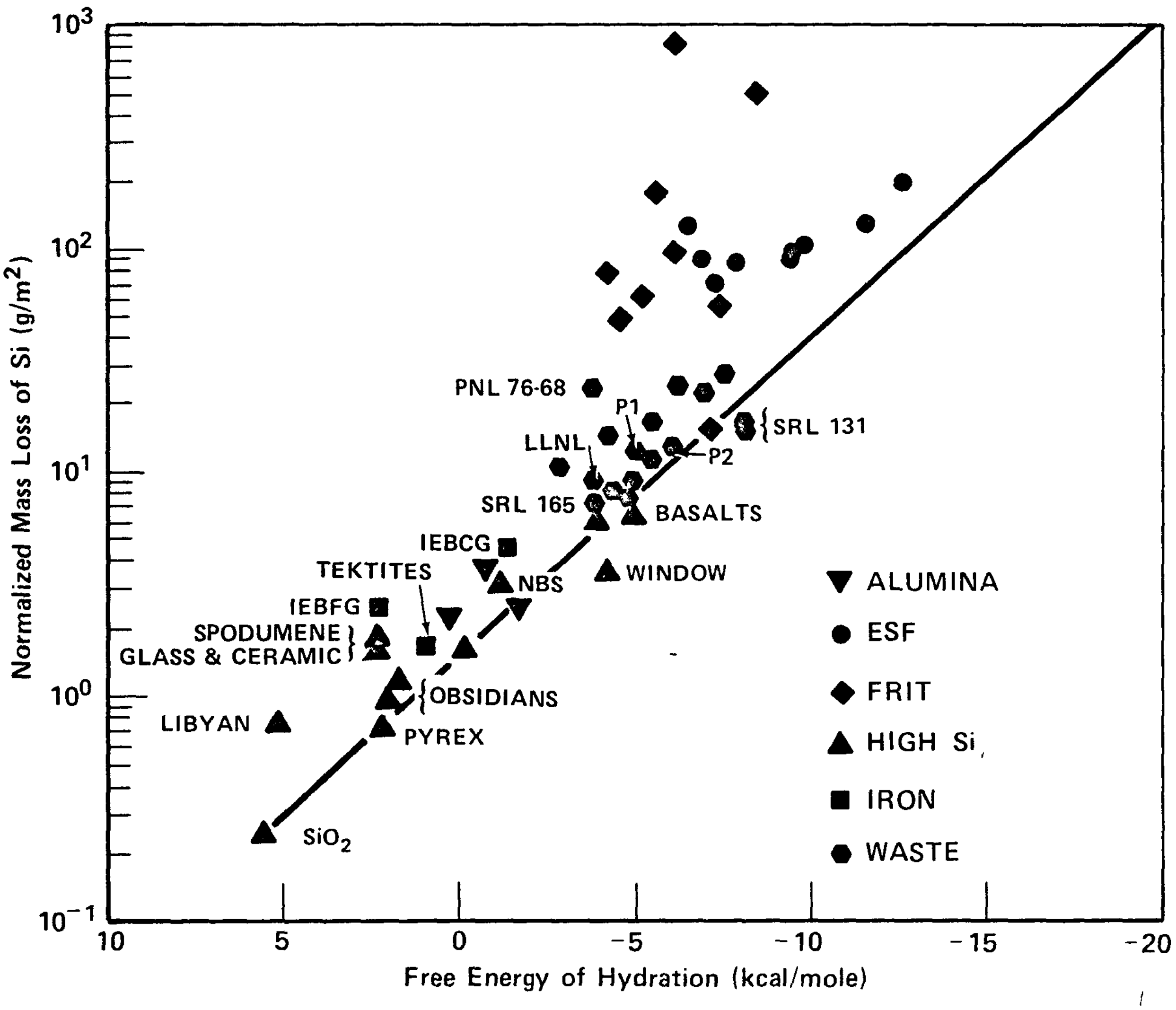
FIGURE CAPTIONS

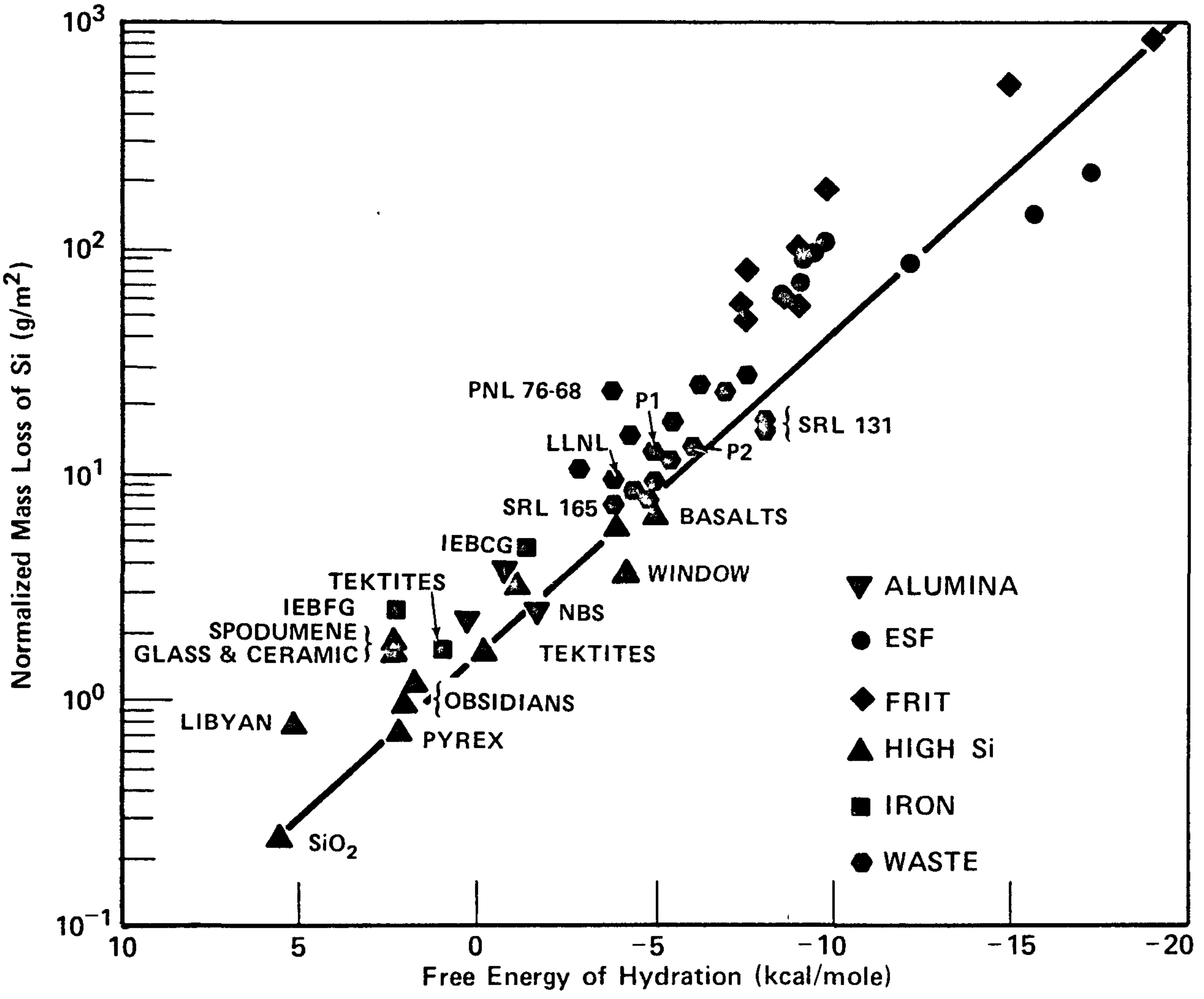
Figure 1a Relation between the normalized mass loss of silicon and the calculated free energy of hydration for a variety of glasses including high alumina glasses, European Science Foundation (ESF) simulated medieval window glasses, frit glasses, glasses high in silica, high ferrous iron containing glasses and nuclear waste glasses. The free energy of hydration assumes that all the silicate components of these glasses hydrate to H_2SiO_3.

Figure 1b Relation between the normalized mass loss of silicon and the calculated free energy of hydration for a variety of glasses. For the ESF and frit glasses an additional contribution to the hydration free energy is included. This arises from the additional hydration free energy for the dissociation of $H_2SiO_3^-$ at the high pH values achieved during the standard leach test.

