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**EFFECT OF GLASS COMPOSITION ON WASTE FORM
DURABILITY: A CRITICAL REVIEW**

by

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ABSTRACT

This report reviews literature concerning the relationship between the composition and durability of silicate glasses, particularly glasses proposed for immobilization of radioactive waste. Standard procedures used to perform durability tests are reviewed. It is shown that tests in which a low-surface area sample is brought into contact with a very large volume of solution provide the most accurate measure of the intrinsic durability of a glass composition, whereas high-surface area/low-solution volume tests are a better measure of the response of a glass to changes in solution chemistry induced by a buildup of glass corrosion products. The structural chemistry of silicate and borosilicate glasses is reviewed to identify those components with the strongest cation-anion bonds. A number of examples are discussed in which two or more cations engage in mutual bonding interactions that result in minima or maxima in the rheologic and thermodynamic properties of the glasses at or near particular optimal compositions. It is shown that in simple glass-forming systems such interactions generally enhance the durability of glasses. Moreover, it is shown that experimental results obtained for simple systems can be used to account for durability rankings of much more complex waste glass compositions. Models that purport to predict the rate of corrosion of glasses in short-term durability tests are evaluated using a database of short-term durability test results for a large set of glass compositions. The predictions of these models correlate with the measured durabilities of the glasses when considered in large groupings, but no model evaluated in this review provides accurate estimates of durability for individual glass compositions. Use of these models in long-term durability models is discussed.

1.0 INTRODUCTION

Borosilicate glasses have been selected worldwide to stabilize high-level radioactive waste. Benefits of borosilicate glasses include ready accommodation of a large range of waste components at relatively high concentrations, ease of processibility, good physical and chemical durability, and low-cost and readily available frit materials. Vitrification also destroys organic material in the waste streams and substantially reduces the volume of waste. Borosilicate glass waste glasses are formulated to provide high waste loading, to facilitate processing, and to yield high chemical durability. Generally, compositions that are easy to process have poor durabilities, and compositions that have high durability are difficult to process, so final waste glass compositions usually represent a compromise between processing and durability properties.

The objective of waste immobilization is to limit the release of radioactive elements to the environment over the course of some large number of half-lives. In a geologic repository, the most important avenue of release of radionuclides into the environment is reaction of a waste glass with ground water. When a glass comes in contact with liquid water or water vapor, reactions take place that result in chemical and physical alteration of the glass and release of glass components into solution. The resistance of a glass to this type of chemical attack is referred to as its chemical durability. One would expect that a relationship exists between the composition of a glass and its durability, but many years of research on this topic for the simplest of glasses has shown that the relationship is very complex indeed. The glasses proposed (and used) as waste glasses for immobilizing nuclear wastes have exceptionally complex compositions, and it may not be possible to precisely control the glass composition during processing. In fact, because variations in waste stream composition are likely, it is necessary to identify glass-forming systems that can tolerate moderately large deviations from a reference composition while maintaining an acceptable level of durability. Moreover, simply identifying a durable glass is not enough: it must also be economically and technologically possible to produce the glass in substantial volumes. For these reasons, vast effort is involved in identifying durable waste glasses, developing experimental methods to reliably measure their durabilities, modeling their long-term performance characteristics, and developing short-term tests that give a fairly reliable measure of their long-term durability. The ways in which composition affects glass durability and the tests used to describe and categorize this relationship are the subjects of this critical review.

Waste glasses will be produced continuously in a remote melter and will be sampled to assure product compliance. It is essential to determine as quickly as possible whether a glass is an acceptable product. This requires not only reliable short-term tests but also models for predicting the outcomes of those tests so that the feed mixture to the melter can be quickly adjusted in response to variations in the waste stream composition. The tests performed to make this assessment and several proposed models for estimating waste glass durability are central topics of this report. In the long view, it is desirable to be as certain as possible that, in the event of an unforeseen breach of other protective barriers, the glass is durable enough over an extended time frame (10^4 - 10^5 years). It is impossible to experimentally verify performance on this time scale. Instead, researchers have developed ways to accelerate glass corrosion so as to gauge long-term performance. The extent to which the results of accelerated tests can be applied to long-term performance of a waste glass in a repository is key to evaluating repository performance. The details of the performance of such models and the tests used to provide information for them have been the subjects of other critical reviews, but these topics will be discussed here as well, insofar as waste glass composition plays a role in long term performance.

As alluded to above, waste glass design is driven not only by the quest for durability, but by the need for processibility. Broadly speaking, processibility means that when the glass is molten at typical melter temperatures (1050-1200°C), its viscosity must be low enough to extract the melt from the melter (2-10 Pa•s). Another concern is that the starting materials should not exsolve excessive amounts of volatiles at melter temperatures, which can result in frothing (and a bubble-filled product) and melter failure. A cautionary example is the oxidation state of iron: too much trivalent iron (Fe^{3+}) results in excessive release of oxygen and can result in the formation of a stable foam that retards heat transfer in a melter, whereas too little lowers melt conductivity and can cause an electrical short in a joule-heated furnace [1,2]. Just as it is important to be able to quickly ascertain whether or not a waste-form in production will be sufficiently durable, it is also important to be able to determine during processing whether melt viscosity and redox state are appropriate for melter performance. While these are not the main topics of this report, melt viscosity and oxidation state will be discussed to some extent because they are a driving force behind the choice of alkali borosilicate glasses as the dominant waste glasses in development or production today.

In this report, Section 2 outlines precisely what is meant by "durability" and what means are used to test it, with particular emphasis on tests used in the United States. Section 3 addresses broad aspects of the chemistry of cations in silicate glasses, with particular emphasis on components found in high concentrations in waste glasses. Section 4 discusses the composition-durability relationships found in simple systems and the extent to which they can be extended to multicomponent waste glasses. Section 5 discusses several models or approaches that have been used to predict the durabilities of glasses of various compositions, generally by interpolation or extrapolation of functions used to fit a database of durability measurements. Section 6 discusses the applicability of models that predict short-term corrosion rates to models of the long-term corrosion of glasses. Finally, Section 7 summarizes what is known and what remains to be done to understand the relationships between composition and durability in waste glasses.

2.0 LABORATORY TESTS

Several laboratory tests have been used to provide a measure of the corrosion rate of high-level waste glasses and to assess the effects of the glass composition on the corrosion rate. Tests commonly used to assess composition effects or to correlate the corrosion behavior with the composition are briefly described below. The relevance of these tests to determining the compositional dependence of glass durability is then discussed.

Before turning to test methods, it is important to clarify precisely what is meant by glass "corrosion." A considerably body of experimental evidence leads to a useful generalization of this process. The path of corrosion is divided into three distinct stages: (1) the short-term stage, when the solution is still dilute in glass corrosion products; (2) the intermediate stage, in which the concentration of glass components is relatively high; and (3) the long-term stage, in which the concentrations of more glass components are so high that crystalline phases precipitate from solution. Note that corrosion will follow this path regardless of whether or not the glass in question is an alkali borosilicate glass, though the details of the corrosion path depend on the identities and concentrations of components released into solution.

The interactions between the glass and solution, and between the glass, solution, and secondary crystalline phases, have characteristic effects on the rate of glass corrosion. These effects are depicted schematically in Fig. 1. In the short-term stage, the chemical potential gradient between the glass components in the glass and the solution is steep, and therefore in this stage glass components are released to solution at a comparatively high rate. In particular, components with high solubilities in aqueous solution, such as alkalis and boron, are generally released to solution at a disproportionately high rate compared to less soluble components, such as zirconium. This results in the formation of a layer on the glass surface that is depleted in soluble components relative to the bulk glass. As the concentration of components approaches the saturation concentration of crystalline phases, the chemical potential gradient between glass and solution flattens, and the rate of glass reaction slows. In the reaction of alkali borosilicate glasses with aqueous solution in static tests, this stage is characterized by relatively high solution pH, which increases the solubility and rate of reaction of the SiO_2 component in the glass. In the long-term stage, crystalline phases act as "sinks" for less soluble glass components (see Appendix 1). The chemical potential gradient between glass and the crystalline phase assemblage is steeper than that between the crystal and solution, and thus the rate of glass corrosion will change. Whether this change is large or small depends on the identity, distribution, and surface area of the secondary crystalline phases, but in general this change will result in an increase in the rate of corrosion. Moreover, the first phase assemblage to form is unlikely to be the final phase assemblage because the solution will continue to evolve and the crystals may end up in reaction relationships with one another. Therefore, the long-term stage is unlikely to be characterized by a single reaction rate, but rather a variable rate that accelerates or decelerates with changes in the phase assemblage.

The transitions between these stages are not likely to be as sharp as depicted in Fig. 1. Furthermore, different glasses will reach the various stages at different rates: for example, a durable glass might take months or years to settle into the intermediate stage of corrosion in an MCC-1 test (see below), whereas a nondurable glass may approach this stage in hours or days. As a result, a single test performed for a fixed length of time is subject to the following biases: (1) the corrosion state is a single point on the path indicated in Fig. 1, and not necessarily the same point for all glasses, and (2) good performance at a particular stage in the corrosion path may have nothing to do with the long-term performance of a glass under repository conditions. This point cannot be emphasized enough: a single test provides data concerning a single point on the corrosion path. Different tests must be performed to obtain information about all three stages of corrosion.

Fig. 1. Reaction Progress Diagram for the Reaction of Glass

2.1 MCC-1 Test

The MCC-1 static leach test (sometimes referred to as the MCC-1P test) was developed by the Material Characterization Center, Pacific Northwest Laboratory, to provide a comparison of the durabilities of candidate final waste glasses developed for the stabilization of high-level nuclear wastes [3]. The method calls for placing a monolithic specimen of known surface area into a volume of leachant such that the ratio of surface area to volume (SA/V), calculated by using the geometric surface area, is 10 m^{-1} . The test may be performed in deionized water, a silicate solution, or a brine. The reference temperature is 90°C and the reference test time is 28 days, although temperatures of 40 or 70°C and other testing times can be used. (The MCC-2 test procedure permits reaction temperatures of 110 , 150 , and 190°C .) The measured solution concentrations of component species are used to monitor the extent of glass corrosion.

Monolithic specimens can be prepared for testing by fracturing, cutting, or grinding sample material. The surface finish resulting from the surface preparation has a measurable effect on the corrosion rate, which increases with surface roughness [4,5]. The increase is due to both the increase in the actual surface area with the surface roughness (the geometric surface area is sensitive to the surface finish) and increased surface strain. Test results for short-term tests of a few days are strongly influenced by the initial surface condition and the presence of fines. Long-term tests are affected by the leachate solution chemistry. The MCC-1 test provides a solution-dominated system in that the SA/V is very low. However, because the leachate remains dilute as the glass dissolves, there is little interaction between released glass components and the glass, and the corrosion process is dominated by the glass composition. Samples corroded in MCC-1 tests show details of the chemical and physical alteration of the glass surface that cannot be seen in other tests. Detailed analyses of monolithic samples corroded during this test have provided valuable insight into the mechanism controlling the initial stage of corrosion [6-8].

While the MCC-1 method was originally designed to compare the chemical durabilities of candidate waste glasses, the test can be used to characterize several aspects of the corrosion process; for example, buffer solutions or solutions spiked with various glass components can be used to determine the effects of the leachate chemistry on the rate of glass corrosion. More importantly, in short-term MCC-1 tests (e.g., one to several days) the concentration of glass corrosion products in solution remains low, and the chemical potential gradient between glass and solution is steep. Such conditions provide information about the inherent capacity of a glass to resist aqueous attack, and thus information germane to the short-term stage of glass corrosion (Fig. 1). Longer tests can be run to monitor the alteration of the glass surface during corrosion to investigate the intermediate and long-term corrosion regimes, though years may be required to obtain high enough concentrations of corrosion products in solution to cause secondary crystalline phase formation.

2.2 The Product Consistency Test

The Product Consistency Test (PCT) was developed at the Defense Waste Processing Facility (DWPF) to monitor the chemical durabilities of the glasses to be produced [9,10]. The concept of the PCT test was developed from the MCC-3 test, which used grains of glass in a static test to increase the SA/V [3]. Two variations of the PCT are used. In the PCT A method, a mass of crushed glass in the size fraction between 100-mesh and 200-mesh sieves is combined with a mass of deionized water 10 times that of the glass. The test time is seven days and the test temperature is 90°C. At the end of the test, the solution is filtered to remove suspended glass and analyzed to measure the boron, sodium, and silicon concentrations in solution. The PCT A method was developed to remotely monitor the product consistency of radioactive glass produced by the DWPF. This method specifies that stainless steel reaction vessels be used, since the glasses to be tested will be highly radioactive, and other materials, such as Teflon, may be affected by the radiation fields. The PCT A method is a "response test," in which the response of a sample glass is compared to the benchmark response of a reference glass, which for the DWPF has been identified in an environmental assessment report as the "SRL EA" glass [11].

The PCT B method allows variation in the size fraction of the glass used, the ratio of glass and leachant mass, the leachant composition, the test temperature, and the test duration. The PCT B method was designed to investigate the effects of various parameters on the response of a specimen, so that the results could be used in further development of waste glasses. In effect, the PCT B method encompasses all variations of crushed-sample, static leach tests. The method does not specify the use of a particular reaction vessel, and some studies have shown the choice of vessel does not strongly affect PCT test results. A similar test procedure to the PCT B test is the MCC-3 test [3], which differs in that the vessel is agitated during the test.

There is some concern regarding the effect of using crushed glass in tests, since waste glasses placed in storage will not be crushed, and there are uncertainties regarding the effects of the particle size on the test results. Particle size effects are very difficult to distinguish from other effects in laboratory tests, in part because the surface area of crushed glass is hard to measure. The surface area is an important test parameter, usually considered with the solution volume as the parameter SA/V. The SA/V of a test determines the rate of change of solution concentrations as a waste glass dissolves, which in turn affects the corrosion rate. The PCT A method partially avoids surface area effects by specifying that a mass of glass of a particular size fraction be used. The total surface area can be reproduced by accurately weighing the glass. However, different glass compositions may fracture differently, and the total surface areas in tests with different glasses cannot be expected to be same. This is an unavoidable limitation of using crushed glass.

Use of the PCT A method as a response test does not require computation of the normalized mass loss, since all results are compared to other PCT A results. However, use of the PCT A or PCT B tests procedures in performance assessment requires an estimate of the surface

area of the sample, as the surface area must be known to compute the normalized mass loss for comparison with the results of other types of tests. Measurement of the surface area by gas adsorption gives unrealistically high surface areas, which also vary with the gas used. It is also important to note that the surface area of relatively reactive glasses may change during the test period, thus changing the SA/V of the test. Instead, the surface area is usually estimated by assuming that the crushed particles have a convenient geometric shape, such as a sphere or a cube, that can be related to the sieve sizes. These approximations suggest the SA/V used in the standard PCT A test is about 2000 m^{-1} (higher or lower SA/V can be obtained in PCT B tests by using different solution/sample mass ratios or by using different sieve fractions of the glass at fixed solution/sample mass ratio).

Despite the uncertainty in the surface area, the high SA/V used in the PCT method provides a convenient means of accelerating the approach of the solution chemistry to saturation. The reaction system is dominated by the glass (in contrast to the MCC-1 method, in which the system is dominated by the solution), so the solution chemistry is very responsive to glass corrosion. That is, corrosion of a small amount of glass produces large changes in the solution chemistry. These conditions highlight the effects of the solution chemistry on the glass corrosion process. Tests that are run for only a few days may attain solution compositions that MCC-1 tests would require several years to attain. Thus, PCT tests provide an acceleration of the corrosion process in terms of the solution chemistry. Alteration of the glass surface progresses rapidly in response to the solution chemistry. Alterations observed after a year or more in MCC-1 testing can be observed within a few days in PCT testing [12]. Similarities in the alteration of the glass surface can be used to demonstrate whether the corrosion mechanism is the same under MCC-1 and PCT conditions.

A more important utilization of the PCT method is for access to the interim and long-term stages of the corrosion path (Fig. 1). PCT tests that are run for time periods between a few days and several months can be used to map the evolution of the solution chemistry as it approaches saturated conditions. The composition of the saturated solution is needed for computer modeling of the corrosion process. In addition, secondary phases can be generated in PCT tests conducted for periods on the order of several months or more, depending on the glass durability. These tests can be used to determine the corrosion rate attained upon the formation of secondary phases, which represents the long-term corrosion rate needed for performance assessment (Appendix 1). Analysis of the corroded solids in tests which have progressed into the long-term corrosion stage provides insight into the corrosion mechanism, allows corrosion products to be identified, and confirms that the corrosion mechanism has not changed [13].

Saturated solution conditions, secondary phase formation, and the long-term corrosion rate are attained faster in tests at higher SA/V. Higher SA/V conditions can be attained by simply performing the PCT test using a greater glass mass-to-solution volume ratio or by using a smaller particle size. Again, the absolute amount of surface area provided by a particular grain size can only be approximated, although the relative surface area is expected to scale with the mass of glass used in the test. Therefore, tests performed with different masses of the same grain size are expected to scale according to the masses used. Tests with different grain sizes may not scale in a predictable fashion. If different grain sizes are used to attain a particular SA/V, some tests should be conducted using glass in the 100- to 200-mesh size fraction for comparison.

2.3 ANL Vapor Hydration Tests

The vapor hydration test developed at Argonne National Laboratory (ANL) is a static test in which a monolithic sample is exposed to water vapor in a sealed vessel [12,14-16]. At relative humidities above about 80%, a thin film of water condenses on the sample which corrodes the glass. Tests are commonly performed in 100% relative humidity at temperatures above 100°C .

These tests combine the effects of high SA/V and high temperature to accelerate the corrosion process. At the completion of a test, the sample is removed from the vessel, and the reacted surface is analyzed. Corrosion of the sample results in the formation of discrete secondary mineral precipitates and alteration of the surface. Glasses convert to clays and oxidation layers form on metal and metal oxide inclusions. The solution evaporates from the sample when the test is terminated and is not available for analysis. Evaporite material is left as a residue as the solution evaporates. The extent of corrosion is determined by measuring the thickness of the alteration layer, exclusive of secondary phases precipitated on the surface. Secondary phases can be analyzed in situ or removed from the sample for analysis.

These tests provide a convenient means of generating secondary phases for analysis within a short period. Knowledge of the assemblage of phases that form during glass corrosion is needed to perform computer simulations of the corrosion process (see Section 6 and Appendix 1). Also, these tests provide a qualitative measure of the effect of secondary phase formation on the long-term corrosion rate (Fig. 1). This information is important to final waste glass development because the long-term corrosion rate depends on the glass composition and the assemblage of phases formed. From these test results, it can be determined whether a candidate final waste glass will show an unacceptable increase in the corrosion rate upon secondary phase formation. Such compositions can therefore be avoided. Similar information can be obtained from PCT B tests run for long periods.

Vapor hydration tests can be performed at any temperature, though higher temperatures significantly accelerate the corrosion rate. The rate measured at high temperatures can be extrapolated to lower temperatures if the activation energy is known. Tests have shown that the hydration processes exhibit Arrhenius behavior. Tests at lower temperature may also be required to confirm that the same secondary phases form, but the known stability ranges of specific phases can be utilized instead.

Corrosion in a vapor environment represents a high SA/V system dominated by the solution chemistry, since very little glass must corrode to saturate the thin film of sorbed water. While the surface area of the specimen is easily measured, the volume of water can only be estimated. Therefore, these tests cannot be quantitatively related to either MCC-1 or PCT tests through the SA/V. However, the alteration of the glass surface has been demonstrated to be the same in MCC-1, PCT, and vapor hydration tests, which indicates that the corrosion mechanism is the same under these very different conditions. In addition, the same secondary phases have been shown to form in vapor tests at 200°C after a few days and in PCT tests at 90°C after a year. This result demonstrates the temperature stability of the particular secondary phases that form and the consistency of the corrosion mechanism.

Vapor hydration tests are performed in a batch mode in which a separate test is run for each period. Tests can be run for several different durations to determine when the secondary phases form and how they affect the corrosion rate. As for the MCC-1 test, if a waste glass contains crystalline phases, the distribution at the sample surface of the crystalline phases can be analyzed before and after testing to characterize the corrosion behavior of individual phases.

2.4 Buffered Solution/pH-Stat Tests

The "pH-stat" tests are static tests in which the solution pH is maintained by periodic addition of strong acid or base solutions. These tests are similar to static tests performed in buffer solutions, except buffers include counter-ions that may influence the corrosion of the waste glass. Strong acid and base solutions are used in pH-stat tests so the counter-ions will not interfere with the waste glass. In static tests in which pH is not controlled, corrosion of borosilicate waste glasses generally results in a large increase in the solution pH because of the release of alkali metals. The increased pH affects the glass corrosion rate. Tests in buffer solutions and pH-stat

tests prevent changes in the solution pH as the waste glass corrodes. Control of the solution pH is important when analyzing materials that dissolve congruently, but it constricts the corrosion of borosilicate glasses by suppressing the natural pH change.

2.5 Soxhlet Tests

Soxhlet tests are performed by reacting a monolithic sample with condensate in a refluxing apparatus [17]. Water is boiled from a reservoir and recondensed in a reflux tube. Condensate is allowed to drip into a small cup that contains the sample. The solution in the sample cup is refreshed continuously, and complete replacement occurs every few minutes; the precise replenishment time depends on the refluxing conditions. The refluxing action provides an effective flow rate that can be varied by controlling the condensation of the vapor. Tests are usually run to attain a flow rate sufficiently high that the solution in the sample cup does not affect the corrosion rate. The corrosion rate is measured by periodically removing a sample of the solution in the reservoir for analysis. Different reaction temperatures can be tested by varying the pressure in the apparatus. One such device was used to measure the corrosion rate of the high-level waste glass R7T7 over a temperature range of 90 to 250°C [17]. Because the leachant solution is recondensed vapor, only deionized water or azeotrope solutions can be used as the leachant. A minor shortcoming of the Soxhlet test method is that the apparatus is relatively complex. Soxhlet tests provide a measure of the corrosion rate in highly dilute solutions and over a wide range of temperatures.

Either crushed or monolithic specimens can be used; however, the flow rate must be such that crushed glass is not flushed out of the sample cup. Most tests are conducted using monolithic samples. Because the test conditions maintain a highly dilute solution in the sample cup, these tests highlight the effects of the glass composition on the corrosion rate and, therefore, provide information about the short-term rate of corrosion (Fig. 1).

2.6 Single-Pass Flow-Through Tests

In single-pass flow-through tests, leachant solution is passed over a monolith surface or through crushed glass at a constant rate. The sample is contained in a reaction cell that can be modeled as a well-stirred reactor with leachant solution entering and exiting the cell at the same rate. Solution is pumped through the cell by using a peristaltic pump; the solution leaving the cell is periodically collected and analyzed. The corrosion rates of waste glasses are known to increase with the leachant flow rate up to a maximum corrosion rate, which is the forward reaction rate [18]. The flow rate can be adjusted for different purposes. Low flow rates can be used to simulate conditions in particular disposal sites. Alternatively, the solution can be pumped through the cell at a rate high enough that the glass reacts at a characteristic forward rate. The forward rate has been reached if further increases in the flow rate do not increase the corrosion rate. The forward corrosion rate is an important characteristic of waste glasses that is needed for computer simulations of corrosion behavior. It is the maximum rate of corrosion attained in the short-term stage of glass corrosion (Fig. 1).

The forward rate represents the maximum corrosion rate of the waste glass at a particular solution pH and temperature. The corrosion rate is known to slow as silicic acid and other glass components become concentrated in the solution. The leachant solution used in a single-pass flow-through test can be varied to measure the effects of the solution composition on the forward reaction rate. Such tests have been applied to determine the effects of pH and of silicon, calcium, aluminum, and other glass components on the glass corrosion rate [19,20]. In addition, the reaction cell can be placed in an oven to determine the effect of temperature on the corrosion rate. Such tests are valuable in assessing the corrosion mechanism of waste glasses, and they provide values for parameters needed to simulate their corrosion behavior.

Tests are usually conducted for several days at a constant flow rate, with samples being collected periodically until the analyses show a constant rate has been reached. Highly reactive waste glasses may dissolve to such an extent that the available surface area decreases significantly over the test duration. Thus, the measured corrosion rate would decrease over time. This effect is more pronounced when crushed samples are used. The loss of surface area can be determined by measuring the reacted glass directly or by making estimates based on the solution analyses and the test duration. Tests must be conducted so that the loss of surface area is negligible during the course of the experiment, and so that the solutions are concentrated enough for analysis, but not so concentrated that they affect the corrosion rate.

