



**THE ROLE OF TEST PARAMETERS ON THE KINETICS AND
THERMODYNAMICS OF GLASS LEACHING**

by

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THE ROLE OF TEST PARAMETERS ON THE KINETICS AND THERMODYNAMICS OF GLASS LEACHING

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Abstract

The relative durabilities of nuclear waste, natural, and ancient glasses have been assessed by standard laboratory leach tests. Different test conditions result in different glass surface areas (SA), leachant volumes (V), and test durations (t). Leachate concentrations are known to be a parabolic function of the kinetic test parameter $SA/V \cdot t$. Based on durability experiments of glass monoliths at low $(SA/V) \cdot t$ glass durability has been shown to be a logarithmic function of the thermodynamic hydration free energy, ΔG_{hyd} . The thermodynamic hydration free energy, ΔG_{hyd} , can be calculated from glass composition and solution pH.

High surface area tests at longer time durations are more representative of the conditions anticipated in geologic repository environments. In the repository environment high effective glass surface areas to solution volume ratios may occur as a result of slow groundwater flow rates. The application of hydration thermodynamics to crushed glass, high $(SA/V) \cdot t$, durability tests has been demonstrated. The relative contributions of the kinetic test parameters, $(SA/V) \cdot t$, and the thermodynamic parameter, ΔG_{hyd} , have been shown to define a plane in ΔG_{hyd} -concentration- $(SA/V) \cdot t$ space. At constant test conditions, e.g. constant $(SA/V) \cdot t$, the intersection with this surface indicates that all ΔG_{hyd} -concentration plots should have similar slopes and predict the same relative durabilities for various glasses as a function of glass composition. Using this approach, the durability of nuclear waste glasses has been interpolated to be $\sim 10^6$ years and no less than 10^3 years.

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 silicates¹¹⁻¹⁴ 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, (silicic acid, cations or complexes in solution, precipitates, and /or solids). Such an ontological approach to glass durability was formulated by Newton and Paul¹⁵ 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 composition¹⁵ 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 selected¹⁶ 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.

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.¹⁷⁻²² The thermodynamic approach of Newton and Paul¹⁵ 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 Paul¹⁵ was expanded and shown to be applicable to a wide variety of glasses¹⁷⁻²² in various environmental conditions.²³

The durability of 107 nuclear waste glasses was compared²² to the remaining 200 natural and man-made glasses in a standard laboratory (MCC-1) durability test. Since the following parameters are known¹ 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

parameters 1-4 were kept constant and only the glass composition was varied.¹⁷⁻²³ The MCC-1 test protocol tests glass monoliths at low (SA/V). In later studies, the glass composition was kept constant by choosing a representative "reference set" of about 10 glasses.²⁰ The test temperature was kept constant at 90°C, but the test duration was varied. Crushed glasses were tested at various time durations according to the MCC-3 leach test protocol which has a high (SA/V). The (SA/V) ratio was varied by testing glasses crushed to various mesh sizes. The high surface area tests are more representative of the conditions that nuclear waste glasses will be exposed to in geologic repository environments where high effective surface areas to volume ratios may occur as a result of low groundwater flow rates.²⁴

The slopes of the ΔG_{hyd} -durability plots for low (SA/V)•t laboratory tests (MCC-1 test protocol) and for high (SA/V)•t laboratory tests (MCC-3 test protocol) are similar. In this study the relative contributions of the kinetic test parameters, (SA/V)•t, and the thermodynamic parameter, ΔG_{hyd} , will be examined. The application of hydration thermodynamics to various durability test conditions is shown to predict the same relative durabilities for various glasses as a function of glass composition.

Slide Commentary

Figure 1 The objective of this study is to demonstrate the relative role of kinetics and thermodynamics in predicting the long term performance of nuclear waste glasses. The kinetic contribution is primarily a function of the test geometry. In particular, the test parameters such as the exposed glass surface area (SA), the solution volume (V), and the test duration (t) alter the kinetic contribution. The thermodynamic contribution represents the long term glass stability as a function of glass composition and structure (bonding).

- Figure 2 Glass durability is a function of both kinetic and thermodynamic stability.
- Figure 3 The dissolution of a glass in solution as a function of time follows a parabolic curve. Kinetic diffusion models with, time dependent dc/dt (Δ concentration/ Δ time) terms, can be fit to the parabolic curve but the mathematical solutions are not unique. Also the kinetic dissolution models cannot readily distinguish the relative durabilities of a sequence of glasses. Thermodynamics can be used to model the long term "equilibrium" or steady state saturation concentrations where the slope of the dc/dt terms approaches zero. 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.
- Figure 4 The free energy of hydration can be calculated from the glass composition by assuming that the glass is composed of orthosilicate and oxide species. A hydration reaction can be written for the hydration of each species and weighted by the mole fraction of that component present in the glass. The summation of weighted contributions from all the species represents the overall hydration free energy of a glass based on its composition. The formalism is

$$\Delta G_{\text{hyd}} = \sum x_i \cdot (\Delta G_{\text{hyd}})_i$$

where $(\Delta G_{\text{hyd}})_i$ is the free energy change of the thermodynamically most stable hydration reaction of component i at mole fraction x_i . The original approach is attributed to Newton and Paul¹⁵ and was modified by Jantzen and Plodinec¹⁷⁻²³ to include additional species and the effects of solution pH.

Figure 5 The parameters known to affect durability are

- (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

All of these were kept constant except glass composition which was the variable studied.

Figure 6 Over 150 different glasses of widely varying composition were examined. Glass monoliths with a geometrically measured surface area of 4 cm² were immersed in 40 cm³ of high-purity water (ASTM Type I) according to the MCC-1 leach test protocol.²⁵ In this manner, the SA/V ratio was always kept constant at 0.1 cm⁻¹. The durability test was performed at 90°C for 28 days duration. All the durability tests were run in duplicate.

Figure 7 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. 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

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

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)

Figure 8 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.²⁰ These included natural obsidians, tektites, basalts, pure SiO_2 , pyrex, modern window glass, and simulated medieval window glasses from the European Science Foundation (ESF). 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 are shown. 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.²¹ The computer generated equation of best fit relating glass composition to silicon released from the glass gave a mathematically determined slope of -0.2240.

Figure 9 Since many natural and man-made glasses do not contain boron, only 140 experimental observations (70 glasses) could be statistically fit. 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.

Figure 10 Since the slopes relating ΔG_{hyd} to $\log(NL_{Si})$ and to $\log(NL_B)$ are similar, it is not surprising that a plot of $\log(NL_{Si})$ and $\log(NL_B)$ has a slope of ~1. 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.

Figure 11 In three dimensions ΔG_{hyd} , $\log(NL_{Si})$, and $\log(NL_B)$ are seen to be colinear due to the highly correlated variable pair interactions, e.g. by defining any two variables the third is fixed. The computer calculated colinearity equation is shown.

Figure 12 In the initial studies of glass durability as a function of glass composition, leachants of high-purity water were used. In order to quantify the effects of silica saturated groundwater (solution) chemistry on glass durability, a "reference set" of ~10 glasses were chosen for study in two groundwaters representative of a tuff repository (J-13) and a basalt repository (GR-4). The thermodynamic approach was applied to the glass compositions including pure SiO_2 , tektites, basalts, waste glasses, two ESF glasses, and a poorly durable frit glass. The test temperature, test duration, and SA/V ratio were kept the same as the studies in high-purity water.

Figure 13 The silica-saturated groundwaters were found to minimize the amount of silica released to solution. The chemistry of the groundwaters 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 curve determined is an expression of the response of both glass and solution pH. 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, superimposed on the linear curve defined by the high-purity water experiments.²³ 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.

Figure 14 In separate durability 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. Crushed glasses were tested at various time durations. Crushed glasses weighing 1.5 grams were immersed in 40 cm³ of high-purity water (ASTM Type I) according to the MCC-3 leach test protocol. The SA/V ratio was varied by testing glasses crushed to various mesh sizes.

- Figure 15 The "reference set" of crushed glasses tested by the MCC-3 test protocol at various SA/V conditions and at various test durations paralleled the relative durabilities determined from monolithic MCC-1 tests. Because the SA/V term dominates the denominator of the normalized mass loss calculation (Figure 7) the glass response does not exhibit good separation. Note that the slopes of $\log(NL_{Si}) - \Delta G_{hyd}$ for monolithic tests (low SA/V $\cdot t$) and crushed glass tests (high SA/V $\cdot t$) are the same.
- Figure 16 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) $\cdot t$ parameter.^{26,27} Measures of reaction progress such as $\log(NL_{Si})$ or $\log(Si)$ in ppm have been shown to be a function of (SA/V) $\cdot t$ for the sequence of "reference glasses" discussed above.²⁰ 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 sensitive to glass composition when plotted against leachate concentration in ppm rather than in normalized mass loss. The relative position of the $\log(NL_{Si})$ verses (SA/V) $\cdot t$ curves for the various glasses increases in the order predicted by their relative ΔG_{hyd} values.
- Figure 17 A simplified version of Figure 16 demonstrating that small (SA/V) $\cdot t$ and large (SA/V) $\cdot t$ follow a parabolic relationship. Normally the origin represents the smaller (SA/V) $\cdot t$ as shown.
- Figure 18 The origin of the (SA/V) $\cdot t$ plot is reversed to orient the viewer for the 3-dimensional plot of $\log(NL_{Si}) - (SA/V) \cdot t - \Delta G_{hyd}$ to be shown next.
- Figure 19 Since $\log(NL_{Si})$ is a function of both (SA/V) $\cdot t$ and ΔG_{hyd} , a plot of over 120 data points collected on the "reference set" of glass was plotted in three dimensional $\log(NL_{Si}) - (SA/V) \cdot t - \Delta G_{hyd}$ space. The data formed a plane which could be fitted statistically with an interpolated spline function. Note how the curvature of the (SA/V) $\cdot t$ verses $\log(NL_{Si})$ sections of the surface is like that shown in Figure 18.
- Figure 20 A scatter plot of the 120 data points that formed the spline function surface of the previous slide.
- Figure 21 A different perspective of the spline function surface.
- Figure 22 Scatter plot of the 120 data points corresponding to the perspective shown in Figure 21.

