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FIRST-ORDER MODEL FOR DURABILITY OF HANFORD WASTE GLASSES
AS A FUNCTION OF COMPOSITION

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ABSTRACT

Two standard chemical durability tests, the static leach test MCC-1 and product consistency test PCT, were conducted on simulated borosilicate glasses that encompass the expected range of compositions to be produced in the Hanford Waste Vitrification Plant (HWVP). A first-order empirical model was fitted to the data from each test method. The results indicate that glass durability is increased by addition of Al_2O_3 , moderately increased by addition of ZrO_2 and SiO_2 , and decreased by addition of Li_2O , Na_2O , B_2O_3 , and MgO . Addition of Fe_2O_3 and CaO produce an indifferent or reducing effect on durability according to the test method. This behavior and a statistically significant lack of fit are attributed to the effects of multiple chemical reactions occurring during glass-water interaction. Liquid-liquid immiscibility is suspected to be responsible for extremely low durability of some glasses.

INTRODUCTION

Selected pretreated Hanford high-level and transuranic wastes are planned to be converted to borosilicate glass in the Hanford Waste Vitrification Plant (HWVP). After being vitrified, these wastes will be ready for final disposal in a geologic repository. The most important waste glass property for disposal in a geologic repository is its chemical durability, which is a function of composition of both glass and the corroding aqueous medium. A large variability in chemical composition of these wastes will result in a similar variability in composition of the resulting glasses. Therefore, mathematical models relating glass durability to glass composition are necessary for the design and operation of the vitrification process. The present study reports on the first step towards such models: generation of experimental data and development of first-order empirical models.

Chemical durability was experimentally determined for a large number of glasses within the expected range of compositions to be produced in the HWVP. Deionized water was used as a corrosive medium. The durability results were fitted to first-order empirical models.

COMPOSITION RANGE

We reduced the overall composition range of HWVP glasses to nine major components (the mass fraction ranges are shown in parentheses): SiO₂ (0.42-0.57), B₂O₃ (0.05-0.20), Li₂O (0.01-0.07), Na₂O (0.05-0.20), CaO (0-0.10), MgO (0-0.08), Fe₂O₃ (0.02-0.15), Al₂O₃ (0-0.15), and ZrO₂ (0-0.13). The remaining waste constituents (Nd₂O₃, CdO, La₂O₃, NiO, MoO₃, F, SO₃, CeO₂, Cs₂O, CuO, MnO₂, RuO₂, Cr₂O₃, BaO, Pr₆O₁₁, SrO, P₂O₅, PdO, Rb₂O, Rh₂O₃, Sm₂O₃, and Y₂O₃) were treated as a tenth component, "Others" (0.01-0.10).

From this reduced composition range, we investigated only the region of compositions that could be processed in a joule-heated ceramic melter equipped with Inconel electrodes. The following limits were imposed on glass viscosity (η), electrical conductivity (ϵ), and liquidus temperature (T_L):

$$\begin{aligned} 2 < \eta (\text{Pa s; at } 1150^\circ\text{C}) < 10; \\ 18 < \epsilon (\text{S/m; at } 1150^\circ\text{C}) < 50; \\ T_L < 1050^\circ\text{C}. \end{aligned} \quad (1)$$

A limited number of compositions outside this range of properties were also included in the study. Seventy nine test compositions were generated using statistical methods.¹ The work was done in three successive phases such that the results from the preceding phases were factored into the planning of successive phases.

EXPERIMENTAL PROCEDURE

Batches sufficient to make 0.5 kg of glass were blended from oxides and carbonates, homogenized, melted in a platinum crucible, crushed, homogenized again, and then remelted. Glass samples were tested for viscosity, electrical conductivity, liquidus temperature, glass transition temperature, and other characteristics. Two standard durability tests were performed: the MCC-1^a and PCT^b.

The concentration of the dissolved solids in the solution was determined after exposing the glass

^a MCC-1 Static Leach Test Method, developed by the Material Characterization Center, Pacific Northwest Laboratory, Richland, Washington, 1983.