2.7 Periodic Replenishment Tests

Several test methods have been developed in which leachate solution is periodically removed from an ongoing static test and replaced with an equal volume of fresh leachant solution. Such replacement tests can be used to simulate very low flow rates that cannot be attained by using mechanical pumps [21]. Either monolithic or crushed samples can be used, and different leachant compositions can be used. Specific test methods have different replacement schedules and call for different amounts of solution to be replaced. For example, the test designated by the International Organization for Standardization (ISO) calls for the entire solution volume to be replaced daily for the first five days, every third day for four replacements, every seven days for four replacements, and monthly thereafter [22]. The American Nuclear Society test ANS 16.1 [23] and a variation of the ANS 16.1, the Dynamic Leach Test [24], also require the total volume of leachant to be exchanged. Other replacement tests call for removing a small fraction of the leachate for analysis and replacing it with an equivalent volume of fresh solution.

The effect of the solution replacements on the corrosion of the waste glass depends on the amount of leachate replaced and on the frequency of the replacement. If the solution is refreshed often and completely, as in the ISO and ANS 16.1 methods, the solution will remain diluted and the solution chemistry will have a reduced effect on the corrosion of the waste glass. These tests will be similar to static tests with very low SA/V. If only a small amount of leachate is replaced, the solution will approach saturation, and the corrosion rate will slow between refreshments but then attain a slightly higher rate after refreshment until the solution returns to near saturation. These tests will be similar to static tests with high SA/V.

Leachant replacement results in a cycling of the corrosion process as control over the corrosion rate alternates between the glass and the solution chemistry. These perturbations to pH, solution composition, etc., may have a significant effect on the observed corrosion behavior. Even small perturbations of an otherwise static test may prevent precipitation of secondary phases and progress of the corrosion into the long-term stage. For example, in tests with SRL 131 high-level waste glass conducted using a variant of the PCT procedure, periodic replacement of a small amount of solution resulted in very different long-term behavior than that obtained when PCT tests were conducted with the same glass but without leachant replacement [21]. The PCT tests without leachant replacement showed that the corrosion entered the long-term stage after about 180 days, while in the periodic replacement tests, the low interim rate was maintained through the longest times tested, which were well beyond one year. The difference can be attributed to the periodic dilution of the leachate, which prevented secondary phases from forming.

Replacement tests cannot be used conveniently for characterizing the corrosion process because of these uncertainties about the effects of solution perturbation. They are better used as response tests to index durabilities of candidate waste glasses relative to a benchmark of performance. When comparing different glasses, it is important that identical replacement schedules be used.

2.8 Regulatory Tests

Vitrification has been identified as a potential treatment for some mixed waste streams containing toxic components. Incorporation of toxic materials into the glass structure may result in a waste glass that is no longer toxic under the guidelines of the Resource Conservation and Recovery Act (RCRA). Such waste glasses can then be disposed of more economically as low-level radioactive wastes. The long-term stability of these waste glasses and their durabilities under likely storage conditions must be adequate to contain radioactive and hazardous constituents to within regulatory guidelines. While the toxicity of radioactive waste components continually decreases with time, the toxicity of the hazardous components will not diminish. Therefore, mixed waste glasses must mitigate the release of toxic components over long periods.

2.8.1 Toxicity Characteristic Leaching Procedure

The Toxicity Characteristic Leaching Procedure (TCLP) was developed by the U.S. Environmental Protection Agency (EPA) as a means of determining whether waste glasses are characteristically toxic in terms of RCRA [25]. The test requires the waste glasses to be sized so they pass through a 0.95-cm (3/8-in.) sieve. The samples are leached in a dilute acetic acid solution at room temperature for 16 to 20 h. The system is mechanically agitated for the entire test duration. The leachate is then analyzed for regulated elements. The elements tested and their regulatory levels (given in parentheses in units of parts per million) include arsenic (5.0), barium (100.0), cadmium (1.0), chromium (5.0), lead (5.0), mercury (0.2), selenium (1.0), and silver (5.0). Several organic compounds are regulated under this test, but organics will be destroyed during vitrification and are not considered further here.

The TCLP does not provide information on the stability of the waste glass that can be used to develop final waste glass compositions or to characterize the corrosion mechanism or long-term behavior. Most vitrified final waste glasses will be sufficiently leach-resistant in acidic media to comply with RCRA regulations, and it is anticipated that the criterion that the final waste glass pass the TCLP will not disqualify any vitrified waste glass. Nevertheless, current regulations require that waste glasses regulated under RCRA pass the TCLP.

2.8.2 Other Tests

Other tests and test variations are described in a report by the International Atomic Energy Agency [26]. Some waste glasses may be required to meet specific state regulations, such as the California Waste Extraction Test [27]. These tests do not provide information regarding the corrosion behavior of waste glasses and are not useful for development or long-term testing of candidate final waste glasses. However, they may be required to demonstrate that selected final waste glasses comply with regulations for disposal. These tests are not considered further in this report.

2.9 Relevance of Test Methods to Determining Composition Effects

As described previously, the corrosion of high-level waste glasses is complicated by interactions between glass components dissolved in solution and the reacting glass surface. The significance of these effects increases as the solution concentrations increase. As the fluid becomes more concentrated, the reaction rate is controlled more by the fluid chemistry and less by the glass composition. The response of the glass to a buildup of its own corrosion products in solution is, in effect, a compositional dependence, but this response is coupled with the response of the solution and secondary phases to this process. That is, tests performed with a relatively evolved solution are measuring the response of the glass/solution/secondary-phase system, not the isolated response of the glass.

The effects of glass composition on the corrosion behavior are most prominent during the early stages of corrosion when the fluid is free of dissolved glass components. These conditions are best maintained either in tests in which the SA/V is very low, such as in short-term MCC-1 tests, or in tests in which the fluid is replenished with fresh leachant solution, such as in single-pass flow-through, Soxhlet, or periodic replenishment tests. For this reason, tests in which the fluid becomes highly concentrated, such as the PCT and ANL vapor hydration tests, do not provide direct measures of the effect of composition on the short-term glass corrosion rate. They do, however, provide insight regarding the effect of composition on the secondary phases formed during corrosion, and they are an integral part of efforts to determine the best—not just the most durable—composition for candidate waste glasses.

When comparing the response of different glasses in a standard test, it should be borne in mind that different glasses may attain different extents of corrosion within a common reaction time. This effect is expected to occur mainly in static tests, where the buildup of corrosion products for a given composition changes the chemistry of the solution from its starting state. For example, alkali-bearing glasses produce high solution pH values in static tests due to alkali loss to solution (dealkalization), which in turn increases the release rate of SiO_2 into solution. Dynamic tests at high effective flow rates maintain sufficiently dilute conditions that corrosion products do not affect the corrosion rate, but tests at lower flow rates will still be affected by corrosion products.

Most work with waste glasses has utilized MCC-1 or PCT test protocols, both of which are expected to show effects of the buildup of corrosion products (smaller effects are expected from the more dilute MCC-1 tests). Efforts have been made to separate effects due to changes in solution pH from effects due to composition (see discussion concerning the Free Energy of Hydration Model, Section 5.2), but the effects of corrosion products upon the observed corrosion rate are usually ignored. This results in a comparison of glasses at different stages in their corrosion process, which may obscure the actual effects of components upon the corrosion rate. The use of response tests to determine the effects of specific components on the corrosion rate is necessarily complicated by the fact that different extents of corrosion are attained during any fixed test period, unless different glasses corrode at exactly the same rate. For this reason, comparison of glasses with very different responses is less reliable than comparison of glasses with similar responses. Therefore, when analyzing schemes for correlating durability and composition (Section 5), subsets of data for glasses having similar compositions and/or similar responses in tests are considered to highlight composition effects over the effects of differences in corrosion progress.

As a final note in this overview of test methods, all of the tests described above except the ANL vapor hydration test are initiated with large volumes of water relative to the volume of glass. This method of test initiation is not particularly relevant to studying glass corrosion in a repository environment, where only a small amount of water will initially contact a much larger volume of glass: e.g., drops of water falling through a crack in a cask and onto the surface of a glass monolith. Over time water may collect in containers, but the solution will have been previously concentrated in glass corrosion products from the initial contact of water with the glass. The "effective" SA/V will be different from that of a test in which an unaltered glass is brought in contact with fresh solution.

The slow ingress of water under repository conditions will result in solution that becomes rapidly concentrated in corrosion products, although the final effective SA/V may decrease due to dilution from subsequent additions of water. In the particular case of alkali borosilicate glasses, the pH of the solution (and its impact on the rate of glass dissolution) is likely to increase more rapidly under repository conditions than would be inferred from static or replacement tests initiated with fresh solutions. It is therefore important to discuss the equivalency of reaction mechanisms when evaluating glass corrosion as measured under different test conditions.

3.0 STRUCTURAL CHEMISTRY OF SILICATE GLASSES

A mechanistic understanding of glass corrosion requires an understanding of the structural chemistry of oxide glasses. Each element is expected to have a distinct behavior in glasses and aqueous solutions, but one can still delineate distinct types of cation behavior in silicate glasses. Very little work has been performed to determine the role of anions in silicate glasses. This is quite important for waste streams with high concentrations of fluoride, sulfate, etc. The following discussion necessarily includes generalizations and simplifications that may not find universal applicability. Its purpose is not to be exhaustive, but to set the groundwork for evaluating the ability of structural and thermodynamic models to predict waste glass durability.

3.1 Structural Models: The Silicate Network and Its Modification

The logical starting point for a discussion of the structural chemistry of silicate glasses is vitreous silica, $v\text{-SiO}_2$. It has been known for many years [e.g., 28] that in $v\text{-SiO}_2$, Si^{4+} is surrounded by a nearly regular tetrahedral array of O^{2-} , each of which is bonded to two Si^{4+} atoms. Oxygen atoms bonded to two silicon atoms are referred to as bridging oxygen, or BO. As noted by Zachariasen [29], Si-O-Si linkages can extend indefinitely in three dimensions without the need for regular, crystal-like order, leading to what has since been described as a continuous random network. In this role, silicon is referred to as a network-forming cation. The continuous random network model has been extensively tested with regard to its application to $v\text{-SiO}_2$ [e.g., 30-32], and with the advent of sophisticated computer models for producing truly random networks [e.g., 32], this model can now be used to predict properties of $v\text{-SiO}_2$.

The continuous random network model does not apply to multicomponent glasses because the addition of other cation oxides destroys Si-O-Si bonds, rendering the "network" discontinuous. The precise form of these modifications depends upon the identity and concentration of the cations in question and, in many cases, the identities and concentrations of other cations and anions already in the glass. The effects that the addition of a cation oxide M_xO_y has on the coordination states of oxygen are discussed in Appendix 2 and are briefly reviewed here. Aside from the BOs of $v\text{-SiO}_2$, multicomponent silicate glasses and melts contain two new "types" of oxygen atoms, nonbridging oxygen atoms (NBO) bonded to one Si^{4+} and an indeterminate number of other cations, and free oxygen (FO) bonded exclusively to cations other than Si^{4+} . It is shown in Appendix 2 that if the coordination number of the added cation M, $n(\text{M})$, exceeds its formal valence, $z(\text{M})$, then the average coordination number of oxygen atoms in a $\text{M}_x\text{O}_y\text{-SiO}_2$ liquid or glass must be greater than 2, the coordination number of oxygen atoms in $v\text{-SiO}_2$. Furthermore, it is shown that if BO coordinate with two silicon atoms alone, then the average coordination number of NBO must be substantially greater than 2. Finally, it is shown that BO atoms must be present in any silicate glass or liquid for which the bulk O/Si ratio is 4 or less. Since the glass-forming regions of most multicomponent silicate systems is bounded on the low- SiO_2 end by a composition with O/Si on the order of 3, this means that as a practical matter nearly all silicate glasses contain substantial numbers of bridging oxygen.

It is doubtful whether it could be demonstrated experimentally that electropositive cations in silicate glasses coordinate solely with NBO, rather than a mix of NBO and BO. This doubt arises because there are many examples of silicate crystals in which BO coordinate with one or more cations other than silicon, particularly +1 or +2 cations, and in many cases the coordination numbers of NBO and BO are comparable. On the other hand, there appears to be no example of a silicate crystal in which NBO coordinate with only one low-valence, electropositive cation, and thus it is taken as a working principal that NBO always coordinate with two cations other than silicon. Such coordination schemes clearly will disrupt the network structure of a silicate glass,

and thus low-valence, electropositive cations are referred to as network-modifying cations, or network modifiers. It has been pointed out that if more than one network modifier coordinates with each NBO, then each cation need not be the same element [33]. For example, there is no reason why sodium and potassium cannot share the same NBO, and indeed arrangements of this type would help explain many peculiarities in the physical and chemical properties of multicomponent silicate liquids. This interpretation is germane to bonding arrangements in aluminosilicate and borosilicate glasses, as shown below.

Thus, the addition of low-valence, electropositive cations to pure SiO_2 results in the destruction of the network of Si-O-Si bonds and the formation of $[\text{M}]_n\text{-O-Si}$ and $[\text{M}]_{n1}\text{-O-}[\text{M}]_{n2}$ species, where $[\text{M}]_n$ denotes the n cations M1, M2, etc., that coordinate with the oxygen atom. This suggests that the structural chemistry of silicate glasses can be described entirely in terms of different kinds of oxygen atoms, leading to a homogeneous equilibrium in $n\text{M}_x\text{O}_y \cdot (1-n)\text{SiO}_2$ liquids written

where M-O-M, Si-O-Si, and M-O-Si represent the relative proportions of FO, BO, and NBO, respectively. This formulation was originally proposed by Fincham and Richardson [34] to explain anomalies in equilibria involving sulfur in silicate liquids, and it was expanded to a complete thermodynamic model by Toop and Samis [35]. It is referred to here as the oxygen species model. Hess [36] showed that the chemical potentials of the oxygen species are directly related to the chemical potentials of the metal oxides; thus, the oxygen species model can be used to describe the thermodynamic mixing properties of silicate liquids. More recently, it is often assumed that the equilibrium in Eq. 1 lies entirely to the right; that is, all FO bonds are consumed to form NBO bonds. This assumption is not valid, as it implies an activity of 0.0 for NBO. Free oxygen atoms are always present, and their chemical activity determines in part the redox ratios of cations in simple silicate glasses [e.g., 37], though the FO concentration in glasses containing low-valence, electropositive cations may be very low.

When applied to real systems, the activities of the oxygen species show sizable deviations from values required for solution ideality, meaning that oxide components are in general a poor representation of speciation in silicate liquids [36]. This arises from three factors: (1) distributions of NBO species over the various Si atoms in a glass; (2) differences in the strengths of M-O bonds compared to Si-O bonds; (3) cooperative interactions between different cations in silicate glasses. Evidence for the third factor is seen in interactions between alkali cations and Al^{3+} , B^{3+} , and Fe^{3+} , discussed in detail in Section 3.2.

To discuss the distributions of NBO over silicon atoms, it is easiest to consider their distributions in two random distribution scenarios. If NBO were randomly distributed over all silicon atoms, the probability of finding one NBO bonded to a silicon atom would be identical to the probability of finding four NBO bonded to a silicon atom, and likewise for all intermediate combinations. The distributions of NBO over silicon atoms is generally discussed by using Q_n notation, where n paradoxically represents the number of BO bonded to a central silicon atom (i.e., $4-n$ is the number of NBO). In this notation, the probability of finding that an NBO in a particular Q_n species, $P(Q_n)$, is such that

$$P(Q_3) = 2P(Q_2) = 3P(Q_1) = 4P(Q_0) \quad (2)$$

On the other hand, if NBO were distributed in such a way as to maximize the numbers of each Q_n species, then

$$P(Q_0) = P(Q_1) = P(Q_2) = P(Q_3) \quad (3)$$

Any distribution of NBO that differs from one of these scenarios implies a nonrandom distribution of NBO over silicon atoms.

Vibrational spectroscopy—particularly Raman spectroscopy—and nuclear magnetic resonance (NMR) spectra of simple alkali and alkaline earth silicate glasses show that NBO tend to be distributed over silicon atoms in a way that minimizes, or nearly minimizes, the number of Q_n species present in the glass; that is, a glass may consist entirely of Q_3 and Q_4 species. Moreover, the Q_n species tend to have adjacent values of n (e.g., a mixture of Q_3 and Q_2 species rather than a mixture of Q_4 and Q_0 species) [38]. The Raman spectroscopic study of $x\text{Na}_2\text{O} \cdot (1-x)\text{SiO}_2$ glasses by Furukawa et al. [39] is representative of these trends. At Na_2O concentrations less than 20 mol%, the only species in the glass are Q_4 and Q_3 species (species containing no NBO or one NBO, respectively). The concentration of Q_3 species reaches a maximum at or near 33 mol% Na_2O , the composition for which there is nominally one NBO for every silicon atom in the glass. Q_2 species first appear near 20 mol% Na_2O and reach their highest concentration near 50 mol% Na_2O , the composition for which there are nominally two NBO per silicon atom. Glasses with higher Na_2O concentrations cannot be produced by using normal quench techniques, but it has been shown that the only Q_n species present in $0.67\text{Li}_2\text{O} \cdot 0.33\text{SiO}_2$ glass is the Q_0 species, as would be predicted from this trend [40]. Alkaline earth silicate glasses exhibit similar trends [41,42]. Likewise, at 67 mol% MO concentration, nearly the only Q_n species in the glasses is the Q_0 species. Thus, the order of appearance of Q_n species with increasing $M_{2/z}\text{O}$ concentration is $Q_3 \rightarrow Q_2 \rightarrow Q_1 \sim Q_0$, a highly nonrandom distribution of NBO. This results in nonideal mixing between $M_x\text{O}_y$ and SiO_2 in multicomponent silicate liquids and glasses.

Variations in the strength of M-O bonds also can produce solution nonideality in $M_x\text{O}_y\text{-SiO}_2$ systems. Higher valence M cations form stronger bonds with oxygen, and consequently they affect the strength of Si-O bonds. Furthermore, because their higher valence requires more NBO in their coordination polyhedra, higher valence M cations will in general form different local atomic arrangements with silicate anions than will lower valence M cations. In silicate minerals, high-valence cations tend to share the edge of SiO_4 tetrahedra containing two NBO, which suggests that in silicate glasses, high-valence cations will form Q_n species containing at least two NBO (e.g., Q_2 species) at relatively low $M_{2/z}\text{O}$ concentrations, especially when compared to large, low-valence cations such as the alkalis. Evidence that this occurs is seen in the Raman spectra of alkaline earth silicate glasses [43,44], where evidence of Q_2 species first appears at 10 mol% CaO or MgO, as compared to nearly 20 mol% Na_2O in Na-silicate glasses [39]. This observation implies the existence of a homogeneous equilibria of the form

$$2Q_n = Q_{n-1} + Q_{n+1} \quad (4)$$

which are often referred to as disproportionation reactions. This equilibrium shifts increasingly to the right with increasing valence/decreasing ionic radius of M. From this, any tendency to form Q_2 species early, as observed in alkaline earth silicate glasses, implies that the number of Q_4 species will be "anomalously" high. It is perhaps not surprising that cations that form low-index (i.e., low n) Q_n species earlier than expected tend to show stable or metastable two-liquid fields in the high-silica regions of their $M_{2/z}\text{O-SiO}_2$ binary systems [e.g., 45, pp. 142, Fig. 365]. The high-silica liquid is rich in Q_4 species, whereas the composition of the low-silica liquid generally implies

that it is rich in Q_2 species. Disproportionation reactions contribute substantially to solution nonideality in the oxygen species model. (Nonideal mixing of cations is considered in Section 3.2.)

Now consider a case in which an alkali silicate liquid and an alkaline earth silicate liquid, both with the same SiO_2 concentration, are mixed. From the above discussion, the Q_n distributions of the end-member liquids would differ, but would the Q_n distribution of the mixture be a weighted sum of these distributions? If alkalis and alkaline earths behaved entirely independently from one another in a mixed liquid, then one would answer this question in the negative, because there are no other factors save steric limitations (probably unimportant in a liquid) that could affect Q_n distributions. On the other hand, if alkalis and alkaline earth cations shared the same NBO, then the Q_n distributions might change, and, more importantly for glass durability, the chemistry of alkalis in the glass would be strongly coupled to the behavior of alkaline earth cations. Evidence for coupled interactions between alkali and alkaline earth cations has been reported by Ellison and Hess [33], though much more work on a broader spectrum of compositions would be needed to confirm this result. If this result is correct, interactions of this kind might explain the high durability of Na-Ca silicate glasses, as discussed in Section 4.

While much of the discussion thus far—and much of the parlance of glass chemistry—derives from the oxygen species model, two other paradigms of silicate glass structure must be discussed: quasi-crystalline models and polymer models. Just as Q_n species are observed in glasses, they are also found in crystals, and perhaps for this reason the distribution of Q_n species can be used to model the phase diagrams of certain near-ideal binary systems. The best example of this is the study of the $\text{K}_2\text{O}-\text{SiO}_2$ system presented by Dorfeld [46], in which most details of the system are accurately modeled by using thermodynamic data obtained from crystal analogs to various Q_n species. Quasi-crystalline models have been used to model phase equilibria in more complex systems, such as $\text{CaMgSi}_2\text{O}_6 \cdot \text{CaAl}_2\text{Si}_2\text{O}_8 \cdot \text{NaAlSi}_3\text{O}_8$ [47], but these generally show substantial deviations from ideal mixing of the end-members. Quasi-crystalline "fragments" of silicate anions have been used successfully to describe the vibrational spectra of simple silicate glasses [39,48], though more recent work shows that constrained Q_n species produce essentially identical results [49]. Quasi-crystalline analogs have also been used for qualitative descriptions of speciation in silicate glasses [e.g., 43], though Q_n notation—had it existed at the time—could have been used interchangeably. However, diffraction data show that multicomponent silicate glasses do not contain crystal-like fragments of silicate anions [e.g., 28], and, as a consequence, quasi-crystalline structural models find little application in describing the structure of silicate glasses.

References to the "polymer" structure of silicate glasses extends at least as far back as Toop and Samis [35], but efforts to quantify this relationship originated with Masson [50] and Hess [51]. The point of reference is not pure SiO_2 , as assumed above, but rather a melt of pure $\text{M}_{2/z}\text{O}$ to which SiO_2 is added. At low SiO_2 concentrations, the liquid contains only free oxygen and isolated SiO_4 tetrahedra (referred to as monomers). As the concentration of SiO_2 is increased, and certainly by the time its concentration is 33 mol% or greater (see Appendix 1), monomers condense to form larger, more polymerized species such as $\text{Si}_2\text{O}_7^{6-}$ (dimers), $\text{Si}_3\text{O}_{11}^{10-}$ (trimers), and still larger species. The superficial resemblance of such species to organic polymers leads to the application of classical polymer theory to the thermodynamics of low-silica liquids. This approach has some success in very simple systems, but as noted by Hess [51], polymer models fail when branched polymers form because the simple linear equations used to describe polymer growth no longer apply. Nevertheless, the expected "connectivity" of SiO_4 tetrahedra is often referred to as the degree of polymerization, and high-silica liquids or glasses are quite often referred to as "more polymerized" than low-silica glasses. As with all the models discussed above, this terminology has outlasted the relevance or applicability of the polymer model.

To summarize the discussion in this section, low-valence, electropositive cations added to pure SiO_2 liquid consume BO to form NBO until the concentration of SiO_2 is so low that no BO exist. By assuming that metals added to a pure SiO_2 bond solely to NBO, one can compute the absolute maximum number of NBO in the liquid, and likewise the absolute minimum number of BO. NBO are generally multiply coordinated by cations other than Si, whereas BO are always shared by two silicon atoms and possibly one or more low-valence cations. In simple systems, NBO are not randomly distributed over SiO_4 tetrahedra, but rather are dispersed, so that SiO_4 tetrahedra containing a single NBO form first, followed by SiO_4 tetrahedra containing two NBO, etc. A trend for increasingly early formation of SiO_4 tetrahedra with comparatively high NBO concentrations is seen as the valence of the cation increases. These results apply to most simple alkali silicate and alkaline earth silicate glasses. The existence of several different models of cation-anion interactions in silicate glasses and liquids results in a bewildering array of terms to describe essentially the same melt/glass properties: in particular, "high polymerization" = "extended network formation" = "high index Q_n species."

Finally, this discussion has drawn a sharp distinction between the behavior of silicon and that of any other cation, so it is reasonable to ask under what conditions a cation can be said to behave "just like silicon." For this to occur, the nominal valence of the cation must be +4, it must coordinate with a regular tetrahedron of oxygen atoms, and it must form relatively covalent bonds with oxygen [52,53]. A cation that serves in this role could freely substitute for silicon in silicate minerals and glasses, and in the latter it would be miscible in all parts. The only cation that fills this role other than Si^{4+} itself is Ge^{4+} [54], which is a negligible component of most waste streams. Therefore, to a first approximation, the behavior of Si^{4+} is taken to be unique.

