A MODIFIED THERMODYNAMIC MODEL OF GLASS DISSOLUTION UNDER STRONG INTERACTIVE CONDITIONS

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ABSTRACT

An extensive series of leach tests were carried out on silicate glasses, in particular borosilicate glasses developed for the West Valley HLW immobilization project, under highly interactive, modified MCC-3 conditions. The results can be systematized in terms of the Plodinec-Jantzen additive hydration energy model. However, the original hydration energies used in applying this model to data obtained under high-dilution MCC-1 test conditions have to be modified when applied to the analysis of results obtained under highly interactive test conditions. In particular, under the latter conditions the hydration energy corresponding to alumina in the glass is much higher, i.e. alumina is very effective in stabilizing the glass against corrosion. This conclusion is based on best-fit calculations for all the glasses included in the study, as well as on the direct observation that: (a) the leachate concentrations obtained with commercial aluminosilicate glasses are lower than those observed for fused silica; (b) the addition of a given amount (e.g. 2%) of alumina to the West Valley glass composition is much more effective in reducing the extent of leaching than the addition of a corresponding amount of silica or of other ingredients.

INTRODUCTION

In recent years the attempts to obtain highly durable glass compositions for High-Level-Waste vitrification and the need for systematic understanding of the effects of glass composition on durability have resulted in the development of a thermodynamic model by Jantzen and Plodinec which correlates leach rates with the weighted sum of the hydration energies of the individual glass components (1-2). This model has been remarkably successful in correlating observed leach rates with calculated values for a large variety of nuclear as well as non-nuclear glasses spanning a range of four orders of magnitude in leach rates. The experimental data used in this model have been obtained using the MCC-1 test procedure, which involves a relatively small extent of influence of the leached species on leachant composition and reactivity because of the high dilution conditions employed in this test.

We have recently concluded a series of tests based on a modified MCC-3 powder test procedure (3,4), which involves very high surface-to-volume ratios and therefore reflects the strong-interaction case. In this case the chemistry of the aqueous phase is heavily influenced by the leach products. The glasses used in this test included compositions developed for waste vitrification at West Valley as well as glasses developed at the Savannah River Laboratory and a variety of non-nuclear glasses (e.g., commercial fused silica, borosilicate, aluminosilicate and soda-lime glasses). The results indicate that the Jantzen-Plodinec model is also applicable to situations which involve strong interactions between the glass and the surrounding leachant, giving rise to effects such as saturation, re-crystallization, surface alteration, etc. It was noted, however, that the data-base used by Jantzen and Plodinec requires certain modifications when used under highly interactive conditions, which may be more relevant to geologic repository scenarios. In particular, under such conditions the role of alumina in stabilizing glass compositions against dissolutions, compared with the role of silica, becomes much more important. This is reflected in the necessity to assign a much higher hydration energy to the alumina component of the glass in order to obtain satisfactory correlation with the experimental data. This effect may be ascribed to the significance of the presence of more stable complex aluminosilicate units in the glass.

EXPERIMENTAL

A modified Materials Characterization Center MCC-3 type powder test (3,4) was used to determine the durability of all glasses tested. 4.00 gram of -100 +200 mesh glass powders were leached in 40.0 mL de-ionized water with a surface to volume ratio of 2700 m^{-1} in a Teflon PFA container (Savillex Corp., Part #560 plus Part #501-37). Each leach vessel was fitted with a rubber septum cap so that the leachate could be withdrawn several times for analysis without opening the vessel. The leachant was not replenished. The leach vessels were placed in a sealed container in the presence of Ascarite™ II to prevent CO_2 ingress. The test temperature was 90°C. The samples were agitated every 24 hours. All the tests were carried out in duplicate or in triplicate. The test duration was 7, 28 and 56 days. At the end of each of these periods a 4.0-mL sample of the leachate was withdrawn from the vessel with a syringe and a part of it was immediately diluted with a 20-fold excess of de-ionized water to avoid possible precipitation before analysis. The rest of the sample was immediately placed in a cup surrounded by water at room temperature and its pH measured by means of a Ross-type glass electrode. Elemental concentrations were analyzed by means of dc plasma spectroscopy and atomic absorption/flame emission.

