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LINEAR FREE ENERGY RELATIONSHIPS IN GLASS CORROSION

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ABSTRACT

Various theoretical models that have been proposed to correlate glass durability to their composition for a wide variety of silicate, borosilicate, and aluminosilicate glasses are examined. Comparisons are made between the predictions of these models and those of an empirical formulation extracted from existing data in the present work. The empirical approach provides independent confirmation of the relative accuracy of the silica release rate predictions of the different theoretical models in static leaching systems. Extensions of the empirical approach used in this work are discussed.

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INTRODUCTION

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Interest in the quantitative prediction of chemical durability of glasses from knowledge of their composition transcends a number of disciplines. Natural and man-made glasses react with water, aqueous solutions and atmospheric media, leading to dissolution of glass surfaces and/or formation of structurally and chemically modified surface layers. Archaeologists and geologists have for some time used the thickness of reacted layers on obsidian and other natural glasses to determine exposure ages of glass objects and volcanic glasses [1]. The temporal information thus derived has been used by archaeologists to infer human activities in the past and by geologists to unravel Nature's past behavior. More recently, the subject of glass-water reaction has also concerned scientists interested in the behavior of nuclear waste glasses in geologic repositories.

Caution should be exercised in making broad generalizations about the relationship between glass composition, structure, and durability. The type of sites (i.e., with respect to the glass anionic framework) as well as the chemical environment within those sites can change as a function of bulk composition. Therefore, the corrosion behavior of a particular glass component can change from one bulk glass composition to another. For example, addition of Al_2O_3 [where $Al_2O_3/(R_2O+RO)^* < 1$] in an alkali silicate glass results in the formation of two distinct sites (i.e., charge compensating and network modifying sites) for the alkali ions [2,3]. Alkali ions in these different structural sites cannot be expected to have identical chemical responses to corrosion. The same may be said for trigonally and tetrahedrally coordinated boron, both of which are likely present in complex borosilicate matrices [4,5].

The primary aim of the present communication is to examine some of the methodologies that have been proposed to predict glass durability from its composition. Comparisons will be made between the predictions of these theoretical models and those of an empirical formulation developed in the present work, in each case using the MCC-1 (Materials Characterization Center Test 1) data base as the standard of comparison.

* R_2O and RO are generic designations for univalent and divalent oxides respectively.

MASTER

Theoretical Models

Several composition-related theoretical parameters have been proposed as indicators of relative glass durability. Following the original suggestion of Paul [6], Plodinec et al. [7] proposed the following formulation to account for composition-durability relationships for glass corrosion:

$$\ln LR_{Si} = k_1 \Delta G^*_{\text{hydration}} + k_2 \quad (1)$$

In this formulation, k_1 and k_2 are constants, LR_{Si} is the normalized leach rate of silica, and $\Delta G^*_{\text{hydration}}$ is the standard free energy of hydration of the bulk glass calculated from:

$$\Delta G^*_{\text{hydration}} = \sum (\Delta G^*_{i, \text{hydration}} X_i) \quad (2)$$

where X_i is the mole fraction of component i , and $\Delta G^*_{i, \text{hydration}}$ is the corresponding standard free energy of hydration of i . Equation 1 was originally cast in terms of normalized mass loss (as opposed to leach rate) and was applied to the MCC-1 tests. Plodinec et al. [7] and Jantzen et al. [8] tabulated free energy of hydration values of selected glass species in multicomponent silicate glasses (see Table I). Figure 1a shows the correlation observed between $\ln LR_{Si}$ and $\Delta G^*_{\text{hydration}}$ based on 28-day MCC-1 experiments. MCC-1 is a static unbuffered leaching experiment; pH and dissolved glass species concentrations in such experiments are effectively controlled by the initial glass composition. Because of the nature of the experiment, the significance of LR_{Si} needs to be clarified. The 28-day LR_{Si} is an integrated normalized leach rate, not an instantaneous leach rate on the 28th day. Because instantaneous silica leach rates can change as a function of time, the 28-day rate represents the average rate from the beginning of the experiment up to the 28th day. Because the solution pH is also allowed to drift in these experiments, the silica release rate for each glass composition represents an integrated rate over the entire pH range of each experiment.