3.2 Structural Chemistry of Aluminosilicate and Borosilicate Glasses

Virtually all silicate waste glass candidates contain substantial amounts of Al^{3+} , B^{3+} , and Fe^{3+} . These components induce substantial changes in the structural chemistry of silicate glasses and must be considered separately from nearly all other cations. In particular, when the concentrations of alkali and alkaline earth cations are high enough, Al^{3+} , B^{3+} , and Fe^{3+} occupy tetrahedral sites with T-O bond distances (where T is Al, B, Fe) comparable to Si-O bond distances. In this guise, they appear to participate in the network structure of the glass, and, more importantly, have a dramatic effect on the structural chemistry of low-valence cations. This behavior does not appear to be important for other sesquioxides (R_2O_3). Trivalent aluminum is the archetype of this type of interaction and is discussed first, followed by B^{3+} , which is arguably the more important component in current candidate waste glasses. The chemistry of Fe^{3+} in simple alkali silicate and alkaline earth silicate glasses has not been so extensively studied, nor is it very relevant to silicate-based waste glasses; therefore, greater emphasis will be placed on its structural role in aluminosilicate and borosilicate glasses.

3.2.1 Aluminosilicate Glasses

Dramatic evidence of the unusual structural role of Al^{3+} is seen in the report by Reibling [55] of viscosities of liquids of the general composition $x\text{Na}_2\text{O} \cdot (y-x)\text{Al}_2\text{O}_3 \cdot (1-y)\text{SiO}_2$. Data for a representative composition, $x\text{Na}_2\text{O} \cdot (25-x)\text{Al}_2\text{O}_3 \cdot 75\text{SiO}_2$, at 1700°C , are shown in Fig. 2. Viscosity is a minimum in the Al-free and Na-free liquids, but it increases steeply as Al_2O_3 is substituted for Na_2O , reaching a maximum very close to the composition for which $\text{Na}/\text{Al} = 1$, but decreases with further increases in Al_2O_3 beyond this point. The same trend, in particular the maximum at $\text{Na}/\text{Al} = 1$, is observed regardless of SiO_2 concentration, showing that it is a result of changes in Na/Al alone. Noting that alkali feldspar crystals, such as $\text{NaAlSi}_3\text{O}_8$,

Fig. 2. Viscosities of $(25-x)\text{Na}_2\text{O} \cdot x\text{Al}_2\text{O}_3 \cdot 75\text{SiO}_2$ and $(33-x)\text{Na}_2\text{O} \cdot x\text{Al}_2\text{O}_3 \cdot 67\text{SiO}_2$ Liquids at 1700°C (adapted from ref. 55).

have aluminum atoms in tetrahedral coordination with oxygen, and sodium atoms in irregular cages formed by Al-O-Si and Si-O-Si bonds, Reibling proposed that aluminum is similarly stabilized in four-fold coordination with oxygen by Na^+ in liquids with $\text{Na}/\text{Al} < 1$. When aluminum atoms were in excess of sodium, the feldspar-like bonding arrangements were no longer viable for some of the aluminum atoms, and this "excess" aluminum had to seek new coordination environments, which Reibling proposed involved aluminum in six-fold coordination.

Further evidence that the mechanism of viscous flow depends mainly on the coordination state of Al^{3+} is seen in resistivity data for $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ glasses, which show a minimum at the $\text{Na}/\text{Al} = 1$ composition [56,57]. This means that Na-O bonds are weaker in the $\text{Na}/\text{Al} = 1$ composition than in other compositions, whereas the expectation from the viscosity data is that some cation-oxygen bonds are far stronger in the $\text{Na}/\text{Al} = 1$ composition. The only other possibility is that the strength of Al-O bonds has been increased. Furthermore, the quite plausible

expectation that stronger bonds would imply a more compact structure is challenged by the observation that the permeability of helium in sodium aluminosilicate glasses is a maximum in compositions for which $\text{Na}/\text{Al} = 1$ [58].

A number of physical properties of sodium aluminosilicate glasses and liquids have been shown to take on extreme values at the $\text{Na}/\text{Al} = 1$ composition—a review of some of the literature is presented by Alexander et al. [59]. A wide variety of structural probes confirm that (1) Al^{3+} is exclusively four-fold coordinated by oxygen atoms when $M^+/\text{Al} > 1$, and (2) the structures of glasses for which $M^+/\text{Al} = 1$ are very similar to the structure of $v\text{-SiO}_2$ glass itself. Persuasive evidence for the first statement is seen in Raman spectroscopy studies of alkali aluminosilicate glasses [60-65], aluminum extended X-ray absorption fine structure (EXAFS) spectra of sodium aluminosilicate glasses [66], and ^{27}Al and ^{29}Si NMR spectra of sodium aluminosilicate glasses [67,68]. Evidence that +1 cations are stripped away from NBO to stabilize Al^{3+} in tetrahedral coordination with oxygen is seen in sodium EXAFS spectra of sodium aluminosilicate glasses [69] and potassium EXAFS spectra of mixed sodium-potassium aluminosilicate glasses [70], Tl^+ luminescence and X-ray photoelectron spectroscopy studies of sodium aluminosilicate glasses doped with minor amounts of Tl_2O [59,71], ^{23}Na NMR spectra of sodium aluminosilicate glasses [67,68,72], and Raman spectra of alkali aluminosilicate glasses [61,62]. Evidence that Al^{3+} takes part in the formation of the network structure of aluminosilicate glasses is seen in X-ray diffraction analyses of $\text{MAIO}_2\text{-SiO}_2$ glasses [73-75] and sodium aluminosilicate glasses [76]. Alkaline earth cations also appear to be able to stabilize Al^{3+} in tetrahedral coordination with oxygen, as evidenced in diffraction studies [77,78], ^{27}Al NMR spectroscopy studies [79,80], and vibrational spectroscopic studies [61,65,81,82] of calcium aluminosilicate glasses. The structural chemistry of Al^{3+} in glasses for which $\text{Na}/\text{Al} < 1$ is a matter of some debate [e.g., 83,84], but in nearly all studies it appears to be four-fold coordinated by oxygen atoms in alkali aluminosilicate glasses (to very high Al_2O_3 concentrations). This debate is not germane to waste glass compositions because high- Al_2O_3 compositions are generally very refractory and cannot be considered viable waste glass candidates.

The mechanism by which Al^{3+} is stabilized in four-fold coordination by low-valence cations is referred to as "charge-balance" and is based on an electrostatic representation of glass/liquid structure. Taken as a collection of ions, the SiO_4 tetrahedron consists of a cation of valence +4 and 1/2 each of four anions of valence -2, giving a net charge of $4 + (4 \times (-2)/2) = 0$. If Si^{4+} were removed and replaced with Al^{3+} , the effective valence of the tetrahedron would become $3 + (4 \times (-2)/2) = -1$. By this logic, a +1 cation (or 50% of a +2 cation) nearby balances the negative charge of the AlO_4 tetrahedron and produces an electroneutral structure. In this role, alkali (and alkaline earth) cations are referred to as a charge-balancing cations, or charge balancers. This behavior is quite distinct from their more usual roles as network modifiers, and it is worth briefly considering what these differences are.

As can be inferred from Appendix 2, when the ratio of the valence z and the coordination number v of cation M (z/v) is less than 1.0, oxygen bonded to only one Si atom will coordinate with two or more M cations, which in the case of the charge-balance mechanism will include Si, Al, and M . A formalism for expressing such species was proposed by Ellison and Hess [33]: if M^{z+} coordinates with $v(M^{z+})$ oxygen atoms, then each NBO "owns" $1/v(M^{z+})$ of the contributed electron density of M^{z+} . In the case of an oxygen atom bonded to Al^{3+} and Si^{4+} , the net contribution to oxygen is $[(+3/4) + (+4/4)]$, or $(+7/4)$. The optimal coordination number for a

charge-balancing M^+ or M^{2+} cation would provide an additional charge contribution of $+1/4$ to the oxygen atom, meaning that $v(M^{z+}) = 4zm$, where n is an integer. Thus, the stoichiometry of the oxygen atom is written

$$[M_{1/4zm}]_m[Al_{1/4}]_n-O-Si_{1/4} \quad (5)$$

Trivalent aluminum is usually considered a network-forming cation when charge-balanced by a low-valence cation, but Eq. 5 shows that it is the coupled species $[M_{1/4zm}]_m[Al_{1/4}]_n$ that is the network former.

As shown elsewhere [33], this approach leads to new types of equilibria beyond those that can be represented by the oxygen species model. In the particular case of Al^{3+} , these new equilibria can be expressed as follows:

$$[M_{1/zi}]_i-O-Si_{1/4} + [Al_{n/3n}]_n-O-Si_{1/4} = [M_{1/4zm}]_m[Al_{1/4}]_n-O-Si_{1/4} \quad (6)$$

where $[M_{1/zi}]_i-O-Si_{1/4}$ is simply a NBO coordination environment, $[Al_{n/3n}]_n-O-Si_{1/4}$ is the coordination state of aluminum when not charge-balanced by M^{z+} , and the charge-balanced species is on the right. The experimental studies cited above suggest that whenever M is a monovalent cation, the equilibrium in Eq. 6 lies entirely to the right; thus, the formation of charge-balanced species is energetically much more favorable than the formation of NBO. Furthermore, Ryerson [85] has shown that the component $NaAlO_2$ mixes very nearly ideally with SiO_2 in high-silica liquids, so it is probably a viable mixing component for thermodynamic analyses of silicate glasses and liquids. As a consequence, the statement that "aluminum is stabilized in four-fold coordination by alkali cations" is only partially correct because the reverse is equally true: alkali (and alkaline earth) cations are stabilized in silicate glasses through their mutual bonding interactions with Al^{3+} . As shown in Section 4.3, charge-balancing of aluminum (and boron) has an enormous impact on the durabilities of multicomponent glasses and vitreous borosilicate waste glasses.

A number of studies have examined the efficacy of charge-balance produced by different cations. The thermochemical data of Roy and Navrotsky [86] show that the stability of charge-balance arrangements involving Al^{3+} and monovalent or divalent cations increased in the order $Mg < Ca < Sr < Pb < (Ba, Li) < Na < (K, Rb, Cs)$. In other words, small, high-valence cations are much less effective as charge-balancing cations than are large, low-valence cations. This is thought to result from the competition for electron density that results when Al^{3+} and the charge-balancing cations have similar valences and ionic radii [52,53]. These results presumably apply to charge-balance arrangements adopted by B^{3+} and Fe^{3+} as well (Sections 3.2.2 and 3.2.3).

One might expect that two large alkali cations, such as sodium and potassium, would mix ideally as charge-balancing cations, but in fact the thermochemical data of Hervig and Navrotsky [87] of mixed Na-K aluminosilicate glasses show significant deviations from ideal mixing. This implies that the structural units involved in the charge-balance interaction are substantially larger than individual AlO_4 tetrahedra, or the somewhat larger species implied by Eq. 5. Therefore, interactions between charge-balancing cations may be important in determining the properties of aluminosilicate glasses.

3.2.2 Borosilicate Glasses

Boric anhydride (B_2O_3) is an excellent glass former, but unlike $v-SiO_2$, the boron atoms in $v-B_2O_3$ are three-fold coordinated by oxygen [e.g., 88-90], and in this state the B-O bond

is stronger than the Si-O bond [89]. Though B_2O_3 is obviously an important component in borosilicate waste glasses, its chemistry is closely coupled with the chemistry of alkali cations, which are also inevitably present in durable borosilicate waste glasses. Therefore, $M_2O-B_2O_3-SiO_2$ glasses (where M is mainly Na^+ , but also Li^+ or K^+) are the simplest boron-bearing compositions germane to the structural chemistry of waste glasses.

Extensive ^{11}B NMR studies of $Na_2O-B_2O_3-SiO_2$ glasses [91-95] have led to a consistent picture of the structural chemistry of B^{3+} in borosilicate glasses. Using the $SiO_2-B_2O_3$ join as a reference point, the addition of moderate amounts of Na_2O to a high-silica liquid along this join will result in one-for-one conversion of three-fold (trigonally) coordinated boron atoms into four-fold coordinated boron atoms through a charge-balance mechanism. At constant SiO_2 concentration, as the concentration of Na_2O increases and the composition approaches the $Na/B = 0.5$ composition, structural units much like those in the mineral reedmergnerite ($NaBSi_3O_8$) form in high-silica glasses [91], whereas Na-O-Si (nonbridging oxygen) bonds form in low-silica glasses (all boron remains four-fold coordinated by oxygen). Increases in Na_2O past the point at which $Na_2O/B_2O_3 = 2$ result in the formation of Na-O-B (nonbridging oxygen), with boron in three-fold coordination. Bunker et al. [96] have proposed that in silica-poor, sodium-poor compositions, the local atomic arrangements resemble those of the mineral danburite ($CaB_2Si_2O_8$), in which silicon and boron are four-fold coordinated by oxygen, but which contains Si-O-Si, Si-O-B, and B-O-B bonds. Broadly speaking, most boron atoms in high-silica liquids are four-fold coordinated by oxygen, and at high Na_2O concentration, most NBO are shared between Si and Na, rather than between B and Na. X-ray photoelectron spectroscopy data [84,97] support the Yun model [91]. Qualitatively similar results have been obtained for $Li_2O-B_2O_3-SiO_2$ glasses [98], though the onset of the formation of NBO bonds occurs at higher SiO_2 concentrations than in the $Na_2O-B_2O_3-SiO_2$ system.

Because B and Si compete with each one another to form stable bonding arrangements with oxygen atoms, the activities of SiO_2 and B_2O_3 in binary $B_2O_3-SiO_2$ liquids show significant positive deviations from ideality [99]. This solution nonideality extends to compositions in the $Na_2O-B_2O_3-SiO_2$ system, which is quite famous for a very large, cigar-shaped metastable two-liquid field lying below the solidus [100,101], with its major axis roughly parallel to the $SiO_2-(Na_2O \cdot 4B_2O_3)$ join (Fig. 3). Substantial solution nonideality in liquids/glasses with $Na/B < 1.0$ was reported by Hervig and Navrotsky [102]. These data were interpreted in terms of highly unfavorable interactions between trigonally coordinated boron atoms and the network of four-fold coordinated silicon atoms. Solution nonideality in this system, and more specifically in the alkali-poor region of the system, is of practical importance to waste glass development because immiscibility can potentially have a deleterious impact on melt viscosity [103] and because one of the end-members is a highly soluble, nearly pure sodium borate glass [104]. A similar metastable two-liquid field has been identified in the $K_2O-B_2O_3-SiO_2$ system [105], suggesting that the improved charge-balance afforded by a larger cation cannot counteract the negative impact of the presence of trigonally coordinated boron atoms in the glass. In fact, at least one candidate high-level waste glass, ABS-41, undergoes amorphous phase separation when annealed at 600°C for three hours [106].

Where four-fold coordinated boron atoms are prominent, it is logical to compare the physical and/or chemical properties of borosilicate and aluminosilicate glasses. There are dramatic differences between the viscosities of $Na_2O-B_2O_3-SiO_2$ and $Na_2O-Al_2O_3-SiO_2$ liquids at the same temperature. For example, a viscosity study by Tait et al. [107,108] indicates that at 1200°C a liquid with the composition $0.33NaBO_2 \cdot 0.67SiO_2$ has a viscosity of approximately 20 Pa•s

(200 poise), whereas the viscosity data taken by Stein and Spera [109] show that the viscosity of molten $0.33\text{NaAlO}_2 \cdot 0.67\text{SiO}_2$ at 1200°C is approximately $10^5 \text{ Pa}\cdot\text{s}$. The reasons behind this enormous discrepancy are not entirely clear, but it probably reflects the relatively small energetic

Fig. 3. Metastable Two-Liquid Field in the System $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ Showing Isothermal Sections of the Solvus (adapted from ref. 100).

difference between boron in trigonal coordination and boron charge-balanced in four-fold coordination by alkali cations. A "pourable" liquid will have a viscosity on the order of $20 \text{ Pa}\cdot\text{s}$, which indicates that it is advisable to include B_2O_3 in waste glasses to improve processibility.

Waste glasses invariably contain Al_2O_3 as well as B_2O_3 , so it is worthwhile to consider to what extent Al^{3+} and B^{3+} compete with one another for charge-balancing cations. Enthalpies of solution for $\text{NaTO}_2-\text{SiO}_2$ glasses ($\text{T} = \text{Al}^{3+}, \text{Fe}^{3+}, \text{B}^{3+}, \text{and Ga}^{3+}$) were analyzed by De Yoreo and Navrotsky [110]. They found that the energetics of the charge-balance mechanism

are far more favorable for the $[\text{NaAl}^{3+}]$ species than for $[\text{NaFe}^{3+}]$, $[\text{NaGa}^{3+}]$, or $[\text{NaB}^{3+}]$, and the energetics of the charge-balanced $[\text{NaB}^{3+}]$ species appear to be the least favorable of all. This implies that in a mixed sodium boroaluminosilicate liquid, sodium will be used first to charge-balance Al^{3+} , and only when nearly all Al^{3+} is charge-compensated will the sodium be diverted to charge-balance B^{3+} [111]. It is not surprising, then, that in glasses along the join $\text{NaAlSi}_3\text{O}_8$ - NaBSi_3O_8 (albite-reedmergnerite), the concentration of trigonal B^{3+} increases with increasing concentration of the albite component. If charge-balance is a desirable effect (and the durability studies cited below indicate that it is), then the ratio of alkalis/Al+B should be on the order of one or more.

3.2.3 Trivalent Iron in Alkali Silicate, Aluminosilicate, and Borosilicate Glasses

Ferric oxide (Fe_2O_3) is a common component of high-level radioactive waste streams, and, in several domestic vitrification programs in particular, the need to incorporate high concentrations of iron into vitreous waste glasses is acute. The single most important means of studying local atomic environments of iron atoms in crystals and glasses is ^{57}Fe Mossbauer spectroscopy. The Mossbauer emission spectrum is sensitive to the oxidation state of the iron atom and also to its coordination state at fixed oxidation. In alkali silicate glasses prepared in air, 80-100% of the iron atoms are in the trivalent oxidation state [112,113], and a substantial body of evidence suggests that under these conditions Fe^{3+} is four-fold coordinated by oxygen and behaves, like Al^{3+} , as a coupled network former. This is not universally the case: Dingwell and Virgo [112] show evidence from a viscosity study of Na_2O - FeO - Fe_2O_3 - SiO_2 liquids that under fairly reducing conditions, Fe^{3+} behaves as a network modifier. Divalent iron always appears to behave as a network modifier. It has also been reported that alkaline earth cations are capable of charge-balancing Fe^{3+} , as in CaO - FeO - Fe_2O_3 - SiO_2 liquids [114].

Of greater practical interest is the behavior of Fe^{2+} and Fe^{3+} in aluminosilicate and borosilicate glasses. Dickenson and Hess [115,116] examined the dependence of the $\text{Fe}^{2+}/\text{Fe}_{\text{tot}}$ ratio on the ratio $\text{K}_2\text{O}/(\text{K}_2\text{O}+\text{Al}_2\text{O}_3)$ in K_2O - Al_2O_3 - SiO_2 liquids with (nearly) constant SiO_2 concentrations. Data for liquids equilibrated at 1400°C and containing 1 mol% Fe_2O_3 (nominal) are shown in Fig. 4. When $\text{K}_2\text{O}/(\text{K}_2\text{O}+\text{Al}_2\text{O}_3) < 0.5$, there are not enough K^+ ions to charge-balance all Al^{3+} ions, and therefore Fe^{3+} competes with Al^{3+} for charge-balancing cations. In these compositions, the $\text{Fe}^{2+}/\text{Fe}_{\text{tot}}$ ratio increases steeply with decreasing $\text{K}_2\text{O}/(\text{K}_2\text{O}+\text{Al}_2\text{O}_3)$. At $\text{K}_2\text{O}/(\text{K}_2\text{O}+\text{Al}_2\text{O}_3) = 0.5$, there are exactly enough K^+ ions to charge-balance all Al^{3+} ions, and, at still higher values of $\text{K}_2\text{O}/(\text{K}_2\text{O}+\text{Al}_2\text{O}_3)$, K^+ ions are in excess of total aluminum concentration. It is not surprising, then, that $\text{Fe}^{2+}/\text{Fe}_{\text{tot}}$ reaches a minimum value at $\text{K}_2\text{O}/(\text{K}_2\text{O}+\text{Al}_2\text{O}_3) \sim 0.5$ and shows very little change for further increases in $\text{K}_2\text{O}/(\text{K}_2\text{O}+\text{Al}_2\text{O}_3)$. From these results, it is evident that Al^{3+} competes more effectively than Fe^{3+} for charge-balancing cations, and that only when alkalis are in excess of Al^{3+} will they be used to charge-balance Fe^{3+} . When insufficient alkalis are present, $\text{Fe}^{2+}/\text{Fe}_{\text{tot}}$ increases in order to place more iron ions in network-modifying positions and to reduce the need for charge-balancing cations. A similar, but much weaker trend of this type is seen in CaO - Al_2O_3 - SiO_2 liquids [116], indicating that Fe^{3+} loses the competition with Al_2O_3 for any type of charge-balancing cation. It is not widely appreciated that the redox ratio of iron varies with melt composition at constant oxygen fugacity (f_{O_2}), but as is shown below, high concentrations of Fe^{2+} significantly degrade waste glass durability, so detailed studies of the dependence of the iron redox ratio on composition in boroaluminosilicate glasses are sorely needed.

Fig. 4. The Ratio of Ferrous Iron to Total Iron (Fe^{2+}/Fe_{tot}) in $(20-x)K_2O \cdot xAl_2O_3 \cdot 80SiO_2$ Containing 80 mol% SiO_2 and Approximately 1 mol% Fe_2O_3 (nominal). Liquids equilibrated at 1400°C in air (data from ref. 116).

There have been few detailed efforts to determine the solution chemistry of iron in alkali borosilicate liquids. The coordination environments of Fe^{3+} in a base glass of the composition $10Na_2O \cdot 30B_2O_3 \cdot 60SiO_2$ have been studied by means of X-ray diffraction [117], EXAFS [118], and X-ray photoelectron spectroscopy (XPS) [119]. The data indicate that with additions of Fe_2O_3 up to 12 wt% (5.1 mol%), all Fe^{3+} is four-fold coordinated, most likely in a charge-balance arrangement. This result is interesting because the concentration of B^{3+} considerably exceeds that of Na^+ , suggesting that Na^+ will charge-balance Fe^{3+} before B^{3+} . This result is supported by the trends in stabilization enthalpies reported by De Yoreo and Navrotsky, as discussed above [110], which suggest that Fe^{3+} should be less effective than Al^{3+} but more effective than B^{3+} in competing for charge-balancing cations. Though no study has reported such a result, it implies that high Fe_2O_3 concentrations in sodium borosilicate glasses may drive B^{3+} out of four-fold coordination and into three-fold coordination. Determining whether this is true or not is a point of considerable interest for the treatment of high-iron waste streams.

3.3 High-Valence Cation Behavior in Silicate Glasses

This section addresses what is known about the chemistry of cations of valence +3 or greater in silicate glasses and melts. The most important trivalent cation components in waste glasses other than B^{3+} , Al^{3+} , and Fe^{3+} are the trivalent lanthanides. The EXAFS study of La, Gd, and Yb in silicate glasses by Ponader and Brown [120] showed (1) that the coordination numbers of small lanthanide cations are generally smaller than those of large lanthanide cations in equivalent glasses and (2) that in sodium aluminosilicate glasses in which all Na^+ are nominally involved in charge-balancing Al^{3+} , the differences between the coordination numbers of the lanthanides are the greatest. Similar coordination numbers were obtained for lanthanides dissolved in an SRL frit, a borosilicate glass considered as a candidate for immobilizing nuclear waste [121]. Raman spectroscopic data of alkali silicate glasses doped with high concentrations of lanthanides showed that lanthanides coordinate with NBO and do not share these to a significant degree with alkali cations [122]. Therefore, lanthanides can be considered network-forming cations in the classic sense.

Lanthanides have potentially important interactions with two anions common in nuclear waste glasses, F^- and PO_4^{3-} . Ponader and Brown [123] found that lanthanides form complexes with F^- in alkali silicate and alkali aluminosilicate glasses—in other words, F^- anions compete effectively with NBO to coordinate with lanthanide cations. This result is consistent with the aqueous solution chemistry of lanthanides: it is known that the only simple anion to form an inner-shell complex with lanthanides is F^- [124]. In principle, this reduces the activity of R_2O_3 (where R is a lanthanide) and increases the compatibility of lanthanides in silicate glasses; however, it also means that the fate of lanthanide cations might be tied to the behavior of F^- in waste glasses with significant F^- concentrations. Ryerson and Hess [125] measured the partitioning of lanthanides between immiscible silicate liquids and found that the addition of P_2O_5 to the system affected the behavior of lanthanides far more than any other cation. The authors interpreted this as the result of the formation of RPO_4 complexes in the liquids. (The compositional dependence of the solubility of RPO_4 is discussed below.)