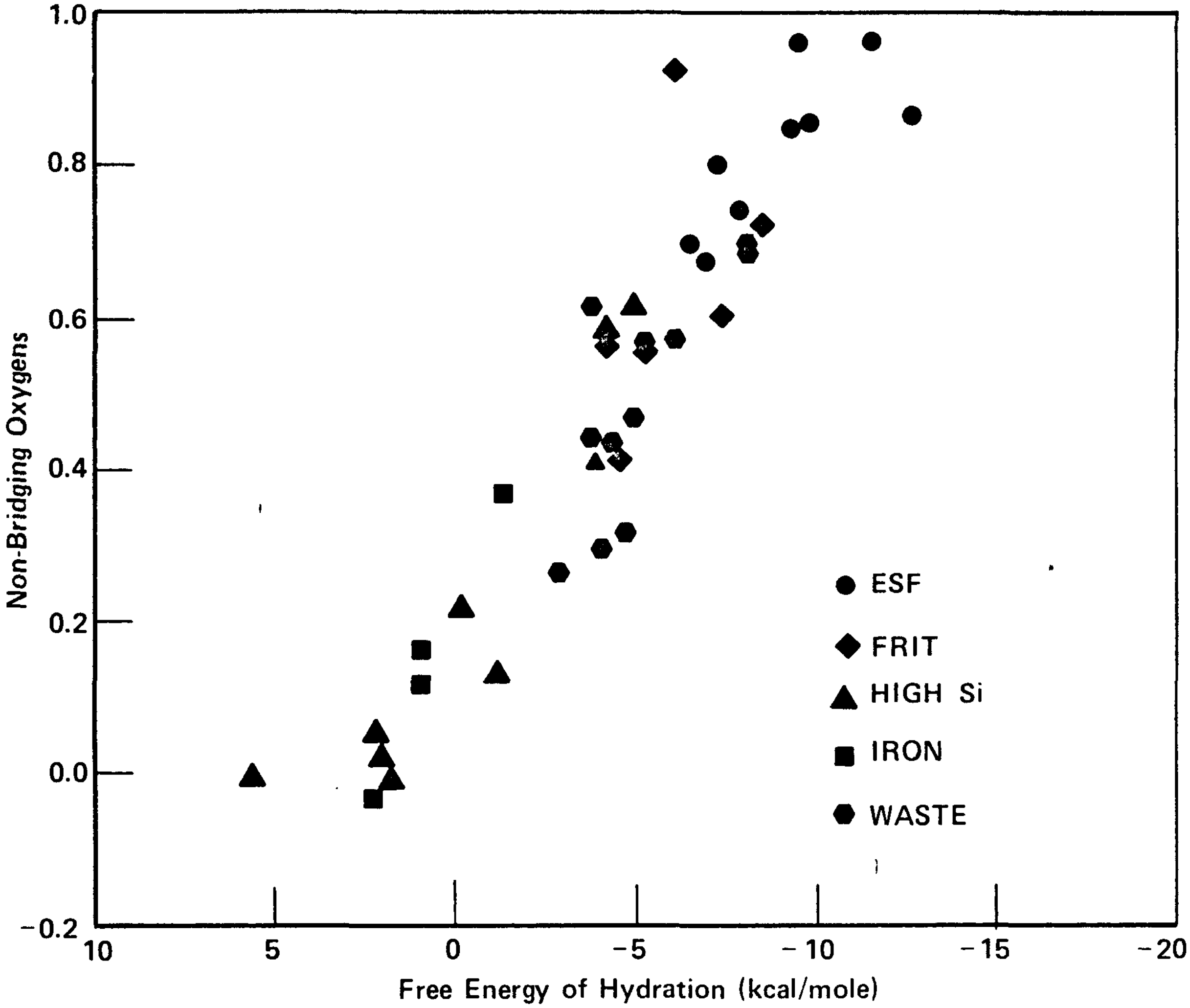
Figure 2a Relation between the calculated number of non-bridging oxygen bonds and the calculated free energy of hydration. The glass structure is the only component considered and the free energy for the dissociation of H_2SiO_3 to $HSiO_3^-$ in the solution does not need to be considered.