Figure 23 The slopes of the $\Delta G_{\text{hyd}} - \log(NL_{\text{Si}})$ plots for monolithic tests (low $SA/V \cdot t$) and for crushed glass tests (high $SA/V \cdot t$) are similar because they intersect the three-dimensional plane at constant $(SA/V) \cdot t$. 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 as demonstrated by Grambow.²⁸

Figure 24 Conclusions

- hydration thermodynamics has wide applicability to the prediction of natural, ancient, modern, and nuclear waste glass durability.
- hydration thermodynamics furnishes a quantitative frame of reference to explain how varying test parameters affect glass durability
- the kinetic $(SA/V) \cdot t$ parameter determines the relative deviation from equilibrium, e.g. the steady state leachate concentration, for any given test geometry.

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**THE ROLE OF TEST PARAMETERS
ON THE KINETICS AND THERMODYNAMICS
OF GLASS DISSOLUTION**

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OBJECTIVE

TO DEMONSTRATE THE RELATIVE ROLE OF

- KINETIC TEST PARAMETERS**
- HYDRATION THERMODYNAMICS**

**IN PREDICTING THE LONG TERM PERFORMANCE
OF NUCLEAR WASTE GLASSES**

$$\text{DURABILITY} = f(\text{KINETIC STABILITY}) \times f(\text{THERMODYNAMIC STABILITY})$$

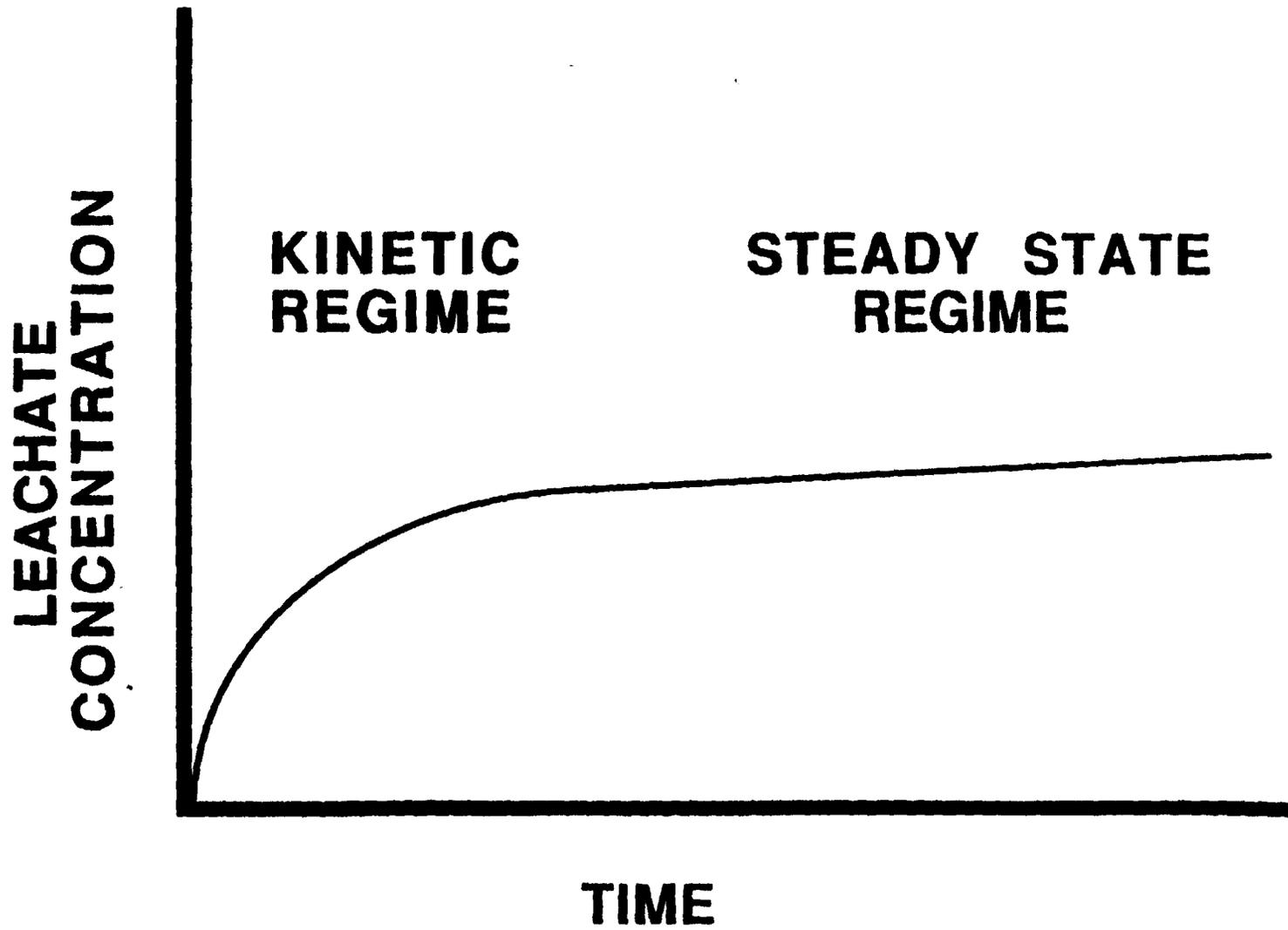
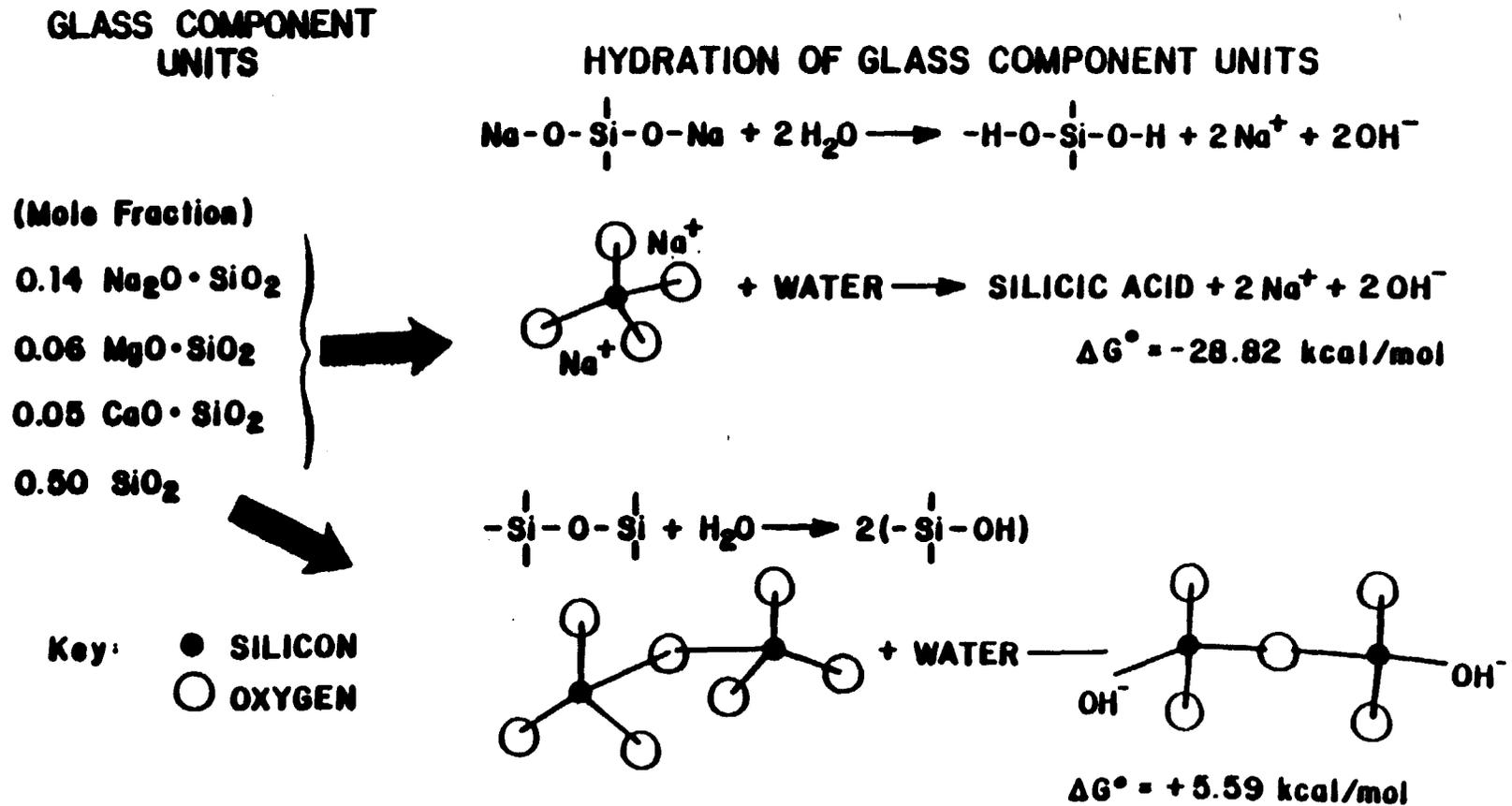