Most of the glasses studied here were developed for the immobilization of the high-level-radioactive waste at West Valley around the WV205 central composition (3). These glasses, melted at the Catholic University of America (3) included compositions containing Th and U as well as glasses based on Zr as a simulant. Other glasses tested here included borosilicate compositions developed at the Savannah River Laboratory (1,3) and a variety of non-nuclear glasses. The commercial aluminosilicate glass used in the test is corning #1720. The fused silica was obtained from Quartz Scientific, Inc.

RESULTS AND DISCUSSION

Calculations

The normalized mass loss $NLi(g \cdot m^{-2})$ of an element i from the glass was calculated according to:

$$NLi = \frac{Ci}{Fi \cdot (S/V)} \qquad (1)$$

where Ci(mg/L) is the measured concentration of element i in the leachate, Fi is its mass fraction in the glass, and S/V (m^{-1}) is the ratio of glass surface to leachant volume.

The relative thermodynamic stability of each glass, in terms of total free energy of hydration, was calculated with the assumption that the total free energy of hydration of a glass is the weighted sum of the free energies of hydration reactions of the individual silicate and oxide components according to Jantzen's formulae (2):

$$DG(hyd) = \Sigma\ Xi \cdot (DGhyd)i \qquad (2)$$

where (DGhyd)i is the free energy change of the hydration reaction of component i present at a mole fraction Xi.

The DG(hyd) term was corrected with the following two formulae introduced by Jantzen (2) due to the contributions to the total free hydration energy from the dissociation of silicic acid and boric acid:

$$DG'hyd = DG(hyd)-1.364\log(1 + \frac{10^{-10}}{10^{-pH}} + \frac{10^{-21.994}}{10^{-2pH}}) \qquad (3)$$

$$DG''hyd = DG'hyd-1.364\log(1 + \frac{10^{-9.18}}{10^{-pH}} + \frac{10^{-21.89}}{10^{-2pH}} + \frac{10^{-35.69}}{10^{-3pH}}) \qquad (4)$$

where DG'hyd is the total free hydration energy after the correction by Eq. (3) and DG''hyd is the total free hydration energy after correction by Eq. (4). In cases where the glass does not contain boron, only Eq. (3) was used.

A least squares regression analysis was applied to produce the best linear fit of the mass loss data plotted against the calculated D(hyd) value for each glass corrected for the observed rise in pH. The fitting expression had the form:

$$\log(NLi) = a[DG(hyd)]-b \qquad (5)$$

The results of the linear fitting procedure for the 41 nuclear waste glasses used in the experiments are given in Table I. R is the linear correlation coefficient of the fit and a is the slope of the straight line of the fit.

Some examples of the corresponding plots are shown in Fig. 1 to Fig. 5. It should be noted that the values of the slope a for Si at 28 days are the same in the case of Jantzen's MCC-1 results (2) and in the case of the present MCC-3 results. However, the slope a for boron at 28 days is higher than that of the silica data by almost a factor of 2 in the case of the MCC-3 data. It is not surprising that the observed congruent dissolution of glasses under MCC-1 conditions breaks down in the strongly interactive case of MCC-3 - type tests due to saturation and possible precipitation or alteration of Si (5). This results in a lower loss of Si than that of boron or sodium.