Other models have been proposed to explain the relationship between glass composition and durability without invoking the concept of hydration free energies. For example, it was recently suggested that the contribution of cations to chemical durability of glasses depends primarily on their valence [9]. The fundamental basis of this hypothesis is yet to be explored in detail, but results based on the same data set used in the hydration model shows valence parameter correlation with $\ln LR_{Si}$ that is comparable to the hydration free-energy model (Figure 1b). Another "thermodynamic" model using the enthalpy of oxide components to weigh the contributions of glass components to durability has also been proposed [10]. The enthalpy values used were not the oxide enthalpy of formation; rather, they were formation enthalpies "corrected" for structural positions in the glass network. Figure 1c shows the correlation between formation enthalpy (computed using the procedure suggested in [10]) and $\ln LR_{Si}$.

Another example of composition-durability correlation is that shown in Figure 1d. The compositional-structural parameter is the concentration of non-bridging oxygen in the glass computed following the procedure used in [8]. As expected, glasses of lower interconnectivity (higher NBO concentration) generally showed higher silica release rate.

All the composition-durability formulations noted above are "quasi-chemical" in nature, in that they invoke thermodynamic or structural principles, yet the relationships themselves have yet to be rigorously justified by theory. Whereas some suggestions have been made that net

TABLE I
Linear Coefficients of Theoretical and Empirical (MULTR) Models

Oxide Components	FEHMA ^a kcal/mol	VPAR ^b	Enthalpy (F) ^c kcal/mol	NBO	MULTR
Al ₂ O ₃	3.04	-2.00	-790.40	-2.00	-9.77
CaO	-16.12	-0.67	-151.79	2.00	4.19
Fe ₂ O ₃	15.50	-2.00	-197.09	-2.00	-2.81
FeO	-14.61	-0.67	-65.01	2.00	7.27
MgO	-13.89	-0.67	-143.76	2.00	3.98
MnO	-14.87	-0.67	-92.144	2.00	6.04
Na ₂ O	-28.82	2.00	-100.14	2.00	13.55
Li ₂ O	-22.74	2.00	-144.09	2.00	10.70
SiO ₂	5.59	-1.33	-435.32	0.00	0.00
B ₂ O ₃	-9.93	0.00	-306.37	0.00	3.44
UO ₂	-6.80	-1.33	-259.30	4.00	-11.15
ZrO ₂	45.10	-1.33	-526.08	4.00	-7.56
K ₂ O	-41.74	2.00	-87.80	2.00	17.10
BaO	-30.57	-0.67	-131.00	2.00	6.26
ThO ₂	-2.53	-1.33	-293.12	4.00	-52.84

^aFree energy of hydration model values are for the species specified in [7,8] (e.g., Na₂SiO₃ instead of Na₂O). The ΔG^* hydration values computed using these coefficients (Figure 1) were further corrected for a pH-effect [8].

^bVPAR values assumed an approximate $\bar{C}$ value of 1.5 (see Eq. 6 in [9]). For the glass compositions considered, $\bar{C}$ actually ranged from 0.8 to 2.0.

^cEnthalpy values assumed an approximate $\bar{E}_{\text{net}}$ of 2.0 (see Eq. 3 in [10]). For the glass compositions considered, $\bar{E}_{\text{net}}$ actually ranged from 0.01 to 4.31 kcal/mol.

reaction rates could be related to the free energy of reaction, the theoretical justifications that have been presented clearly cannot be applied to systems far from thermodynamic equilibrium boundaries [11-13]. Confidence in the use of one or more of these models largely hinges on the fact that a correlation between the compositional parameters proposed and durability has been observed empirically (Figure 1).