Figure 3

FREE ENERGY OF HYDRATION FOR A SIMPLE GLASS COMPOSITION



Jantzen and Plodinec (1984)

FACTORS AFFECTING DURABILITY OF GLASSES

- | | |
|--|-------------------------|
| o Exposed surface area | SA/V CONST |
| o Volume of leaching solution | SA/V CONST |
| o Nature of leaching solution | DEIONIZED WATER |
| o Frequency of replenishing/
changing leaching solution | STATIC 28-DAY |
| o Temperature of leaching | 90°C |
| o Glass composition | VARIABLE STUDIED |

MATERIALS CHARACTERIZATION CENTER (MCC)

LEACH TEST DESCRIPTION

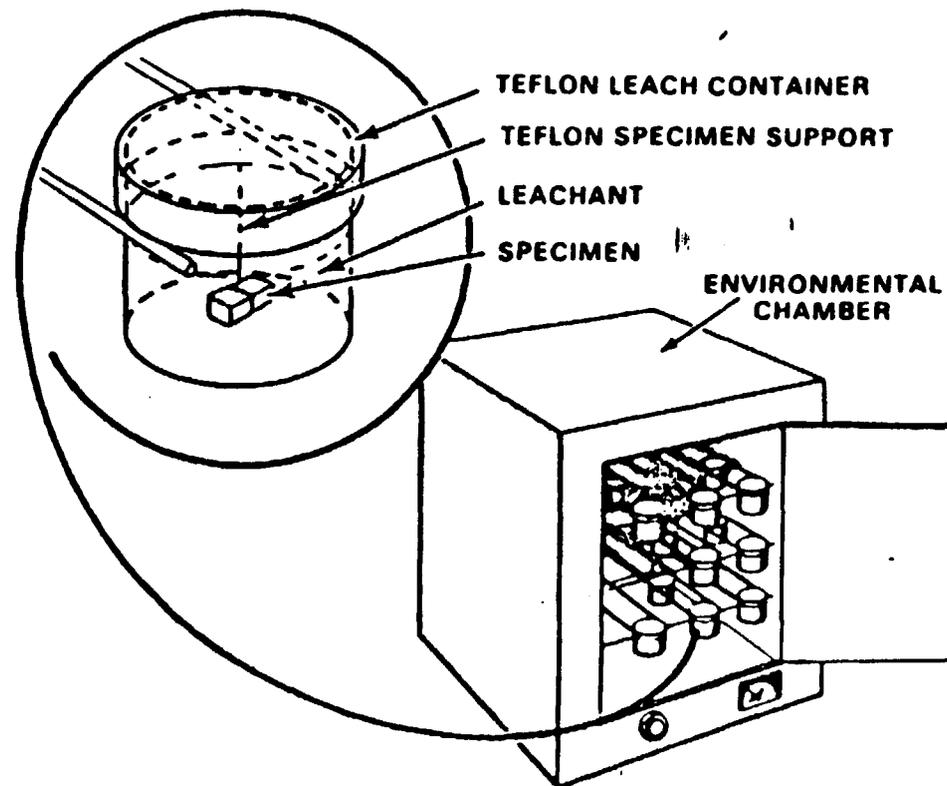


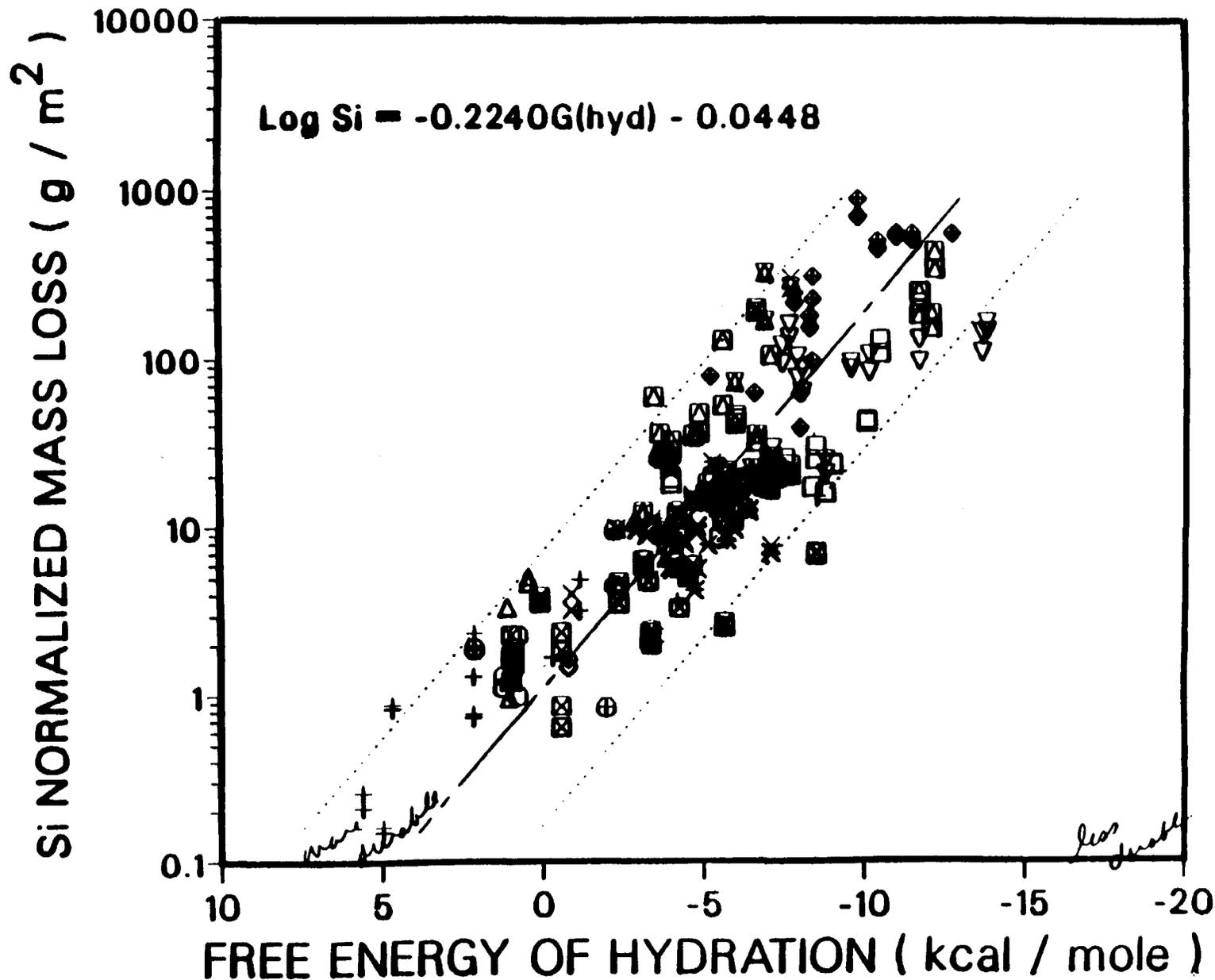
Figure 6

$$\text{NLi (element)} = \frac{\text{ppm}}{\left(\frac{\text{element mass}}{\text{fraction in glass}}\right) \left(\frac{\text{SA}}{\text{V}}\right)}$$