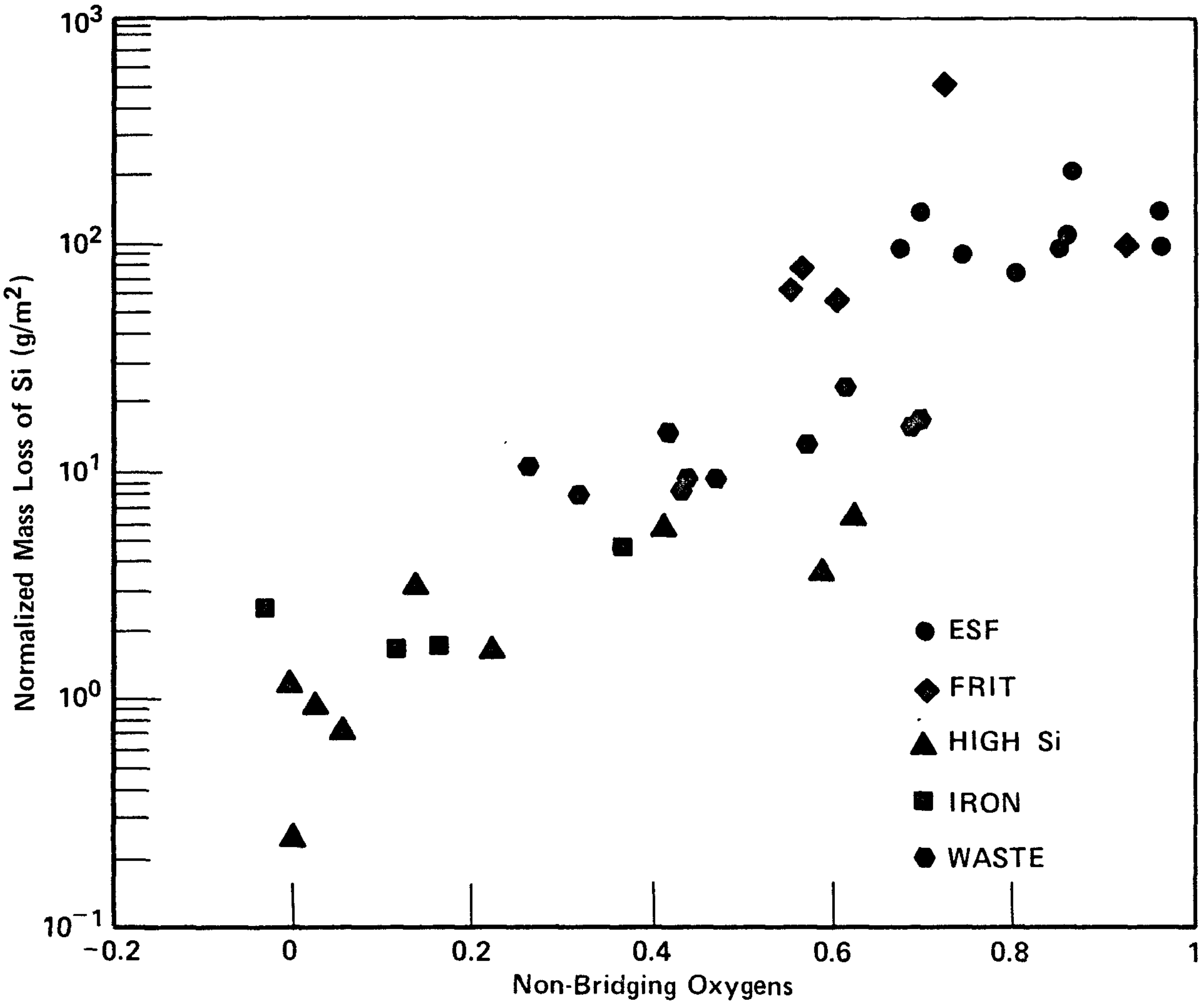
Figure 2b The relation between the number of non-bridging oxygen bonds and the amount of elemental silicon released by these glasses demonstrate the control of bond energetics during leaching of glass.


Normalized Mass Loss of Si (g/m^2)
Free Energy of Hydration (kcal/mole)
10^3
10^2
10^1
10^0
10^{-1}
10
5
0
-5
-10
-15
-20
PNL 76-68
P1
LLNL
P2
SRL 131
SRL 165
BASALTS
IEBCG
TEKTITES
NBS
WINDOW
IEBFG
SPODUMENE
GLASS & CERAMIC
OBSIDIANS
LIBYAN
PYREX
SiO_2
▼ ALUMINA
● ESF
◆ FRIT
▲ HIGH Si
■ IRON
⬣ WASTE