Correlations of the type shown in Figure 1 are also well known in the field of organic chemistry and are referred to as linear free energy relationships (LFER). Examples are the correlations suggested by Polanyi [14] for hydrogen abstraction reactions, Bronsted and Pederson [15] for base-catalyzed decomposition of nitramide, and Hammett [16] for the hydrolysis of substituted ethyl benzoates. These and subsequent workers have found that, for certain restricted classes of organic reactions, a correlation often exists between the reaction rate constant and a thermodynamic or structural characteristic of the reactants. This relationship can be formally described by:

Fig. 1. Correlation (r = Correlation Coefficient) of $\ln LRS_1$ with (a) $\Delta G^\circ_{\text{hydration}}$, (b) Valence Parameter [9], (c) Enthalpy [10], (d) NBO [8], and (e) Empirically Predicted LRS_1 (See Text for Discussion) for MCC-1, 28-Day Results. Symbols are for the following final pH ranges: (X) > 11; (◇) 10-11; (□) 9-10; (△) 8-9; (○) < 8. Data from C. Jantzen (pers. comm.), [9], and Argonne National Laboratory [unpublished data.].

$$\Delta G^\dagger = k_1(E) + k_2 \quad (3)$$

where $\Delta G^\dagger$ is the free energy of formation of the critical activated complex, E is a free energy or structural parameter associated with a reactant, and k_1 and k_2 are constants. Such relationships have also been recently recognized in other types of reactions including dissolution of inorganic solids [e.g., 17].

Empirical Relations

The dependence of silica leach rate on glass composition can be independently derived from existing data (i.e., data used in Figure 1). An empirical equation that expresses the best estimate of the partial

dependence of $\ln LR_{Si}$ on the molar concentration of individual glass components may be generated using a least squares technique (multiple linear regression) [18,19]. The empirical equation generated, when compared to theoretically-based expressions, could yield insights into the parameters of reaction that are most important in determining the reaction rates.

In the regression analysis, unstandardized partial regression coefficients of the mole fraction (X_i) of oxide components (predictor variables) on $\ln LR_{Si}$ (criterion variable) were derived (Table I). The coefficients shown in Table I are statistical measures of the contribution of specific oxide components on the durability; large coefficients (e.g., for the alkalis) imply large contributions to enhancing LR_{Si} (i.e., reduction of durability). Because mole fractions of glass components cannot be fully independent of each other (i.e., the statistical closure problem), silica was not incorporated in the multiple regression equation. This approach is equivalent to using pure silica as the hypothetical base glass so that only addition of oxide components other than SiO_2 can result in a change in the silica release rate (thus the zero coefficient for SiO_2 in Table I). The constant of regression is the predicted silica leach rate ($\ln LR_{Si}$) of pure silica glass. This constant is an adjustable parameter in the regression analysis so that it could change as a function of the data set being evaluated. An alternative approach would have been to fix this regression constant to the experimentally observed leach rate of silica glass. The assumed linear dependence of $\ln LR_{Si}$ on composition is not an inherent limitation of the regression approach, but only a reasonable starting point.

Figure 1e compares the normalized silica release rates predicted by the regression analysis to those actually measured in the experiments. It is evident that the residuals (i.e., $\ln LR_{Si, predicted} - \ln LR_{Si, observed}$) are more tightly constrained than in Figures 1a-d (also compare correlation coefficients, r). This is to be expected because there is no better linear predictor equation (in a least squares sense) of the normalized leach rate than the multiple linear regression equation.

DISCUSSION

Our aims in providing an empirical predictor equation for the silica leach rate based only on existing data are (1) to objectively evaluate the statistical accuracy of the theoretical predictive equations and (2) to compare the empirical coefficients with the coefficients suggested by the theoretical models (Table I). In line with the first objective, it is quite impressive that the prediction of the free energy of hydration model produced a correlation that is almost as good as the best statistical linear fit to the existing data. The other theoretical models also approached the correlation produced by the unbiased "best fit" model (Figure 1e) to varying degrees. This is remarkable because a completely accurate linear theoretical model could produce a correlation only as good as that shown in Figure 1e for the data set considered.