^b Product Consistency Test Method for Defense Waste Processing Facility Glass. E. I. du Pont de Nemours & Company, Inc., Aiken, South Carolina.

samples to deionized water at 90°C for 7 days (PCT) and 28 days (MCC-1) in sealed polytetrafluoroethylene containers. A glass monolith was used in the MCC-1 test and glass powder (75 to 150 μm particles) was used in the PCT. The glass-surface-to-water-volume ratio was 10 m^{-1} for MCC-1 and $2 \times 10^3 \text{ m}^{-1}$ for PCT.

DATA ANALYSIS

The durability was measured as the mass of glass that has been dissolved from a unit surface area during the test exposure time, determined from the concentration of boron in the solution using the formula

$$r = Vc_B/Ag_B. \quad (2)$$

Here r is the normalized boron release (equivalent to the mass of the glass dissolved per unit glass-water interface area), V the solution volume, A the glass surface area, c_B the mass density of boron in the solution, and g_B the mass fraction of boron in the glass. A lower value of r indicates a greater glass durability and vice versa.

The data from each test procedure were fitted by first-order empirical mixture models² of the form

$$r = \exp\left(\sum_{i=1}^n a_i g_i\right), \quad (3)$$

where g_i is the i -th component mass fraction in glass, a_i is the i -th component coefficient, and $n(=10)$ is the number of components (nine major components and "Others"). Addition of the i -th component decreases glass durability (i.e., increases the normalized boron release) if

$$a_i > \ln r. \quad (4)$$

This inequality is derived in the Appendix.

Concentrations of silicon, sodium, lithium, and cesium in the solutions were also obtained, and equation (3) was fitted to the data. Releases of elements other than boron do not provide an adequate measure for the extent of glass dissolution because these elements are involved in solid products of secondary reactions.

RESULTS

All MCC-1 and PCT test results generated in this study are displayed in Figure 1. The normalized boron releases varied from 3 to 691 g/m² per 28 days for MCC-1 and 0.07 to 21 g/m² per 7 days for PCT. Because of the strong nonlinear dependence of $\ln r$ on composition, we decided to delete six data-points (those represented by full circles in Figure 1) before fitting the first-order mixture model for MCC-1. The normalized boron releases for the remaining glasses varied from 3 to 118 g/m² per 28 days. A first-order mixture model for PCT was fitted to all data.

The a_i -coefficients (Table 1) were obtained by least squares regression. The fraction of variability in $\ln r$ accounted for by the fitted model is represented in Table 1 as R^2 . The $R^2(\text{adj})$ was adjusted for the number of parameters and number of data points used in fitting the model. In $R^2(\text{press})$ each data point was left out of the fit to evaluate how well the model predicts the property for the data point. Thus $R^2(\text{press})$ estimates the fraction of variability that would be explained in predicting new observations. The $R^2(\text{press})$ values for MCC-1 and PCT show that the first-order mixture models provide some predictive ability but leave considerable room for improvement. In addition, plots of predicted versus measured MCC-1 and PCT boron release values (Figure 2) reveal that the low and high values of r tend to be overpredicted and medium values underpredicted. This lack-of-fit is statistically significant.

Using inequality (4), we can assess the effect of individual glass components on durability by the difference ($a_i - \ln r_S$) between the release coefficient, a_i , for the i -th component and the logarithm of the normalized boron release, r_S , from a selected glass. The experimental values of $\ln r$ vary from 1.1 to 4.8 for MCC-1 data (excluding the six data points not fitted) and from -2.7 to 3.0 for PCT

Table 1. MCC-1 and PCT Normalized Boron Release Model Coefficients (a_i)