in solution

Where NLi = g/m²

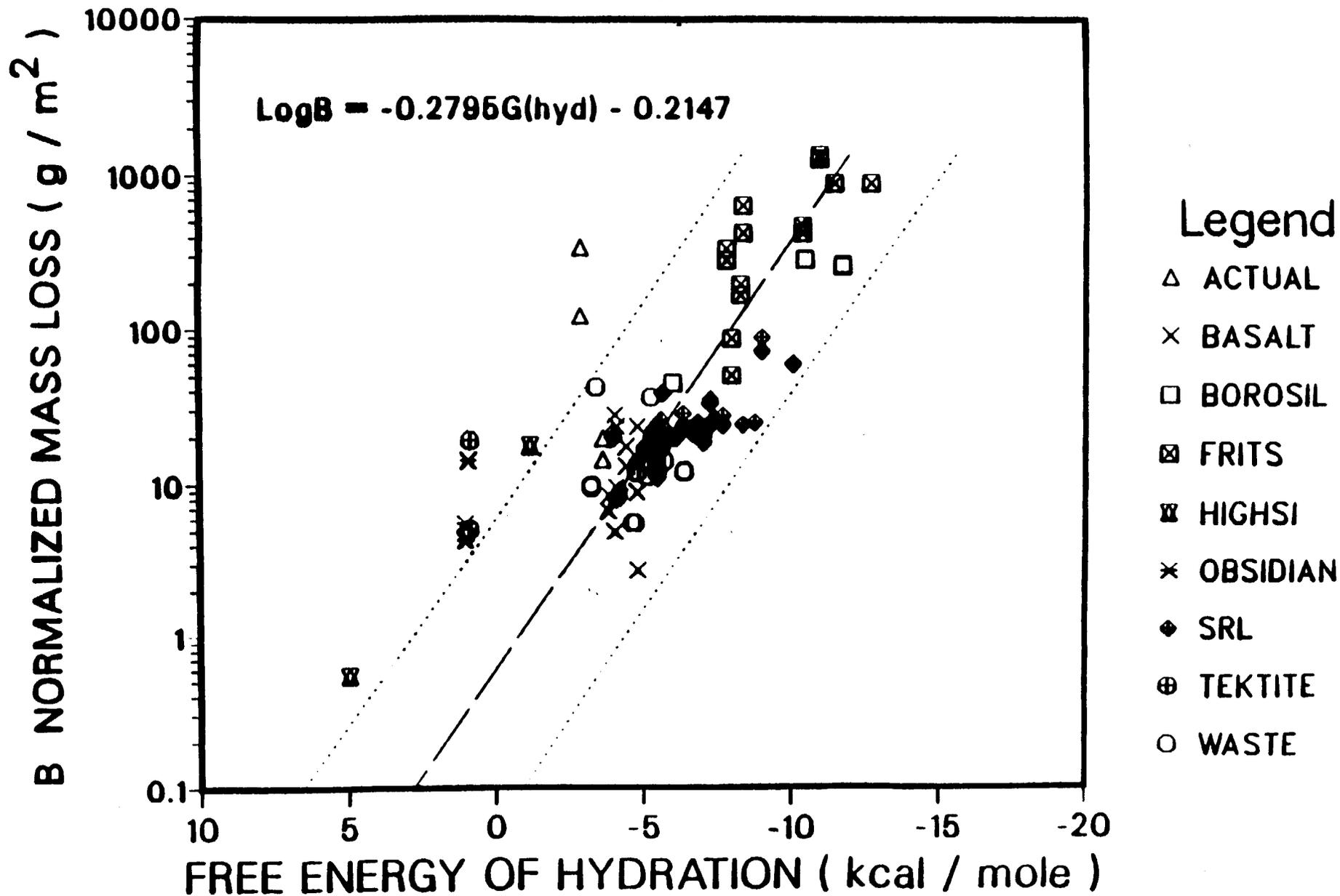
REGRESSION ANALYSIS OF 28 DAY MCC-1 GLASS DURABILITY CORRECTED FOR pH EXCURSIONS



- Legend**
- △ ACTUAL
 - × BASALT
 - BOROSIL
 - CHINESE
 - EGYPTIAN
 - × FRENCH
 - ◆ FRITS
 - GLCERAM
 - GRANITE
 - + HIGHSI
 - ◇ ISLAMIC
 - LUNAR
 - ▽ MEDIEVAL
 - MISC
 - MIXALK
 - △ OBSIDIAN
 - × ROMAN
 - SRL
 - TEKTITE
 - VENETIAN
 - × WASTE

Figure 8

REGRESSION ANALYSIS OF 28 DAY MCC-1 GLASS DURABILITY CORRECTED FOR pH EXCURSIONS



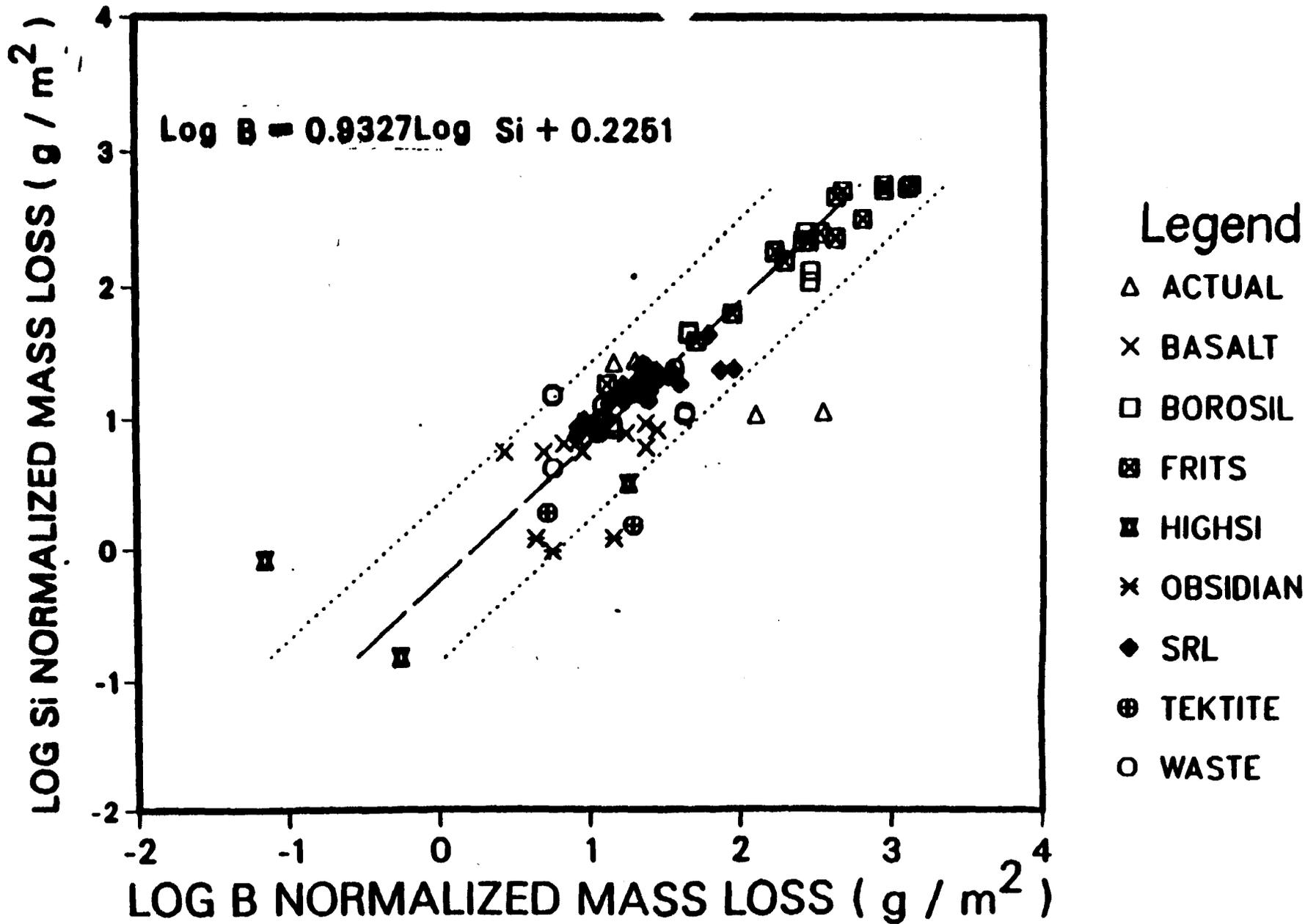
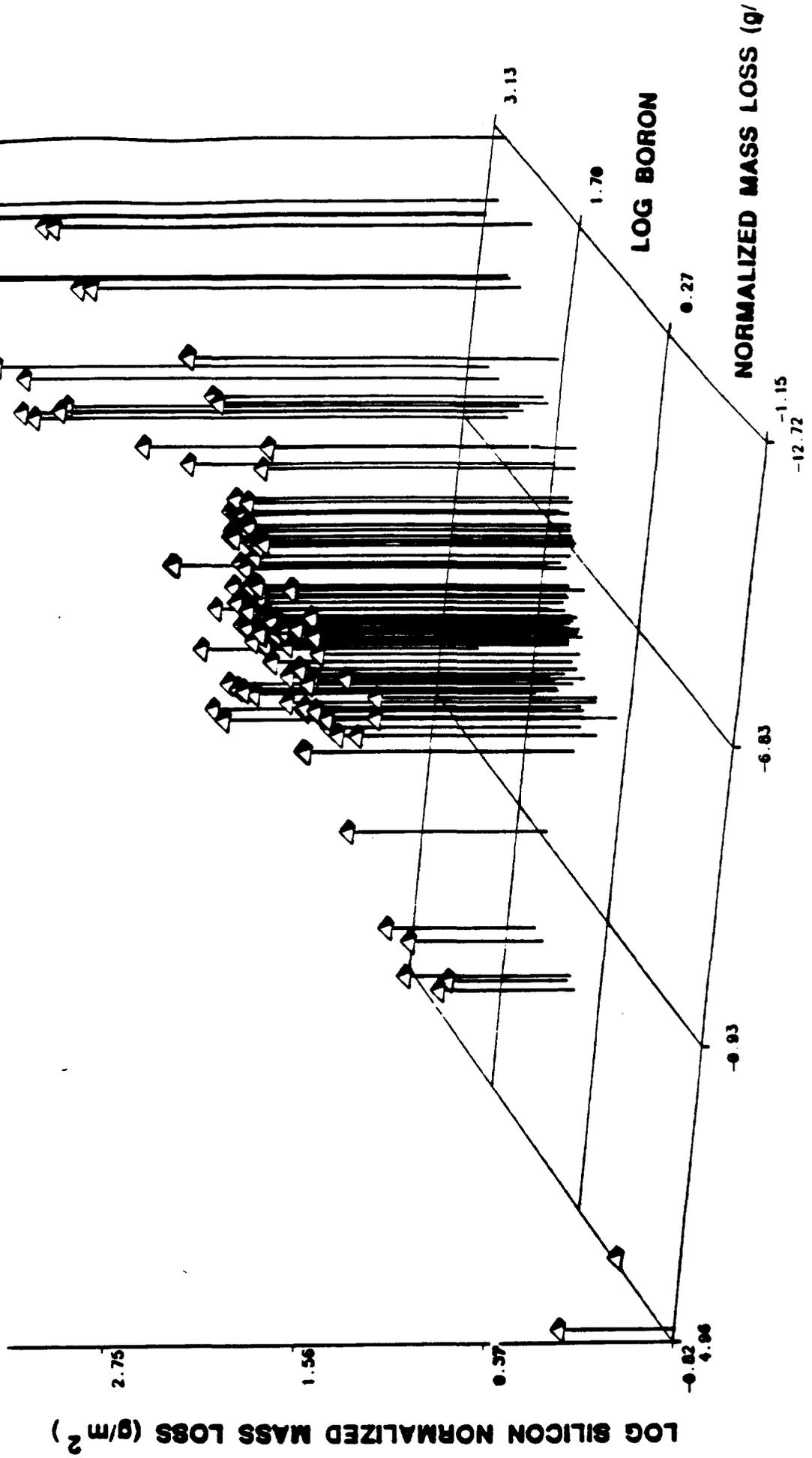


