

CHEMICAL DURABILITY OF SIMULATED NUCLEAR GLASSES
CONTAINING WATER

DISCLAIMER

H. Li
M. Tomozawa^(a)

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

April 1995

Presented at the
1995 American Ceramic Society Annual Meeting
April 30 - May 4, 1995
Cincinnati, Ohio

Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Richland, Washington 99352

(a) Rensselaer Polytechnic Institute, Troy, New York

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Chemical Durability of Simulated Nuclear Waste Glasses Containing Water

Hong Li, Pacific Northwest Laboratory,^(a) Richland, WA 99352
Minoru Tomozawa, Materials Engineering Department, Rensselaer Polytechnic Institute
Troy, NY 12180-3950

ABSTRACT

The chemical durability of simulated nuclear waste glasses having different water contents was studied. Results from the product consistency test (PCT) showed that glass dissolution increased with water content in the glass. This trend was not observed during MCC-1 testing. This difference was attributed to the differences in reactions between glass and water. In the PCT, the glass network dissolution controlled the elemental releases, and water in the glass accelerated the reaction rate. On the other hand, alkali ion exchange with hydronium played an important role in the MCC-1 test. For the latter, the amount of water introduced into a leached layer from ion-exchange was found to be much greater than that of initially incorporated water in the glass. Hence, the initial water content has no effect on glass dissolution as measured by the MCC-1 test.

INTRODUCTION

Immobilization of radioactive nuclear waste materials using borosilicate-based glasses requires that the final glass waste form be chemically durable. Vitrification of waste streams involves mixing waste slurry with glass frit and vitrifying the mixture at high temperature. In the process, waste glass is melted under an atmosphere containing water vapor and, hence, water entry into the molten glass is expected. The effect of water content on chemical durability of waste glass is unknown. It is known, for sodium-silicate glass, that water in the network adversely affects glass chemical durability [1]. This paper reports a systematic study of the effect of water content on the chemical durability of simulated nuclear waste glasses.

EXPERIMENTAL

Three simulated high-level nuclear waste glasses, provided by Pacific Northwest Laboratory (Richland, Washington) were used for this investigation. Table I summarizes the glass compositions. The glasses were separately remelted at 1150°C under three water vapor pressures: 93, 355, and 760 mmHg. The detailed procedures of melting glass and determining water content in the glass are reported elsewhere [2].

(a) Pacific Northwest Laboratory is operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

Table I. Chemical Compositions of High-Level Simulated Nuclear Waste Glasses (wt%)

Oxide	CVS2-18	CVS2-52	CVS2-74
SiO ₂	53.53	60.00	56.60
B ₂ O ₃	10.53	8.17	7.81
Al ₂ O ₃	2.31	2.33	8.16
Fe ₂ O ₃	7.19	7.20	3.34
ZrO ₂	3.85	3.85	0.05
MgO	0.34	0.09	0.32
CaO	0.83	0.08	0.79
Li ₂ O	3.75	7.88	7.13
Na ₂ O	11.25	4.50	6.64
Others	5.92	5.90	9.16

Glass dissolution in deionized water was evaluated at 90°C using the product consistency test (PCT) and MCC-1 test methods [3,4]. For the PCT, the ratio of sample surface area to solution volume, (S/V), was 2000 m⁻¹ and the test duration was 7 days. For the MCC-1 test, the S/V ratio was 10 m⁻¹, and the test duration was 28 days. Solution pH values before and after each test were measured using a 701A digital pH/mV meter.

After each test, concentrations of sodium, boron, lithium, and silicon were measured using a Beckman Spectran-V DC plasma emission spectrometer. Each elemental release was calculated in terms of the normalized elemental mass loss [3]:

$$(NL)_i = C_i / [f_i(S/V)], \quad (\text{g/m}^2) \quad (1)$$

where C_i (g/m³) is the concentration of element i in the 0.45- μm filtered solution, and f_i is the mass fraction of element i in the unleached specimen.

RESULTS

Figure 1 illustrates the infrared spectra for three as-received glasses. An absorption peak at $\sim 3550 \text{ cm}^{-1}$ is attributed to asymmetric vibration of hydroxyl [5], and another peak at $\sim 2700 \text{ cm}^{-1}$ is a combination band of B-O vibrations [6,7]. Hence, water content in the glass is proportional to the intensity of the absorption peak at 3550 cm^{-1} per unit of specimen thickness.