Oxide	MCC-1	PCT
SiO ₂	0.3	-3.5
B ₂ O ₃	9.0	10.5

Na ₂ O	9.1	15.3
Li ₂ O	9.2	18.7
CaO	7.3	-9.0
MgO	6.3	10.9
Fe ₂ O ₃	5.1	-2.2
Al ₂ O ₃	-7.0	-26.1
ZrO ₂	-0.5	-8.7
Others	0.5	1.7
R ²	0.71	0.78
R ² (adj)	0.67	0.75
R ² (press)	0.57	0.70

data. When a_j values are compared with these ranges, we can see that the MCC-1 and PCT durabilities of a typical glass are greatly increased by an addition of Al₂O₃, moderately increased by additions of ZrO₂ and SiO₂, and decreased by additions of Li₂O, Na₂O, B₂O₃, and MgO. An addition of "Others" has little effect. Although ZrO₂ is reported in the literature³ as an oxide that increases glass durability, its effect is much weaker than that of Al₂O₃. Additions of CaO and Fe₂O₃ produce a moderately positive (CaO) or indifferent (Fe₂O₃) effect on PCT durability, whereas MCC-1 durability is reduced.

DISCUSSION

Because space limitations prevent reporting compositions and elemental releases of all 79 glasses tested, the following discussion is restricted to general remarks regarding the lowest and highest normalized boron releases observed, reaction progress reached in MCC-1 and PCT, non-linear behavior of some glasses, and releases of elements other than boron.

General Observations

Of the glasses with $\eta \leq 10$ Pa s at 1150°C, those which were the most durable ($r \leq 11$ g/m² per 28 days for MCC-1 and $r \leq 0.32$ g/m² per 7 days for PCT) were high in SiO₂ (≥ 0.465) and Al₂O₃ (≥ 0.06), moderate in B₂O₃ (0.07-0.17), low in Na₂O+Li₂O (≤ 0.19), MgO (≤ 0.02), ZrO₂ (≤ 0.04), and Fe₂O₃ (≤ 0.045), and had a wide range of CaO and "Others". The high content of Al₂O₃ and SiO₂ and low content of Na₂O, Li₂O, and MgO can be explained by the corresponding values of a_j -coefficients (Table 1). Limitations in other components were caused by property constraints,

such as glass viscosity, electrical conductivity, and liquidus temperature, as expressed in inequalities (1). For example, the content of ZrO_2 and Fe_2O_3 was limited by the requirement that $T_L < 1050^\circ C$. A high content of ZrO_2 or Fe_2O_3 would require a low Al_2O_3 content to keep liquidus temperature below $1050^\circ C$. However, a low Al_2O_3 content would result in a low chemical durability. A minimum level of alkali oxides, B_2O_3 , or CaO was necessary to maintain viscosity below 10 Pa s at $1150^\circ C$. If glasses with a higher viscosity were acceptable, a higher durability could be attained. However, such glasses would require a higher melting temperature than $1150^\circ C$, which is not permitted in a melter heated by Inconel electrodes.

The glasses with the lowest chemical durability as determined by both the MCC-1 test and PCT had a low content of Al_2O_3 and ZrO_2 or a high content of B_2O_3 and alkali oxides. This observation also confirms the general trends indicated by the coefficient values listed in Table 1.

Although there is a satisfactory qualitative agreement between the a_i -coefficients and the expected effects of individual glass components, closer inspection of Figure 2 reveals that the predictive ability of the first-order models is far less satisfactory. For example, a glass with a predicted normalized boron release equal to 2 g/m^2 per 7 days as determined by the PCT can have an actual release as high as 8 g/m^2 . To ensure that the actual release is not higher than 2 g/m^2 , the predicted values must be lower than 0.8 g/m^2 . Similarly, predicted 28 g/m^2 per 28 days for the MCC-1 test corresponds to actual values as high as 120 g/m^2 . A predicted value must be at least 10.5 g/m^2 if the actual release should not to exceed 28 g/m^2 .

