HIGH-LEVEL NUCLEAR WASTE BOROSILICATE GLASS:
A COMPENDIUM OF CHARACTERISTICS*

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ABSTRACT

With the imminent startup, in the United States, of facilities for vitrification of high-level nuclear waste, a document has been prepared that compiles the scientific basis for understanding the alteration of the waste glass products under the range of service conditions to which they may be exposed during storage, transportation, and eventual geologic disposal. A summary of selected parts of the content of this document is provided.

Waste glass alterations in a geologic repository may include corrosion of the glass network due to groundwater and/or water vapor contact. Experimental testing results are described and interpreted in terms of the underlying chemical reactions and physical processes involved. The status of mechanistic modeling, which can be used for long-term predictions, is described and the remaining uncertainties associated with long-term simulations are summarized.

INTRODUCTION AND BACKGROUND

Current plans call for startup of facilities for vitrification of high-level nuclear waste, stored in tanks at Savannah River, South Carolina, and West Valley, New York, within the next few years. The products from these facilities will be canistered high-level nuclear waste borosilicate glass. These products will be stored, transported, and eventually disposed of in a geologic repository. The behavior of the glass, under the range of service conditions that tit is likely to experience, is a subject of considerable scientific and public interest. Fortunately, an enormous body of pertinent scientific information has been generated, worldwide, over the past few decades, regarding this subject. The document entitled "High-Level Nuclear Waste Borosilicate Glass: A Compendium of Characteristics" has been prepared to consolidate this information. The intent of this ambitious undertaking is to support resolution of issues concerning waste glass degradation that may arise during startup of the vitrification facilities.

The history of the development of borosilicate glass as a waste form reflects a broad international consensus on its suitability as a waste form for immobilization of high-level nuclear waste. After the initial recognition of glass as a promising medium for immobilization of high-level nuclear waste in the mid 1950's [1], the technology for vitrification of high-level nuclear waste has been pursued internationally for four decades. The first production facility to vitrify high-level radioactive waste began operation, at Marcoule, in France, in 1978. Borosilicate glass has now been selected as the final waste form in most countries that have high-level nuclear waste from reprocessing of nuclear fuels. In the U.S., borosilicate glass was selected as the reference waste form for tank wastes stored at Savannah River [2], West Valley [3], and Hanford [4] after a review and evaluation of alternatives [5,6].

Subjects discussed in the full compendium include waste glass production, plausible environmental service conditions, experimental effects of glass composition and environmental factors on borosilicate glass corrosion and weathering, observations of alterations in natural glasses, glass dissolution modeling, and uncertainties in long-term simulations. Rather than attempt to summarize all these areas, in the limited space available, this paper focuses on summarizing the parts of the compendium related to experimental and modeling investigations of the corrosion and weathering of the borosilicate waste glass matrix.

OVERVIEW OF EXPERIMENTAL INVESTIGATIONS OF WASTE GLASS CORROSION AND WEATHERING

Because waste glasses are metastable solids, they cannot reach thermodynamic equilibrium with the aqueous and/or humid air environments to which they may be exposed. In this paper, the alterations that occur upon immersion in aqueous solutions are referred to as "corrosion" processes, whereas those that occur as a result of humid air or intermittent water contact are referred to as "weathering" processes. In such environments, waste glasses undergo a variety of complex changes, including leaching and dissolution of some components, and formation of a variety of secondary phases. The complete reactions that take place depend on glass composition and the chemistry of the aqueous environment. Given the variety of glass compositions and testing environments that have been studied, it is not surprising that a rich diversity of experimental observations has been reported. However, the experimental evidence suggests that corrosion and weathering of glass can be interpreted in terms of a limited number of underlying processes. These include ion exchange of network modifiers, hydrolysis of the glass network, dissolution of glass components, nucleation and precipitation of secondary phases, and associated mass transport (diffusion) of reactants and products through surface alteration layers. The key heterogeneous chemical reactions that occur at the glass/water interface and the associated nomenclature are summarized in Table I [7]. Homogeneous reactions that occur in the bulk leachate as a result of dissolution of glass components include nucleation and precipitation of secondary phases.