Effects of Alumina and Silica on Leach Behavior

The above results indicate that the Jantzen-Plodinec model is generally suitable for analysis of the modified MCC-3 test results. However the correlation coefficients show that the fit is not very good and there is room for improvement. Most significantly, the modified MCC-3 results in Table II demonstrate that the commercial aluminosilicate glass is even more durable than fused silica glass. However, in the Jantzen-Plodinec data base, the hydration energy of silica is 5.59 kcal/mole, a value which is larger than the 3.04 kcal/mole for the hydration energy of Al_2O_3. This indicates that the replacement of SiO_2 by Al_2O_3, e.g. when aluminosilicate glass is substituted for fused silica, should cause a decrease in durability even without considering the presence of other leachable elements such as boron, sodium, calcium and magnesium in the aluminosilicate glass composition. This is contrary to the experimental observations. Therefore, it has been attempted to assign higher free energy of hydration to alumina. This has resulted in more positive DG(hyd) values for alumina-containing glasses and better correlation with the MCC-3 test data. Fig. 6 shows that as the value of free energy of hydration increases, the least squares fit becomes better and it gives the best correlation coefficient around 40 kcal/mole for Al_2O_3. By using 40.04 kcal/mole as the free energy of hydration for Al_2O_3, the analysis of the B, Si and Na leach data for the 41 HLW glass compositions included in this study gives much better correlation than the original Jantzen-Plodinec model. The correlation results are detailed in Table I. Examples of the correlation plots are shown in Figs. 1-5. Similar correlations can also be established between Li or K release and DG(hyd). The higher value for the free energy of hydration of Al_2O_3 which results in better correlations between the glass composition and chemical durability reflects a more significant role of Al_2O_3 in stabilizing the glass against dissolution under highly interactive conditions.

The higher value of the free energy of hydration of Al_2O_3, could be explained in the following way. In the original Jantzen-Plodinec model AlO(OH) is assumed to be the product of the hydration reaction of Al_2O_3 (6). This results in a value of 3.04 kcal/mole for the hydration energy:

$$Al_2O_3 + H_2O \longrightarrow 2AlO(OH) \qquad (6)$$
$$DGhyd(Al_2O_3) = 3.04 Kcal/mole$$

However, under the MCC-3 conditions AlO(OH) undergoes ionic dissociation because of the sharp rise in pH. The following hydration reaction can therefore be invoked to account for the much higher hydration free

TABLE I

Parameters of Least Squares Regression Analysis

Element	Time (days)	Original Jantzen-Plodinec Hydration Energies			Corrected Hydration Energies		
		a	b	R	a	b	R
Si	7	-0.2100	2.1296	0.8394	-0.1598	1.8634	0.9549
	28	-0.2240	2.1054	0.7497	-0.1650	1.7849	0.9151
	56	-0.2694	2.3915	0.8309	-0.1636	1.7666	0.9451
B	7	-0.3744	2.5738	0.8507	-0.2792	2.0651	0.9489
	28	-0.4190	2.5365	0.6958	-0.3113	1.9520	0.8562
	56	-0.5426	3.0759	0.7031	-0.3482	1.9168	0.8449
Na	7	-0.2487	1.9566	0.7121	-0.2500	1.9582	0.9482
	28	-0.3293	2.1799	0.5212	-0.2829	1.8848	0.8497
	56	-0.4186	2.5303	0.6115	-0.2628	1.6046	0.7189

TABLE II

Durabilities and Free Energies of Hydration of Glasses

Glass	7 Day (Si)		28 Day (Si)		DGhyd (kcal/mole)		
	Conc. mg/L	Normal Conc.	Conc. mg/L	Normal Conc.	Al=3.04	Al=40.04	Al=70.04
ALSI #1	19.10	0.02455	16.75	0.01938	-0.9187	2.9300	6.0503
ALSI #2	21.50	0.02764	20.8	0.02406	-0.9187	2.9300	6.0503
Fused Silica #1	71.28	0.05724	100.1	0.07235	5.4546	5.4546	5.4546
Fused Silica #2	66.35	0.05297	80.50	0.05785	5.4546	5.4546	5.4546
WV205+2% SiO_2	70.55	0.12146	166.8	0.25844	-5.3620	-4.5579	-3.9060
WV205+2% Al_2O_3	46.3	0.08316	54.3	0.08455	-5.4976	-4.1939	-3.1371