Only partial improvement was achieved when formula (3) was extended by adding second-order terms (second-order models are currently being developed). When applied to chemical durability, the predictive power of empirical mixture models is not as good as when applied to viscosity or electrical conductivity because durability is not a mixture property in a strict sense. Glass durability involves equilibria and kinetics of multiple chemical reactions that occur at the glass-water interface. Because of these processes, glass durability as a response function is far more complex than empirical models can fit.

Reaction Progress

The reaction progress, ξ , is measured as the mass of glass released per unit volume of solution. In terms of boron release, this variable can be expressed as $\xi = c_B/g_B$; hence, by equation (2), $\xi = rA/V$. The reaction progress reached during MCC-1 test, ξ_M , varied between 0.03 and 6.9 kg/m³ and the reaction progress reached during PCT, ξ_P , varied between 0.14 and 42 kg/m³. Their ratio

$$\beta = \xi_M/\xi_P \quad (5)$$

varied from $\beta = 1.6$ to 154, and was between 5 and 20 for most compositions. This wide span of β indicates that some glasses acceptable by the MCC-1 test may not be acceptable by the PCT and vice versa. Generally, an acceptable glass must satisfy the inequality $r < r_R$, where r_R is the normalized boron release from a reference glass determined by a given test method.

For nine out of 79 glasses tested, β was >45 ; these glasses were low in CaO and Fe₂O₃ (all but one had zero CaO and seven had 2 wt% Fe₂O₃, the minimum level used in testing). Glasses with $\beta < 0.07$ had 6 to 10 wt.% CaO. This is as expected, considering the differences between MCC-1 and PCT values of a_j -coefficients for CaO and Fe₂O₃ (see Table 1). However, some glasses with minimum or maximum levels of CaO and Fe₂O₃ had medium values of β , probably as a result of the compensating effect of other components.

Assuming for simplicity surface reaction control,⁴ the driving force for glass dissolution is the discontinuity in orthosilicic acid activity at the glass-water interface (see Ref. 4 for detailed discussion). This discontinuity changes with time as a result of SiO₂ release from glass and SiO₂ precipitation in the form of solid silicates in the gel layer. The kinetics of this change is complex, because it is controlled by multiple simultaneous and subsequent chemical reactions. Therefore, the reaction progress versus time function, $\xi(t)$, is not similar for all glasses. The differences in the functional form of $\xi(t)$ account for the wide range in the value of β .

Consider a chemical reaction in which SiO₂ is involved. If this reaction begins at $\xi = \xi_c$ such that

$\xi_c \equiv \xi_M$ and $\xi_c < \xi_P$, then the reaction will not affect MCC-1 but will affect PCT significantly. If this reaction precipitates a silicate at a sufficiently high rate, then the orthosilicic acid concentration in the solution will be lower and the driving force for glass dissolution will be higher relative to the case when such reaction does not occur. A higher driving force leads to a higher dissolution rate and, hence, higher values of ξ_P and β . By the same token, the value of β will be low if the chemical reaction starting at ξ_c dissolves a silicate precipitated previously.

The glass with the lowest β value of the 79 glasses tested ($\beta=1.6$, $\xi_M=0.11 \text{ kg/m}^3$ and $\xi_P=0.17 \text{ kg/m}^3$) did not experience any substantial precipitation of silicates up to $\xi_c \equiv 0.06 \text{ kg/m}^3$, at which chalcedony^a began to form. This glass was rich in CaO (8 wt%) which was precipitated by ambient CO₂. Hence, the orthosilicic acid concentration in the solution was high, glass dissolution was slow, and precipitation of silicates did not reduce it with progressing reaction. A small amount of mesolite, which began to form before formation of chalcedony, dissolved in later stages.

The glass with the highest β value of the 79 glasses tested ($\beta=154$, $\xi_M=0.16 \text{ kg/m}^3$ and $\xi_P=25 \text{ kg/m}^3$) experienced massive precipitation of magnesium silicates (talc began to precipitate at $\xi_c \equiv 0.06 \text{ kg/m}^3$). This precipitation reduced the orthosilicic acid concentration in solution and caused enhanced dissolution of glass at final stages of MCC-1 testing and during PCT, thus making PCT release unusually high relative to MCC-1.