WASTE GLASS CORROSION

Upon initial contact, water (as H_2O, H_3O^+, or OH^-) diffuses into the glass and reacts with Si-O-Si and SiO-M bonds, preferentially at nonbridging oxygen sites [8], to form silanol groups (-Si-OH) (see reactions 1-5 in Table I). Cations such as Na^+ and Li^+ are released and diffuse out of the glass and enter the solution. Hydrolysis of the glass network allows boron to be released at about the same rate as the alkalis, even though much of the boron exists in the glass in anionic tetrahedral sites similar to those of silicon [9]. Likewise, other elements in the glass are free to diffuse through, and be released from, the partially hydrated glass.

During leaching, the hydrolyzed glass network apparently opens up, releases metals, and repolymerizes to form a more stable hydrous gel that can incorporate components originally incorporated in the glass. Raman and nuclear magnetic resonance spectroscopic studies of alkali borosilicate glasses [10] show that there is extensive condensation (i.e., repolymerization) of the silicate structure, after water hydrolysis. After Si-O bonds are hydrolyzed to form silanols, and cations are released from the glass, the structure quickly reforms through condensation of the silanols. The evidence for this is that ^{17}O doped into the leachant is found later to be present in Si-^{17}O-Si groups *in the gel layer*. This gel layer eventually reacts again with water at the water-gel boundary, to dissolve as silicic acid. This latter step in the reaction process is also referred to as "etching" (see reactions 6 and 7 in Table I).

The combined effects of these reactions is that when waste glass is exposed to water, it experiences an initial transient reaction period wherein ion exchange and surface gel layers develop on the glass surface. Surface analytical methods indicate [11] that a steady-state period, characterized by nearly constant thicknesses of the diffusion and gel layers, follows the initial transient period when the rate of etching or dissolution of the gel layer is equal to the rate of penetration of the diffusion layer into the underlying glass. For nuclear waste glasses reacted over sufficiently long periods of time, this simple steady-state picture is complicated by precipitation of secondary phases from solution or by *in situ* aging of the gel layer [12].

Table I
Glass Corrosion and Weathering Reactions

	Reaction / Process	Nomenclature
1	$n(\text{Si-O}^-)\text{-X}^n + n\text{H}_3\text{O}^+ = n(\text{Si-OH}) + \text{X}^n + n\text{H}_2\text{O}$	Ion exchange
2	$2\text{Si-O-Na} + \text{H}_2\text{O} = 2\text{Si-OH} + \text{Na}_2\text{O}$	Hydrolysis reactions at non-bridging oxygen sites
3	$\text{Si-O-Na} + \text{H}_2\text{O} = \text{Si-OH} + \text{Na}^+ + \text{OH}^-$	
4	$\equiv\text{Si-O-Si}\equiv + \text{OH}^- = \equiv\text{SiOH} + \equiv\text{Si-O}^-$	Network hydrolysis (forward reaction) Condensation (backward reaction)
5	$\equiv\text{Si-O-Si}\equiv + \text{H}_2\text{O} = \equiv\text{SiOH} + \equiv\text{Si-OH}$	
6	$\begin{array}{c}\text{OH}\\|\\\equiv\text{Si-O-Si-OH} + \text{OH}^- = \equiv\text{Si-O}^- + (\text{H}_4\text{SiO}_4)_{aq}\\|\\\text{OH}\end{array}$	Network dissolution or etching (forward reaction). Condensation (backward reaction)
7	$\begin{array}{c}\text{OH}\\|\\\equiv\text{Si-O-Si-OH} + \text{H}_2\text{O} = \equiv\text{Si-OH} + (\text{H}_4\text{SiO}_4)_{aq}\\|\\\text{OH}\end{array}$	

Note: - X is a glass modifier of valence n.
- Although the reactions are written explicitly for Si, similar reactions occur for other network-forming elements.

Two principal hypotheses have been advanced concerning the controls on the overall reaction rate after the initial transient development of surface layers, viz., (1) mass transport through the surface alteration layers and (2) dissolution affinity control. It has been pointed out by Bourcier [13] that it is difficult, if not impossible, to distinguish between these two hypotheses by curve-fitting alone. This point is illustrated in Figure 1, which shows that leaching data can be fitted equally well using either hypothesis. However, several investigations have reported experimental results that discriminate between the two rate control hypotheses.