10^3
10^2
10^1
10^0
10^{-1}
Normalized Mass Loss of Si (g/m^2)
PNL 76-68
P1
LLNL
P2
SRL 131
SRL 165
BASALTS
IEBCG
TEKTITES
WINDOW
IEBFG
NBS
SPODUMENE
GLASS & CERAMIC
TEKTITES
OBSIDIANS
LIBYAN
PYREX
SiO_2
▼ ALUMINA
● ESF
◆ FRIT
▲ HIGH Si
■ IRON
⬢ WASTE
10
5
0
−5
−10
−15
−20
Free Energy of Hydration (kcal/mole)


1.0
0.8
0.6
0.4
0.2
0.0
−0.2
Non-Bridging Oxygens
10
5
0
−5
−10
−15
−20
Free Energy of Hydration (kcal/mole)
● ESF
◆ FRIT
▲ HIGH Si
■ IRON
⬢ WASTE



Normalized Mass Loss of Si (g/m^2)
10^3
10^2
10^1
10^0
10^{-1}
−0.2
0
0.2
0.4
0.6
0.8
1
Non-Bridging Oxygens
● ESF
◆ FRIT
▲ HIGH Si
■ IRON
⬢ WASTE

APPENDIX I CALCULATION OF HYDRATION FREE ENERGY FOR A GLASS

(after Paul, References 5, 23)

1. Convert the normal glass composition by weight to the molar composition expressed as mole fraction.

2. Convert moles of R_2O, RO, and ZrO_2 to moles of silicate structural units, e.g., R_2SIO_3, $RSiO_3$ and $ZrSiO_4$. Leave excess SiO_2 and all other components as oxide structural units, e.g., SiO_2, U_3O_8, UO_2, Fe_2O_3, Al_2O_3.

3. Multiply the mole fractions of each structural entity by the appropriate free energy of hydration (Table 1) for

$$M_xSiO_2 + H_2O \qquad H_2SiO_3 + xM$$

$$\text{or } R_xO_y + H_2O \qquad xR(OH)_y$$

4. Sum values from step 3 to obtain a free energy of hydration (in kcal/mol) for the entire glass.

APPENDIX II GLASS AND GLASS CERAMIC COMPOSITIONS IN WEIGHT PERCENT AND LEACH PARAMETER DATA

ESF GLASSES (EUROPEAN SCIENCE FOUNDATION)

GLASS	AL2O3	B2O3	BAO	CAO	CS2O	FEO	FE2O3	K2O	LI2O	MGO	MNO	NA2O	NIO	SIO2	SRO	TIO2	UO2	ZRO2	RAREARTH	DELTAGI	DELTAGII	PH	NLSI	REFERENCE
144	3.88	0.00	0.00	20.59	0.00	0.00	2.10	29.49	0.00	0.06	0.10	0.09	0.00	43.68	0.00	0.00	0.00	0.00	0.00	17.143	-17.604	10.7500	210.0000	58
147	3.93	0.00	0.00	30.91	0.00	0.00	0.00	14.99	0.00	0.06	0.00	0.10	0.00	50.01	0.00	0.00	0.00	0.00	0.00	9.346	-11.561	9.7000	95.0000	58
148	4.01	0.00	0.00	26.13	0.00	0.00	0.50	14.68	0.00	0.06	0.22	0.10	0.00	54.29	0.00	0.00	0.00	0.00	0.00	7.889	-9.210	9.2700	90.0000	58
149	4.20	0.00	0.00	21.84	0.00	0.00	0.08	14.46	0.00	0.06	1.80	0.10	0.00	57.54	0.00	0.00	0.00	0.00	0.00	8.076	-10.962	10.2000	95.0000	58
150	4.33	0.00	0.00	22.01	0.00	0.00	0.27	1.44	0.00	6.64	0.00	9.58	0.00	55.73	0.00	0.00	0.00	0.00	0.00	8.808	-11.125	10.2400	75.0000	58
151	4.08	0.00	0.00	20.03	0.00	0.00	0.27	7.55	0.00	3.36	0.47	5.28	0.00	58.96	0.00	0.00	0.00	0.00	0.00	6.481	10.0000	9.9400	134.0000	58
158	3.89	0.00	0.00	28.56	0.00	0.00	0.00	24.42	0.00	0.06	0.11	0.09	0.00	42.87	0.00	0.00	0.00	0.00	0.00	15.556	-16.121	10.6300	140.0000	58
159	4.05	0.00	0.00	35.45	0.00	0.00	0.00	14.66	0.00	0.06	1.13	0.00	0.00	44.65	0.00	0.00	0.00	0.00	0.00	13.518	-13.979	10.6000	97.0000	58
77/33	4.14	0.00	0.00	22.68	0.00	0.00	2.59	0.00	0.00	0.07	0.00	21.74	0.00	48.78	0.00	0.00	0.00	0.00	0.00	9.820	-12.193	9.8000	110.0000	58