Figure 2(a-c) depicts hydroxyl absorption intensity versus specimen thickness for the three glasses melted under three water vapor pressures. It is apparent that the slopes of the lines increase with water vapor pressure. Knowing the hydroxyl absorbance (A) and the specimen thickness (d), the water concentration, C , in each glass was calculated using Beer's law, $A = \epsilon Cd$, where ϵ is the extinction coefficient of hydroxyl previously determined for these glasses [2]. Table II summarizes water concentrations in the prepared glass samples. Under a given water vapor pressure, it can be seen that the water solubility of CVS2-18 was the highest, while that in CVS2-74 was the lowest.

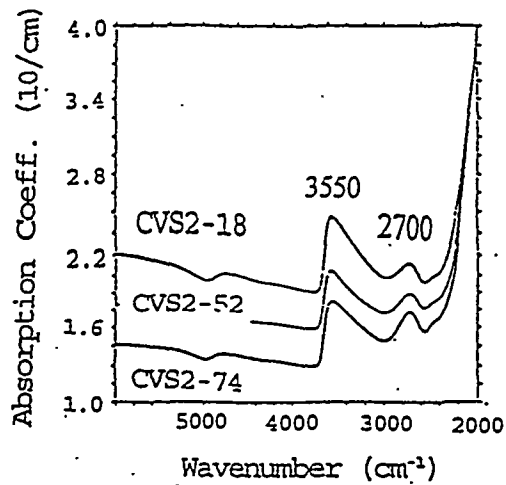


Figure 1. FTIR spectra of CVS2-18, -52, and -74 simulated nuclear waste glasses, which are displaced upward, relative to CVS2-74, for clarity.

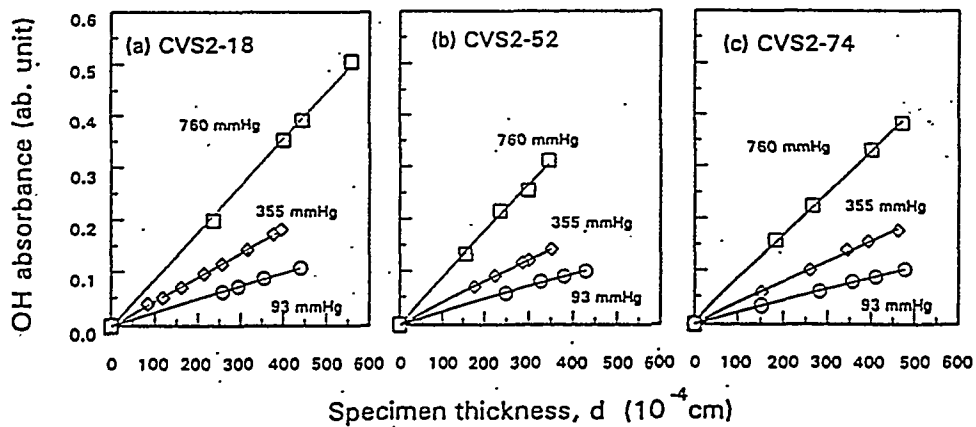


Figure 2. Hydroxyl absorbance as a function of specimen thickness for CVS2-18, -52, and -74 glasses melted at 1150 °C under three water vapor pressures as indicated.

Table II. Water Contents (wt%) in the Glasses Melted under Various Water Vapor Pressures

Vapor Press. (mmHg)	CVS2-18	CVS2-52	CVS2-74
93	0.20	0.14	0.11
355	0.36	0.24	0.21
760	0.73	0.53	0.44

For the PCT, the initial pH was about 8.5 for all solutions after the sample powder was immersed in water for about 30 min at room temperature. The pH of the deionized water was 5.0. After the 7-day test, the pH values were close to 10.0. Figure 3 (a,b) illustrates the normalized elemental mass losses versus water content for sodium and boron, respectively. The error bars of the data measurements are less than the size of the symbols used here. Among the three glasses, CVS2-18 was more susceptible to water attack than CVS2-52; CVS2-74 was the most resistant to such an attack. The general trend of Figure 3 indicates that glasses with higher water content exhibited a greater amount of dissolution. Comparing the releases of sodium and boron between glasses having the lowest and the highest water contents, the increases are about 7 %, 10 %, and 38 % for CVS2-18, -52, and -74, respectively. Similar trends were also found for the releases of both lithium and silicon.