Figure 2 shows the results of Chick and Pederson [14]. In the experiment shown in Figure 2a, the glass was leached in deionized water for a period of 56 days, at which point the leachate was replaced. The observation that the subsequent leaching behavior was similar to the initial behavior suggests that the leachate composition is more important than the effects of the surface alteration layers. This result indicates that dissolution affinity control is more important than diffusion through the surface layers. Figure 2b shows the results obtained when the reacting glass sample was replaced with a fresh glass sample. The results show that the fresh glass exhibits only a slightly increased reaction rate when compared with the original glass. This again was interpreted as indicating that the surface alteration layers exert little control on the reaction rate and supports the hypothesis that dissolution affinity represents the primary factor controlling the reaction rate. Many other investigators have reported experimental results supporting the hypothesis that the overall reaction rate is controlled by dissolution affinity, under a wide variety of conditions [15-18].

The hypothesis that the rate of corrosion of borosilicate glass is controlled by the dissolution affinity and in particular by the silicic acid concentration in solution can be used to explain observed surface area-to-solution volume (SA/V) ratio [19,20] and flow effects [21,22]. However, despite the broad evidence for, and success of the dissolution affinity rate control hypothesis, there is evidence that the surface alteration layers can be important under some circumstances. Conradt et al. [18] have shown that the corrosion
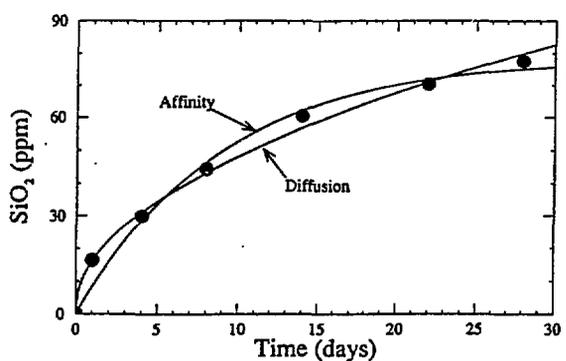
Figure 1. Silica Release Data for SRL 165 Glass Reacted at 150°C in 0.003$\underline{M}$ NaHCO$_3$ Solution. (Curves are regressed to the data using equations for diffusion control (rate = A + Bt$^{1/2}$ and affinity control (rate = Ak$_+$(1 - Q/K)) for reaction rate. Both models fit the data to within experimental error) [13].
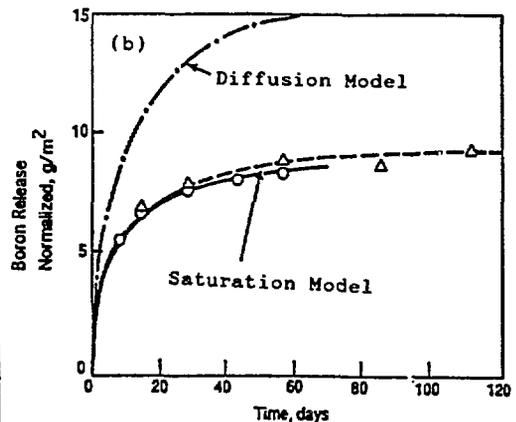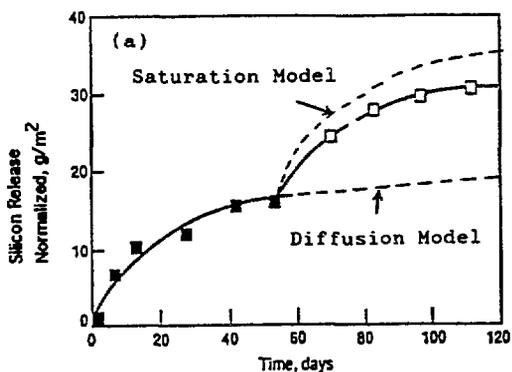

Figure 2.   Waste Glasses Tested at 90°C, in Deionized Water, at 10 m^{-1} [14].
(a) Comparison of results obtained in a leachate replacement test with solution saturation model and diffusion model.
(b) Comparison of results obtained in a glass sample replacement test with solution saturation model and diffusion model.

rate of SM58LW11 nuclear waste glass is almost completely controlled by the surface alteration layers in 0.01$\underline{M}$ NaOH solution. Van Iseghem [23] has found that the surface alteration layers formed on SM527 and WG124 glasses are somewhat protective at 190°C. Several authors have found that surface layers formed in magnesium-rich leachates can be protective [24–26]. Isotopic data [27] has shown that transport control of reaction rate is important for durable (Na-Al-Si) glasses during early reaction times. Also, the recent work of Grambow [28] on R7T7 glass in silica-saturated brines suggests that diffusion of water through the growing surface layers may be important in controlled long-term corrosion rates, under certain conditions.