The specific mechanism by which glass dissolution evolves can be determined using phase diagrams^{4,5} based on geological codes. The scenario based on surface reaction control is perhaps oversimplified because the gel layer may consist of two or more strata of different compositions, which impose an orthosilicic activity at the interface different from that in the bulk. This situation is analogous to that observed by Grambow and Strachan:⁶ transport of orthosilicic acid through and outer layer was rate-controlling when glass was corroded by MgCl₂ solution.

^a Computer simulation courtesy of Peter McGrail.

Nonlinear Behavior

Five test glasses exhibited extremely high MCC-1 normalized boron release (121 to 691 g/m² per 28 days), which was not predicted by equation (3). Four of those glasses were rich in boron oxide and all had a low level of Al₂O₃ (three glasses had 20 wt% B₂O₃ and zero Al₂O₃; one glass 20 wt% B₂O₃, 4 wt% Al₂O₃, and 19 wt% Na₂O+Li₂O; and one glass 5 wt% B₂O₃, zero Al₂O₃, and 19 wt% Na₂O+Li₂O). A likely cause of this behavior is liquid-liquid phase separation, a well-documented phenomenon in sodium borosilicate and lithium borosilicate ternary glasses.⁷ The R₂O-B₂O₃-SiO₂ submixture (R = Na+Li) was in the immiscibility dome for two of these five glasses, near to it for two, and distinctly outside it for one. Phase separation was clearly evident on SEM micrographs of two glasses (no TEM examination was undertaken to detect the presence or absence of phase separation in the remaining three glasses). Apart from the glasses exhibiting non-linear behavior, the R₂O-B₂O₃-SiO₂ submixture was in the immiscibility dome for three other glasses that did not show any irregularity in MCC-1 had. However, their Al₂O₃ and ZrO₂ content was high. According to Tomozawa, Al₂O₃ and ZrO₂ suppress immiscibility.⁸

The effect of phase separation on glass durability was discussed by Tomozawa⁸ and Shelby.⁹ The overall durability of a phase-separated glass is controlled by the durability of the connected phase. If the connected phase is depleted of the components that increase durability, the overall glass durability will decrease.

Other Elements

Normalized releases, as defined by equation (2), of elements other than boron were also determined. We obtained empirical coefficients for the normalized releases of Si, Li, and Na by fitting the normalized release of these elements to Equation (3). Elements other than boron form, or can be absorbed in, a gel layer. In addition, alkali ions are extracted from glass at the beginning of the dissolution process. Therefore, the normalized releases of these elements in solutions do not represent the amount of glass dissolved and are not suitable for durability assessment. However, when compared with the normalized boron release, the releases of other elements provide information

about their participation in gel layer formation or initial extraction.

Normalized releases of Na and Li are generally smaller than releases of B, but can be larger for some glasses if the initial alkali extraction supplies more alkali to the solution than chemical reactions and absorption deposits into the gel layer. The a_i -coefficients based on normalized releases of Na and Li tend to have similar values as the normalized boron release. As a result, the component coefficient differences between Na and Li and that of B are small or negligible. In contrast, the normalized release of Si is smaller than the normalized release of B because of the presence of the silica precipitated and sorbed in the gel layer. The differences between the a_i -coefficients for normalized releases of silicon, $a_i(\text{Si})$, and boron, $a_i(\text{B})$, are plotted in Figure 3 for MCC-1 and PCT.

The lower (or more negative) the difference between $a_i(\text{Si})$ and $a_i(\text{B})$ is, the more the i -th oxide reduces the concentration of orthosilicic acid in solution. As Figure 3 indicates, large negative differences exist between $a_i(\text{Si})$ and $a_i(\text{B})$ for MgO and B₂O₃, followed by Na₂O and Li₂O. The value of $a_i(\text{Si})-a_i(\text{B})$ for CaO is large and negative in the MCC-1 test and small and positive in the PCT. Al₂O₃ exhibits a large positive difference between $a_i(\text{Si})$ and $a_i(\text{B})$. Other components (SiO₂, Fe₂O₃, ZrO₂, and Others) affect the value of $a_i(\text{Si})-a_i(\text{B})$ to a small or negligible extent.