The relative magnitude (or hierarchy) of the partial regression coefficients associated with each glass component can be compared with thermodynamic or structural properties of each component thought to control composition-durability correlations. At the outset, it is notable that the empirically generated coefficients naturally fall into cation groups such as R_2O , RO , etc. (Table I). The "coefficients" of the free-energy of hydration model and the valence-parameter model showed the best correlation with the empirical coefficients (Figures 2a and 2b). Both these theoretical models predicted the relative durability effects of elemental groups (R_2O , RO , R_2O_3 , and RO_2) in a manner generally consistent with the empirical equation. In contrast, the NbO (Figure 2c), enthalpy

Fig. 2. Correlations of Empirical (MULTR) Coefficients with (a) Free Energy of Hydration Model (FEHM) Coefficients, (b) VPAR Coefficients, (c) Enthalpy Coefficients, and (d) NBO Coefficients (See Notes in Table I). Symbols are for the following elemental groups: (o) R₂O; (◊) RO; (Δ) RO₂; (X) B₂O₃; (◻) R₂O₃.

(Figure 2d), formation free energy (not shown), and formation enthalpy (not shown) formulations did not predict these group effects as satisfactorily. It cannot be emphasized too strongly that the empirical coefficients were derived totally independently of any of the theoretical models.

Other discrepancies between the theoretical models and empirical observations are notable. For example, whereas the valence parameter model was successful in predicting relative contributions of elemental groups, it failed to account for the relative durability effects within individual groups suggested by the empirical analysis [9]. This contrasts with the fact that the relative durability contributions within the alkali and, to a lesser extent, alkaline earth element groups stipulated by the hydration model is borne out by the empirical analysis. However, agreement between the durability effects predicted by the hydration model and the empirical observation for the RO₂ and R₂O₃ groups is not as satisfactory. For example, the hydration model predicts a beneficial effect of substituting Fe₂O₃ for Al₂O₃ contrary to the results of the empirical analysis. Furthermore, the relative beneficial effects of adding ThO₂ and UO₂ to glass durability appears to be underestimated by the hydration model.

The differences between the empirical and theoretical coefficients, where observed, could imply inadequacy of either of the two approaches. The results of the empirical analysis obviously depends on the accuracy of the data used and on artifacts that could result from the statistical

procedure. Systematic errors in the data set cannot be precluded and cannot be controlled during the analysis. Random analytical errors, however, are inherently considered by any statistical analysis. Statistical artifacts arising from multicollinearity of the compositional variables and use of statistically "unstable" variables were tested during the regression analysis using both standard and hierarchal methods [19]. All compositional variables used in the empirical analysis passed the statistical test at 99% level of confidence which suggests that the coefficients derived by the analysis (Table I) are stable and are not statistical artifacts.

The alternative possibility that the differences observed between the theoretical models and the empirical analysis are due to inadequacies in the former should also be explored. Whereas a detailed analysis of problems which may be associated with the fundamental assumptions of all the theoretical models is obviously outside the scope of this presentation, a few comments seem warranted at this point. For example, all the models discussed above used mole fractions as weighting parameters whereas activities may be the more appropriate values in a truly thermodynamic treatment [6]. The use of mole fractions in place of activities will introduce apparent changes in the coefficients of the empirical equation if component mixing in the glass is highly non-ideal. For the NBO formulation, the assumption that durability correlates with the concentration of non-bridging oxygens regardless of the types of cations associated with the NBO site is clearly disputed by the empirical analysis. The same may be said about the indifference, inherent in the valence parameter model, to the cation types in a particular valence group. This problem was recognized by Geldart and Kindle [9]. It is interesting that the hierarchy of empirical coefficients within individual valence groups (i.e., differentiating alkaline earths from divalent transition metals) show some relation to Pauling's electronegativity values. Consideration of this additional effect (or alternatively, cation polarizability effect) may thus be a potential avenue of improving the valence parameter model as presently formulated [cf. 8, 20]. The hydration model as originally proposed by Paul [6] stipulated a correlation between durability and $\Delta G_{\text{hydration}}$, not $\Delta G^{\circ}_{\text{hydration}}$. These two terms are related by:

$$\Delta G_{\text{hydration}} = \Delta G^{\circ}_{\text{hydration}} + RT \ln Q \quad (4)$$

where Q is the activity product of dissolved glass components. If the correlation justified by the theoretical treatment is between $\Delta G_{\text{hydration}}$ and durability, then a potential problem inherent in the approximate nature of Eq. 1 is its lack of consideration of the solution chemistry term ($RT \ln Q$) in Eq. 4. Jantzen et al. [8] actually have partially taken this into account by applying a pH correction to the hydration free energies. However, iterative computational procedures are required for full incorporation of solution chemistry effects into the hydration model [e.g., 21,22].