WASTE GLASS WEATHERING – A SPECIAL CASE OF GLASS CORROSION

As pointed out earlier, weathering is a special case of glass corrosion that must be considered for unsaturated repository settings. Unfortunately, it has not been studied to the same extent as the aqueous corrosion discussed above. The available results indicate that the experimental observations can be interpreted as a high glass surface area-to-solution volume aqueous corrosion condition. When waste glass is exposed to humid air, water molecules adsorb onto the glass surface, with the number of monolayers adsorbed increasing rapidly, with relative humidity in the range 80-100% [29,30]. For alkali-containing

glass, the initial release of alkali lowers the water vapor pressure of the adsorbed surface films, with the result that additional water vapor condenses on the surface, or that refluxing can occur.

The large surface area-to-volume ratios that characterize glass weathering lead to some interesting experimental observations. Among these are the following:

- enhancement of the significance of radiolysis effects, due to the high solution concentrations that can be achieved as a result of dissolution of humid air radiolysis products in the small volumes of water involved [31],
- the promotion of nucleation of secondary phases that can lead to increases in the rate of glass reaction attributable to the increased dissolution affinity accompanying secondary phase precipitation [32].

Although the reaction processes and rate-controlling steps are the same as those discussed above for waste glass corrosion, the set of overall phenomena involved in radionuclide release may differ in important ways. These include the refluxing of water that contacts the glass surface under humid air experimental conditions, due to condensation on the surface (as mentioned above, leached salts on the glass surface lower the vapor pressure of the surface solution films) and runoff. This phenomenon provides a mechanism for radionuclide release in humid air environments, even when the relative humidity is less than 100% [33,34]. In addition, the formation of colloidal materials appears to be enhanced due to contact of weathered glass with water [35].

WASTE GLASS DISSOLUTION MODELING

Experiments alone are insufficient to predict waste glass alteration, because they cannot be performed over the extended time periods of up to tens of thousands of years or over the numerous sets of possible conditions of interest. The goal of chemical modeling of the reaction of nuclear waste glass is to make accurate long-term predictions of the rates of glass degradation and the associated radionuclide release rate in a repository environment. Key steps in the development of such a model are the identification of the reaction steps that control the rate, as well as the development and validation of models to simulate the rates of these steps under the range of conditions of interest. The former has been discussed above and the latter is discussed briefly in the following paragraphs.

Several approaches have been used to model glass dissolution. One approach involves the solution of diffusion equations, assuming that the rate of reaction is controlled by water diffusion [36,37] or ion exchange [38-40]. This approach has its origins in studies of dissolution of simple glasses over short time periods, where reaction rates are diffusion-limited and rates are not affected by saturation effects. Another approach combines rate control by transport or ion exchange, with a term to account for the effect of a growing surface layer providing a diffusion barrier for subsequent reaction [41].

The approach most widely used to model borosilicate glass corrosion assumes that the reaction rate is controlled by a surface dissolution process and explicitly accounts for the formation of alteration and secondary phases, with feedback from the evolving solution composition. Although diffusion takes place, it is assumed not to be rate-limiting. at least under most experimental conditions, and is therefore not explicitly included (see experimental evidence discussed earlier). The following rate equation, based on macroscopic irreversible thermodynamics, is used to model the dissolution kinetics [42]:

$$\frac{dn_i}{dt} = A \upsilon k_f (a_{H^+})^n (1 - e^{A_f/RT}) \tag{1}$$

where
n_i = number of moles of species i in solution
A = surface area
υ = stoichiometric factor
k_f = forward rate constant (moles/cm^2/sec)
n = exponent for pH dependence of rate
A_f = affinity to dissolve (kcals/mole)
R = gas constant
T = temperature, Kelvins

The dissolution affinity is given by $A_f = RT\ln(Q/K)$. The term $(1 - e^{A_f/RT})$ can be rearranged to $(1 - Q/K)$, where Q is the activity product of aqueous species involved in the dissolution reaction for the dissolving solid, and K is the equilibrium constant for that same solid. The models incorporate this or similar rate equations into a general reaction path computer program that provides for aqueous speciation and precipitation of secondary phases, as the solutions become saturated. Nonstoichiometric release is accounted for by incorporation of elements into amorphous and crystalline secondary phases.