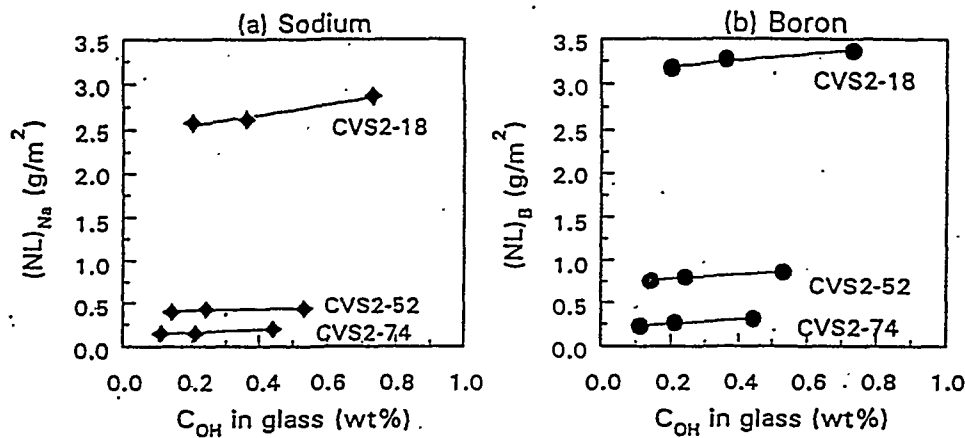


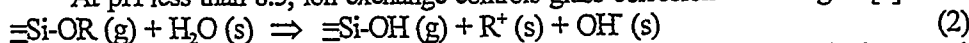
Figure 3. PCT normalized elemental mass loss versus water content for CVS2-18, -52, and -74 simulated nuclear waste glasses.

For the MCC-1 test, after 28 days, the pH increased to about 9.0. Figure 4(a,b) illustrates the elemental releases of sodium and boron versus water concentration, respectively. Analogous to the PCT results, the elemental release of CVS2-18 was the highest, while that of CVS2-74 was the lowest. However, the releases appeared to be unaffected by the water content in the glass. The same conclusion is true for the releases of both lithium and silicon.

DISCUSSIONS

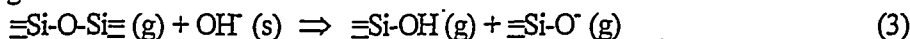
The adverse effect of water content on glass chemical durability was observed in the PCT, but not in the MCC-1 test. Because of the great difference in the S/V values for the two tests, the initial pH levels were also very different. For alkali-silicate glasses, glass reaction with water proceeds via ion exchange, network hydrolysis, and subsequent network dissolution. Solution pH strongly influences which process dominates.

At pH less than 8.5, ion exchange controls glass corrosion according to [8]:

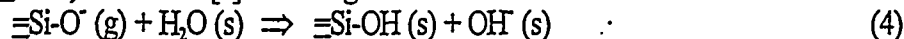


where R⁺ is the alkali ion, and (g) and (s) refer to glass and solution, respectively. Reaction (2) increases the solution pH and at the same time produces silanol group, ≡Si-OH, in the glass.

increases the solution pH and at the same time produces silanol group, $\equiv\text{Si-OH}$ or $\text{Si-O}(\text{H}_3\text{O}^+)$, in the glass. For the PCT, a massive ion exchange raised the solution pH to such a level that the glass network dissolution is expected almost from the beginning of the test [9,10]. Therefore, the releases were mainly controlled by the network dissolution. These processes can be described in terms of free hydroxyl formed by reaction (2) attacking siloxane bonds at the water/glass interface [8] according to:



and then followed by the dissolution of the leached layer via the reaction of nonbridging oxygen (NBO), $\equiv\text{Si-O}^-$, with water [8] according to:



Surfaces of the PCT sample powders were examined using an optical microscope. No surface alteration was found, which indicated the dominating role of the network dissolution in the PCT. Therefore, the increase of glass dissolution for the glasses having higher water content may be related to the formation of more NBOs, which in turn promotes reaction (4).