The behavior of large +4 cations in alkali aluminosilicate glasses has been extensively investigated because of its importance to trace element geochemistry. Watson [126] demonstrated experimentally that the solubility of ZrO_2 in alkali aluminosilicate liquids is tied to the M^+/Al^{3+} ratio. When $M^+/Al^{3+} \leq 1$, ZrO_2 solubility has a minimum, but as M^+/Al^{3+} increases beyond 1.0, the solubility of ZrO_2 increases strongly and approximately linearly. A similar effect has since been reported for TiO_2 [127], Fe_2TiO_5 [128], and RPO_4 [129-131], and is likely to exist for Sn^{4+} and Th^{4+} as well. Figure 5 shows experimental results for TiO_2 in $xK_2O \cdot (20 - x)Al_2O_3 \cdot 80SiO_2$ liquids from the study of Dickinson and Hess [127]. The number of high-valence cations accommodated by a unit increase in alkali oxides varies from one cation/cation complex to another, implying a specific chemical interaction with a stoichiometry much like the 1:1 ratio observed for alkali cations and Al^{3+} . In the absence of alkali cations, the high-valence cations turn to other, less satisfactory bonding arrangements, which in general drastically lowers their solubilities in silicate glasses.

Ellison and Hess [33] propose that at least in the case of Zr^{4+} , this alkali stabilization results from the sharing of NBO by alkalis and Zr^{4+} . The stoichiometry of the alkali/zirconium complex implied a coordination number for Zr^{4+} of 6, the value obtained by Farges et al. [132] in an EXAFS study of Zr in alkali silicate and aluminosilicate glasses. It is important to confirm whether alkalis share NBO with other +4 cations. Sharing of NBO by high-valence cations and

Fig. 5. Saturation Concentration of TiO_2 in Rutile-Saturated Liquids in the System $(20-x)K_2O \cdot xAl_2O_3 \cdot 80SiO_2$ Equilibrated at $1450^\circ C$ (data from ref. 127).

alkalis would tie up alkalis in much the same way as does charge-balance of Al^{3+} by alkalis and, given the very low solubility of ZrO_2 in aqueous solutions, would tend to increase the resistance of a glass to aqueous attack.

The most important +5 cation in waste glasses is P_2O_5 , which in some instances, such as the West Valley candidate waste glass WV-205, may reach a level of 2-3 wt% [133]. Nelson and Tallant [134] showed that P_2O_5 is not incorporated into the silicate network structure of alkali silicate glasses but instead forms discrete anions that strip alkali cations from network-modifying positions. This behavior suggests that the stabilization of $CePO_4$ by alkalis in excess of Al^{3+} , reported by Montel [129], may be due to the formation of alkali-phosphate complexes. Dupree et al. [135] suggest that different alkali cations form different phosphate anions, with larger alkalis tending to form the largest anions.

In many systems, however, the solution chemistry of P_2O_5 in silicate oxide glasses is determined by the interactions between the PO_4^{3-} anion and trivalent cations. For example, Toplis et al. [136] show that at high concentrations, PO_4^{3-} increases the solubility of Fe_3O_4 in synthetic basalts, implying favorable interactions between PO_4^{3-} and Fe^{3+} . This is potentially quite important in iron-rich waste glasses. As noted above, the interactions between PO_4^{3-} and trivalent lanthanides are very strong and result in extremely low solubility for RPO_4 (monazite) in aluminosilicate liquids. In most waste glasses, the CaO concentration is much greater than the cumulative concentration of all lanthanide cations. Under these circumstances it may be $Ca_3(PO_4)_2$, and not RPO_4 , that controls P_2O_5 solubility [137]. As its density is likely to differ from that of the bulk liquid, formation of $Ca_3(PO_4)_2$ will result in a stratification of the melt and may interfere with heat transfer or with extracting the liquid from the melter.

Finally, we consider what little is known about the behavior of actinide elements in silicate glasses. Farges [138] used EXAFS to characterize the coordination environments of Th^{4+} in silicate glasses and reports bond lengths and coordination numbers very similar to those for Zr^{4+} . This result suggests that the solution mechanisms of Zr^{4+} and Th^{4+} are similar: i.e., Th^{4+} solubility will be relatively low in a glass in which all alkalis are involved in charge-balancing Al^{3+} but will increase strongly and nearly linearly with alkali concentration. Depending on the stoichiometry of the alkali/ Th^{4+} complex, this type of interaction may result in a modest improvement in waste glass durability. The chemistry of uranium in borosilicate and aluminosilicate glasses produced under modestly oxidizing conditions appears to be entirely confined to the uranyl ion, $(UO_2)^{2+}$ [139,140]. The effective valence of this species, +2, means U^{6+} behaves as a large, moderately soluble divalent cation in silicate glasses, in contrast with Pu^{4+} and Th^{4+} , which are much less soluble. On the basis of the electromotive series proposed by Schreiber and others [141,142], the +5 and +4 valence states of uranium are not likely to be accessible in most waste glasses because of the presence of minor amounts of Cr_2O_3 and MnO .

Karraker [143] determined the valences of uranium and transuranic elements in an alkali borosilicate glass to be +6 for U, +4 for Pu and Np, and +3 for Am. Muller [144] reports a compositional dependence of the valence state of neptunium that involves an increase in the Np^{4+}/Np^{3+} ratio with increasing alkalis in excess of B^{3+} in simple borosilicate glasses. If true, this behavior is qualitatively similar to that shown by iron in alkali aluminosilicate glasses, as shown in Fig. 4 [116]. Tetravalent plutonium probably shows behavior comparable to the behavior inferred above for Th^{4+} , with alkalis stabilizing its coordination polyhedron of NBO. The coordination chemistry of other transuranic elements varies wildly with their valences; therefore, more information is needed concerning precisely what these valences are in borosilicate glasses as a function of glass composition. Determining the positions of these elements in the electromotive series of multivalent cations in borosilicate glasses [141,142] would be a very important contribution to waste glass development, as it might be possible to tailor the relative proportions of other cations to force transuranic elements into the most favored oxidation states.

3.4 Summary of Cation Solution Chemistry in Silicate Melts and Glasses

The oxygen in silicate glasses can be loosely divided into bridging, nonbridging, and free oxygen atoms (BO, NBO, and FO, respectively), depending on whether they coordinate solely with network-forming cations, a combination of network formers and network modifiers, or with network modifiers alone. The network structure of a silicate glass arises from interconnections between network-forming cations linked by common BO, and these structures are terminated by bonds through NBO to network-modifying cations. The NBO are the principal means of interaction between silicate anions and electropositive cations such as the alkalis and alkaline

earths. A simple structural argument shows that the coordination numbers of NBO are likely to be three or greater; i.e., they generally coordinate with more than one network-modifying cation. These modifiers need not be the same cation.

Trivalent aluminum, boron, and iron can be stabilized in four-fold coordination with oxygen by large, low-valence cations such as the alkalis or alkaline earths, a process referred to as charge-balancing. All evidence indicates that alkalis are used to stabilize Al^{3+} first, then Fe^{3+} , and finally B^{3+} . If sufficient alkalis are not available to charge-balance Fe^{3+} in aluminosilicate liquids, or if some other cation is still more effective at competing for alkalis, then the redox ratio $\text{Fe}^{2+}/\text{Fe}_{\text{tot}}$ will increase. Likewise, if insufficient alkalis are available to charge-balance B^{3+} in boroaluminosilicate glasses, B^{3+} reverts to three-fold coordination, in which guise it competes effectively with Si^{4+} for NBO.

Lanthanide chemistry is like that of a relatively incompatible network modifier, with the caveat that its solution chemistry in the melt may be strongly affected by the presence of fluorine or P_2O_5 . The solubilities of the oxides of all +4 cations studied thus far, save Si^{4+} and Ge^{4+} , show a marked dependence on the concentration of alkali oxides in excess of Al_2O_3 in silicate glasses, in general increasing with the concentration of so-called "excess" alkalis. The mechanism proposed to explain this phenomenon for Zr^{4+} is quite similar to the charge-balance mechanism proposed for Al^{3+} . This similarity suggests that Zr^{4+} may be effective in decreasing alkali loss during aqueous attack. The chemistry of actinide elements varies strongly with their valences. The behavior of Th^{4+} and Pu^{4+} is anticipated to be qualitatively similar to the behavior of Zr^{4+} , but very little is known about the solution mechanisms of neptunium, americium, or other transuranic elements in silicate melts and glasses.

4.0 EMPIRICAL CORRELATIONS BETWEEN COMPOSITION AND DURABILITY

The purpose of this section is to discuss what is known empirically about the effects various components have on the durability of simple silicate glasses and to examine the extent to which these relationships can be extended to multicomponent waste glasses. A great deal of information is available about composition-durability relationships in simple systems, but, unfortunately, results from one study cannot be compared quantitatively with results from other studies because of the absence of a uniform approach for testing or measuring durability. Much of the discussion, therefore, is qualitative. In waste glass durability studies, by contrast, a potentially large database exists of MCC-1-type experiments performed on various glass compositions, but very few studies have examined more than one glass composition at a time. Again, direct comparison is difficult, but, nevertheless, certain general rules can be discerned. For simplicity, all compositions are in terms of moles or mole-fractions unless otherwise noted. In the discussion that follows and in much of the remainder of this critical review, it is assumed that the compositions in question are homogeneous glasses, i.e., they have not undergone liquid-liquid or glass-glass phase separation and are free of crystals. The effects that crystallinity and phase separation have on glass durability are discussed in Section 5.1.

4.1 Composition Space of Candidate Waste Glasses

Table 1 in Appendix 3 shows the compositions of a number of candidate waste glasses (mol% of oxide components). (The table shows only those components with a mole fraction of at least 0.1% in at least one waste glass.) Also shown are average values for each component taken over all waste glasses, the average over all waste glasses containing the component, the extreme values for the component, and the percentage of waste glasses containing the component. The components are arranged in decreasing order of their average concentration taken over all waste glasses. All waste glasses contain SiO_2 , B_2O_3 , Na_2O , Fe_2O_3 , Al_2O_3 , in order of decreasing average abundance. These components represent an average of 82 mol% of the oxide components of candidate waste glasses. Nearly all the glasses contain ZrO_2 , NiO , and BaO , though at a level of 1 mol% or less. When present, Li_2O , CaO , and MgO are major components, and the same is true to a lesser degree of TiO_2 and ZnO . Taken together, these oxides account for at least 93 mol% of all candidate waste glasses. Actual waste components typically comprise only 10-15 mol% (oxide basis) of a waste glass, and a great many of these are present only very low concentrations, so their impact on waste glass durability is negligible. Since each of these waste glasses is a relatively durable material, the range of values for each component is a measure of the compositional space of greatest relevance to waste glass durability, provided that in developing the waste glasses an adequate region of compositional space has been explored.

From this, the glass chemistry of waste glasses is expected to be largely described by the subsystem $\text{SiO}_2\text{-B}_2\text{O}_3\text{-A}_2\text{O-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3(\text{FeO})\text{-MO-FO}_2$, where A represents alkali cations (mainly Na^+), M represents alkaline earth cations (mainly Ca^{2+}), and F represents Ti and Zr. A comprehensive study of the dependence of glass durability on compositional variations in this system would greatly aid the development of better waste glasses. Unfortunately, most systems that have been subjected to detailed studies are either considerably simpler, such as the soda-lime silicate glasses ($\text{Na}_2\text{O-CaO-SiO}_2$), or a good deal more complex, e.g., real waste glasses. Nevertheless, a number of trends emerge from these studies that—by accident or design—seem to account for broad aspects of the observed durability of candidate waste glasses. These trends are discussed in the following sections, with a final section covering the relatively few comparative studies of the durabilities of candidate waste glasses.

Many of the experiments reported in the academic studies discussed below were performed for relatively short periods of time on relatively nondurable glasses using nonstandard test methods, often with little or no information about the actual SA/V of the system. For simplicity, then, tests will be referred to as "solution dominated" when the apparent SA/V is on the order of a standard MCC-1 test (or even less) and as "glass dominated" when the apparent SA/V is on the order of the PCT test. Sometimes not even this much information is available, in which case reference is made to durability ranking alone.

4.2 Durability Relationships in A_2O -MO Silicate Glasses

The bulk of academic studies of the corrosion of silicate glasses concerns what are probably the least durable simple glasses, the alkali silicates. Useful information has been obtained from these studies, particularly concerning the mechanisms of alkali loss in aqueous dissolution, but their applicability to waste glasses is so remote that they will not be considered in this review. It is common knowledge in glass chemistry, however, that as the alkali concentration of a glass increases, its resistance to aqueous attack decreases: for example, residual K_2O - SiO_2 glass in a platinum crucible can be cleaned out simply by holding the crucible under flowing tap water. The deleterious impact of alkali cations upon glass durability also extends to more complex systems. Clark et al. [145] performed glass-dominated durability tests on $xNa_2O \cdot 10CaO \cdot (90-x)SiO_2$ glasses that showed that as Na_2O concentration increases, glass durability decreases very sharply. It would seem desirable, then, to avoid including alkalis in waste glass compositions; however, the processing temperatures and melt viscosities of alkali-free silicate compositions are usually too high for these glasses to be considered as waste glasses. Furthermore, as indicated in Section 3.3, alkalis may be important in enhancing the solubility of otherwise incompatible elements in the glass. Thus, the principal, though unstated, objective of waste glass development is to identify means to keep alkalis (and boron) in the glass.

As alkali cations are removed from a reacting glass, the pH of the corroding solution tends to increase, particularly if it started out as deionized (DI) water. Therefore, adding a component that is not very soluble in basic aqueous solutions will tend to decrease the rate of glass corrosion. A practical example is virtually any divalent cation, the hydroxides of which—if they exist—tend to be sparingly soluble in basic aqueous solutions [146]. This principle is quite important to the production of window glass, which to a first approximation falls in the system Na_2O - CaO - SiO_2 . The common names for Na_2O and CaO are soda and lime, respectively, and therefore window glasses are often referred to as soda-lime silicate glasses. Sodium hydroxide is many times more soluble in water than CaO [146], so adding CaO should enhance the resistance of sodium silicate glass to aqueous attack.

In fact, a large number of experimental studies have demonstrated that sodium silicate glasses corrode much more rapidly than Na-Ca silicate glasses. Clark et al. [147] showed that in glass-dominated experiments, the concentrations of Na and Si obtained from $20Na_2O \cdot 80SiO_2$ glass were 2.5×10^5 and 8.5×10^5 ppm, respectively, after 12 h of aqueous attack, but for $20Na_2O \cdot 10CaO \cdot 70SiO_2$ glass, these concentrations were only 566 ppm each after 9 days of aqueous attack, implying a difference in the rate of glass corrosion on the order of 10^3 . Das [148] examined the durabilities of Na-Ca silicate glasses in glass-dominated experiments using solutions with fixed initial pH ranging from 4 to 11. These experiments demonstrated that the much greater durability of Na-Ca silicate glasses relative to sodium silicate glasses is independent of pH through this range. The results also show, however, that the rate of Na extraction and the rate of Si extraction are different as a function of pH: the highest Na extraction rates were obtained in acidic solution, whereas the highest Si extraction rates were obtained in basic solutions. Boksay and Bouquet [149] showed that below a pH of 3,

Si extraction from Na-Ca silicate glasses increases with decreasing pH, though it is still two orders of magnitude greater at a pH of 11 than at a pH of 4. This illustrates that glass durabilities are a function not only of the chemistry of the glass, but of the solution as well.

In short tests, A_2O -MO- SiO_2 glass durabilities also appear to depend upon the identity of the alkali cation. For example, Dilmore et al. [150] showed that in glass-dominated systems, $15K_2O \cdot 10CaO \cdot 75SiO_2$ glass is leached much more rapidly than $15Na_2O \cdot 10CaO \cdot 75SiO_2$ glass. Das [148] showed that this durability ranking is independent of imposed solution pH in solution-dominated systems. Interestingly, the presence of a different alkali in solution than in the glass (e.g., as a component of a buffer solution or as part of a brine) appears to affect aspects of glass corrosion as well. For example, Smets and Tholen [151] showed that when $20Na_2O \cdot 10CaO \cdot 70SiO_2$ glass is leached in potassium-bearing solutions, potassium is incorporated into the leached layer, though its penetration is not as deep as the level of sodium leaching.

A mixture of two alkalis in A_2O -MO- SiO_2 glasses decreases the rate of dealcalization relative to a mechanical mixture of the end-members. Dilmore et al. [150] found that $(15-x)Na_2O \cdot xK_2O \cdot 10CaO \cdot 75SiO_2$ glasses are more durable than the Na or K end-members, and more durable than mechanical mixtures of the end-members. The main impact of this "mixed alkali effect" is to suppress alkali loss rates and to delay the onset of network dissolution. Interestingly, the mechanical mixtures of the end-members were more durable than indicated by a mixing line between the end-members, suggesting that even at the SA/V of the study (7 m^{-1}) the buildup of corrosion products in solution still strongly affects the corrosion. What has not been established in any study of simple glass-forming systems is whether or not the same solution pH is eventually reached regardless of the alkali mixture, and whether or not network dissolution rates are affected by the presence of two or more different alkalis in solution.

Different divalent cations also have different effects on glass durabilities, at least at low concentrations. Smets and Tholen [152] examined the Na depletion profiles obtained when $20Na_2O \cdot 10MO \cdot 70SiO_2$ glasses ($M = Ca, Mg, \text{ or } Zn$) were leached in DI water at extremely low SA/V (solution-dominated system). After reaction for a fixed period, the amount of Na remaining in the corrosion layer increased depending on M in the order $Ca < Mg < Zn$, and the depth of corrosion decreased in the same sense. Smets et al. [153] examined Na and H profiles in leached $20Na_2O \cdot xMO \cdot (70-x)SiO_2$ glasses and found that this effect is most important at relatively low MO concentrations. By the point at which $x = 15 \text{ mol\%}$, there is little difference between the performances of the glasses. In particular, such differences are dwarfed by the magnitude of the increased durability resulting from an increase in the concentration of MO.

To summarize, the rate of dealcalization of A_2O -MO- SiO_2 glasses is orders of magnitude lower than in their A_2O - SiO_2 counterparts, regardless of whether MO is added to a glass with a fixed A:Si ratio or substituted for A_2O or SiO_2 , regardless of whether the system is solution- or glass-dominated, and regardless of the initial solution pH in solution-dominated systems. A modest mixed-alkali effect produces somewhat more corrosion-resistant A_2O -MO- SiO_2 glasses, but this is much smaller than the effect produced by small changes in MO concentration. The benefit of adding MO is greatest at low MO concentrations and falls off for relatively high MO concentrations (15-20 mol%). There is no suggestion, however, of a point at which the durability of A_2O -MO- SiO_2 glasses decreases with MO concentration. Finally, ZnO appears to be more effective than CaO or MgO for slowing glass corrosion in short-term experiments, though the differences are negligible at high MO concentrations.

4.3 A₂O-T₂O₃-SiO₂ Glasses

The compositional dependence of the durabilities of A₂O-T₂O₃-SiO₂ glasses is somewhat more relevant to the question of the durabilities of high-level radioactive waste glasses because, as noted above (and in Appendix 3, Table 1), while some waste glasses do not contain significant quantities of any divalent cation oxides, nearly all contain significant quantities of B₂O₃, Al₂O₃, and Fe₂O₃. As noted in the previous section, each of these sesquioxides exhibits unique behavior in its glass chemistry, so it is not surprising that each shows unique behavior in glass corrosion. In the case of B₂O₃, the peculiarities arise from the relative proportions of tetrahedrally coordinated BO₄ species and trigonally coordinated BO₃ species, and from the high intrinsic solubility of B₂O₃ in aqueous solutions. In the case of Fe₂O₃, the concern is the Fe³⁺:Fe²⁺ redox ratio, which is seldom measured in multicomponent glasses (including waste glasses), but which varies not only with the imposed oxygen fugacity, but with composition as well (see above, Section 3.2.3). Trivalent aluminum does not have mixed coordination states in the range of glass compositions that are important for waste glass development, but it is unusual for the enormous range of crystalline silicates in which it is a central constituent.

4.3.1 A₂O-B₂O₃-SiO₂ Glasses

Short-term durability/composition relationships for glasses in the Na₂O-B₂O₃-SiO₂ system were determined by Adams and Evans [154]. They reacted glasses with water in a solution-dominated system at 25°C for 24 h. The weight losses shown by the glasses during this time were projected onto the ternary system, and lines were interpolated between the data representing compositions with "equivalent" durabilities (Fig. 6). These "isodurs" surround the SiO₂ apex and project toward the Na₂O-B₂O₃ join along an axis nominally identified as Na₂O/B₂O₃ = Na/B = 0.85. Adams and Evans point out that the true axis could lie anywhere from 0.7 to 1.0, and they use the latter in their model. The substance of the model is that compositions that maximize the concentration of BO₄ tetrahedra and put all Na⁺ in a charge-balancing role (as nearly as possible) tend to have the highest durabilities. By itself, this does not explain the substantial durability decrease with decreasing SiO₂ concentration along this join. On the other hand, the NMR data discussed above show that BO₃ trigons are increasingly favored with decreasing SiO₂ concentration; so in the context of the Adams and Evans model, one would anticipate that durabilities decrease with decreasing SiO₂ concentration, as observed. The magnitude of the decrease for a net change in SiO₂ concentration is much greater away from the Na/B = 1.0 line than near it.

Other short-term studies have confirmed the relationships identified by Adams and Evans. LaCourse and Stevens [155] obtained results for short-term leaching of sodium-rich, boron-depleted glasses in the xNa₂O•(y-x)B₂O₃•(1-y)SiO₂ compositional joins. As B₂O₃ increases at the expense of Na₂O, the time required to obtain a pH of 9.0 increases exponentially, implying that sodium release rates decrease in the same sense. Kaps et al. [156] examined sodium self-diffusion vs. short-term durability in sodium borosilicate glasses. They showed that, in general, where sodium self-diffusion rates are highest, the glasses have the lowest durabilities, and that the lowest self-diffusion rates are obtained in the vicinity of the Na:B = 1:1 join. Harvey and Jensen [157] performed a 30-day, solution-dominated static leach test on Na₂O•B₂O₃•nSiO₂ glasses, and showed that for n = 5 to 12 moles, the mass loss was essentially independent of SiO₂ concentration, but for n < 5 moles, mass losses increased steeply and exponentially with decreasing SiO₂ concentration.

Fig. 6. Curves Representing Equivalent Mass Loss ("Isodurs") for Glasses in the System $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ (adapted from ref. 154).

These trends extend to long-term durability tests as well. Bunker et al. [158] performed pH stat/buffered leaching experiments with sodium borosilicate glasses, measuring durability as a function of the $\text{Na}_2\text{O}/\text{B}_2\text{O}_3$ ratio at 60 mol% SiO_2 and as a function of SiO_2 for $\text{Na}_2\text{O}/\text{B}_2\text{O}_3 = 1$. In general, the durabilities follow the isodurs of Adams and Evans [154], regardless of pH. Sodium and boron were preferentially leached from glasses with Na:B ratios $< 1:1$, regardless of pH, whereas glasses with $\text{Na}_2\text{O}/\text{B}_2\text{O}_3 \geq 1$ leached more or less congruently in base (though sodium loss was enhanced in acid). Glasses with $\text{Na}_2\text{O}/\text{B}_2\text{O}_3 = 1$ were several orders of magnitude more durable than those with (substantially) lower or higher Na:B ratios. Using NMR data, these results were correlated with the concentration of four-fold coordinated boron, which not only appears to enhance glass durability but which also is selectively retained in the leached layer, relative to three-fold coordinated boron, in the early stages of leaching. The presence of abundant four-fold coordinated boron also increases the likelihood of stoichiometric dissolution. It was concluded that the dissolution of most sodium borosilicate glasses was controlled by network dissolution, though the range of compositions analyzed seems too sparse for this generalization.

Few studies have tried to quantify durability relations in mixed alkali borosilicate glasses. However, the results of a detailed analysis of the leaching behavior of $67.4\text{SiO}_2 \cdot 17\text{B}_2\text{O}_3 \cdot 8\text{K}_2\text{O} \cdot 3\text{Na}_2\text{O} \cdot 0.7\text{Li}_2\text{O} \cdot 3.6\text{Al}_2\text{O}_3$ glass, performed by Buckwalter et al. [4], can also be used to address this issue. Their results show that normalized B release was always greater than normalized Na or K release, but generally lower than (Na+K) release. In addition, while Na and K concentrations were low in the leached layer, B was almost entirely removed. The ratio of these components to Si released into solution was substantially greater than implied by stoichiometry at all times. This result appears to be consistent with the results reported by Bunker et al. [158]: since the (Na+K+Li):B ratio of this composition is substantially less than 1:1, stoichiometric dissolution would not be expected. A very useful contribution to the literature in this field would be a study of mixed alkali borosilicate glasses, particularly glasses containing Na and Li, as both are common in durable waste glasses.