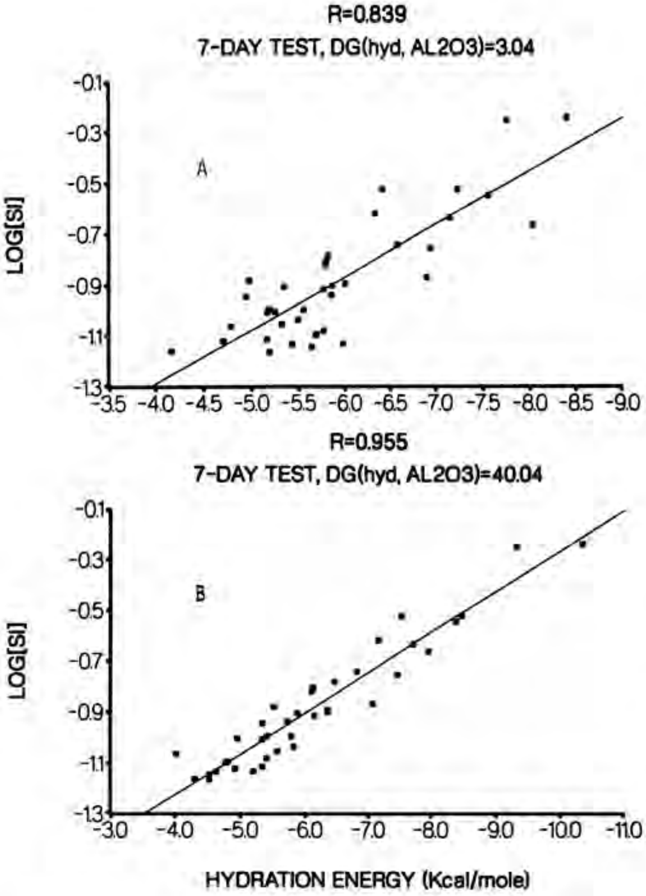

Fig. 1. 7-Day SI Release Data.
A. DG(HYD, AL2O3)=3.04 KCAL/MOLE
B. DG(HYD, AL2O3)=40.04 KCAL/MOLE

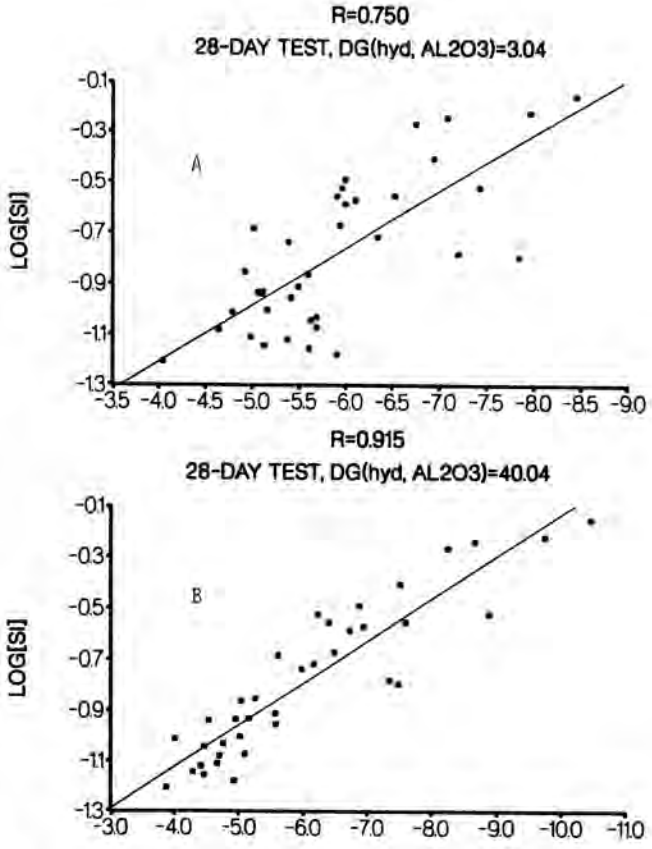

Fig. 2. 28-Day SI Release Data.
A. DG(HYD, AL2O3)=3.04 KCAL/MOLE
B. DG(HYD, AL2O3)=40.04 KCAL/MOLE