FRIT GLASSES

GLASS	AL2O3	B2O3	BAO	CAO	CS2O	FEO	FE2O3	K2O	LI2O	MGO	MNO	NA2O	NIO	SIO2	SRO	TIO2	UO2	ZRO2	RAREARTH	DELTAGI	DELTAGII	PH	NLSI	
FRS12	0.00	20.00	0.00	0.00	0.00	0.00	0.00	0.00	15.00	1.00	0.00	3.00	0.00	60.00	0.00	0.00	0.00	1.00	0.00	7.1257	9.4500	9.4500	15.7850	—
FRS15	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	15.00	1.00	0.00	8.00	0.00	75.00	0.00	0.00	0.00	1.00	0.00	18.632	12.2000	12.2000	854.0500	—
FRS17	0.00	9.50	0.00	0.00	0.00	0.00	0.00	0.00	7.50	1.00	0.00	13.50	0.00	67.50	0.00	0.00	0.00	1.00	0.00	9.551	10.7500	10.4500	180.5500	—
FRS2	0.00	20.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	18.00	0.00	60.00	0.00	0.00	0.00	1.00	0.00	7.336	10.4000	9.4500	50.5000	—
F131	0.00	15.96	0.00	2.42	0.00	0.00	0.00	0.00	6.16	1.33	0.00	18.62	0.00	53.11	0.00	1.21	0.00	0.55	0.64	13.565	11.1000	11.0100	513.0000	—
F153	0.00	10.00	0.00	0.00	0.00	0.00	0.00	0.00	4.50	2.00	0.00	13.50	0.00	67.01	0.00	1.99	0.00	0.99	0.00	7.356	10.5000	9.6000	79.0000	61
F165	0.00	10.00	0.00	0.00	0.00	0.00	0.00	0.00	7.00	0.98	0.00	13.01	0.00	68.02	0.00	0.00	0.00	0.99	0.00	8.47	10.5000	9.8500	62.7000	62
F21	0.00	9.53	0.00	4.26	0.00	0.00	0.00	0.00	3.65	2.13	0.00	17.43	0.00	53.19	0.00	9.82	0.00	0.00	0.00	9.13	10.5000	10.3000	97.8000	61
F211	0.00	11.69	0.00	0.59	0.00	0.00	0.00	0.00	4.63	0.00	0.00	21.68	0.00	61.41	0.00	0.00	0.00	0.00	0.00	8.87	10.2300	10.0500	56.1000	61