4.3.2 $\text{A}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ Glasses

Another important waste glass subsystem is $\text{A}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$, particularly where A = Na or Li. Smets and Lommen [159] used secondary ion mass spectroscopy (SIMS) to determine the sodium-loss profiles of $20\text{Na}_2\text{O} \cdot x\text{Al}_2\text{O}_3 \cdot (80-x)\text{SiO}_2$ glasses ($x = 0, 5, 10, 15, 20$) that had been reacted in a solution-dominated system for very short periods, generally less than 1 h. The depth of sodium depletion was taken as the measure of relative durability. The depth of sodium depletion decreased markedly with increasing Al_2O_3 . The greatest change in the depth of depletion was obtained for the smallest amounts of added Al_2O_3 , $x = 5$: leached layers of the $x = 15$ and $x = 20$ glasses were far thinner than in glasses with lower Al_2O_3 concentrations, but did not differ significantly from each other. For $x = 5$ or 10, sodium-loss profiles show a plateau, interpreted as evidence that sodium atoms were involved in charge-balancing AlO_4 tetrahedra. They also inferred that H_2O diffusion into the glass was strongly inhibited by the addition of Al_2O_3 .

Dilmore et al. [160] measured corrosion of $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ glasses in a glass-dominated system at 100°C for periods of up to 41 days. They found that as the Al_2O_3 concentration increased, the release rates of lithium decreased: for example, in glasses with equivalent mole fractions of Li_2O , the pH of the solution and the dissolved Li^+ concentration were far higher for the glass with the lower Al_2O_3 concentration. Transmission electron microscope (TEM) images of corroded glasses were quite telling: high aluminum glasses still showed scratch marks from sample preparation, whereas high lithium glasses were extensively corroded. It should be noted that no glass analyzed by Dilmore et al. had a Li:Al ratio as large as 1:1.

Tait and Mandelosi [161] examined the durability of sodium aluminosilicate glasses as a function of the Na:Al ratio and (Na+Al):Si ratio in solution-dominated experiments run on an ISO replacement schedule for periods of up to 60 days. To obtain bubble-free melts, it was necessary to melt compositions at exceptionally high temperatures, and experience shows that this process can lead to substantial alkali loss. A great limitation on the application of the results of this study is that no compositional analyses were performed on the glasses. Nevertheless, the authors found that for sodium aluminosilicate glasses relatively close to the Na:Al = 1:1 join, glass durabilities as determined after 30- to 60-day tests were very weakly affected by changes in the SiO_2 concentration or the Na:Al ratio, though there is a tendency for glasses to become more durable as the Na:Al ratio is decreased towards 1:1. Taken at face value, changes in the Na:Al ratio when it is already close to 1:1 have little impact on durability. This is analogous to the wide field of durable glasses found in the $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ system, which encompasses a range of Na:B ratios from approximately 1.1:1 to 0.7:1.

Very few studies have examined the possibility of a mixed alkali effect in the durabilities of alkali aluminosilicate glasses. Tait and Mandelosi [161] also performed ISO-based solution-dominated durability measurements on glasses containing variable amounts of Na and K and having (Na+K):Al ratios of 1:1. Normalized Na, K, and Si losses were relatively insensitive to the Na:K ratio, though the glasses were never found to undergo stoichiometric dissolution, so an effect at still greater reaction times cannot be ruled out. On the other hand, Klonkowski and colleagues have reported a mixed-alkali effect in Na-K aluminosilicate glasses [162] and Li-Na aluminosilicate glasses [163] with alkali-to-aluminum ratios substantially greater than 1:1. It was found that intermediate Na-K bearing glasses were less durable than those on a mixing line connecting the end-members, whereas Na-Li bearing glasses were more durable than those on a mixing line connecting the end-members. The experimental methods used to obtain the durability-composition relations were not stated in either study, however, and therefore the results must be regarded with some skepticism and will not be discussed further.

To summarize, composition-durability relationships observed in $A_2O-B_2O_3(Al_2O_3)-SiO_2$ systems can be generalized as follows:

- At fixed SiO_2 concentration, durability is poorest along the A_2O-SiO_2 join, increases very strongly (exponentially?) as $(Al,B)_2O_3$ is substituted for A_2O , and is a maximum at or near the composition where $A_2O:T_2O_3 \sim 1.0$. Further increases in T_2O_3 concentration in $A_2O-B_2O_3-SiO_2$ systems degrade durability, but a similar relationship has not been quantitatively established in aluminum-bearing systems.
- A substantial gain in durability is obtained by a relatively modest increase in $(Al,B)_2O_3$ concentration. At or near the A:T = 1:1 composition, durabilities appear to be weakly affected by the A:T ratio.
- At fixed A:B ratios, durability deteriorates with decreasing SiO_2 concentration. In aluminosilicate glasses, this has only been established for relatively alkali-rich compositions.
- Durability is least sensitive to SiO_2 concentration near the A:B = 1:1 composition, and probably near the A:Al = 1:1 composition as well.

4.3.3 Extension to $A_2O-Fe_2O_3-SiO_2$ Systems

A very important T cation in waste glasses that has not been considered explicitly in simple systems is Fe^{3+} . As noted above, calorimetric and spectroscopic evidence suggests that Fe^{3+} is stabilized in four-fold coordination by alkali cations, though with a net energy gain that is smaller than that obtained for Al^{3+} . As noted above, the Fe^{3+}/Fe^{2+} ratio can be changed at fixed f_{O_2} simply by reducing the number of charge-compensating alkali cations at fixed total iron concentration. This suggests that in $Na_2O-FeO_x-SiO_2$ glasses prepared at constant f_{O_2} , durability will increase steadily from the Na_2O-SiO_2 join to the point where the Fe^{3+}/Fe^{2+} ratio is as high as allowed by the imposed f_{O_2} . For samples in this system prepared in air at typical melter temperatures, the optimal Na:Fe ratio would be very close to the 1:1 composition. It has been shown in multicomponent borosilicate glasses that durability deteriorates with decreasing Fe^{3+}/Fe^{2+} [e.g., 133], so further increases in Fe concentration past the optimal Na:Fe value would decrease glass durability.

With the generalizations made above for borosilicate and aluminosilicate glasses, we can conclude that durable waste glasses will tend to have A_2O/T_2O_3 ratios close to 1.0 (where $T = Al^{3+}, B^{3+}, Fe^{3+}$), or perhaps slightly lower (T_2O_3 -rich). Whether an intentional act of design or an artifact of the composition selection process, this is manifestly the case in durable waste glass compositions (Appendix III, Table 1). It should be noted that iron in waste glasses is virtually always identified as " Fe_2O_3 ," despite insufficient quantities of other multivalent cations with higher reduction potentials to assure that this is the case. In those instances in which $Fe^{3+}:Fe^{2+}$ ratios have been determined, they are generally rather low (0.0 - 0.5). Nevertheless, failure to report the redox state of such a large component in most waste glasses needlessly complicates the quest for data on durability/composition relationships, and a greater effort should be made to verify iron redox ratios.

4.3.4 Mixing of T^{3+} Cations

Most waste glasses contain both Al and B, usually with molar $Al/B < 1:1$. Very little work has been published on the ways in which glass durabilities vary with this ratio. Brezneva et al. [164] report leaching rates of twelve glasses in the $Na_2O-Al_2O_3-B_2O_3-SiO_2 \pm CaO$ system, though their test methods are neither identified nor reported. The range of compositions is very broad, and it is somewhat difficult to generalize the results—perhaps for this reason, the authors made no effort to do so. Given this caveat, in general the most durable glasses had $Na_2O/(B_2O_3+Al_2O_3) \leq 1.0$. In CaO -free compositions with fixed Na_2O and Al_2O_3 , an increase in B_2O_3 concentration at the expense of SiO_2 substantially increased glass durability, and a one-for-one increase in Na_2O and B_2O_3 at the expense of SiO_2 resulted in only a slight decrease in durability. Tait and Mandelosi [161] examined Na-Al-B silicate glasses with $Na_2O/(Al_2O_3+B_2O_3)$ ratios of 1 but with variable Al/B ratios (up to 1). As the B_2O_3 concentration increased, there was essentially no change in glass durability; however, the authors cite unpublished data that purports to show that at Al/B ratios of 0.25, the glasses are markedly less durable than glasses with higher $Al:B$ ratios. Trotignon et al. [165] conducted a more limited durability study of compositional variations in a sodium borosilicate base glass with $Na_2O/B_2O_3 \sim 1.1$, using static dissolution tests performed at 10 m^{-1} . Substitution of 4 mol% Al_2O_3 for SiO_2 resulted in a ten-fold decrease in normalized release rates for Na, B, and Si. These results suggest that the most durable glasses will contain both B_2O_3 and Al_2O_3 , and they perhaps indicate that the $Al:B$ ratio should optimally be 1:3 or greater. It is possible that at this level, boron atoms that might otherwise occupy three-fold coordinated sites are compelled to occupy charge-balanced four-fold coordinated sites by the presence of sufficient Al^{3+} . These results also illustrate the overall importance of the charge-balance mechanism in alkali boroaluminosilicate glasses.

4.4 $A_2O-T_2O_3-MO-SiO_2$ Glasses

Smets and Tholen [152] performed short-term solution-dominated durability tests that examined a large range of glass compositions of the general composition $20Na_2O \cdot 10MO \cdot xAl_2O_3 \cdot (70-x)SiO_2$, where $M = Ca, Mg, \text{ or } Zn$, and x varied from 0 to 20. In each case, the depth of sodium extraction decreased very rapidly with increasing x , with a substantial increase between $x = 0$ and 10 and a more modest change from $x = 15$ -20. Unlike sodium aluminosilicate glasses [159], low-aluminum glasses did not show a plateau in sodium concentration in the leached layer. On the basis of this result, they suggest that all sodium atoms are bonded to NBO for $x < 10$. At low Al_2O_3 , the durabilities appeared to increase depending on M in the order $Ca < Mg < Zn$, but at high aluminum concentrations there is relatively little difference. Tait and Mandelosi [161] looked at Na-Ca aluminosilicate glasses with $(Na_2O+CaO)/Al_2O_3$ ratios of 1:1 as a function of the Na:Ca ratio. Durability (as measured by

Na loss) showed little correlation with the Na:Ca ratio, though Ca and Si loss increased slightly with increasing CaO concentration. Data from Brezneva et al. [164] for $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$ -CaO glasses with fixed Na_2O , Al_2O_3 , and B_2O_3 concentrations show that an increase in CaO to 12 mol% (at the expense of SiO_2) increased glass durability, but further increases in CaO concentration somewhat diminished durability. These results suggest there is an optimal CaO concentration for glass durability, even in complex, multicomponent glasses. If so, an addition of small amounts (5-10 mol%) of CaO may produce a larger net effect than addition of large amounts. This result is probably generally true for relatively electropositive divalent cations.

In the study by Trotignon et al. [165] involving sodium borosilicate base glass with $\text{Na}_2\text{O}/\text{B}_2\text{O}_3 \sim 1.1$, substitution of 5 mol% CaO for SiO_2 and the addition of 1-2 mol% Fe_2O_3 and ZnO had a small impact on normalized Si release but resulted in a four- to five-fold decrease in Na and B losses. Unfortunately, it is not possible to decouple the various effects of the latter compositional variation, but given the results of Brezneva et al. and Tait and Mandelosi [164,161], it is reasonable to conclude that the improved durability was the result of a combination of the effects of CaO and ZnO. This suggests that +2 cations modify the chemistry of alkalis in the glass, possibly by sharing NBO with alkalis.

4.5 $\text{A}_2\text{O}-\text{M}_x\text{O}_y-\text{SiO}_2$ Glasses

As evidenced by Table 1, in Appendix 3, waste glasses contain many cations other than those considered above, but few studies have examined the effect of the addition of other cations on the durabilities of simple silicate glasses. Ohta and Suzuki [166] examined durabilities of $73\text{SiO}_2 \cdot 12\text{CaO} \cdot 15\text{Na}_2\text{O} \cdot n\text{M}_x\text{O}_y$ glasses (weight basis), where $n\text{M}_x\text{O}_y$ was 5-25% ZrO_2 ; 5-15% SnO_2 , TiO_2 , Al_2O_3 , or La_2O_3 ; 10% PbO ; 5% P_2O_5 , MnO_2 , or Fe_2O_3 ; or 1.5-3% Cr_2O_3 . The glasses were boiled in DI water, 20% HCl, or 2N NaOH. Addition of relatively small amounts of Ta_2O_5 , La_2O_3 , Cr_2O_3 , and TiO_2 had very little impact on durability in DI water; P_2O_5 greatly decreased durability; and low concentrations of ZrO_2 , MnO_2 , Al_2O_3 , and SnO_2 (in order) substantially enhanced it. At higher concentrations, all components but P_2O_5 enhanced glass durability in DI water. By contrast, all components but TiO_2 and ZrO_2 actually caused durability to decrease in strong acid. This effect was particularly pronounced for Al_2O_3 and La_2O_3 . In strong base, Cr_2O_3 , SnO_2 , La_2O_3 , and ZrO_2 improve durability; MnO_2 , Ta_2O_5 , and TiO_2 have little effect; and Fe_2O_3 , PbO , P_2O_5 , and Al_2O_3 degrade durability. Shelby and Vitko [167] found that the tin-rich side of soda-lime silicate float glass was much more resistant to weathering under undersaturated, high humidity conditions than the side that had not been in contact with molten tin. Tin oxide is not a significant component of any waste glass, but as it inevitably appears to enhance the durability of simple glasses, it perhaps deserves closer scrutiny.

A number of studies have focused on the relationship between ZnO concentration and enhanced short- and intermediate-term glass and waste glass durabilities. Tait and Jensen [168] examined the effect of the addition of 8.5 mol% ZnO to a base glass of the composition $70.3\text{SiO}_2 \cdot 12.1\text{Na}_2\text{O} \cdot 17.6\text{B}_2\text{O}_3$. The zinc-bearing glass releases all elements at a lower rate than the zinc-free glass, such that after 21 days of leaching in DI water the solution concentrations of Si, Na, and B are 10 times lower than in the zinc-free glass. Analysis by SIMS revealed a peak in zinc concentration near the surface of the leached layer. They attribute the enhanced durability to surface adsorption of zinc onto the leached layer, which passivates surface silanol groups. Lewis et al. [169] examined a complex candidate waste glass containing 23 mol% ZnO and loaded with from 0% to 25% of a simulated high-level nuclear waste. It was found that sodium and total mass losses decreased with waste loading, but that zinc losses increased. Zinc and silicon concentrations in the leached layer increased from 0% to 15% waste loading, but

silicon decreased and zinc increased markedly in the 25% glass. X-ray diffraction (XRD) analyses revealed $\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$ in the leached layers of glasses containing 15% waste and Zn_2SiO_4 in the leached layer of the glass containing 25% waste.

Calestani et al. [170] examined the durability of lithium borosilicate glasses in DI water (on an ISO schedule). The glasses had a base composition of $55.5\text{SiO}_2 \cdot 29.2\text{B}_2\text{O}_3 \cdot 5\text{Li}_2\text{O} \cdot 10.3\text{Na}_2\text{O}$ (by weight) and were doped with 9.1 or 16.7 wt% SrO , Cs_2O , or U_3O_8 , or 4 wt% ZnO . All glasses except the zinc-bearing composition show a rapid increase in Si and Li concentrations in solution that flattens out after four days. The zinc-bearing glass, by contrast, shows much lower initial Si and Li losses and shows a slow, steady increase in the solution concentrations of those elements over time. The greatest overall weight loss is observed for the cesium-bearing glass, followed by glasses containing Sr and U. The glass containing uranium performed similarly to the glass containing no waste. Mass losses from zinc-bearing glasses were several times lower than those for the other glasses. Scanning electron microscope (SEM) images of the glasses show substantial leaching of all materials except the zinc-bearing glass, which still shows abrasion marks from its preparation for leaching.

To summarize, the addition of ZrO_2 , ZnO , PbO , and possibly SnO_2 to glasses that do not otherwise contain them enhances the durability of the glasses in a wide variety of systems and under extreme variations in imposed solution conditions. Addition of ZnO appears to enhance glass durability in the short and intermediate term, but also increases the likelihood of producing crystalline secondary phases. The addition of Cs_2O (and presumably other alkali cations) and P_2O_5 to an otherwise durable glass enhances mass losses under a wide variety of conditions.

4.6 Composition/Durability Relationships in Candidate Waste Glasses

Many studies have determined the performance characteristics of specific candidate waste glasses, but few have directly compared the durabilities of two or more waste glasses under identical conditions. Those few are the subject of this section. Glass compositions referenced by name are compiled in Appendix 3. Three things must be borne in mind in analyzing these studies. First, in a system such as $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$, small changes in composition can affect durability by orders of magnitude, whereas in waste glass development one is usually interested in an incremental improvement in the durability of an already durable glass. Second, while the experiments in the academic studies discussed above were conducted for hours or a few days, nearly all waste-form durability tests are performed for a minimum of 7 days and in glass-dominated systems that greatly accelerate the rate of solution evolution. Third, it is often difficult to isolate the effect of a change in the concentration of a single component in a multicomponent waste glass because of the effect the variation has on the concentration of all other components, whether they are diluted by its addition (simple addition) or whether the concentration of one or more particular components is decreased while that of the addend is increased (simple substitution). Most studies cited below employ still more complicated means of varying glass compositions. As a result, whether it was the increase in component A or the decrease in component B that produced the observed change in waste glass performance cannot be assessed with perfect certainty. Also, the longer a static test is performed, the further one gets from evaluating the forward glass reaction, and the closer one gets to the possibility of solubility effects on the reaction rate. We therefore cannot expect perfect correlation between the results obtained in durability studies of waste glasses and the durability relationships found for the simple systems discussed above.

4.6.1 Comparisons of Related Glass Compositions

A very important cautionary note to all of the following discussion is obtained from the study of Advocat et al. [171], who analyzed the effect on short-term and long-term durability of adding MgO to R7T7 glass and M7 glass (Appendix 3, Table 1). Short-term tests were conducted on coupons of glass using a Soxhlet apparatus with a refresh rate of approximately 8 min (very high flow) at 100°C (to 28 days), or in a modified MCC-1 static leaching experiment performed at 90°C at an SA/V of 50 m⁻¹ (to 91 days). In all cases, the addition of MgO results in a decrease in glass durability, but the effect is much more pronounced in static tests than in Soxhlet tests, and much greater for high SA/V than for low SA/V. The decrease in durability in all tests was more pronounced for M7 than for R7T7.

The cautionary note arises from the following observation. The R7T7 and M7 glasses have very similar (Na+Li)/(B+Al) ratios (on the order of 0.9) and comparable concentrations of all major oxide components, except that SiO₂, CaO, and Al₂O₃ concentrations are somewhat lower in M7 than in R7T7. On the basis of the discussion in the previous sections, these differences should combine to make R7T7 the more durable glass. In fact, the Soxhlet results are equivocal, showing nearly the same normalized boron release for both glasses, whereas the normalized boron release in static tests is much higher for M7 than for R7T7. This shows that changes in solution composition due to buildup of corrosion products in static tests can significantly impact durability rankings, even for relatively durable glasses such as these. The importance of this point cannot be understated: the response of a composition to aqueous attack is a manifestly different property than its response to buildup in solution of the products of its dissolution. Most of the remaining studies in this section involve static tests, so the durability rankings must be taken in this light. In general, the more durable glasses respond better to elevated pH than the less durable glasses, or they have lower alkali release rates that slow the rate of pH increase. There are legitimate structural chemistry reasons why these results might be expected, but the feedback between corroding glass and evolving solution must always be kept in mind.

Nogues et al. [172] compared the durabilities of seven candidate waste glasses (Appendix 3, Table 2) containing 42-51 wt% SiO₂, 8-13 wt% Na₂O, 14-22 wt% B₂O₃, 3-6 wt% Fe₂O₃, and 1.5-2.5 wt% MoO₃, combined with simulated waste products (composition not reported). In addition to these components, six of the glasses contained 3-9 wt% Al₂O₃; four of the compositions included 2-4 wt% CaO; two included 2 wt% Li₂O; and one included a very low concentration of MgO. No glass contained all four of these components, though one contained Al₂O₃, CaO, and Li₂O. Durabilities were determined by using a MCC-1 type experiment performed at 90°C at an SA/V of 10 m⁻¹; the normalized release rates of Si, B, and Na were used to monitor glass dissolution. Normalized elemental releases from the Al₂O₃-free glass were one to two orders of magnitude higher than those for the remainder of the glasses: its Na₂O/B₂O₃ molar ratio was approximately 2:3, and it also had the highest Fe₂O₃ and nearly the highest MoO₃ concentrations of any of the glasses studied. On the basis of this study and studies of the effects of minor components on liquid immiscibility in Na₂O-B₂O₃-SiO₂ glasses [173,174], it is likely that this glass was phase separated.

The compositions studied by Nogues et al. [172] were more in line with conventional candidate waste glasses and therefore are discussed in some detail. In general, compositions with (Na+Li)/(B+Al) ratios furthest from 1.0 were the least durable, e.g., in the most durable glass (Na+Li)/(B+Al) = 0.9, whereas in the least durable glass (Na+Li)/(B+Al) = 0.67. For glasses with similar (Na+Li)/(B+Al), the more durable of the two had a higher SiO₂ concentration. The three most durable glasses also contained CaO. There was no obvious correlation between durability ranking and the concentration of simulated waste

products, and, likewise, the Fe_2O_3 concentration did not vary enough to give an accurate picture of its possible effects on durability. Overall, these results are consistent with the conclusions reached above: the most durable glasses have $M^{1+}/T^{3+} \sim 1.0$ or less; for compositions with $B/Al > 1.0$, the most durable glasses also contain CaO ; and so on. Interestingly, substitution of 2 wt% Li_2O for 2 wt% Al_2O_3 had a relatively minor effect on the durabilities of glasses M7 and M5, suggesting that at low concentrations, Li_2O and Al_2O_3 may be similarly effective in improving the durability of these compositions. (This is not expected to be a general result, however, and probably does not apply to SRL-type waste glasses.)

Nogues and Hench [175] performed MCC-1 tests on the candidate waste glasses (Appendix 3, Table 1) ABS 29 and ABS 41. These waste glass candidates have very similar compositions, except that in ABS 41, 3 wt% of the ZnO found in ABS 29 is replaced with an equivalent mass of Fe_2O_3 . The $(\text{Na}+\text{Li})/(\text{B}+\text{Al})$ ratio of the glasses is 0.6, and in this and other respects they resemble the glass M5 from the study by Nogues et al. [172]. Durability was measured using MCC-1 tests at 90°C at $\text{SA/V} = 10 \text{ m}^{-1}$ for durations up to 28 days. The normalized release rates of ABS 29 were consistently lower than those of ABS 41, suggesting that ZnO suppresses glass dissolution. The authors report that both glasses performed better than a glass containing 6 wt% Fe_2O_3 and no ZnO , though no data were shown. They suggest that a "critical concentration" of multivalent cations is necessary to suppress glass dissolution, and thus this study is an early indication that glass "complexity" can enhance durability (see Section 4.6.2). These results are not easily explained using data from simple systems because so few studies of simple systems have examined the role of Fe_2O_3 in glass dissolution. The redox state of iron in aqueous solution is very unlikely to be the same as that in a glass, and this difference in the chemical potentials of FeO and Fe_2O_3 between glass and solution is likely to have a deleterious impact on durability.

Hermansson et al. [176] report a detailed study of the physical and chemical properties and durabilities of a suite of 10 compositionally-related waste glass candidates (Appendix 3, Table 3), including ABS 39, ABS 41 (about which there is an extensive literature), and ABS 118, a glass very similar in composition to JSS-A, the reference glass for radioactive waste disposal for Japan, Switzerland, and Sweden. Earlier, Hermansson et al. [177,178] had compared the durabilities of ABS 39 and ABS 41, but the results do not differ from those reported later [176] and will not be discussed in detail. All glasses contained 46-52 wt% SiO_2 , 14-19 wt% B_2O_3 , 9.5-13 wt% Na_2O , 2.5-5 wt% Al_2O_3 , 3-6 wt% Fe_2O_3 , 1-2 wt% UO_2 , and 9 wt% simulated waste products. (ABS 118 contained 11.3 wt% simulated waste.) In addition, five compositions contained 2.5-3 wt% ZnO , and four contained 2-3 wt% Li_2O . (Three glasses had no ZnO or Li_2O .) In addition to all of these components, ABS 118 contained 4 wt% CaO and 0.4-1 wt% P_2O_5 , Cr_2O_3 , NiO , and ZrO_2 . In all cases, the $(\text{Na}+\text{Li})/(\text{B}+\text{Al})$ ratio was on the order of 0.7 or less. All variations in composition, except the concentrations of minor components in ABS 118, were substitutional: for example, in comparing the composition EXP 1 to ABS 49, 3 wt% SiO_2 replaced 3 wt% Li_2O , and EXP 3 differs from EXP 1 in that 3 wt% ZnO is replaced with 3 wt% Li_2O . The $(\text{Na}+\text{Li})/(\text{Al}+\text{B}+\text{Fe})$ ratios of all glasses were substantially less than 1.0, ranging from a low of approximately 0.6 to a high of nearly 0.9. Durabilities were measured using normalized Si, B, Na, and Li losses and total weight change obtained in 28-day MCC-1 tests conducted at 90°C and at an SA/V of 10 m^{-1} .