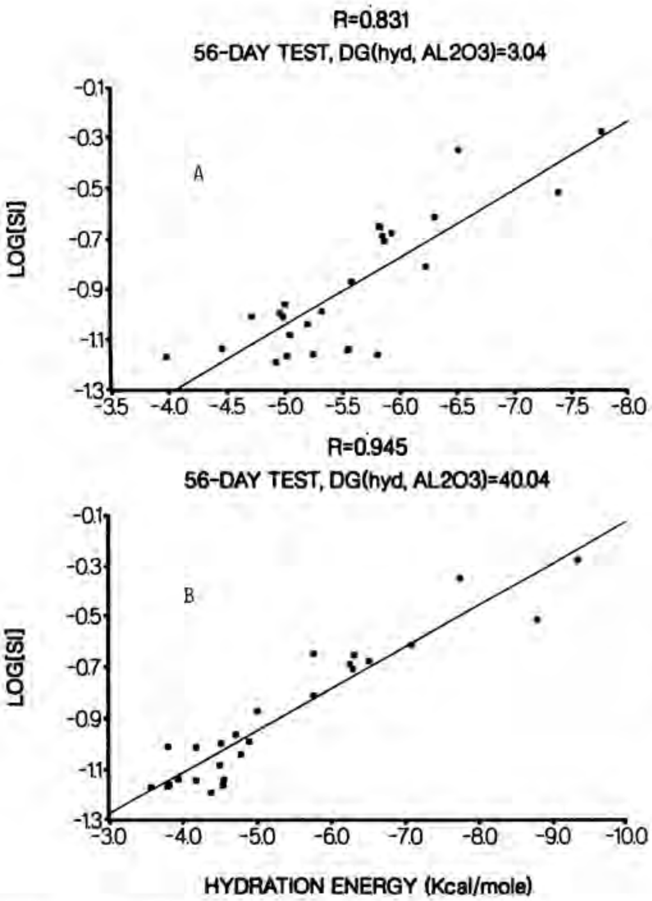

Fig. 3. 56-Day SI Release Data.
A. DG(HYD, AL2O3)=3.04 KCAL/MOLE
B. DG(HYD, AL2O3)=40.04 KCAL/MOLE