Figure 10

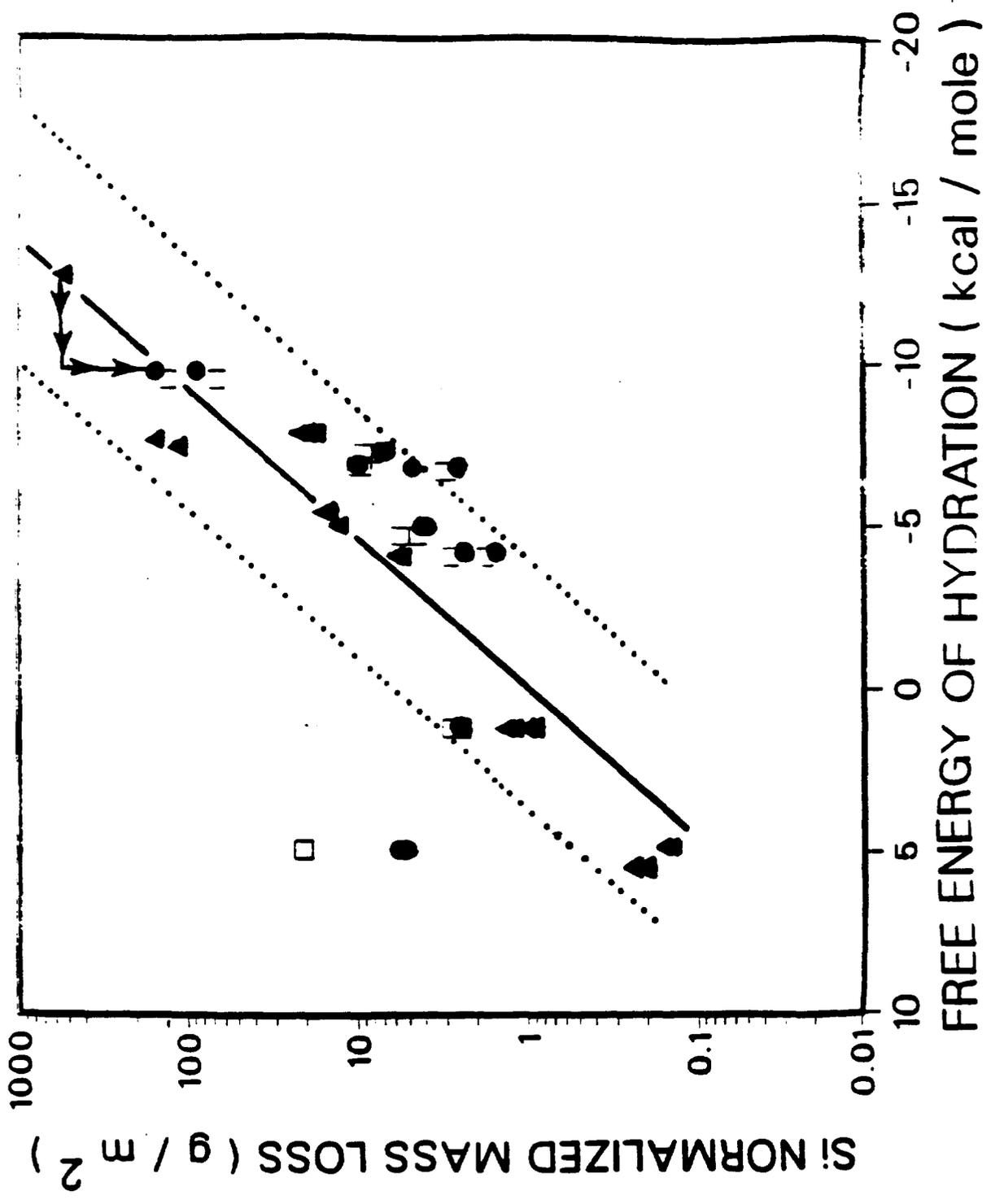
$$\Delta G_{hyd} = -4.33 \log(NL_{Si}) - 0.26 \log(NL_B)$$



FREE ENERGY OF HYDRATION (Kcal/Mole)

FACTORS AFFECTING DURABILITY OF GLASSES

- o Exposed surface area** **SA/V CONST**
- o Volume of leaching solution** **SA/V CONST**
- o Nature of leaching solution** **SILICATE WATER**
- o Frequency of replenishing/
changing leaching solution** **STATIC 28-DAY**
- o Temperature of leaching** **90°C**
- o Glass composition** **CONSTANT**



Legend
 ▲ DI-WATER
 ● GR-4
 □ J13

FACTORS AFFECTING DURABILITY OF GLASSES

- Exposed surface area $(SA/V) \cdot t$ VARIED
- Volume of leaching solution $(SA/V) \cdot t$ VARIED
- Nature of leaching solution DEIONIZED WATER
- Frequency of replenishing/
changing leaching solution $(SA/V) \cdot t$ VARIED
- Temperature of leaching 90°C
- Glass composition CONSTANT