The normalized total mass losses of all waste glasses differ by only a factor of three, suggesting that the waste glasses lie within a fairly broad valley of relatively high durability. In the seven most durable glasses, the normalized release rates of Na, B, Si, and Li (where appropriate) were very nearly equal, indicating congruent dissolution—the range of normalized sodium release from these glasses was $2.9\text{--}8.7 \text{ g/m}^2$ in 28 days. In the three least durable glasses, the normalized Na (or Na+Li) release was much greater than that for Si and B,

and overall mass losses were greater than those for any of the other glasses as well. It is of interest, then, to consider how these three differ from the others. They are identified as EXP 7, EXP 6, and ABS 39, in order of increasing normalized mass loss and normalized boron release. EXP 6 is similar to ABS 39, save that 3 wt% SiO_2 replaces 3 wt% Fe_2O_3 , and EXP 7 is similar to ABS 39 except that 3 wt% Li_2O replaces 3 wt% Na_2O in ABS 39. Within these compositions, an increase in SiO_2 concentration at the expense of Fe_2O_3 improves durability (though it also increased the working temperatures [176]), and a mixed alkali glass is somewhat more durable than a single-alkali glass. Similar conclusions are reached in analyzing the relative durabilities of the seven more durable compositions, as discussed in the following paragraphs.

The unifying feature of the least durable glasses is that their B_2O_3 concentrations were the highest of any in the study, 19.1 wt%. (Interestingly, the glass ranked seventh in durability, EXP 4, has the next highest B_2O_3 concentration, at 18.5 wt%.) Since the variable components were SiO_2 , Na_2O , Li_2O , ZnO , Fe_2O_3 , and B_2O_3 , this result suggests that substitution of B_2O_3 for any of these oxides when the $(\text{Na}+\text{Li})/(\text{Al}+\text{B})$ ratio is already less than one results in a decrease in glass durability. This interpretation is supported by comparing the performance of these glasses with the material labeled EXP 5, which is third in durability rank. EXP 5 was very similar to the least durable glass, ABS 39, except that 3 wt% SiO_2 was substituted for 3 wt% B_2O_3 , at the cost of increased processing temperature. It was similar to EXP 6 except that 3 wt% Fe_2O_3 was substituted for 3 wt% B_2O_3 , resulting in a much more modest enhancement in durability. Finally, it was somewhat similar to EXP 7, save that it did not contain Li_2O and that 3 wt% SiO_2 was substituted for 3 wt% Na_2O . Therefore, an increase in SiO_2 concentration produced a greater improvement in durability than did the mixed alkali effect in these somewhat alkali-deficient glasses.

The durability ranking of the six most durable glasses is EXP 1 > EXP 2 > EXP 5 > ABS 41 > ABS 118 > EXP 4, based on normalized mass loss, Na release, and Si release. The most durable glass contained ZnO and had the highest SiO_2 concentration of any of the glasses in the study (again, at the cost of increased processing temperature). At this SiO_2 concentration (54 wt%), substitution of 3 wt% Li_2O for 3 wt% ZnO (i.e., composition EXP 3) increased normalized elemental releases and total mass loss by a factor of three, but modestly improved processing temperatures. Replacement of 2.5 wt% SiO_2 in EXP 1 with 2.5 wt% Na_2O (i.e., composition EXP 2) had a very small impact on durability, increased the $\text{Na}/(\text{Al}+\text{B})$ ratio, and greatly lowered the processing temperature. These results suggest that the presence of ZnO results in a greater enhancement to glass durability than the mixed alkali effect or higher SiO_2 concentration. On the other hand, EXP 5 has no ZnO , and is lower in SiO_2 and higher in Na_2O , Fe_2O_3 , and Al_2O_3 than EXP 1, EXP 2, or EXP 3, but has a durability very similar to EXP 1 and EXP 2. As noted above, $\text{Na}/(\text{Al}+\text{B})$ of this glass is the closest to 1.0 of any composition in the study, suggesting that a relatively small change in Al_2O_3 towards a charge-balanced composition can result in a great improvement in glass durability.

The most interesting of these compositions, however, is ABS 118, which has the lowest SiO_2 concentration of any glass in the study and therefore might be expected to be amongst the least durable. It differs from the other glasses in having a relatively complex composition, a comparatively high Al_2O_3 concentration (4.9 wt%, compared to 2.5-3.1 wt%), and modest amounts of CaO and ZrO_2 (4 and 1 wt%, respectively). Some combination of these factors more than compensates for the low SiO_2 concentration in the glass—evidence discussed below suggests that these factors are glass complexity and elevated Al_2O_3 and ZrO_2 concentrations.

Van Iseghem et al. [179] report static leach test results (90°C , $\text{SA/V} = 10$ to 100 m^{-1}) for a reference glass, WG 124, and three related glasses, WG 119, WG 122, and WG 123 (Appendix 3, Table 4). The glasses have unusually high SiO_2 concentrations (66-70 mol%), high FeO and Fe_2O_3 concentrations (5-10 mol% combined FeO_x , approximately 50% of which is FeO), and high concentrations of CaO and MgO (5-6 mol% each), and they contain no B_2O_3 . WG 124 contains 5 mol% $\text{Na}_2\text{O}+\text{K}_2\text{O}$, whereas the other compositions contain 12 mol% $\text{Na}_2\text{O}+\text{K}_2\text{O}$. In brief, all compositions are comparable to durable soda-lime silicate glasses (a minor exception is WG 124, which contains 1-2 mol% BaO, MoO_3 , etc., as simulated waste). The Al_2O_3 content of the glasses is therefore expected to be a pivotal concern in measured durability: WG 119 and WG 122 contain no Al_2O_3 , WG 124 contains 2 mol% Al_2O_3 , and WG 123 contains 5 mol% Al_2O_3 , so WG 123 is expected to be the most durable. Complete release rate data are reported only for WG 119 and WG 123, though the authors state that results for WG 122 and WG 124 are comparable to those for WG 119. The results indicate that normalized release rates from WG 123 are approximately half an order of magnitude lower than for the other glasses for periods up to one year. This supports the notion that alkaline earth cations can greatly stabilize alkali cations in long-term leach tests and, moreover, that the concentration of Al_2O_3 in alkali-alkaline earth silicate glasses has a very large impact on durability, as discussed above.

Feng et al. [180] report durability tests of a suite of glasses based on WV 205 (Appendix 3, Table 1), a waste glass developed for the West Valley Demonstration Project. Durability was measured using boron release obtained from 7-, 28-, and 56-day tests similar to the MCC-3 protocol (see Section 2.2), conducted at 90°C . Unlike the borosilicate glasses discussed above, WV 205 contains alkali oxide concentrations in excess of Al_2O_3 and B_2O_3 , with $(\text{Na}+\text{K}+\text{Li})/(\text{B}+\text{Al})$ of 1.8 and $(\text{Na}+\text{K}+\text{Li})/(\text{B}+\text{Al}+\text{Fe})$ of 1.3. In such an alkali-rich composition, one can anticipate that the addition of SiO_2 , and especially Al_2O_3 , will improve glass durability and that adding both together would produce a marked enhancement in durability. These predictions are precisely the results observed: the addition of 3 wt% SiO_2 decreases 7-day boron release to solution by nearly a factor of two, while 3 wt% Al_2O_3 decreases boron release by a factor of three. The relative rankings of all glasses to which Al_2O_3 or SiO_2 was added was invariant with time, with the disparity between the modified compositions and the reference composition increasing over time. Zirconium oxide was also found to improve glass durability, though the greatest benefit was obtained with relatively small amounts (1-2 wt%). This is consistent with the assumption that complexation of zirconium and alkalis (Section 3.3) stabilizes the glass as a whole. The same may be true of TiO_2 , which at a level of 4-6 wt% markedly improved durability, but which paradoxically lowered durability at a level of 2 wt%. This may indicate that the solution mechanism of TiO_2 in a glass at low concentrations differs from the mechanism at high concentrations. Addition of Cr_2O_3 and small increases in Fe_2O_3 caused a modest improvement in durability, as did the addition of NiO and CuO: the beneficial effects of these cations may derive more from their low solubility in aqueous solution than their stabilizing impact on glass structure. The addition of 2 wt% La_2O_3 improved durability relative to the reference glass, but further increases decreased durability. The final pH of the glass with 2 wt% La_2O_3 is also anomalously low compared to all other compositions, and, as substantial foaming of the melt was reported when La_2O_3 was added [180], loss of alkalis in sample preparation cannot be ruled out. The addition of ZnO resulted in a marked increase in boron release rates for all concentrations examined (2-6 mol%), showing that the beneficial impact of ZnO on glass durability does not apply to all glass compositions.

More complex combinations were also examined. By adding 1.7 wt% CaO, 2 wt% SiO_2 , or 2 wt% ZrO_2 to a glass that already contained 3.5 wt% excess Al_2O_3 , its durability was improved relative to a glass containing excess Al_2O_3 alone, by about the same

factor in each case. The effects of adding SiO_2 and ZrO_2 are somewhat easier to understand than the effect of adding CaO: alkalis are still far in excess of all tetrahedral +3 cations, meaning charge-balance is unlikely to be a factor, and the CaO concentration is still far too low to consider the composition an alkali-alkaline earth silicate glass. Instead, the relatively low solubility of CaO in basic solutions or increased glass complexity may be the controlling factor. Equimolar substitution of ThO_2 for ZrO_2 degraded glass durability, but combining this substitution with the addition of Al_2O_3 or ZrO_2 improved durability relative to the reference glass. For the most part, the compositional dependence of the durabilities of these glasses is in line with what is expected based on the structural chemistry of the glasses (Section 3), though in glass-dominated tests such as MCC-3 and PCT, feedback effects due to rapid evolution of the solution must play a role as well.

A final study of note is that of Toven et al. [181], who performed 100°C Soxhlet tests on a wide range of borosilicate glass compositions (Appendix 3, Table 5), using normalized B, Na, and Li release as measures of durability. The principal compositional variables were the concentrations of SiO_2 , Al_2O_3 , B_2O_3 , Na_2O , Fe_2O_3 , and CaO, but unfortunately the concentrations of fission products and actinides, denoted (FP+act)ox, are not reported. As a result, it is impossible to determine whether a change in frit components is responsible for a small change in dissolution rate; in particular, where such comparisons are possible, it appears that the durability of the glasses decreases, with increased concentration of (FP+act)ox. Nevertheless, the initial dissolution rates vary by nearly a factor of 50, suggesting that large changes are due mainly to the composition of a frit. It is these that will be addressed in this section. (It must be noted that the intention of Toven et al. was not to perform a parametric study of composition-durability relationships, but to test models purported to predict initial dissolution rates.)

Broadly speaking, high-silica glasses are invariably more durable than low-silica glasses, but as SiO_2 concentration decreases from a maximum of 69.4 wt% to a minimum of 40.4 wt%, the variability within a fixed range of SiO_2 concentration increases, presumably due to the stabilizing/destabilizing influence of changes in the relative concentrations of other frit components. The distinguishing feature of the most durable glasses in the set is that, for the most part, $\text{Na}/(\text{B}+\text{Al})$ is greater than 1.0, B/Al is 1.0 or more, and B_2O_3 is present at a level between 8 and 10 wt%. Within this subset of glasses, fixing the weight fraction of B_2O_3 and Al_2O_3 while increasing Na_2O (and [FP+act]ox) at the expense of SiO_2 results in a very modest decrease in durability. Once again, the charge-balance effect is a very important factor in improving the durabilities of boroaluminosilicate glasses. Glasses containing Fe_2O_3 instead of Al_2O_3 are invariably much less durable than Al_2O_3 -bearing glasses, though a direct comparison is made difficult by the absence of exact analogs in each compositional set: where it is possible, it appears that substituting approximately 6 wt% Fe_2O_3 for 6 wt% Al_2O_3 increases the dissolution rate by roughly four times. A direct replacement of 4 wt% Al_2O_3 with 4 wt% CaO increases the corrosion rate by approximately a factor of six in glasses with Na/B ratios of approximately 1.0, indicating that the benefit of high CaO concentrations may be confined to glasses with alkalis in excess of B and Al.

As noted in Section 3, many fission products and actinides are high-valence cations that are likely to interact directly or indirectly with alkalis not associated with Al^{3+} in silicate glasses. This has the potential to produce a complex interdependence between the concentration of high-valence cations versus Al^{3+} and the durability of a waste glass. For example, the study of Tait and Mandelosi [161] shows that the durabilities of glasses with $\text{Na}/\text{Al} < 1$ are comparable to those for which $\text{Na}/\text{Al} = 1$, meaning that shifting Al^{3+} into a configuration that does not involve charge-balance does not significantly impact glass durability. On the other hand, shifting Ti^{4+} or some other high-valence cation into a configuration that did

not involve alkali cations might reduce the durability of a glass. Thus in some cases, increasing Al_2O_3 at the expense of Na_2O while keeping other components fixed may actually degrade the durability of the glass, as fewer alkalis would be available to interact with components in the waste. This appears to be the case in the compositions presented by Tovená et al. [181], particularly the comparison of samples 4 and 6, though the lack of information about the composition of the waste and the absence of truly systematic variations in bulk composition make this comparison somewhat suspect. On the other hand, if alkalis are far in excess of what could be used by B, Al, Fe, or any waste products—the case most relevant to waste glasses developed at Savannah River Laboratory and the West Valley Demonstration Project—then substitution of B_2O_3 for SiO_2 should improve glass durability. Again, a clear example is not available, but comparison of samples 4 and 26 suggests that this is, in fact, the case. A final interesting and important result is that in flow-through tests such as these, where glass components are given no chance to build up in solution, mass-for-mass an increase in the weight fraction of B_2O_3 has a much more beneficial impact on waste glass durability than a comparable (or even slightly larger) increase in Al_2O_3 concentration when the concentration of alkalis is already in excess of Al+B (e.g., samples 5 and 10). As seen elsewhere in this section, most of this behavior follows directly from considerations of the structural chemistry of glasses and from results obtained for simple systems, though such considerations by themselves do not permit estimation of the magnitude of variations produced by changes in composition.

4.6.2 Changes in Glass Complexity

In the previous section, it was occasionally seen that a glass composition was more durable than related compositions for no obvious reason except, perhaps, that its composition was more complicated than the others with which it was compared, e.g., ABS 118 vs. EXP 4 in the study by Hermansson et al. [176]. For complexity to improve durability, the components added to the glass must be more soluble in the glass than in aqueous solutions (particularly basic solutions in static leach tests) and must not show a great tendency to form crystalline corrosion products. The thermodynamics underlying the relationship between complexity and durability are discussed in Appendix 6.

Evidence that the complexity of a glass composition can contribute to its durability is shown in the studies of McGrail et al. [182] and McVay and Buckwalter [183], among others. In these studies, a relatively simple sodium borosilicate reference glass is modified by adding or subtracting various oxides and waste simulants. In the study by McGrail et al. [182], the durability measure was 28-day MCC-1 tests performed at 90°C using normalized sodium release as the durability measure. Two series of glasses were analyzed (Appendix 3, Table 6). In one series, a glass of the composition $14\text{Na}_2\text{O} \cdot 10\text{B}_2\text{O}_3 \cdot 76\text{SiO}_2$ (Glass 1) was modified by substitution of CaO (Glass 2), then $\text{CaO} + \text{ZnO}$ (Glass 3), then $\text{CaO} + \text{ZnO} + \text{Fe}_2\text{O}_3$ (Glass 5) for SiO_2 , with a final product similar to PNL 3008—a waste glass containing roughly 44 wt% SiO_2 ; 11 wt% B_2O_3 ; 15 wt% Na_2O ; 12 wt% Fe_2O_3 ; and 2.5-5 wt% NiO, CaO, ZnO, and TiO_2 . In the second series, Glass 5 was modified by the addition of ZrO_2 , TiO_2 , and MoO_3 , resulting in a final composition similar to PNL 76-68 (Appendix 3, Table 1). Glass 1 had alkalis somewhat in excess of B_2O_3 , but it lay well within the region of most durable glasses as defined by Adams and Evans [154]: using the model of Dell et al. [95], it is predicted that 80-90% of all boron atoms will be tetrahedrally coordinated by oxygen and charge-balanced in this configuration by Na_2O . As SiO_2 is replaced by other oxides, boron is increasingly shifted into trigonal coordination (forming NBO with sodium and the added metals), and sodium increasingly takes on the role of a network modifier. Glasses 1, 2, 4, 5, and PNL 3008 illustrate this trend. In this case, increasing complexity does not help because the structural chemistry of the glass changes in undesirable ways. On the other hand, ZrO_2 and TiO_2 are believed to use alkalis to stabilize their coordination polyhedra of oxygen, which suggests that at low concentrations they should improve the durability of the glass by using up alkalis that are not

otherwise occupied in charge-balancing B^{3+} . Furthermore, neither ZrO_2 nor TiO_2 has appreciable solubility in aqueous solutions [146]. This appears to be the case in the series of glasses labeled 6, 7, and 8, for which ZrO_2 , TiO_2 , and MoO_3 were added to glass 5, thereby improving its durability.

Greater support for the proposal that the complexity of a composition improves the durability of a glass is seen in a study by McVay and Buckwalter [183], in which very small amounts of a wide range of oxides were added to PNL 3008 (Appendix 3, Table 7). For the most part, the additives were kept at a level of 1-3 wt%, so their individual impacts on the structural chemistry of the glasses were relatively modest. Durability was determined using MCC-1 tests performed at 90°C for periods of up to 700 h. The normalized sodium and boron release rates of PNL 3008 glass were consistently a factor of four greater than those of the more complex glasses, implying that it is the complexity of the glass, rather than its structural chemistry, that is determining its dissolution rate.

It is shown in Appendix 6 that the addition of a component that mixes ideally with other components in a glass results in an overall decrease in the free energy of the glass, and that this decrease is still larger for a component that shows a substantial negative deviation from ideality, such as an alkali oxide. If the chemical potential gradient between glass and corroding solution is a driving force in the rate of dissolution, then simply decreasing the free energy of the glass will always improve its durability. Further study of the relationship between glass complexity and durability would be very valuable: in particular, if complexity generally improves durability, then there is validity to the working premise of the free energy of hydration model, for reasons discussed in Section 5 and in Appendix 6.

4.6.3 Effects of Waste Composition and Waste Loading

Finally, it is appropriate to consider the impact of waste loading on waste glass durability. As noted above, Tovená et al. [181] show that increasing the waste loading of R7T7 glass increases its forward rate of dissolution. This is in contrast to the findings of Clark et al. [184], Rankin and Wicks [185], and Maurer et al. [186] for Savannah River waste streams combined with various SRL frits, where increased concentration of any of three waste streams increased glass durability relative to the frit. The reasons for this appear clear from the discussion thus far. The frit in question is SRL 131, consisting of 57.9 wt % SiO_2 , 17.7 wt% Na_2O , 14.7 wt% B_2O_3 , 5.7 wt% Li_2O , 2 wt% MgO , 1 wt% TiO_2 , and 0.5 wt% each ZrO_2 and La_2O_3 [185]. The $(Li+Na)/B$ ratio of the frit is 2.25, meaning that alkalis are extensively involved in bonding arrangements with NBO. In the Clark et al. and Maurer et al. studies noted above, three waste streams were considered: (1) "high Al"—nearly 50 wt% Al_2O_3 , with most of the balance as MnO_2 (11.3 wt%), Fe_2O_3 (13.8 wt%), and zeolite, an alkali aluminosilicate with an M^+/Al^{3+} ratio of 1:1; (2) "TDS-3A"—47.3 wt% Fe_2O_3 , with the balance being MnO_2 , Al_2O_3 , zeolite, and minor amounts of other cations; (3) "high Fe"—nearly 60 wt% Fe_2O_3 , the balance being zeolite, NiO , and comparatively small amounts of other components. The base frit lies in a region of relatively nondurable glasses when projected onto the isodurs of Adams and Evans [154] (taking all Li_2O to behave as Na_2O), and therefore the presence of anything which forces alkalis into charge-balancing roles will enhance waste glass durability. This is very clearly the case in the waste streams described above: this effect is produced by Al_2O_3 in the high Al waste stream and by a combination of Fe_2O_3 and Al_2O_3 in the TDS-3A and high Fe waste streams. In fact, both studies show that increasing waste loading to as high as 30 wt% substantially improves the durability of the frit. Rankin and Wicks [185] added the TDS-3A waste stream to frit 131 and measured the durabilities of the resulting glasses using 28-day MCC-1 tests in deionized water at 90°C, and 14-day static tests at 90°C using pH-buffered solutions (pH = 3, 7, and 11). The durability measures were normalized mass loss

and normalized element release of a wide spectrum of frit and waste components. Corrosion experiments performed in DI water showed that the durability of the reference frit was improved by waste loading up to a level of 50% waste by mass, though at such high loadings crystallization occurred in the glass on quench or in the melt (see Section 5.1 for the effect of crystallinity on glass durability). In buffers with pH = 7 and pH = 11, increased waste loading also improved durability, though durability decreased with waste loading in the buffer pH = 3. As the authors note, such acidic conditions are highly unlikely in a repository; so, as a practical matter, waste loading improves durability in SRL frits.

It is important to see in this example that it is the combination of frit composition and waste stream composition that determines whether or not waste loading will improve waste glass durability. When a frit is not durable because of very high alkali concentrations, addition of high-valence cations, Al_2O_3 , and Fe_2O_3 will invariably improve durability, but this approach will also leave a waste processor vulnerable in case of a large decrease in these components in the waste stream over time.

4.6.4 Compositional Effects on Long-Term Corrosion

The discussion thus far has focused on the effects of key glass components on the corrosion rate in dilute solutions during to the initial stages of corrosion. Continued corrosion in static or nearly-static environments will produce highly concentrated solutions from which secondary phases may precipitate. These secondary phases may decrease the corrosion rate by settling on the glass surface and inhibiting mass transfer from the glass to solution. They may also increase the corrosion rate by acting as a "sink" for certain glass components in solution, thereby affecting the release of those components from the glass. The phases that form and their influence on the continuing glass corrosion depend on the glass composition, since most of the solute species are derived from the glass. Thus, glass components affect not only the glass structure and dissolution rate but also the identities of secondary phases.

Tests in which secondary phases formed show that the corrosion rate increases upon precipitation of particular phases. Clays are known to form after short exposure times but do not affect the corrosion rate, possibly because the effects of clays on the solution chemistry do not differ significantly from those of the glass itself. Zeolites such as analcime (NaAlSiO_4) are commonly found to accelerate the corrosion rate [14,16,187,188]. Tests with glass compositions that do not support the formation of zeolite, such as the low-aluminum waste glass PNL 76-68 (Appendix 3, Table 1), do not show accelerated corrosion [189]. The French glass R7T7 (SON 68 18 17 L1C2A2Z1 in Appendix 3, Table 1) is likewise not expected to generate secondary phases because of its low aluminum concentration [190]. Since waste glasses generally contain high concentrations of silica and sodium, aluminum appears to be the component that most strongly affects the formation of zeolites.

The effects of secondary phases on the chemistry of the solution has been incorporated into thermodynamic computer models, such as EQ3 [191] and PHREEQE [192]. These models are coupled with corrosion rate models to simulate glass corrosion under a range of conditions. Although the thermodynamically most stable phases can be predicted from a given solution, these are usually not the phases found to form in experiments. As a result, experimentally observed phase assemblages are usually used as input to the models.

The effect of a glass component on the long-term corrosion rate may be very different from its effect on glass dissolution. The role of Al^{3+} is a case in point, as it generally increases durability in the early stages of glass corrosion, but increases the likelihood of the formation of analcime and other secondary phases over the long term, which may in turn increase

the rate of glass corrosion. The effects of key glass components must be understood with regard to all aspects of the corrosion process so that glasses can be designed to provide acceptable long-term immobilization of waste materials.