WASTE GLASSES

GLASS	AL2O3	B2O3	BAO	CAO	CS2O	FEO	FE2O3	K2O	LI2O	MGO	MNO	NA2O	NIO	SIO2	SRO	TIO2	UO2	ZRO2	RAREARTH	DELTAGI	DELTAGII	PH	NLSI	
LL-S29	28.38	0.00	0.00	6.30	1.37	4.67	0.00	0.00	0.00	0.00	1.65	12.62	0.00	36.66	0.22	4.45	0.00	3.68	0.00	-3.7706	2.6127	6.5000	9.4000	63
M2	8.86	18.33	0.67	0.00	1.28	1.85	2.06	0.00	0.00	0.00	0.92	14.63	0.54	43.98	0.38	0.00	0.00	1.86	4.65	-4.7563	-4.3201	8.5000	7.8000	64
M3	4.20	14.05	0.58	4.25	1.11	0.75	0.83	0.00	0.00	0.36	0.79	13.67	0.47	52.99	0.33	0.00	0.00	1.61	4.02	-4.3557	-3.6569	8.3500	8.3500	64
M4	5.08	22.81	0.84	0.00	1.62	1.31	1.45	0.00	0.00	0.00	1.13	9.12	0.67	47.28	0.48	0.00	0.00	2.34	5.86	-2.8590	2.6992	8.5000	10.6000	64
M5	3.11	14.96	0.64	2.08	1.25	1.38	1.54	0.00	2.08	0.00	0.89	12.98	0.52	51.90	0.36	0.00	0.00	1.81	4.51	-4.9363	-6.1955	9.1000	9.2000	64
M6	2.08	19.17	0.64	3.90	1.25	1.38	1.54	0.00	0.00	0.00	0.89	11.71	0.52	50.24	0.36	0.00	0.00	1.81	4.51	-4.2557	-4.7734	8.8000	14.8000	64
P-1	12.21	0.00	0.00	5.21	0.00	3.70	4.10	0.00	0.00	0.00	2.20	18.02	0.60	52.35	0.00	0.00	1.60	0.00	0.00	-5.4197	-8.8211	9.9400	11.4800	65
P-3	8.48	3.03	0.00	4.65	0.00	4.85	5.45	0.00	0.00	0.00	2.32	16.16	1.31	49.70	0.00	3.03	1.01	0.00	0.00	-5.0332	-7.9149	9.7700	12.6100	65
WRS12	7.51	10.95	0.00	2.36	0.00	9.60	10.67	0.00	8.21	0.58	5.33	3.18	1.61	39.45	0.00	0.00	0.00	0.55	0.00	-7.5508	-9.7619	9.7500	27.4200	—
WRS15	7.51	0.00	0.00	2.36	0.00	9.60	10.67	0.00	8.21	0.58	5.33	5.92	1.61	47.65	0.00	0.00	0.00	0.55	0.00	-6.9339	-9.9881	10.0000	22.7800	—
WRS17	5.01	6.63	0.00	1.57	0.00	6.41	7.13	0.00	5.24	0.72	3.56	10.45	1.08	51.50	0.00	0.00	0.00	0.70	0.00	-6.2256	-9.3153	9.9000	24.7100	—
WRS2	5.09	14.16	0.00	1.60	0.00	5.86	6.51	0.00	0.00	0.73	3.61	13.79	1.01	46.95	0.00	0.00	0.00	0.71	0.00	-5.4949	-6.2645	9.0000	16.7600	—
131-30	3.51	10.90	0.00	1.23	0.00	4.93	5.47	0.00	4.10	1.45	3.42	14.07	4.21	45.06	0.00	0.75	0.00	0.39	0.53	-8.0707	-9.7432	9.4800	17.0800	66
131 50	5.81	7.74	0.00	2.10	0.00	10.98	12.20	0.00	2.95	1.06	5.72	11.37	3.01	35.70	0.00	0.55	0.00	0.34	0.47	-8.1430	-9.3024	9.3900	15.9900	66
165 GGW	12.18	6.75	0.00	1.44	0.39	0.00	6.36	0.00	4.72	0.81	2.35	8.31	0.96	52.70	0.48	0.00	1.88	0.67	0.00	-3.8551	-4.2820	8.8000	7.2800	67
165MM	3.98	7.14	0.00	1.49	0.00	5.27	5.85	0.21	5.10	0.71	2.68	11.55	0.77	54.42	0.18	0.00	0.00	0.71	0.00	-6.0676	-5.4461	8.5000	13.2000	—
76-68	0.68	10.05	0.60	2.69	1.16	5.09	5.66	0.15	0.00	0.17	0.07	13.15	0.29	46.59	0.48	3.46	0.00	1.92	7.78	-3.7913	-6.7432	9.7500	23.8000	68