Alternatively, it may be appropriate to analyze the "successes" or "failures" of the theoretical models from mechanistic grounds. Assuming the following reaction is the rate-determining step in the silica detachment process:

a description of the forward rate can be formulated [22]:

$$\text{rate} = k_{\text{TST}} (\text{Si-O-Si}^*)(\text{H}_2\text{O}) \exp(-\Delta G^\ddagger/\text{RT}) \quad (6)$$

The constant k_{TST} incorporates the activity coefficient of the activated complex, the transmission coefficient, and the Plank's and Boltzmann constants in the usual transition state formulation, (Si-O-Si^*) and (H_2O) are the activities of the reactants (reaction 5) forming the activated complex, χ is the activated complex, and $\Delta G^\ddagger$ is the free energy change associated with formation of the activated complex. The effect of glass composition on the silica detachment rate could result from the restriction imposed by the presence of particular glass components on $(\text{Si-O-Si}^*)(\text{H}_2\text{O})$ [21] and/or the magnitude of the activation barrier. If it is assumed that the compositional effect on silicate detachment rates depends primarily on the influence of specific glass components on the free energy required to form the activated complex [e.g., 14-17] then it could be surmised, from the hydration model, that this effect is proportional to the free energy of hydration of individual glass components. The "success" or "failure" of the hydration model in predicting silica detachment rates is therefore related to the degree of correlation between the free energies of activation and hydration free energies. Similarly, the "success" or "failure" of other models to completely account for the observed compositional effects on silica detachment rates may be related to the degree of dependence of the free energy of activation on the suggested compositional parameter.* Alternatively, both the activities of the reactants forming the activated complex and the free energy of activation (Eq. 6) could be strong functions of glass compositions. If this is the case, more complex (e.g., non-linear) formulations may be necessary to completely account for observed composition-durability relationships.

CONCLUDING COMMENTS

Correlations of durability to glass composition in static glass leaching systems considered in this communication are well characterized by a number of existing formulations. The general correlations predicted by the free energy of hydration model and, to a lesser extent, other related theoretical models have been independently confirmed by an independent empirical formulation developed in the present work. Discrepancies between compositional effects predicted by the theoretical models and those borne out by the empirical analysis could be used as a basis for (1) modifying theoretical models so as to be more consistent with observations or (2) experimental verification of durability effects of component substitution (e.g., Al_2O_3 vs. Fe_2O_3).

The empirical approach used in this study could be extended further to examine other composition-durability correlations in glasses. For example, obsidian hydration rates of importance in archaeological applications are measured in terms of growth of hydrated layers, not silica detachment rates. Furthermore, the parameter of interest in these applications is vapor durability, not the durability in aqueous solutions discussed above. Experimentally measured obsidian hydration rates together with the obsidian compositions used could be employed to generate multiple linear regression equations similar to those derived here. This experimentally generated composition-hydration rate correlation can be used to predict intrinsic hydration rates of other compositions as well as to theoretically examine the significance of the compositional effects observed. There is no reason, a priori, to believe that correlations in

*Note that it is also possible for a model to fail with an adequate theoretical foundation but an inadequate data set or method for parameter estimation.

these types of systems should follow the predictions of any of the above theoretical models. Another example of possible extended utility of the empirical approach is the detailed examination of the correlations observed in the MCC-1 experiments used in this paper. We noted above that the role of glass components in silica detachment reactions could change as a function of glass composition. This role is influenced further by the conditions (e.g., T, pH) of the reaction [6-8]. It is therefore likely that the partial regression coefficients generated above could depend on (1) the subset of glass compositions considered and (2) the conditions of the experiments (most notably, pH). Our initial attempts to consider compositional subsets such as "aluminosilicates," "silicates," and "borosilicates" suggest that systematic changes in the regression coefficients could indeed be observed. This may imply either that non-linear models may be more appropriate or strictly linear relationships are restricted to particular ranges of glass compositions. Consideration of restricted pH ranges in the regression analysis also suggests possible dependence of empirical coefficients on reaction pH. We will be considering the significance of these effects in the future.

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