4.7 Summary of Compositional Dependence of Glass Durability

The experimental studies in this section demonstrate that, for the most part, the components that form the strongest bonds in glasses result in the greatest improvements to glass and waste glass durability, whereas those that form the weakest bonds prove the greatest detriment to glass and waste glass durability. The durability of an alkali silicate glass will generally be improved by adding Al_2O_3 , B_2O_3 , and divalent cation oxides (MO , where $\text{M} = \text{Ca}^{2+}$, Mg^{2+} , Zn^{2+} , etc.), in order of decreasing estimated impact. The mechanism in each case appears to be the sharing of oxygen anions by alkalis and these cations, resulting in stronger cation-anion bonds for both and a strongly coupled response to aqueous attack. Other components that form strong coupled bonding arrangements with alkalis—particularly Zr^{4+} —may also improve glass durability by the same mechanism. Trivalent iron forms bonding arrangements like Al^{3+} and B^{3+} in glasses, resulting in a modest improvement in glass/waste glass durability, whereas Fe^{2+} reduces the durability of a glass.

It was shown that the compositional effects on durability seen in short-term, solution-dominated tests of glasses in simple systems are germane to more complex waste glass compositions as well, though very few studies have been sufficiently methodical in their testing of candidate waste glasses for these effects to be isolated. In particular, adding Al_2O_3 to a waste glass composition generally improves its durability, substitution of $(\text{M}^+\text{Al}^{3+})\text{O}_2$ or $(\text{M}^+\text{B}^{3+})\text{O}_2$ for SiO_2 results in a relatively small change in durability; adding alkaline earth cations to a waste glass composition has a small impact on durability; and adding ZrO_2 may improve durability of waste glasses with alkalis in excess of Al_2O_3 and B_2O_3 . Adding waste components to an alkali-rich frit, which is otherwise not durable, results in a reduced release rate of the frit components to solution, but adding waste to an intrinsically durable frit may increase the release rate of frit components to solution. It is proposed that this occurs because the alkalis and high-valence cations in the waste share the same oxygen, resulting in stronger cation-anion bonds and enhanced response to aqueous attack.

5.0 MODELING THE RELATIONSHIP BETWEEN GLASS COMPOSITION AND DURABILITY

The previous sections have shown that the structure and bonding relationships in a glass are strongly affected by its composition. Various components may either extend the network structure or terminate it, with concomitant impact upon the properties of the glass and its precursor melt. It stands to reason that there must be a relationship between the composition of a waste glass, its structural chemistry, and its resistance to attack by an aqueous solution. Models that seek to quantify the relationship between composition and chemical durability of a glass are the subject of this section. A list of the models to be discussed is shown in Table 1.

The compositional dependence of the durabilities of high-level waste glasses has been assessed by correlating the experimentally determined corrosion rate with waste glass compositions. For the models discussed in this section, the correlations are of the form

$$\log(\text{rate}) = aR + b \quad (7)$$

where the rate is measured experimentally, R is a model-dependent index determined by glass composition, and a and b are constants giving the slope and y-intercept of a linear regression of R against the rate (linear regression is discussed in Appendix 4). The corrosion rate is measured using MCC-1, MCC-3, PCT, and Soxhlet tests, although the dilute conditions maintained in short-term MCC-1 and Soxhlet tests probably provide the best measure of the glass composition effect. The normalized release of a key glass element, such as silicon or boron, after a certain reaction time is usually used as the rate in the correlation.

Application of Eq. 7 to multicomponent borosilicate waste glasses is based on the premise that the energetics of breaking a particular cation-anion bond during glass corrosion are nearly independent of the other types of cation-anions bonds in the glass. Thus, a glass is modeled as a collection of noninteracting units, and its durability follows solely from the aggregate effect of the stability and abundance of each unit. Models discussed in this section differ in how the units are defined and how the stability of a unit is measured. The validity of explicit and implicit assumptions made in the various models is also discussed.

The most extensively documented models are the free energy of hydration (FEH) model, developed at the Savannah River Laboratory [193,194], and the structural bond strength (SBS) model, developed at The Catholic University of America (CUA) Vitreous State Laboratory [195]. In both models, the correlation index R is obtained by summing the products of the mole fractions of each component in a particular basis and a weighting factor. This is written generically as

$$R = \sum_i (c_i X_i) \quad (8)$$

where the summation is over all components i , c_i is a weight factor for component i (referred to below as the composition index), and X_i is the mole fraction of component i . The composition indices in the FEH model are the hydration energies of (assumed) silicate and oxide components, while in the SBS model, these indices are the enthalpies of formation of oxides, adjusted according to empirical rules. The valence oxygen (VO) model [196] and nonbridging oxygen (NBO) model [194] do not employ composition indices, but they still generate a correlation index based on the bulk composition of the waste glass. In the VO model, the relative proportions of cations of different valences and the oxygen associated with them are used as the correlation index, whereas in the NBO model, an estimate of the number of NBO is used as the correlation index. Yet another approach is to regress the weight fractions or mole fractions of a

Table 1. Models Describing the Relationship between Glass Composition and Durability

Model	Section	Summary
Free energy of hydration	5.2	Free energies of hydration ($\Delta_{\text{hyd}}G_i$) for glass components are summed to obtain an estimated $\Delta_{\text{hyd}}G$ for the glass, which is then used as an index to predict durability.
Structural bond strength	5.3	The heats of formation of the constituent oxides are used to estimate the average characteristic bond strength of a glass, and this is used as an index to predict durability.
Valence oxygen	5.4	Glass durability is modeled as a function of the average cation valence of the overall glass.
Nonbridging oxygen	5.5	The amount of connectivity of glass network is estimated and correlated with glass durability.
Pacific Northwest Laboratory statistical model (Composition Variability Studies)	5.6	Durability is correlated directly with the weight fractions of specific oxide components.
Thermodynamic hydration energy reaction model (THERMO)	5.7	Similar to the free energy of hydration model (Section 5.2) but with a completely revised database and a set of empirical, composition-dependent corrections for changes in solution pH during 7-day PCT tests.

set of compositional components against the durability index [197], without regard to the physical or theoretical significance of the result. The composition variation studies (CVS) model [198,199,200] does just this: in its present form, it is a linear model, but nonlinear approaches are under development.

To evaluate the relative merits of various models, it is important to have a consistent, relevant database of glass compositions and test results. For this purpose, we have employed a subset of the nearly 300 glass compositions discussed by Geldart and Kindle [196]. The following criteria were used to eliminate glass compositions not relevant to waste glass formulations from the data set.

1. The sum of oxide weight fractions was constrained to lie in the range of 95 to 103 wt%. The lower limit is set to avoid considering compositions for which a potentially important component is not listed. The upper limit reflects the concern that high totals mean that the concentration of one or more components is exaggerated.
2. Samples for which the SiO_2 concentration was more than 80 mol% (oxide basis) were eliminated. This limit is dictated by the very high temperatures that would be required to process a material with such a high SiO_2 concentration.
3. Samples with P_2O_5 concentrations greater than 1 mol% were eliminated. This criterion is driven by the observation (noted above) that P_2O_5 substantially stabilizes metastable and stable two-liquid fields in silicate glasses, and therefore it has highly nonideal interactions with the glass structure.

4. Samples with concentrations of ThO_2 , UO_2 , ZrO_2 , SrO , PbO , and Cs_2O greater than 2 mol% were eliminated. These limits were dictated mostly by the absence of waste glasses with higher concentrations of any of these oxides (with the possible exception of ZrO_2).
5. Compositions with $\text{M}_2\text{O}/(\text{Al}_2\text{O}_3+\text{Fe}_2\text{O}_3+\text{B}_2\text{O}_3)$ molar ratios less than 0.5 or $\text{M}_2\text{O}/(\text{Fe}_2\text{O}_3+\text{B}_2\text{O}_3)$ molar ratios less than 0.8 were eliminated ($\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Ca}$). This criterion was only applied to compositions containing at least 3 mol% B_2O_3 . It represents an effort to avoid phase-separated compositions, or compositions that are likely to phase-separate on annealing. Note that we have no information about the thermal history of these samples and no knowledge of whether or not they are single phase, and so we have set somewhat conservative limits.

The glasses that met these criteria were divided into four general categories of known durable glasses:

- Glasses containing at least 3 mol% B_2O_3 and Na_2O and at least 1.5 mol% Al_2O_3 . These are referred to *sodium boroaluminosilicates*, and are taken as the compositions most representative of radioactive waste glass compositions. All waste glasses included in the Geldart and Kindle data set fall into this category.
- Glasses containing at least 3 mol% B_2O_3 and alkali oxide, but less than 1 mol% Al_2O_3 . These glasses are referred to as *alkali borosilicates*. One of the early and extensively studied waste glasses, PNL 76-68, falls into this category, but most waste glasses developed since then have higher Al_2O_3 concentrations.
- Glasses containing at least 3 mol% Al_2O_3 and alkali oxides, but less than 1 mol% B_2O_3 . These are referred to as *alkali aluminosilicates*. Most waste glasses contain far higher concentrations of B_2O_3 , but some (particularly the Canadian nepheline syenite waste glass) are essentially pure aluminosilicates. The availability of melters that can economically operate at high temperatures makes such compositions relatively attractive.
- Glasses containing at least 5 mol% CaO and at least 10 mol% alkali oxides, but less than 3 mol% Al_2O_3 or B_2O_3 . These are referred to as *alkali lime silicates*. Nearly all the compositions that fall into this category contain at least 10 mol% Na_2O , which would serve to classify them as soda-lime silicate glasses, the mainstays of the window and container glass industries. These are often highly durable compositions, and as with aluminosilicate glasses, new melter technologies make them potentially attractive candidates for waste disposal, mainly for low-level waste.

A comparatively small number of glass compositions had very high alkali oxide concentrations and very low concentrations of alkaline earth cations, Al_2O_3 , and B_2O_3 . Such compositions may ultimately be of use in low-level waste glasses, but their durabilities were generally too low for consideration as high-level waste glasses, and they were excluded from further analysis. These sorting criteria left 165 glass compositions: 84 sodium boroaluminosilicates; 21 alkali borosilicates; 28 alkali aluminosilicates; and 32 alkali lime silicates. The identities and compositions of these glasses (normalized weight-fractions, oxide basis) are shown in Appendix 5.

The durability criterion used in testing the models was normalized silicon release at the end of a 28-day MCC-1 test; these values ranged from 0.8 to 813 g/m², or over approximately three orders of magnitude. As discussed in Section 2.1, at very high silicon release, the MCC-1 test no longer measures the inherent durability of the glass, but instead the response of the altered glass surface to a concentrated aqueous solution formed from its own corrosion products. In the earliest stages of the corrosion of alkali-bearing glasses, alkalis are preferentially removed from the near-surface volume of the glass, a process referred to as dealkalization. Dealkalization produces a partially hydrated layer that is enriched in less soluble components, particularly silica, relative to the bulk glass. Normalized Si release mainly measures the rate of breakdown of this layer at the layer/water interface, but preferential removal of the alkalis well below the interface is likely to continue at a higher rate. Therefore, normalized releases of alkalis or boron (which is also preferentially leached) are better measures of the mass of glass that has reacted with water. These data were not provided in the Geldart and Kindle database. Use of normalized Si release may introduce some scatter in the correlations because it is not as good a measure of the rate of glass reaction with water. It has the advantage that Si is necessarily a constituent in all silicate glasses, whereas the same cannot be said of boron or alkalis.

The FEH, SBS, NBO, and VO models have been evaluated elsewhere. The report by Geldart and Kindle [196], from which the data set used in the present review was obtained, compared the 28-day normalized silicon release at 90°C with SA/V of 10 m⁻¹ for 295 glass compositions with predicted values obtained using the FEH, VO, and NBO models. Because that study included an evaluation of each of the models in predicting the performance of actual waste glass compositions, this application is not emphasized in the present review. The correlations between the models and log(LRS_i) obtained by Geldart and Kindle are similar to those obtained here for the compositions listed in Appendix 5.

A similar study examining the correlation of a common data set of dissolution results with various glass composition-durability correlation models was reported by Abrajano et al. [197]. The FEH model, the SBS model, the NBO model, and the VO model were regressed against normalized silicon release measurements obtained from 28-day MCC-1 tests of over 300 different glass compositions, including waste glasses, natural glasses, and historical glasses. The goodness of fit for each correlation was assessed by comparing the correlation coefficients. The data were also fitted to a multiple linear regression equation of the glass compositions, which was found to have the best correlation with the durability measure, and, of the models, the FEH model came closest to reproducing the quality of this correlation. It was concluded that the glass composition/durability correlations, particularly the FEH model, did an excellent job of correlating a large data set of MCC-1 test results and glass compositions. Consideration of narrow compositional ranges or nonlinear relationships were proposed as alternative methods of treating the problem [197].

5.1 Restrictions on the Applicability of Linear Correlative Models

The models discussed in Sections 5.2 through 5.6 assume that the material in question is a homogeneous, crystal-free glass. The presence of crystals or a second glass phase can have unpredictable effects on measured release rates of glass components. The models discussed in Sections 5.2 through 5.6 are not capable of identifying which compositions are likely to form second phases (a linear correlation between a compositional parameter and a tendency to phase separate is proposed in the thermodynamic hydration energy reaction model, or THERMO, discussed in Section 5.7). Furthermore, within the set of appropriate glass compositions, the predictions of the models only apply to the normalized release rates measured in static tests of fixed duration, a single point on the corrosion path shown in Fig. 1. A single test of fixed duration is a tool for verifying product consistency but cannot be regarded as an accurate

measure of the relative durabilities of glasses. The effects of formation of a second phase on measured release rates is briefly outlined in this section, followed by the significance of durability rankings as obtained from application of the models.

Immiscibility usually produces two vitreous phases (though a larger number is not precluded), one of which serves as a matrix to contain the other. The precise morphology and the relative durability of the phases determines the durability of the phase-separated material. The morphology is difficult to control when one has very precise control over the composition and thermal history of a material and is probably impossible to control for vitreous waste forms. The phase-separation scenario of greatest concern is when there are extensive interconnections between pockets of a low-durability phase. This situation can result in bulk durability comparable to that of the least-durable phase. Some glass components could decrease elemental release rates in some compositions, but induce phase separation (and possibly increase release rates) in others. As bulk composition approaches the two-phase region, one expects a smooth variation in bulk properties, but after the boundary is crossed the properties abruptly change, becoming not only a function of composition, but of the time-temperature path followed by the composition. The complexity of this problem argues in favor of confining linear correlation models to single-phase glasses and avoiding wherever possible those compositions that fall near the boundaries of metastable two-liquid fields. In borosilicate glasses, this is generally achieved by keeping the ratios of alkalis to boron well in excess of unity.

The condition that the glass be free of crystals means that quench crystals did not appear after a glass was poured and no crystals coexisted with the liquid in the melter. Accommodation of a significant fraction of particular glass components in crystals changes the true bulk composition of the glass matrix, leading to errors in the predicted performance of the bulk composition. The waste glass production is likely to result in formation of quench crystals, which result when compositions at high waste loadings are poured into canisters. High waste loadings push the composition close to the liquidus (the surface in temperature-composition space at which crystals first appear), and quench crystal growth is favored as the liquid passes metastably through the liquidus during prolonged cooling in a canister. The morphologies of quench crystals tend to be "feathery," with many branches radiating out and away from one another. The glass around quench crystals becomes depleted in whatever components are present in the crystal, and the diffusion gradients that result are frozen in place at or below the glass transition. If the crystal components improved the durability of the glass, then the glass around the quench crystals will be less durable than the bulk glass. The high surface area of quench crystals can potentially result in high release rates for glass components. On the other hand, the crystals themselves are very often more durable than the bulk glass. Neither effect can be described by a linear correlation model.

The role that crystals play in affecting bulk durability could be described by a linear model if the model could also predict the location of the isothermal liquidus as a function of composition. Liquidus surfaces cannot be accurately described by linear correlation models, however, except over very limited compositional ranges in very particular systems. This is quite clearly seen by tracing any isothermal section in a simple binary or ternary system. The topologies of liquidus surfaces in multicomponent systems are very much more complex. Furthermore, particular components may show highly nonlinear changes in solubility as a function of composition at fixed temperature: the saturation surface of TiO_2 in $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ liquids discussed in Section 3.3 (Fig. 5) is a good example. In more complex systems, the interdependencies between different components are likely to be much less clear, resulting in a very complex liquidus topography. As with immiscibility, if a homogeneous, single-phase glass is desired, the best strategy is to remain as far from near-liquidus compositions as possible. Broadly speaking, this is best accomplished by using high concentrations of alkalis relative to Fe_2O_3 , Al_2O_3 , and B_2O_3 , much as is true for avoiding immiscibility.

These considerations show that linear correlation models should not be expected to describe the behavior of systems that have undergone a phase transition, but more importantly they highlight the fact that linear correlation models must be applied only to a relatively circumspect range of glass compositions, i.e., those with little tendency to phase separate or to nucleate crystalline phases. This highlights a limitation of the use of linear correlation models during production in a vitrification facility: they do not predict untoward behavior for compositions that do, in fact, produce two or more vitreous or crystalline phases. While empirical rules-of-thumb can be developed to avoid such compositions in production (e.g., the THERMO model, Section 5.7), the time-temperature path and composition dependence of phase space is too complex for a linear model, and the rules-of-thumb must be regarded as general guidelines.

A final point concerns the relationship between predicted performance of a composition in a static test of fixed duration and long-term durability. In fact, there is no necessary correlation. As noted in Section 2.0, not all glasses enter the same stage of corrosion at the same time in a static test of fixed duration. As shown in Fig. 1, the rate of release of any component follows a complex and decidedly nonlinear function in time, and the rate of approach to any point on this surface will be more or less attenuated by a combination of the composition of the glass, the composition of the solution, the temperature, and the presence or absence of crystalline phases. Clearly a material that disintegrates rapidly in a short-term leach test is unlikely to be considered a suitable waste form; however, low release rates in a short-term test may mean very little if, over time, secondary crystalline phases form and control the rate of glass corrosion thereafter. The inherent resistance of a glass composition to aqueous attack is best monitored in solution-dominated tests, ideally Soxhlet or flow-through tests, though short-term MCC-1 tests are appropriate for durable glass compositions. At the termination of solution-dominated tests, the corrosion path is still in the steep, nearly linear stage of the initial reaction of the glass with water. In a long-term MCC-1 test, or PCT or MCC-3 tests of any duration, the buildup of corrosion products in solution dominates the rate of glass corrosion, and therefore glass composition is important mainly in its integrated impact on solution composition. To accurately compare one glass with another in glass-dominated tests requires that the tests be performed for a period germane to each of the compositions in question. It might be a valid test of linear correlation models to examine a set of glasses with comparable release rates of various components, as these will approach solution saturation at approximately the same rate. For a more general range of compositions, a linear correlation might still be found if the range of release rates is great enough, but it is unlikely to accurately reflect a real functional dependence.

To summarize, use of the linear correlation models discussed below requires that glasses be homogeneous, single-phase, and crystal-free. The correlations obtained using the models provide different information depending on the tests used to generate the data. In the best case, they can predict performance at a single point on the corrosion path of glass, though when the results are correlated with release rates obtained from glass-dominated tests, it is clear where this point lies. At the Defense Waste Processing Facility, product consistency will be measured with 7-day PCT A tests, and therefore models to verify consistency will be based on glass-dominated test results. In this context, a good correlation between a model and cation release rates might be suitable for process control, but validation that a product performs adequately in a 7-day PCT A test says very little about its long-term durability. Under these circumstances, a perfect correlation between model and experiment does not guarantee good long-term durability. For the most part, we will avoid references to "durability" and refer instead to high- or low-mass-loss glasses, leaving implicit the understanding that this speaks only to the results obtained in a 28-day MCC-1 test.

5.2 Free Energy of Hydration Model

One of the best known models relating glass composition to durability is the FEH model. It was derived from concepts originally developed by Paul [201] for simple glasses and later extended to nuclear waste glasses by Plodinec and Jantzen [193,194,202-207]. The original durability measure was normalized silicon loss in 28-day MCC-1 tests performed at 90°C [193], but subsequent reports have indicated that normalized boron losses suffice as well [e.g., 206]. (Normalized boron or alkali release is a better measure of the mass of glass that has reacted with water, for reasons discussed in Section 5.) The primary purpose of the FEH model is to provide information for the development of durable glass formulations, but it has also been used to assess the long-term performance of waste glass [193,194,202-205,207].

5.2.1 Formalism

The FEH model describes the corrosion of a glass as a sum of reactions of simple silicate and oxide components. The model provides a formalism for estimating the cumulative free energy of the hydration reactions of these components, which is used as an index against which glass durability is measured. A free energy of hydration, $\Delta_{\text{hyd}}G_i$, for each component C_i is defined as the free energy of the reaction

where $P_1, P_2, \dots P_n$ are products of the reaction. The composition-weighted sum of $\Delta_{\text{hyd}}G_i$ is taken as the estimated free energy of hydration of the glass, $\Delta_{\text{FEH}}G$:

$$\Delta_{\text{FEH}}G = \sum_i (X_i \Delta_{\text{hyd}}G_i) \quad (10)$$

where X_i is the mole fraction of the i th component.

The value of $\Delta_{\text{FEH}}G$ depends critically upon the choice of components for expressing the glass composition. The recommended components for use in the FEH model calculations are crystalline oxides (cations with valences of +3 or greater) and silicates (+1 and +2 cations and Zr^{4+}), and recommended $\Delta_{\text{hyd}}G_i$ values are shown in Table 2. The silicates have been referred to as "orthosilicates," but with the exception of $ZrSiO_4$ they are, in fact, metasilicates, consisting of chains or rings of $(SiO_3)_n$ species. Silicon oxide is allocated to each silicate component, with the balance being retained as an SiO_2 component. A hazard of using metasilicate components is that their relatively high SiO_2 concentrations occasionally result in a negative concentration for the SiO_2 component [196]; nevertheless, they reflect the chemical certainty that electropositive cations react primarily with the silicate network and secondarily with other components.

Each component is assumed to react with water to form one or more hydrated species, in some cases solvated atoms or molecules (e.g., Na^+) and in others crystalline phases [e.g., $Al(OH)_3$]. Calculation of $\Delta_{\text{FEH}}G$ was amended for instances in which stable hydration products were observed experimentally that were not accounted for in the list shown in Table 2 [208]. If $\Delta_{\text{hyd}}G_i$ is more negative than $\Delta_{\text{hyd}}G_i$ for the aqueous ion, this value should be used in Eq. 10. An example is the three alternative products for distribution of the Al_2O_3 component of the glass (Table 2). Of course, knowing which reaction to use requires detailed knowledge of the test results, which in turn effectively obviates the need for the model (i.e., if a test must be performed to use the model, then the model does not have good predictive capability). For the

Table 2. Calculated Free Energies of Hydration for Glass Components [after 194, 206]

Component	Hydrated Species	$\Delta_{\text{hyd}}G_i$, kcal/mol
Cs_2SiO_3	$\text{Cs}^+ + \text{H}_2\text{SiO}_3$	-46.82
K_2SiO_3	$\text{K}^+ + \text{H}_2\text{SiO}_3$	-41.74
Na_2SiO_3	$\text{Na}^+ + \text{H}_2\text{SiO}_3$	-28.82
Li_2SiO_3	$\text{Li}^+ + \text{H}_2\text{SiO}_3$	-22.74
BaSiO_3	$\text{Ba}^{2+} + \text{H}_2\text{SiO}_3$	-30.57
SrSiO_3	$\text{Sr}^{2+} + \text{H}_2\text{SiO}_3$	-24.40
CaSiO_3	$\text{Ca}^{2+} + \text{H}_2\text{SiO}_3$	-16.12
MgSiO_3	$\text{Mg}^{2+} + \text{H}_2\text{SiO}_3$	-13.89
MnSiO_3	$\text{Mn}^{2+} + \text{H}_2\text{SiO}_3$	-14.87
FeSiO_3	$\text{Fe}^{2+} + \text{H}_2\text{SiO}_3$	-14.61
NiSiO_3	$\text{Ni}^{2+} + \text{H}_2\text{SiO}_3$	-14.35
B_2O_3	H_3BO_3	-9.93
Al_2O_3	$\text{Al}(\text{OH})_3$	-7.73
Al_2O_3	$\text{AlO}(\text{OH})$	-1.63
Al_2O_3	$\text{Al}(\text{OH})_{3(\text{am})}$	+3.04
Fe_2O_3	$\text{Fe}(\text{OH})_3$	+15.50
SiO_2	H_2SiO_3	+5.59
TiO_2	$\text{TiO}(\text{OH})_2$	+15.99
UO_2	$\text{U}(\text{OH})_4$	+8.38
ZrSiO_4	$\text{ZrO}(\text{OH})^+ + \text{H}_2\text{SiO}_3$	+45.10

purposes of this evaluation, all three reactions for Al_2O_3 were tried in correlations against the entire database. The best correlations for the entire database and for all subsets were obtained by assuming $\text{Al}_2\text{O}_3 + 3/2 \text{H}_2\text{O} \rightarrow \text{Al}(\text{OH})_{3(\text{am})}$, where the subscript (am) refers to an amorphous Al-rich phase. This reaction is assumed in what follows.