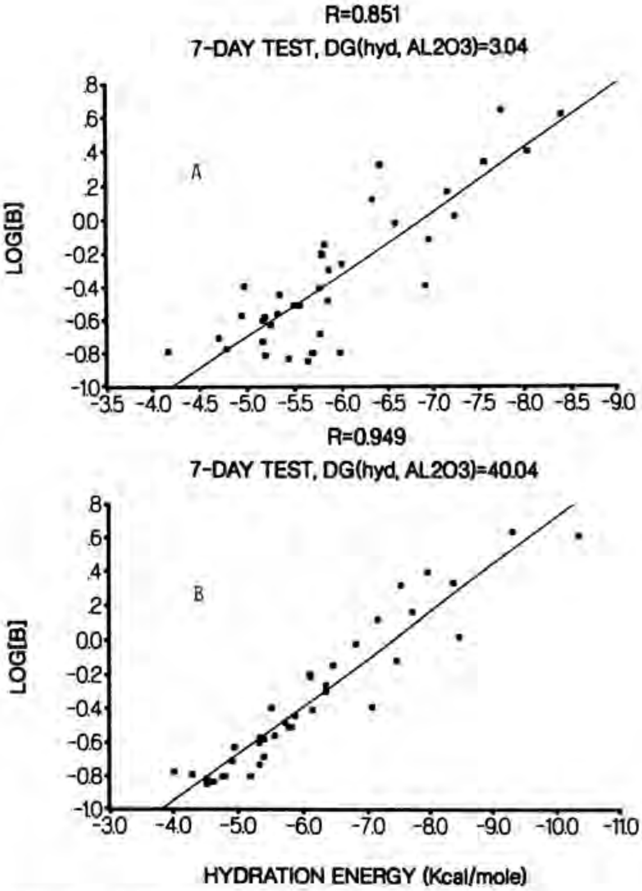

Fig. 4. 7-Day Boron Release Data.
A. DG(HYD, AL2O3)=3.04 KCAL/MOLE
B. DG(HYD, AL2O3)=40.04 KCAL/MOLE

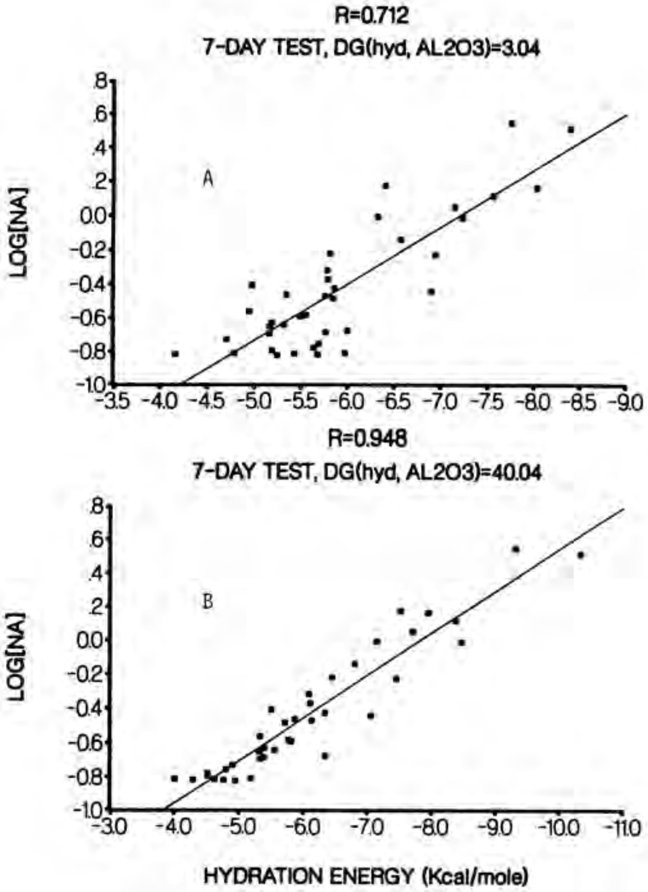

Fig. 5. 7-Day Sodium Release Data.
A. DG(HYD, AL2O3)=3.04 KCAL/MOLE
B. DG(HYD, AL2O3)=40.04 KCAL/MOLE