The differences between $a_i(\text{Si})$ and $a_i(\text{B})$ for different oxides are difficult to rationalize. Some characteristics of individual oxides that may account for these differences are summarized as follows:

- (1) A high normalized boron release (a large extent of glass dissolution) is associated with a large fraction of silica precipitated in the gel layer and, hence, a corresponding decrease in the fraction of silicon in solution. This would result in a lower value of $a_i(\text{Si})$ for SiO₂ relative to $a_i(\text{B})$ for SiO₂.

- (2) Magnesium oxide tends to reduce the normalized release of Si through formation of magnesium silicates, such as talc.

- (3) Alkali oxides increase SiO₂ solubility limit in the solution because they increase pH. This way, the interfacial discontinuity in the orthosilicic acid

concentration is increased, the extent of glass dissolution is increased, and more opportunity is given for silicates to precipitate.

(4) The formation of CaCO_3 , which prevents formation of calcium silicates, allows more silicon to remain in the solution at high concentration when a higher reaction progress is reached, as is the case of PCT.

(5) Aluminosilicates do not form in a sufficient quantity to hold a significant portion of SiO_2 in the gel layer because most of Al_2O_3 precipitates as gibbsite. In addition, Al_2O_3 may affect the equilibrium concentration of orthosilicic acid at the glass-water interface, but this effect was not confirmed by Grambow and Strachan.⁴ According to these authors,⁴ Al_2O_3 decreases the initial rate of dissolution through kinetic factors and by the formation of a layer that limits the transport of orthosilicic acid from the glass.¹⁰

Although these characteristics are linked to the differences between $a_j(\text{Si})$ and $a_j(\text{B})$ for individual glass components, a detailed proof that would establish such a link will require more analysis.

CONCLUSIONS

(1) MCC-1 and PCT durabilities of HWVP glasses increase as the Al_2O_3 or zirconia mass fractions increase, and decrease as the lithium, sodium, magnesium, or boron oxide mass fractions increase. Other components have mild or negligible effect on durability or affect MCC-1 and PCT differently.

(2) Dissolution of glasses with different composition progresses in a non-similar pattern because of differences in precipitation and dissolution reactions that control the orthosilicic acid concentration in the solution. As a result, the mixture models developed in this study provide some predictive ability but leave considerable room for improvement.

(3) Glasses with a combination of high boron oxide fraction and low Al_2O_3 fraction exhibit exceptionally high MCC-1 normalized boron releases that are not predicted by a first-order model fitted to glasses with 5 to 20 wt% B_2O_3 and up to 15 wt% Al_2O_3 . This behavior may be caused by phase separation.

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APPENDIX

Proposition: An addition of the j-th component decreases glass durability if $a_j > \ln r$.

Proof: The first derivative of equation (3) with respect to j-th component mass fraction yields

$$\partial \ln r / \partial g_j = a_j + \sum_{i \neq j}^n a_i \partial g_i / \partial g_j, \quad (A1)$$

where $i \neq j$ under the summation symbol indicates summation from $i=1$ to n except $i=j$. Out of the n mass fractions, only $n-1$ are independent because mass fractions must satisfy the condition that $\sum_i g_i = 1$. Since $\sum_{i \neq j} g_i = 1 - g_j$, then

$$\sum_{i \neq j}^n \partial g_i / \partial g_j = -1. \quad (A2)$$

If all but the j-th component are kept in constant proportions (the j-th component is added to the mixture), then $g_i / (1 - g_j) = \text{const.}$ for $i \neq j$ and thus $\partial g_i / \partial g_j = -g_i / (1 - g_j)$. This expression satisfies condition (A2). Equation (A1) now becomes