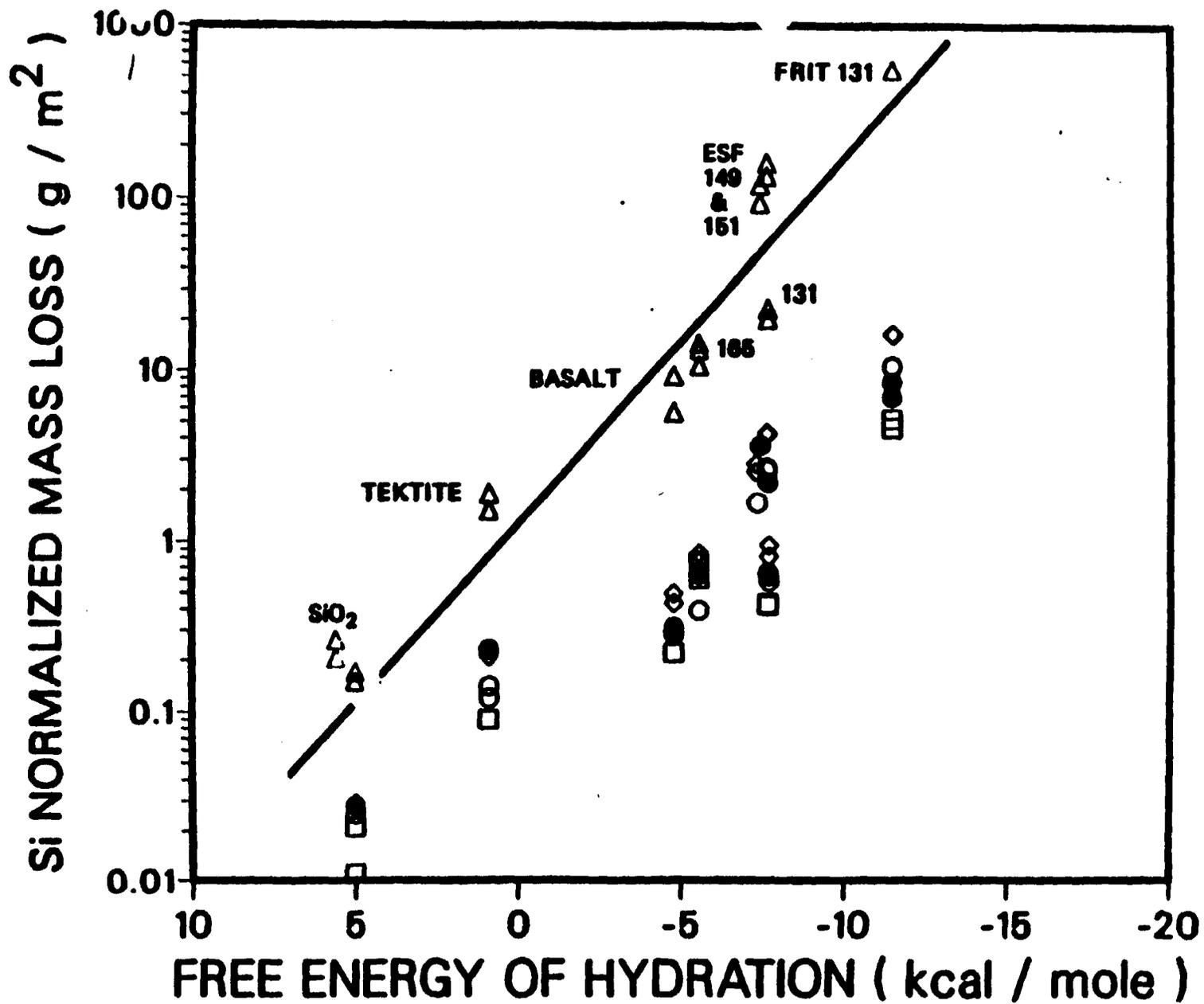


Figure 15

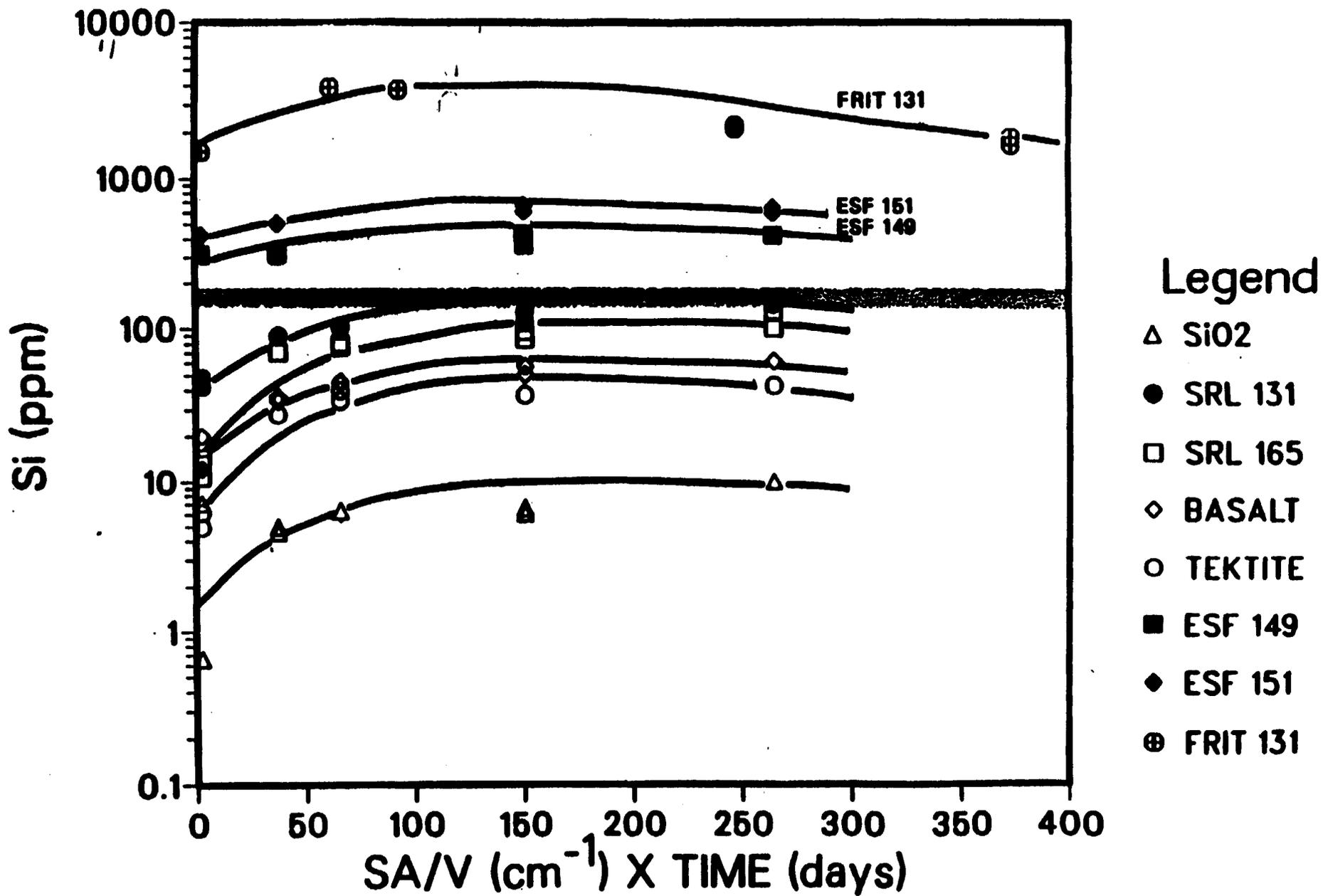


Figure 3b (SA/V) (t) parameter plotted versus silicon release to solution in ppm for durable and non-durable glasses. Glasses above the reference silica saturation at 90°C dissolve by matrix dissolution.