The model developed by Grambow [43] is the most fully developed and widely used model. The model includes dissolution affinity, a transport term for diffusion of aqueous silica through the surface alteration layers, and an empirical term to account for the long-term dissolution rate. In this model, the affinity term uses only the concentration of dissolved silica, to determine Q, and K correspond to a silica "saturation" value, for the particular glass composition involved. A variation of the Grambow model, which has been developed by Bourcier [44], differs mainly in that the rate of reaction is assumed to be controlled by the dissolution affinity of the hydrous gel surface alteration layer. The thermodynamic properties of the gel layer are calculated based on a solid solution of amorphous and hydrous phases whose net composition corresponds to the measured alteration layer composition. The results of using this model to predict the dissolution rate of SRL 165 glass are illustrated in Figure 3. In general, the models based on the assumption that glass corrosion rate is controlled by dissolution affinity have been successful in reproducing a wide variety of experimental data.

SUMMARY OF REMAINING UNCERTAINTIES

The success of models, which are based on the assumption that surface dissolution reactions are rate-limiting, indicates that current understanding is at least qualitatively correct. However, additional work is needed to show that long-term corrosion and weathering can be predicted with confidence. When model parameters, measured in the laboratory, are extrapolated to natural systems, they predict rates of reaction up to several orders of magnitude faster than those observed in nature [45]. While these differences can be readily explained and while the direction of the discrepancy indicates that current modeling approaches are conservative, they do highlight the need for additional work. This is particularly apparent when it is realized that the processes responsible for controlling the long-term dissolution rate have not been identified. Recently, Grambow [46] has suggested two long-term rate-controlling processes. The first involves the long-term nucleation and precipitation of secondary phases that act as sinks for silica and thereby control the residual affinity for the rate-limiting dissolution reactions. The second assumes that as the residual affinity for the dissolution reactions decreases, the rate of these reactions will decrease to the point at which other processes such as ion-exchange/water diffusion (dealkalization) becomes dominant. A general model should, therefore, incorporate provisions to allow these processes to become dominant in the long term.
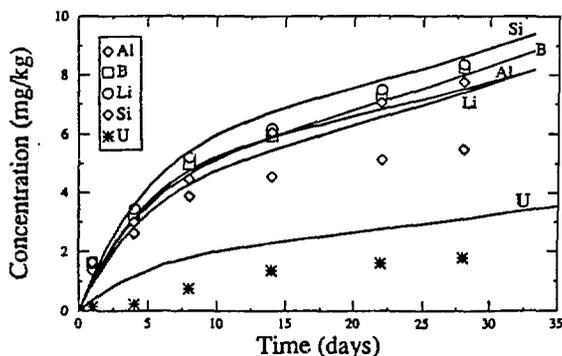

Figure 3. Predicted vs. Measured Concentrations of Elements Leached from SRL 165 Glass at 150°C in 0.003$\underline{M}$ NaHCO$_3$ Solution. (Silica concentrations x 0.1. Lines are concentrations predicted by gel layer glass dissolution model [44], symbols are experimental data. Predicted concentrations are generated using starting solution composition, composition of surface gel layer, and rate constant derived from flow-through glass dissolution experiment.)

Despite the uncertainties identified, current models can be applied to calculate various limiting cases for the rate of glass dissolution [46]. In general, modeling, experimental, field testing, and natural analog results compiled in the Compendium indicate that the long-term rates should not exceed the rates observed for corresponding conditions in laboratory studies. However, validation of the current understanding and models continues to be the major source of remaining uncertainty concerning long-term weathering and corrosion of waste glass.