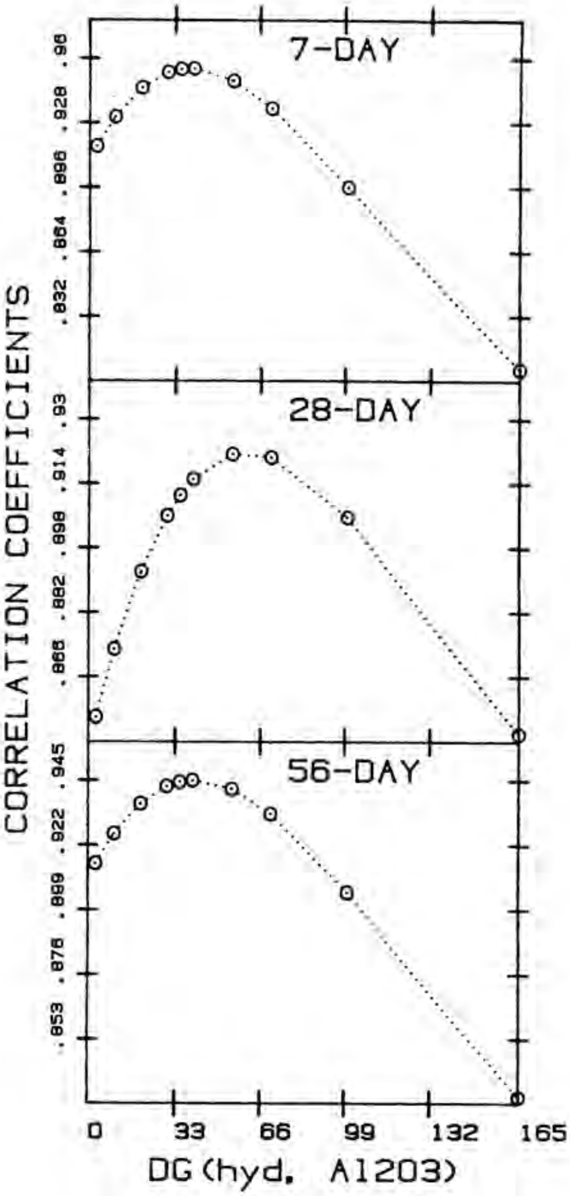

Fig. 6. Correlation Coefficients of the Linear Least Squares Fit as a Function of DG(HYD, AL2O3).

energy of the alumina component of the glass:

$$Al_2O_3 + 3H_2O \rightarrow 2H^+ + 2H_2AlO_3^- \qquad (7)$$

$$DGhyd(Al_2O_3) = 32.4 \text{ kcal/mole}$$

This value is based on the free energies of formation of Al_2O_3, H_2O, H^+ and $H_2AlO_3^-$ in Ref. 7. Furthermore, complex aluminosilicate compounds (8,9), rather than simple alumina and silica, should be considered as the reactants of the hydration reactions. A simple model could be the formation of low albite, $NaAlSi_3O_8$. For each mole of Al_2O_3, 2 moles of low albite could be formed with 6 moles of SiO_2 and one mole of Na_2O. For simplicity, it is assumed that low albite is formed directly from the reactants in the original Jantzen-Plodinec model, as represented by the equation:

$$Na_2SiO_3 + 5SiO_2 + Al_2O_3 \rightarrow 2NaAlSi_3O_8 \qquad (8)$$

$$DG = -41.28 \text{ kcal/mole}$$

where DG is the free energy change of this equation. This value is based on the free energies of formation of SiO_2 and Al_2O_3 (7), Na_2SiO_3 (7) and $NaAlSi_3O_8$ (10). This equation can be used to justify the increase of the empirical free energy of hydration of Al_2O_3 from 3.04 to 40 kcal/mole in the present calculations.

This larger effect of Al_2O_3 compared with SiO_2 in stabilizing glass against hydration is also directly observed upon considering the leach data obtained when 2% of additional Al_2O_3 was added to the basic composition of WV205 glass (3), resulting in a much more durable glass than the corresponding glass with 2% additional SiO_2, as shown in Table II.

CONCLUSION

The thermodynamic approach proposed by Jantzen and Plodinec to correlate glass durability with the overall free energy of hydration is applicable to the highly interactive MCC-3 test conditions. Assigning higher hydration free energy for Al_2O_3 significantly improves the correlation with the understanding that Al_2O_3 plays a much more important rule than SiO2 in stabilizing glasses against dissociation at least under the highly interactive MCC-3 conditions. This is even more directly evident upon comparing leach test data for glasses in which part of the silica has been replaced by alumina with data for the corresponding glasses without this change in composition.

The interactive test data, unlike MCC-1 data, shows a large difference between the mass loss based on boron and on silica, respectively, due to stronger saturation effects in the case of silica.

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