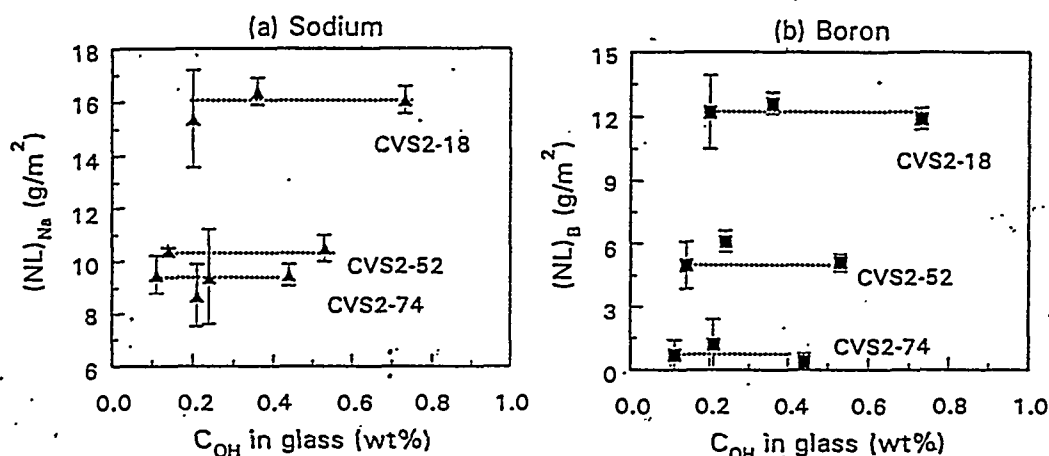
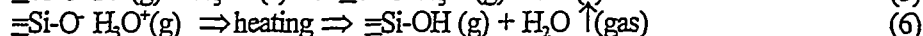
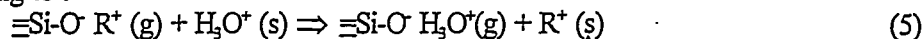


Figure 4. MCC-1 normalized elemental mass loss versus water content for CVS2-18, -52, and -74 simulated nuclear waste glasses.

For the MCC-1 test, the initial solution pH was much lower and, hence, ion exchange was favored during the test [10]. For an ion exchange-controlled leaching process, such as in the MCC-1 test, it is expected that a hydration layer will form on the specimen surface and that the hydroxyl concentration in that layer will be high [10]. After the MCC-1 test, hydration layers were observed for all samples. Hydroxyl concentration changes in the samples were examined using a Perkin-Elmer FTIR-1800 spectrophotometer. An example is illustrated in Figure 5, showing FTIR spectra of a CVS2-18 monolith before and after the MCC-1 test. A substantial increase in the hydroxyl absorption is evident (cf. spectra 2 and 1). The result supports the notion that ion exchange plays the dominant role in the MCC-1 test.

Figure 5 also shows spectra for the same sample (after MCC-1) dehydrated at 300°C in ambient air for 1 and 16 h, respectively (cf. spectra 3 and 4). The dehydration spectra suggest ion exchange introducing both hydroxy and molecular water into the network. The former is strongly bonded to the network, which can be approximated by the differences in hydroxyl absorptions

in the network, which is approximated by the difference in hydroxyl absorptions between spectrum 2 and 3. The presence of the two types of water suggests alkali ions exchanging with hydronium according to :



Reactions (5 and 6) have also been reported for soda-lime silicate glass by Schnatter et al. [11]. Figure 5 demonstrates that the amount of hydroxyl introduced into the leached layer during the MCC-1 test is much higher than that of water initially incorporated in the glass during melting. Therefore, the influence of the initial water content on glass leaching must be minimal as observed in the MCC-1 test.