ACKNOWLEDGMENTS

REFERENCES

1. J. M. White and G. LaHaie, Atomic Energy of Canada, Ltd. Report CRCE-591 (1955).
2. U.S. Department of Energy Report DOE/EIS-0082, 1982.
3. U.S. Department of Energy Report DOE/EIS-0081, 1982.
4. U.S. Department of Energy Report DOE/EIS-0113, 1987.
5. U.S. Department of Energy Report DOE/TIC-11219, 1982.
6. T. A. Benadzowski et al., Ceram. Bull. 62(12), 1364-1390 (1983).
7. T. A. Abrajano, J. K. Bates, and J. J. Mazer, J. Non-Cryst. Sol. 108, 269-288 (1989).
8. B. M. J. Smets and T. P. A. Lommen, Phys. Chem. Glasses 23, 83-87 (1982).
9. B. C. Bunker et al., Phys. Chem. Glasses 31, 30-41 (1990).
10. B. C. Bunker et al., Phys. Chem. Glasses 29, 106-120 (1988).
11. T. A. Abrajano and J. K. Bates, Mat. Res. Soc. Symp. Proc. 84, 533-546 (1987).
12. J. K. Bates et al., Proc. 2nd Annual Internat. High-Level Radioact. Waste Mgmt. Conf. and Exposition, Amer. Nucl. Soc., Las Vegas, NV, pp. 720-727 (1991).
13. W. L. Bourcier, Mat. Res. Soc. Symp. Proc. 212, 3-18 (1991).
14. L. A. Chick and L. R. Pederson, Mat. Res. Soc. Symp. Proc. 26, 635-642 (1984).
15. L. R. Pederson et al., J. Non-Cryst. Sol. 86, 369-380 (1986).
16. B. Grambow, "Influence of Saturation on the Leaching of Borosilicate Nuclear Waste Glasses," Presented at the 13th Internat. Congr. on Glass, Hamburg (1983).
17. F. Lanza et al., Mat. Res. Soc. Symp. Proc. 112, 685-691 (1988).
18. R. Conradt, H. Roggendorf, and H. Scholze, Mat. Res. Soc. Symp. Proc. 50, 203-210 (1985).
19. W. Lutze, "Silicate Glasses," in Radioactive Waste Forms for the Future, W. Lutze and R. Ewing, eds. (1988).
20. L. R. Pederson et al., Mat. Res. Soc. Symp. Proc. 15, 47-54 (1983).
21. Aa. Barkatt et al., Mat. Res. Soc. Symp. Proc. 26, 643-653 (1984).
22. A. J. Machiels and C. Pescatore, Mat. Res. Soc. Symp. Proc. 15, 209-216 (1983).
23. P. Van Iseghem et al., Final Report 1986-1990, R/2869 (1990).
24. G. Malow, Mat. Res. Soc. Symp. Proc. 11, 25-36 (1982).
25. Z. Zhou and W. S. Fyfe, Mat. Res. Soc. Symp. Proc. 112, 725-735 (1988).
26. Aa. Barkatt et al., Appl. Geochem. 4, 593-603 (1989).
27. L. R. Pederson et al., Phys. Chem. Glasses 31, 177-182 (1990).
28. B. Grambow et al., Mat. Res. Soc. Symp. Proc. 257, 143-150 (1992).
29. R. M. Pashley and J. A. Kitchener, J. Coll. Inter. Sci. 71, 491-500 (1979).
30. W. L. Ebert et al., Phys. Chem. Glasses 32(4), 133-137 (1991).
31. D. J. Wronkiewicz et al., Mat. Res. Soc. Symp. Proc. 212, 99-106 (1991).
32. W. L. Ebert et al., Waste Mgmt. 11, 205-221 (1991).
33. J. C. Cunnane and J. K. Bates, Mat. Res. Soc. Symp. Proc. 212, 885-892 (1991).
34. J. W. Cary et al., Mat. Res. Soc. Symp. Proc. 212, 871-878 (1991).
35. J. K. Bates et al., Proc. Internat. High-Level Radioact. Waste Mgmt. Conf., Amer. Nucl. Soc., Las Vegas, NV, p. 1085 (1990).

36. R. H. Doremus, J. Non-Cryst. Sol. 55, 143-147 (1983).

37. K. B. Harvey and C. A. Boase, Adv. Ceram. 20, 495-504 (1986).

38. R. H. Doremus, J. Non-Cryst. Sol. 19, 137-144 (1975).

39. J. O. Isard et al., Phys. Chem. Glasses 23, 185-189 (1982).

40. R. Conradt and H. Seholse, Vister della Staz. Sper. Vetor 5, 2-6 (1984).

41. R. M. Wallace and G. G. Wicks, Mat. Res. Soc. Symp. Proc. 15, 23-28 (1983).

42. P. Aagaard and H. C. Helgeson, Am. J. Sci. 282, 237-285 (1982).

43. B. Grambow, Adv. Ceram. 8, 474-487 (1986).

44. W. L. Bourcier et al., Mat. Res. Soc. Symp. Proc. 176, 209-216 (1990).

45. M. A. Velbel, Am. Chem. Soc. Symp. 323, 615 (1986).

46. B. Grambow, SKB Technical Report 95-59 (1991).