$$\partial \ln r / \partial g_j = a_j - (1 - g_j)^{-1} \sum_{i \neq j}^n a_i g_i \quad (A3)$$

which, by equation (3), yields

$$\partial \ln r / \partial g_j = (a_j - \ln r) / (1 - g_j). \quad (A4)$$

Hence, if an addition of j-th component increases the normalized boron release, that is, if $\partial r / \partial g_j > 0$, then, by equation (A4),

$$a_j > \ln r.$$

Equation (A4) is equivalent to an equation given by Cox.¹¹

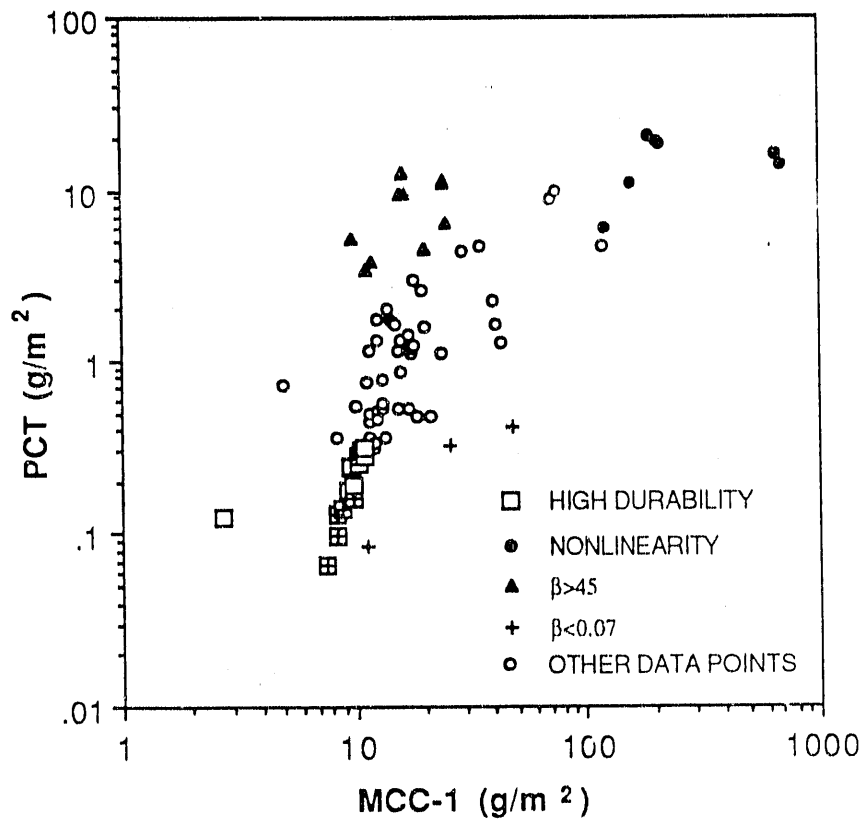


Figure 1. PCT vs MCC-1 Normalized Boron Releases for 82 Test Glasses

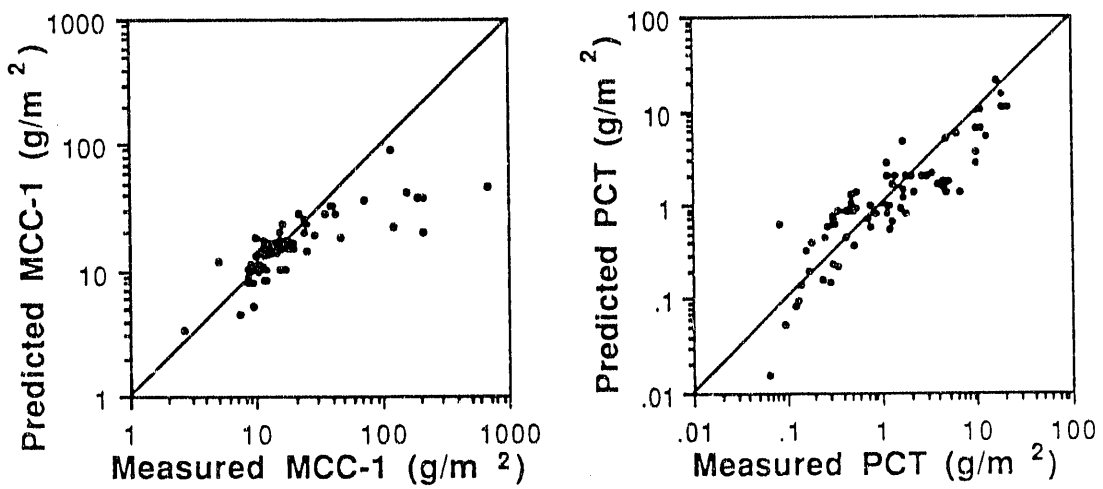


Figure 2. Predicted Versus Measured Normalized Boron Release for the First-Order Mixture Model.

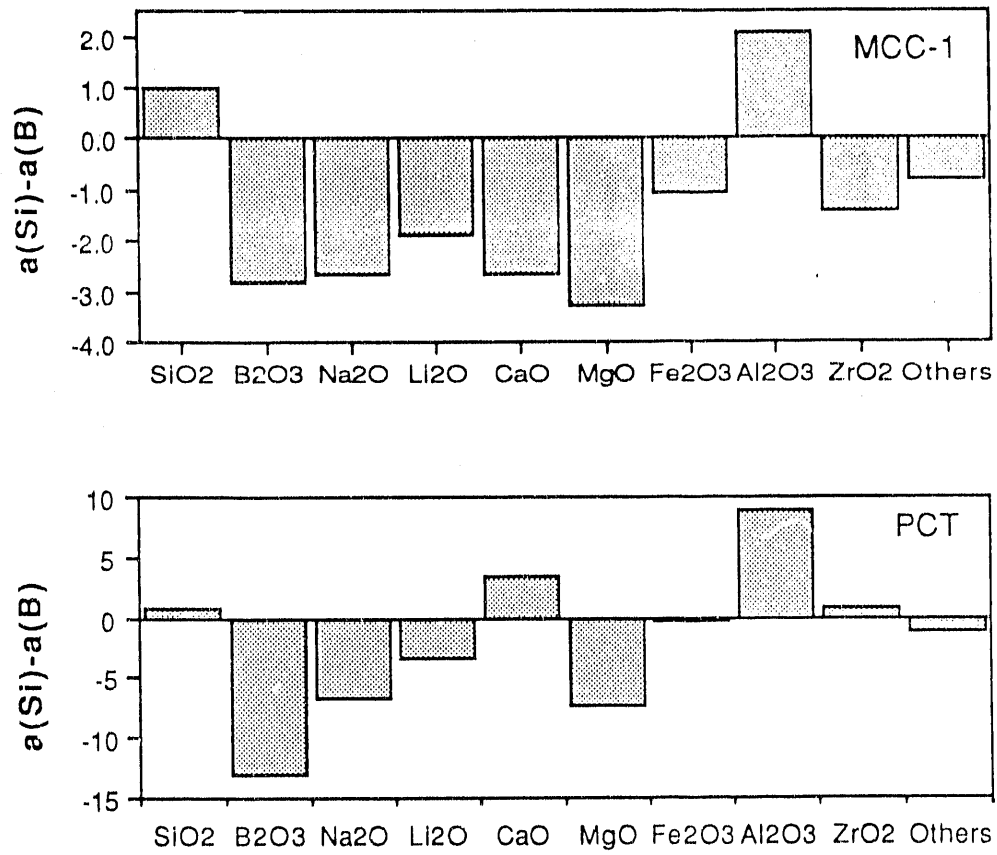


Figure 3 Differences Between a_i -Coefficients for Silicon and Boron.

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