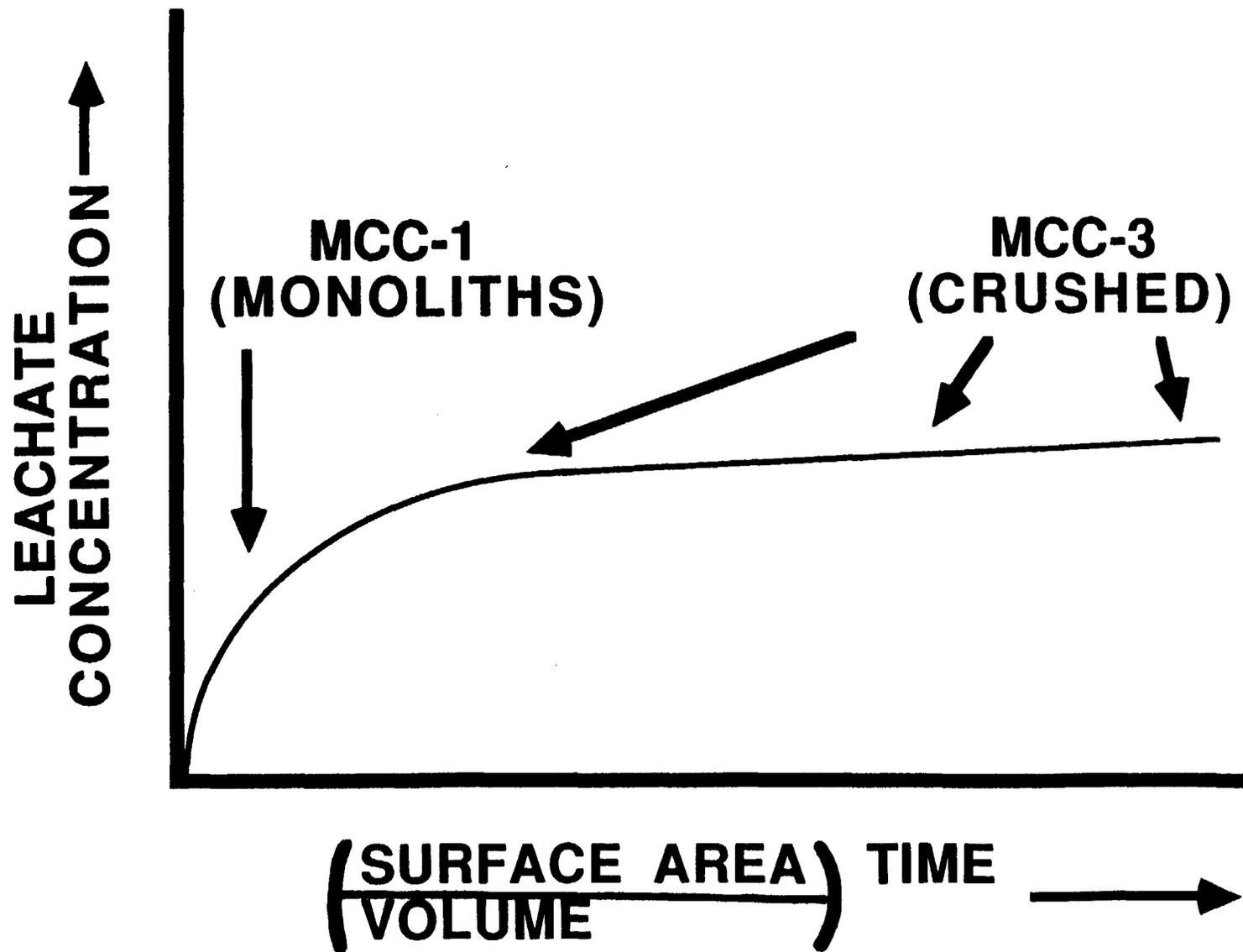


Figure 17

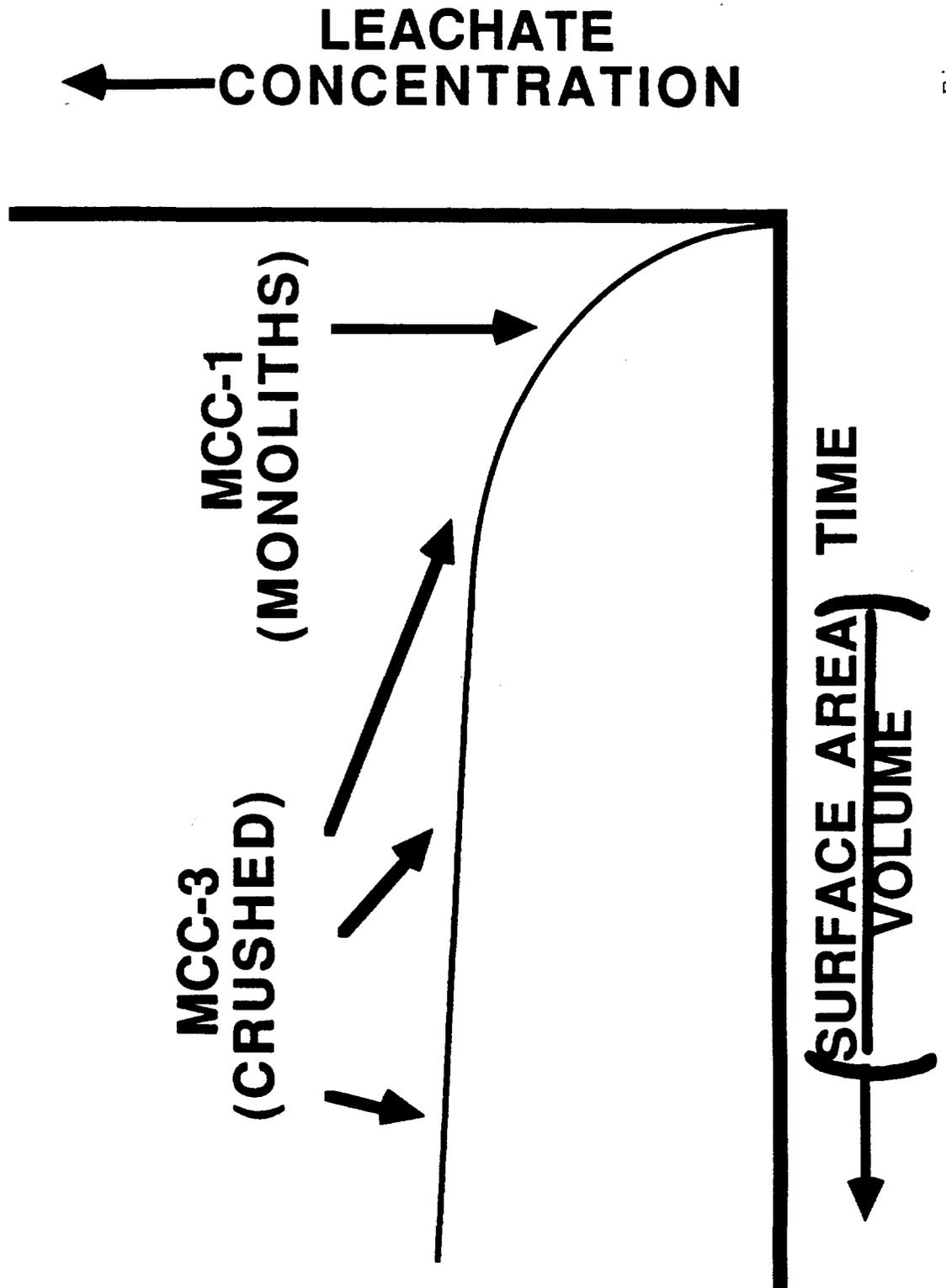


Figure 18

SCATTER PLOT OF FREE ENERGY DATA

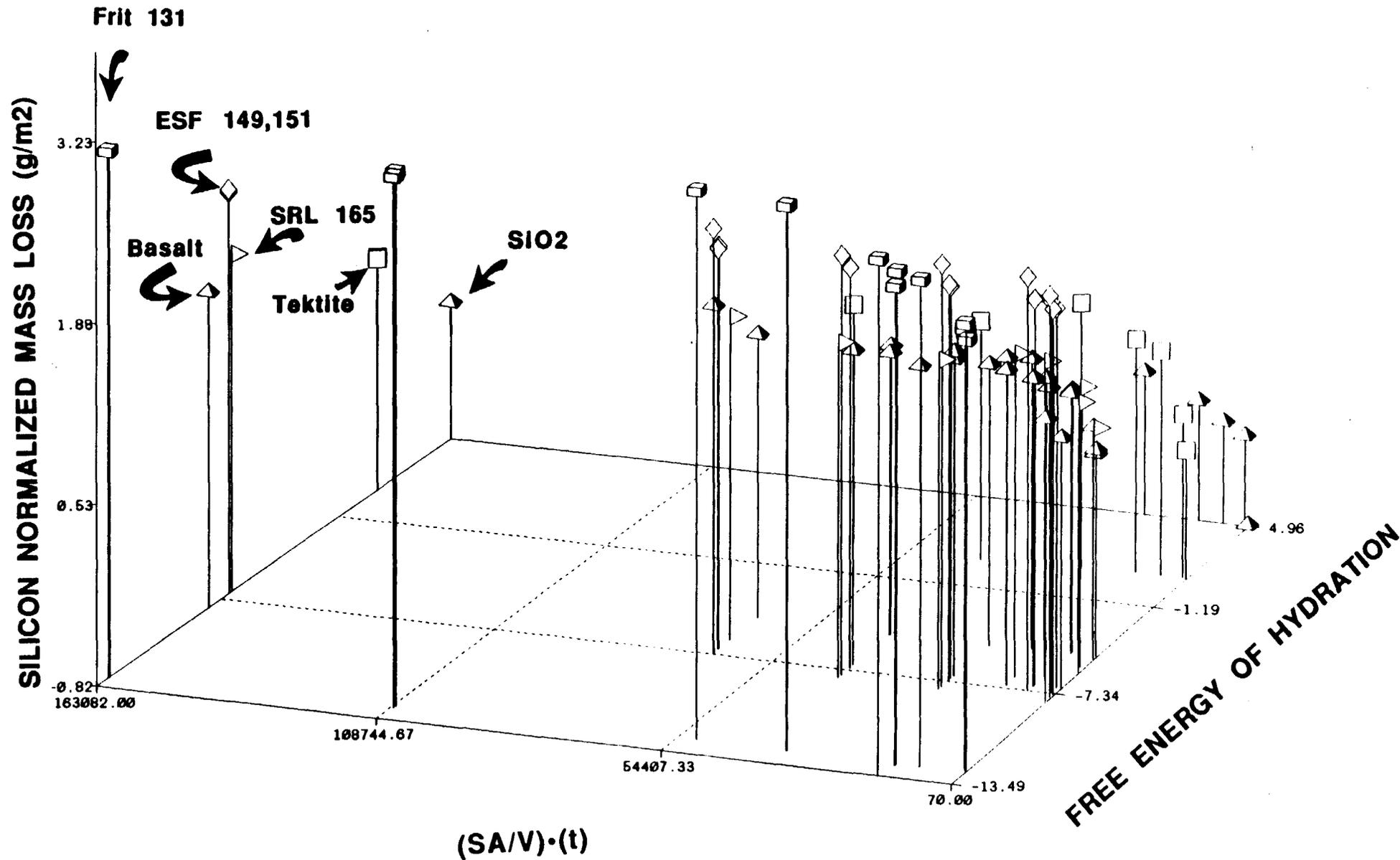
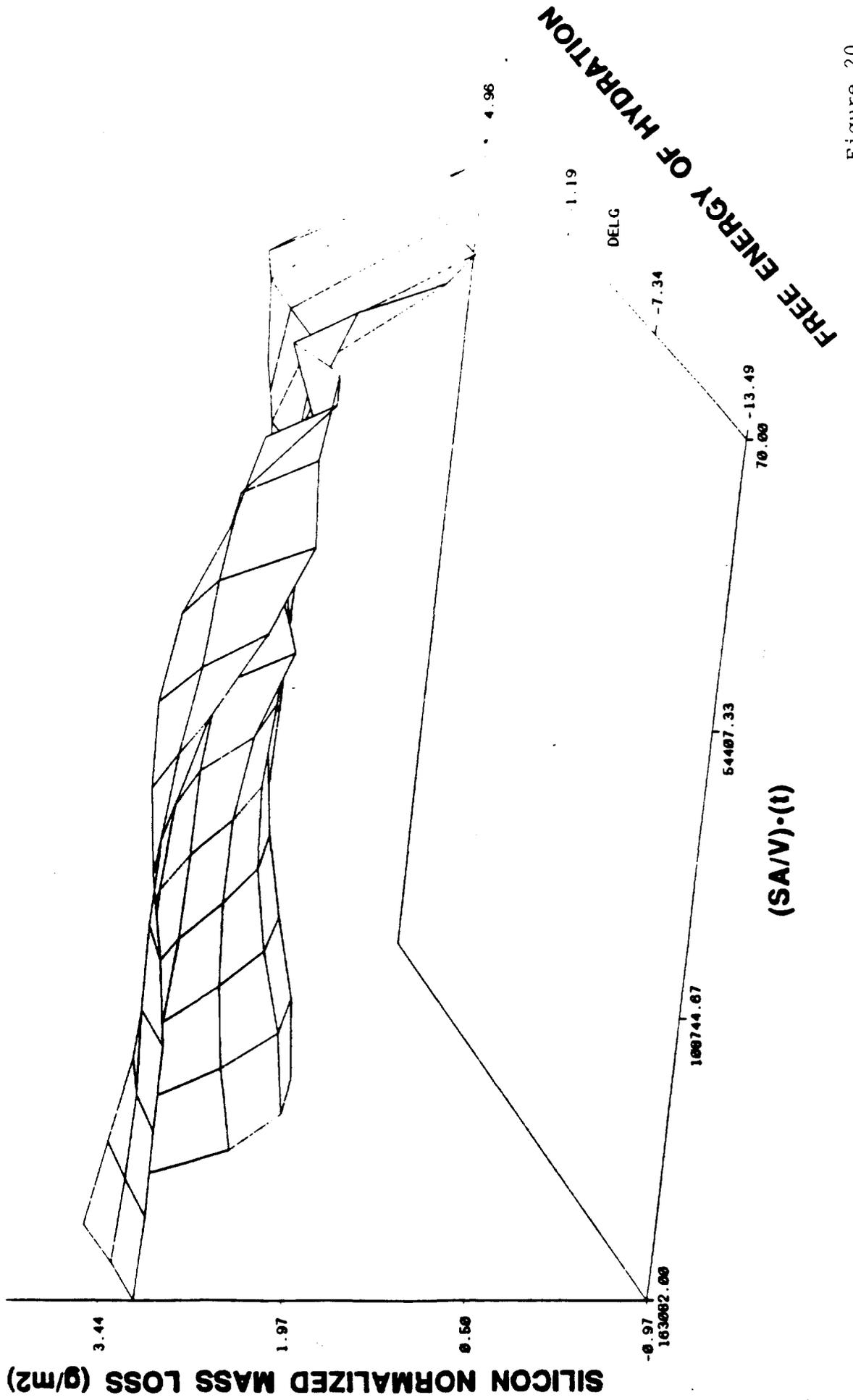