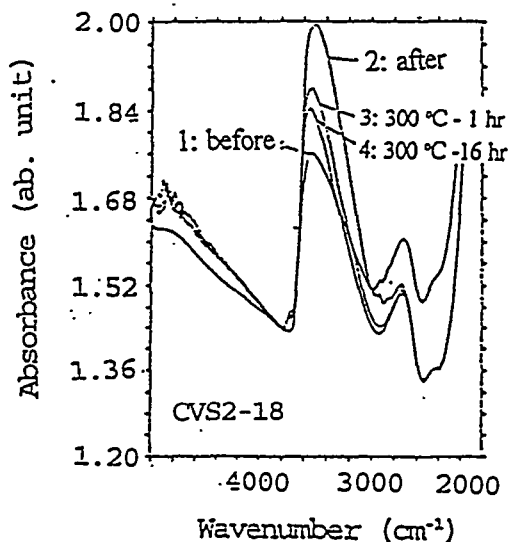


Figure 5: FTIR spectra of CVS2-18 monolith, showing the hydroxyl absorbance changes before and after the MCC-1 test as well as during dehydration at 300 °C.

Chemical durability of a glass depends in part on its network bond strength, which is affected by the presence of nonbridging oxygens, NBO. The extent of the NBO effect not only depends on a total concentration of alkali ions, but is also affected by ionic strength or ionic potential of alkali ions. Sigel [12] reported that glass containing various amounts of NBO showed different positions of ultra-violet (UV) absorption edges, namely the UV edge shifted from a lower wavelength to a higher one with increasing NBO. McSwain et al. [13] studied the UV edge changes for binary borate glasses. For a given concentration of alkali ion, they reported the UV edge shifted to a higher wavelength in the order $\text{K} > \text{Na} > \text{Li}$, in which their ionic potential increased in the order $\text{K} < \text{Na} < \text{Li}$. These results imply there may be a correlation between the UV absorption edge and the glass chemical durability since both are affected by NBO.

A qualitative correlation between the UV edge and the chemical durability was examined. Figure 6 illustrates spectra for CVS2-18, -52 and -74, glasses melted in 760 mmHg water vapor. The wavelength of UV edge was found to increase in the order CVS2-74, CVS2-52, and CVS2-18, which appears to be well correlated with the trend of the glass elemental releases in water,

CVS2-74 < CVS2-52 < CVS2-18. For the same glass, it was also found that the UV edge for a sample having the lowest water content was slightly lower than that of a sample having the highest water content, suggesting that water creates additional NBOs. Based on this preliminary investigation, glass having a higher UV edge appears to be more susceptible to water attack.

Compared to the effect of water content on chemical durability, it is apparent that glass composition has a stronger influence. As expected, the strength of the glass network changes with composition, which may be assessed by using a structural bond strength (SBS) model proposed by Feng and Barkatt [14]. In the SBS model, the total bond energy can be determined from the glass composition. The more negative the value of the bond energy, the higher the strength of the network and, hence, a greater resistance of that glass to water attack. For the three glasses studied here, the total bond energies were calculated to be -3.24, -3.32, and -3.38 kcal/mol for CVS2-18, -52, and -74, respectively. Comparison between the elemental releases with the total bond energy is in good agreement for these glasses.

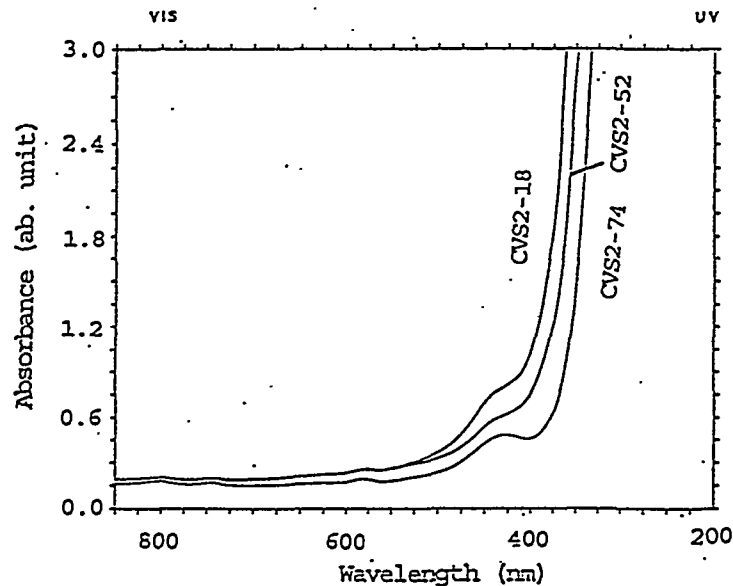


Figure 6. Optical spectra in a range from visible to ultra-violet for CVS2-18, -52, and -74 simulated nuclear waste glasses (specimen thickness: 136. μm).