HIGH SILICA GLASSES

GLASS	AL2O3	B2O3	BAO	CAO	CS2O	FEO	FE2O3	K2O	LI2O	MGO	MNO	NA2O	NIO	SIO2	SRO	TIO2	UO2	ZRO2	RAREARTH	DELTAGI	DELTAGII	PH	NLSI	
BASALT	14.05	0.00	0.03	10.17	0.00	11.55	0.00	0.48	0.00	6.17	0.16	5.02	0.00	50.30	0.26	1.76	0.00	0.03	0.00	-4.9663	-0.0478	7.0000	6.4500	68
CAS (P 16)	16.29	0.00	0.00	15.79	0.04	1.44	1.60	1.89	0.00	3.29	0.00	5.04	0.00	54.24	0.04	0.11	0.00	0.22	0.00	-3.9821	-3.3782	8.5000	5.7900	65
CUA	8.79	3.45	0.00	1.05	0.15	9.42	7.11	0.00	0.00	0.00	4.60	2.30	2.09	59.00	0.10	0.00	1.19	0.00	0.74	-0.1385	3.8714	7.0000	1.6800	69
LIBYAN	2.86	0.00	0.00	0.84	0.00	0.00	2.19	0.00	0.20	0.07	0.00	0.11	0.00	93.53	0.00	0.21	0.00	0.00	0.00	5.1846	4.3664	8.3000	0.7700	—
NBS	3.66	17.24	0.28	0.14	0.00	0.00	0.10	7.31	0.47	0.00	0.00	2.74	0.00	68.05	0.00	0.00	0.00	0.00	0.00	-1.1363	0.8657	7.5800	3.2000	68
OBSID1	13.52	0.00	0.00	1.22	0.00	0.00	2.44	4.67	0.00	0.41	0.10	3.35	0.00	73.98	0.00	0.30	0.00	0.00	0.00	1.7607	10.5649	5.0000	1.2100	—
OBSID2	12.43	0.00	0.00	1.22	0.00	2.41	2.68	5.07	0.00	0.14	0.00	1.44	0.00	73.73	0.00	0.87	0.00	0.00	0.00	2.0490	7.5483	6.2100	0.9600	—
PYREX	2.00	13.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	4.00	0.00	81.00	0.00	0.00	0.00	0.00	0.00	2.1750	14.3219	3.7000	0.7300	67
SIO2 (7740)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	100.00	0.00	0.00	0.00	0.00	0.00	5.5900	13.2023	5.1500	0.2500	—
SPODC	22.11	0.03	0.00	0.57	0.00	0.00	0.22	0.00	4.04	0.03	0.00	0.16	0.37	67.63	0.00	1.49	0.06	1.55	1.73	2.3491	2.2256	8.3700	1.6700	—
SPODG	22.11	0.03	0.00	0.57	0.00	0.00	0.22	0.00	4.04	0.03	0.00	0.16	0.37	67.63	0.00	1.49	0.06	1.55	1.73	2.3491	2.4166	8.3000	1.8400	—
WINDOW	0.50	0.00	0.00	13.10	0.00	0.00	0.00	0.00	0.00	1.70	0.00	13.90	0.00	70.80	0.00	0.00	0.00	0.00	0.00	-4.3616	-2.0826	7.7900	3.6400	67

FERROUS IRON GLASSES

GLASS	AL2O3	B2O3	BAO	CAO	CS2O	FEO	FE2O3	K2O	LI2O	MGO	MNO	NA2O	NIO	SIO2	SRO	TIO2	UO2	ZRO2	RAREARTH	DELTAGI	DELTAGII	PH	NLSI	
ATTEK	12.59	0.00	0.00	2.63	0.00	5.68	0.00	2.41	0.00	1.98	0.00	1.75	0.00	72.12	0.00	0.85	0.00	0.00	0.00	0.9594	5.8924	6.5200	1.6900	—
CORTEK	12.59	0.00	0.00	2.72	0.00	1.78	0.00	1.83	0.00	1.87	0.00	4.45	0.00	74.58	0.00	0.18	0.00	0.00	0.00	0.9515	10.8706	4.6600	1.6500	—
IEBCG	13.38	0.00	0.00	9.36	0.00	5.03	0.00	2.52	0.00	3.42	0.00	1.51	0.00	61.07	0.00	0.00	2.11	1.61	0.00	-1.3315	-1.3429	8.5500	4.6600	39
IEBFG	16.33	0.00	0.00	1.80	0.00	1.80	0.00	3.41	0.00	0.00	0.00	1.90	0.00	73.65	0.00	0.00	0.80	0.30	0.00	2.3197	2.9250	8.0000	2.5200	39

ALUMINA GLASSES

GLASS	AL2O3	B2O3	BAO	CAO	CS2O	FEO	FE2O3	K2O	LI2O	MGO	MNO	NA2O	NIO	SIO2	SRO	TIO2	UO2	ZRO2	RAREARTH	DELTAGI	DELTAGII	PH	NLSI	
SI70AL30	42.11	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	57.89	0.00	0.00	0.00	0.00	0.00	0.69	0.694	4.7400	2.7000	41
SI75AL25	36.13	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	63.87	0.00	0.00	0.00	0.00	0.00	0.55	0.554	4.7200	3.9000	41
SI80AL20	29.79	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	70.21	0.00	0.00	0.00	0.00	0.00	1.77	1.775	5.0000	2.5500	41