Figure 19

SPLINE FUNCTION OF FREE ENERGY DATA



SCATTER PLOT OF FREE ENERGY DATA

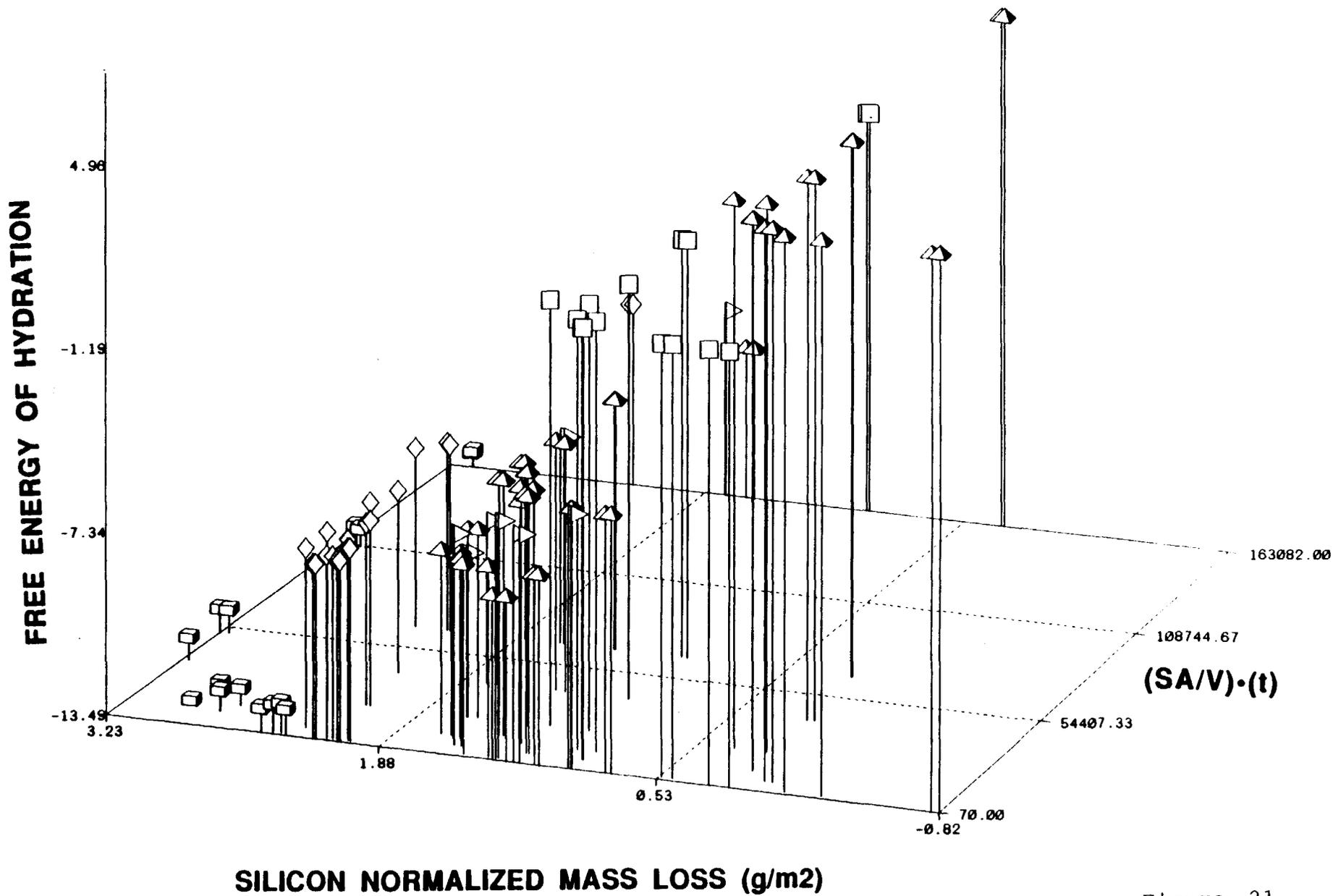


Figure 21

SPLINE FUNCTION OF FREE ENERGY DATA

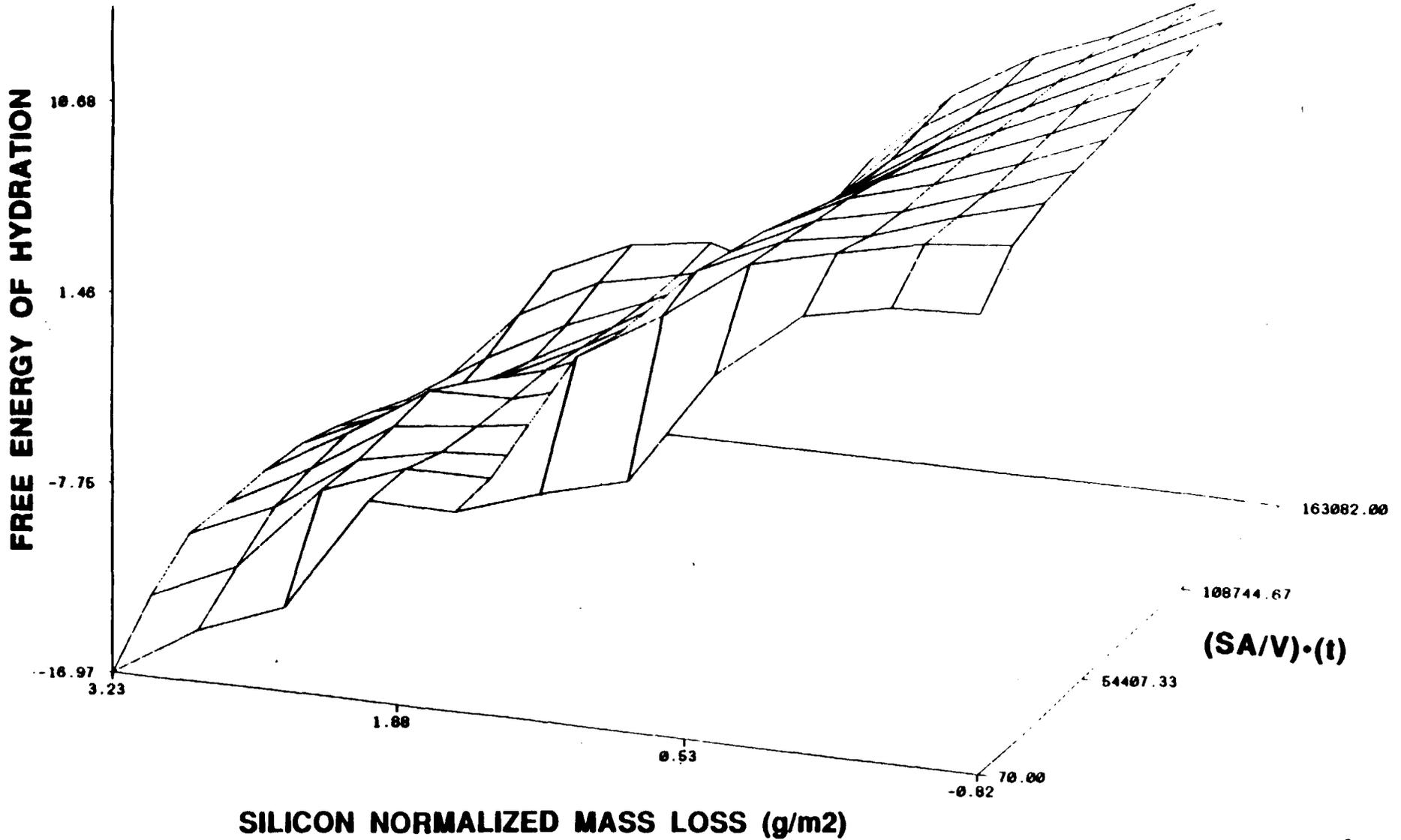


Figure 22

CONCLUSIONS

- **Hydration thermodynamics can be used to predict nuclear waste glass durability for any test geometry**
- **Hydration thermodynamics can be used to understand how various test parameters affect glass durability**
- **The kinetic $(SA/V) \cdot t$ test parameter determines the relative steady state equilibrium (deviation from equilibrium) for each test geometry**