CONCLUSIONS

Using the PCT method, water in the glass was shown to influence chemical durability of simulated nuclear waste glasses. In contrast, such an effect was not detected using the MCC-1 test. The discrepancy was attributed to the differences in reactions of glass with water. Network dissolution was found to be the dominant reaction in the PCT, and ion exchange in the MCC-1 test. Overall, the chemical durability is principally influenced by glass composition. Finally, a correlation between NBO in glass and glass durability was explored using UV spectroscopy. Preliminary results suggested that a glass more susceptible to water attack tends to have a higher UV edge.

ACKNOWLEDGMENTS

This work was sponsored by Pacific Northwest Laboratory, Richland, Washington, under contract grant No. 195074-A-F1. Discussions of the SBS model with Dr. X. Feng at PNL are appreciated. Hong Li is also grateful to Associated Western Universities, Inc. for a postdoctoral fellowship appointment at Pacific Northwest Laboratory.

REFERENCE

1. M. Tomozawa, C.Y. Erwin, M. Takata and E.B. Watson, "Effect of Water Content on the Chemical Durability of $\text{Na}_2\text{O}3\text{SiO}_2$ Glass," *Journal of American Ceramic Society* 65[4] 182-183 (1982).
2. H. Li and M. Tomozawa, "Effect of Water Content on Properties of Simulated Nuclear Waste Glasses," *Journal of Non-Crystalline Solids* (submitted, 1994).
3. J.E. Mendel (Editor), *Nuclear Waste Materials Handbook*, DOE/TIC-1140, Pacific Northwest Laboratory, Richland, Washington (1986).
4. C.M. Jantzen and N.E. Bibler, *Nuclear Waste Glass Product Consistency Test (PCT) Method - Version 3.0 (U)*, WSRC-TR-90-539 Rev. 1, Savannah River Laboratory, Aiken, South Carolina (1990).
5. H. Scholze, "Gases and Water in Glass, Part Two," *Glass Industry* 47[11] 62-68 (1966).
6. A.S. Tenney and J. Wong, "Vibrational Spectra of Vapor-Deposited Binary Borosilicate Glasses," *Journal of Chemical Physics*, 56[11] 5516-5523 (1972).
7. G.A. Pasteur, "Optical Determination of OH in B_2O_3 Glass," *Journal of American Ceramic Society* 56[10] 548 (1973).
8. R.J. Charles, "Static Fatigue," *Journal of Applied Physics*, 29[11] 1549-1553 (1958).
9. R.K. Iler, Chapter 2. Water-Soluble Silicates in *The Chemistry of Silica*, John Wiley & Sons, New York (1979).
10. X. Feng, "Effects of pH on the Leaching Mechanism of Nuclear Waste Glasses," in *Ceramic Transactions, Nuclear Waste Management IV*, Vol. 23, ed. by G.G. Wicks, D.F. Bickford, and L.R. Bunnell, American Ceramic Society, Columbus, OH (1991) p. 95-104.
11. K.H. Schnatter, R.H. Doremus and W.A. Lanford, "Hydrogen Analysis of Soda-Lime Silicate Glass," *Journal of Non-Crystalline Solids*, 102, 11-18 (1988).
12. G.H. Sigel, Jr., "Vacuum Ultraviolet Absorption in Alkali Doped Fused Silica and Silicate Glasses," *Journal of Physics and Chemistry of Solids*, 32, 2373-2383 (1971).
13. B.D. McSwain, N.F. Borrelli and G.J. Su, "The Effect of Composition and Temperature on the Ultra-violet Absorption of Glass," *Physics and Chemistry of Glasses*, 4[1] 1-10 (1963).
14. X. Feng and A. Barkatt, "Structural Thermodynamic Model of the Durability and Viscosity of Nuclear Waste Glasses," in *Materials Research Symposium Proceeding*, Materials Research Society, Vol. 112, 543-554 (1988).