There are two published methods for determining the mole fractions used in Eq. 10. The steps used by Plodinec and Jantzen [193] to calculate $\Delta_{\text{FEH}}G$ are as follows:

1. Express the glass composition in terms of oxides.
2. Compute the number of moles of each oxide.
3. Normalize the bulk composition expressed as oxides to one mole.
4. Convert oxides to the components shown in Table 2, adjusting the SiO_2 concentration to accommodate the silicate components.

5. Multiply the number of moles of each component by $\Delta_{\text{hyd}}G_i$ for each component, and sum over all components to obtain $\Delta_{\text{FEH}}G$.

An alternative method for calculating $\Delta_{\text{FEH}}G$ advocated by Geldart and Kindle [196] is as follows:

1. Express glass composition in terms of oxides.
2. Convert the oxides to the components listed in Table 2.
3. Compute the number of moles of each component.
4. Normalize the bulk composition expressed as components to one mole.
5. Multiply each the number of moles of each component by $\Delta_{\text{hyd}}G_i$ for each component, and sum over all components to obtain $\Delta_{\text{FEH}}G$.

The difference between the two methods is the normalization step. Using the method of Plodinec and Jantzen results in a value $\Delta_{\text{FEH}}G$ that is normalized to one mole of oxides (for a normalization constant on the order of 1.4), whereas using the method of Geldart and Kindle results in a value of $\Delta_{\text{FEH}}G$ that is normalized to a mole of silicate and oxide components (for a normalization constant on the order of 1.2). The ratio of the normalization constants obtained by these two methods varies with composition, particularly when the concentration of silicate components is relatively high, as this greatly reduces the contribution of SiO_2 to the total number of moles of components. These differences mean that the absolute value of $\Delta_{\text{FEH}}G$ is generally larger when using the Geldart and Kindle approach than when using the Plodinec and Jantzen method because the normalization constant is smaller [196].

Since each glass composition has a unique normalization constant, there is no simple relationship between the values for $\Delta_{\text{FEH}}G$ obtained by these two methods. We note that the mole fractions used to calculate $\Delta_{\text{FEH}}G$ in step 5 of the Plodinec and Jantzen method do not sum to 1.0, and in fact these values represent the number of moles of (silicate or oxide) hydration reaction components per mole of simple oxide components. It is a mix of two different bases for representing the glass, namely the oxide basis and the silicate/oxide basis. The different normalization steps also mean that different quantities of glass are considered in obtaining $\Delta_{\text{FEH}}G$; as a result, any correlations obtained between these alternative values of $\Delta_{\text{FEH}}G$ and corrosion rates will be based on different masses of glass, different numbers of atoms, and different numbers of bonds. While the correlations are empirical, it is unfortunate that the basis set for representing the glass does not have a clearer theoretical foundation. The values calculated by the method of Plodinec and Jantzen have units of energy per 1 mole total oxides, while the values calculated by the method of Geldart and Kindle have units of energy per 1 mole of silicate and oxide components. The former is consistent with the general representation of glass compositions, while the latter is consistent with the definition of a mole fraction and with Eq. 10. The method advocated by Plodinec et al. [193] has the merit that $\Delta_{\text{FEH}}G$ is slightly better correlated with glass durability measures. (However, as discussed below, by including an ideal mixing term in the formalism advocated by Geldart and Kindle, one can obtain a slightly better correlation between composition and durability than is obtained using the Plodinec and Jantzen formalism without an ideal mixing term.) Since the FEH model is intended for use during processing at the DWPF, for which the formalism of Plodinec and Jantzen will be used, subsequent discussions in this critical review will focus on this method of calculation.

Plodinec et al. [193] reported that the corrosion rates of some glasses used in their correlation were affected by the high solution pH values attained during 28-day MCC-1 tests. The correlation was adjusted to isolate the glass composition effects from the solution pH effect. This can be done by either subtracting the amount of dissociated silicon or boron in solution from the totals, or, as implemented by these authors, by adjusting $\Delta_{FEH}G$ of compositions that produced high solution pH. The pH correction to $\Delta_{FEH}G$ accounts for dissociation of $Si(OH)_4$ and $B(OH)_3$ at high (> 9) pH. The $\Delta_{FEH}G$ values for glasses containing SiO_2 are adjusted by adding the term

$$\Delta(\Delta_{hyd}G_{Si}) = -1.364 \log \left(1 + \frac{10^{-10}}{10^{-pH}} + \frac{10^{-21.994}}{10^{-2pH}} \right) \quad (11)$$

An additional term is added for glasses containing B_2O_3 :

$$\Delta(\Delta_{hyd}G_B) = -1.364 \log \left(1 + \frac{10^{-9.18}}{10^{-pH}} + \frac{10^{-21.89}}{10^{-2pH}} + \frac{10^{-35.69}}{10^{-3pH}} \right) \quad (12)$$

These equations were derived from the known dissociation constants of silicic and boric acid at high pH conditions [208]. The correction terms make $\Delta_{FEH}G$ more negative, and therefore they have the effect of "destabilizing" the glass relative to similar compositions with lower final pH. An extension of this approach was implemented by Tovenet et al. [181] in applying the FEH model to compositional variations of R7T7 glass: correction terms appear to have been computed for all glass components. The significance of accounting for each component varies with the component's mole fraction in the glass, its pK_a values, and the pH attained in the test.

The pH correction as employed in the FEH model raises several issues. First, it is not clear that terms accounting for the dissociation of components other than one used as the corrosion index should be used to adjust the composition index, because it appears to over-correct the glass corrosion. Second, the rate of glass corrosion has been shown to increase directly with pH for $pH > 6$ [209,210]. This behavior is not wholly accounted for in the dissociation of silicon and boron in the correction terms because this dissociation is negligible at pH values below pK_{a1} . Third, solution pH is usually measured at room temperature, whereas the corrosion rate is measured at $90^\circ C$ or higher. It is uncertain how the room-temperature pK_a values used in the correction terms affect the accuracy of the correction. Finally, use of the correction terms requires that the glass be tested prior to correlating its composition and durability. This detracts from use of the FEH model as a predictive tool, even though predicting final waste glass durabilities is one of its intended purposes. It may be possible to predict pH for experiments of fixed duration from glass composition, in which case this limitation is less important. Fortunately, the pH corrections are only large for nondurable glasses that were included in the Savannah River Laboratory database primarily to fix the correlation, and these glasses are ignored in the following discussion.

5.2.2 Testing the FEH Model Using the Reference Database

The correlation in the FEH model is obtained by linear regression of $\Delta_{FEH}G$ against the durability measure $\log(LR_i)$, where i has historically been Si, B, or Na; $\Delta_{FEH}G$ has been determined for all compositions listed in Appendix 5. The correlations between $\Delta_{FEH}G$ and $\log(LRS_i)$ are shown in Table 3 for the entire database and for the various subsets discussed above. The best fit is obtained for the sodium boroaluminosilicate subset ($R = 0.73$), and the worst fit for alkali borosilicates ($R = 0.11$), where the model is essentially uncorrelated with LR_{Si} . For this reason, alkali borosilicate glasses are excluded from the remainder of this analysis.

Table 3. Free Energy of Hydration Model: Regression Coefficients and Statistics for Linear Correlation between $\Delta_{FEH}G$ (Independent) and $\log(LR_{Si})$ (Dependent)

	No. of Observations	Correlation Coefficient	Standard Error	Intercept	Slope
All Glasses	165	0.593	0.405	0.712	-0.1067
All Glasses with $LR_{Si} \leq 28 \text{ g/m}^2$	120	0.644	0.205	0.719	-0.070
Sodium Boroaluminosilicate Glasses	83	0.733	0.157	0.689	-0.0901
Sodium Boroaluminosilicate Glasses with $LR_{Si} \leq 28 \text{ g/m}^2$	79	0.511	0.128	0.856	-0.0536
Alkali Borosilicate Glasses	21	0.109	0.489	1.702	-0.0259
Alkali Lime Silicate Glasses	32	0.672	0.334	0.939	-0.0877
Alkali Aluminosilicate Glasses	28	0.636	0.564	0.540	-0.1174

The intercept of the correlation varies by approximately a factor of two from one subset to another, from 0.54 for alkali aluminosilicate glasses to 0.94 for alkali lime silicate glasses. The slope of the line also shows approximately a 25% variation from one subset to another.

The standard errors of the correlations provide additional information about the goodness of fit (see Appendix 4). The standard errors for the entire data set, alkali lime silicate glasses, and aluminosilicate glasses are between 0.3 and 0.5, meaning that approximately 67% of predicted values lie within approximately 0.4 log units of the measured values. This discrepancy is relatively unimportant for low-mass-loss glasses, but for intermediate- and high-mass-loss glasses the discrepancy between the predicted and measured value of LR_{Si} can be very large. Figure 7 shows predicted LR_{Si} plotted against measured LR_{Si} for the entire data set as obtained from the correlation shown in Table 3. A large number of points are clustered near a mass loss of 10-15 g/m², and because of this, the correlation is heavily weighted towards these compositions. As a result, the mismatch between the measured and predicted release rate is greatest for low-mass-loss and high-mass-loss glasses. Many of these glasses are sodium boroaluminosilicates, and Fig. 8 shows the correlation between predicted and measured mass losses for this subset. The accuracy of predicted mass losses is noticeably better than for the database taken as a whole, with 67% of the predicted values lying within 0.13 log units of the measured mass losses.

The clustering of points in Figs. 7 and 8 suggests that extreme high and low values may be affecting the correlation. The high-mass-loss values are particularly suspect because the solutions are probably largely glass-dominated in these tests. As a test, correlations were also obtained for the database taken as a whole and for sodium boroaluminosilicate glasses with LR_{Si} no greater than 28 g/m². The correlation statistics are shown in Table 3. The correlation coefficient and standard error for low-mass-loss glasses taken from the entire

Fig. 7. Measured Release Rates vs. Release Rates Predicted by the Free Energy of Hydration Model for All Glass Compositions in the Reference Database (Appendix 5). The line indicates a perfect correlation.

database improve considerably ($R = 0.64$, $\sigma_x = 0.2$), but the correlation for low-mass-loss sodium borosilicate glasses is much worse ($R = 0.51$, $\sigma_x = 0.13$). This indicates that the model is fairly insensitive to compositional dependence of elemental release rates for low-mass-loss glasses in solution-dominated experiments.

Fig. 8. Measured Release Rates vs. Release Rates Predicted by the Free Energy of Hydration Model for Sodium Boroaluminosilicate Glass Compositions (Appendix 5). The line indicates a perfect correlation.

To summarize, the slopes and intercepts vary from one composition subgroup to another, and all subgroup regression coefficients differ from that of the entire database. A relatively strong correlation is obtained for alkali boroaluminosilicate glasses when high-mass-loss glasses are included, but the model is relatively insensitive to compositional dependence of normalized release rates for more durable glasses. The model predictions are uncorrelated with measured release rates for alkali borosilicate glasses. In most subsets, the goodness of fit is strongly affected by inclusion of high-mass-loss compositions, which pin down an extreme end of the line.

5.2.3 Possible Improvements

The FEH model makes four important implicit assumptions:

- The choice of thermodynamic components is adequate;
- The free energies of mixing of the components in the glass or solution can be neglected;
- The free energies of vitrification of the crystalline components used to estimate $\Delta_{\text{hyd}}G$ for the glass can be neglected; and
- Mechanistically, the ways in which any set of components react with water are identical to the ways in which mixed, vitrified components in waste glasses react with water.

The first assumption follows from the observation that the free energy of hydration of a glass estimated using the set of components listed in Table 2 differs from the value obtained using a different set of components. The second assumption is implicit in Eq. 10 in that mixing terms in the glass and aqueous solution are not included. As shown in Appendix 6, the free energies of mixing of ideal components in the glass are of the same order of magnitude as $\Delta_{\text{FEH}}G$, and including mixing might improve the correlation or disprove the model. These two assumptions can be addressed in a meaningful way given the present understanding of glass chemistry and structure. The third assumption follows from the use free energies of hydration of crystalline components and is a necessary consequence of a lack of relevant thermodynamic data. The fourth assumption can be stated differently in the form of an example: does the Na_2SiO_3 component in a soda-lime silicate glass behave differently than it would in Na_2SiO_3 glass itself? It is doubtful whether this can be proved or disproved, but it illustrates the wide gulf between a thermodynamic representation of the corrosion process and the actual reactions that govern the corrosion process.

The thermodynamic relevance of glass components has been addressed in part by Ellison and Navrotsky [211], who point out that enthalpies of mixing between pure SiO_2 and components of the form MTSiO_4 ($M = \text{Na}^+, \text{K}^+$; $T = \text{B}^{3+}, \text{Al}^{3+}$, and possibly Fe^{3+}) are very nearly zero, suggesting near-ideal mixing of these components in silicate liquids. In general, the enthalpies of mixing of electropositive cation oxides with SiO_2 are most exothermic at or near the true orthosilicate composition, for which the O:Si ratio is nominally 4:1. This suggests two possible improvements to the model: (1) treat Al^{3+} , Fe^{3+} , and B^{3+} as though they are components in tectosilicates, rather than as oxides; and (2) convert all silicate components to true orthosilicates, rather than the metasilicates employed in the present model. The first suggestion has been tested in part in studies by Feng and Barkatt [212] and Macedo et al. [213], who treated aluminum as though it were part of an albite species ($\text{NaAlSi}_3\text{O}_8$). They obtained substantially improved correlations between $\Delta_{\text{FEH}}G$ and durability for West Valley composition nuclear waste glasses. These components also address the known failure of any linear model of silicate and oxide components to correctly predict durabilities in such simple systems as $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$, where durability is a highly nonlinear function of the Na:B ratio. The specific failure of the FEH model for glass durabilities in this system has been discussed by Bunker [214].

Even if "correct" vitreous components were used in Eq. 10, $\Delta_{\text{FEH}}G$ would not represent the true free energy of hydration of a glass, but rather the free energy change of the hydration reactions of a set of isolated components. The true free energy of hydration would

account for the free energy of mixing of the components in the glass phase and, if dilute conditions were not maintained during the reaction, the free energy of mixing of corrosion products in the aqueous solution. The issue of the thermodynamic mixing terms is addressed in part by incorporating an ideal mixing term to account for the chemical complexities of waste glasses compared to simple crystals. To do this, it is necessary to adopt Geldart and Kindle's formalism for computing $\Delta_{FEH}G$, as true mole-fractions are needed in the calculation. A formal derivation of thermodynamic mixing terms is discussed in Appendix 6. A test of this approach against the reference data set yields a correlation slightly better than that obtained for the Plodinec-Jantzen formalism. A still better approximation can be obtained by recasting the components listed in Table 2 in terms of equal numbers of oxygen atoms. This is because oxygen atoms tend to account for the largest part of the molar volume of oxide phases, so volumes of mixing are reduced by considering equal-oxygen components. By reducing the importance of these terms, one obtains a more valid representation of $\Delta_{FEH}G$ and a more valid test of the (assumed) correlation between $\Delta_{FEH}G$ and the rate of glass dissolution.

The reactions listed in Table 3 are deficient in two other respects. First, $\Delta_{FEH}G$ for many glasses turn out to be positive, meaning that energy must be added to the system for the reactions to proceed at all. This implies that many glasses should not react with water, whereas all glass in the database do, in fact, react with water. This may be due largely to the energies assigned for the reactions, which for the most part appear to have been taken directly from the values recommended by Paul [201]. Values more consistent with standard compilations might improve this situation. Second, most of the reactions involve H^+ as a reactant, but as dealcalization early in the course of corrosion of alkali-rich glasses quickly produces a solution pH greater than 7.0, very little H^+ would be available to react. Correcting this would require new reactions involve H_2O or OH^- . It must be noted that these concerns have been addressed in large part by an extensively revised version of the FEH model, the Thermodynamic Hydration Energy Reaction Model, or THERMO (see Section 5.7).

Another departure from strict thermodynamic significance is that most of the components are crystalline (with the possible exception of SiO_2), whereas the appropriate standard state for waste glasses is really vitreous. The product of the hydration reaction is independent of the isotope of the reactant material, so the free energy of hydration of each of the components listed in Table 2 ($\Delta_{FEH}G$) differs from the value for the more relevant vitreous standard state ($\Delta_{hyd}G_{vit}$) by the free energy of vitrification of the crystal ($\Delta_{vit}G_{xtal}$):

$$\Delta_{vit}G_{xtal} = \Delta_f G_{vit} - \Delta_f G_{xtal} \quad (13)$$

Free energies of vitrification are on the order of 1-3 kcal/mol for good glass formers, such as SiO_2 , and higher for poor glass formers, such as alkali oxides. Thus, the vitrification term in Eq. 13 can be of the same order of magnitude as the hydration term in Eq. 10. Properly addressing this concern requires experimental data for the reference components in the vitreous state.

A final improvement—less in the model than in its application—is to restrict the range of compositions to those whose mass losses over time closely bracket the range of interest. Even if the FEH model fails to give an accurate estimate of the durability of a glass that lies outside this range, it would nevertheless correctly predict that its durability was unsuitable for use as a waste glass. The range of glass durabilities that have been used to demonstrate the utility of the FEH model is too broad to be of use for predicting waste glass durabilities, and is not necessary to demonstrate the applicability of the approach.

The question of the relationship between the reaction mechanism of the components and the mixed glass has one significant wrinkle: the formation of a "leached" layer

on the surface of the glass effectively means that the solution is attempting to equilibrate not with the bulk glass but with the surface layer, whatever its composition might be. When glasses form very thin surface layers and/or the layers have little impact on the rate of glass dissolution, as is often the case, then this issue is of little consequence. When a thick, relatively nonreactive layer inhibits dissolution of the bulk glass, however, the effective free energy of hydration is not that of the bulk glass but of some average of the glass and the leached layer. There is as yet no way to predict whether a glass will form this type of layer, and this probably limits the generality of the FEH model, regardless of the relative successes obtained by incorporating the changes suggested above. Examples of glasses that rapidly form protective, nonreactive layers include lead silicate glasses, or glasses reacted in Mg-rich brines.

5.2.4 Predictive Utility of the FEH Model

As implemented in this study, FEH model can provide an estimate of which alkali boroaluminosilicate glasses are likely to have very high mass losses, but it does a poorer job of predicting LR_{Si} for glasses with low mass loss (more durable glasses). For these more durable materials, the $2\sigma_x$ confidence interval for a predicted LR_{Si} of 10 g/m^2 is approximately $\pm 8 \text{ g/m}^2$. Provided that predicted mass losses are well below those of the reference EA glass, the FEH model may provide adequate predictive capability for process control at a vitrification facility, but it would be necessary to take this uncertainty into account and test all marginal compositions. The FEH model as described has no capability for predicting crystallization or phase separation, and therefore may give erroneous (low) estimates of mass loss rates if either process occurs. The predictions of the FEH model are essentially uncorrelated with measured LR_{Si} for alkali borosilicate glasses, and therefore compositions that fit this description should be avoided during waste glass production. Because the FEH correlations are obtained against short-term tests, and, as discussed previously, there is no necessary correlation between the predicted durability rankings of the glasses and their rankings in long-term accelerated tests, the model should not be used to rank the long-term durability of glasses.

5.3 The Structural Bond Strength Model

The SBS model, developed at The Catholic University of America, is based on structural considerations and has been proposed to describe the chemical durability and viscosity of nuclear waste glasses [215,216,218]. It was developed to assist in producing durable, processible glasses for the West Valley Demonstration Project. It has long been known that a correlation exists between glass durability and viscosity at melter temperatures. Thus, the goal of this program was to develop a correlation between glass composition, durability, and viscosity that would allow West Valley to develop an optimum glass composition that meets its vitrification needs and specifications.

5.3.1 Formalism

The SBS model assumes that the fundamental mechanism controlling the dissolution of a glass is the breaking of network bonds, such as Si-O-Si bonds. Therefore, if there were a reliable way to measure the average bond strength of the "network" structure of a glass, the bond strength could serve as an index against which to measure glass durability. A bond strength for each component i , V_i , is calculated from its enthalpy of formation, $\Delta_f H_i$. The contribution of $\Delta_f H_i$ to the estimated bond strength of the glass is determined by using a set of empirical rules derived from a model of glass structure proposed by Sun [217]. Sun's model distinguishes between cations that are assumed to form the network structure, cations that are assumed to break down the network structure, and cations whose roles are intermediate between the two extremes. The V_i values thus obtained are weighted by the mole fraction of the oxide and summed together to obtain a correlation index, V_{tot} , for the glass.

In the model as described by Feng and Barkatt [215], the first step is separating the elements into network formers (SiO_2 , Al_2O_3 , and ZrO_2), network modifiers (alkali oxides), and intermediates, which are basically all other components. Network formers are assigned a bond strength of $2\Delta_f H_i$ and intermediate cations a bond strength of $\Delta_f H_i$. Though B_2O_3 is an excellent glass-forming oxide, boron is considered an intermediate cation because of the ease with which it is extracted from borosilicate glasses. The bond strength of network breakers is modified by E_{net} , taken to represent the average strength of a network bond, and calculated assuming coordination numbers of 4, 4, and 6 for Si, Al, and Zr, respectively:

$$E_{\text{net}} = \frac{\sum(X_i V_i)}{\sum(X_i v_i)} \quad (14)$$

where X_i is the mole fraction of component i , V_i is its bond strength, and v_i is its coordination number. The value E_{net} is then used to adjust the bond strength contributions of the network breakers, the alkali oxides. In the published descriptions of the SBS model the bond strength of network breakers is $\Delta_f H_i - E_{\text{net}}$. The quantity E_{net} , however, is intended to account for the reduction in the average bond strength produced by each NBO produced by a network-breaker cation, rather than by each network breaker oxide, and therefore a more logical estimate of the network breaker bond strength is $\Delta_f H_i - 2E_{\text{net}}$. This treatment has been determined to yield substantially improved correlations between average bond strength and durability measures compared to the original formulation, and it is recommended that the original model of Feng and Barkatt [215], $\Delta_f H_i - E_{\text{net}}$, be abandoned. In what follows, the average bond strength of a network breaker is always taken to be $\Delta_f H_i - 2E_{\text{net}}$. The average structural bond strength of a glass is simply the composition-weighted sum of its constituent oxides:

$$V_{\text{tot}} = \sum V_i \quad (15)$$

Values of V_{tot} are regressed against $\log(\text{LR}_i)$ values in an equation of the form

$$\text{rate} = aV_{\text{tot}} + b \quad (16)$$

obtained in short-term hydrothermal leach tests, such as MCC-1, MCC-3, or PCT tests, using Eq. 7.

5.3.2 Testing the SBS Model Using the Reference Database

Values of V_{tot} have been calculated for all compositions listed in Appendix 5. The correlations between V_{tot} and $\log(\text{LR}_{\text{Si}})$ are shown in Table 4 for the entire database and for the various subsets discussed above. As with the FEH model, the best fit is obtained for the sodium boroaluminosilicate subset ($R = 0.80$), and the worst fit for alkali borosilicates ($R = 0.05$), for which the model is essentially uncorrelated. The latter are excluded from the remainder of this analysis. The intercept of the line for the remaining subsets varies by a total of 0.5 log units, though the slope varies by only about 10%. Thus, there is somewhat greater consistency in the slope of the regression one data set to another for the SBS model than for the FEH model. The standard errors of the correlation tend to be better than obtained for the FEH model, a reflection of the improved correlations with most data sets. Figure 9 shows the predicted LR_{Si} plotted against the measured value for the entire data set. The correlation is perceptibly better than for the FEH model for intermediate-mass-loss samples, but high- and low-mass-loss samples still tend to be underpredicted. Figure 10 shows predicted LR_{Si} plotted against the measured value for the sodium boroaluminosilicate subset. The improvement in the correlation for this subset relative to that of the FEH model (Fig. 8) is evident.

Table 4. Structural Bond Strength Model: Regression Coefficients and Statistics for Linear Correlation between V_{tot} (Independent) and $\log(\text{LR}_{\text{Si}})$ (Dependent)

	No. of Observations	Correlation Coefficient	Standard Error	Intercept	Slope
All Glasses	165	0.632	0.389	3.698	8.09×10^{-3}
All Glasses with $\text{LR}_{\text{Si}} \leq 28 \text{ g/m}^2$	120	0.793	0.163	2.745	5.54×10^{-3}
Sodium Boroalumino- silicate Glasses	83	0.800	0.138	3.295	7.28×10^{-3}
Sodium Boroalumino- silicate Glasses with $\text{LR}_{\text{Si}} \leq 28 \text{ g/m}^2$	79	0.798	0.090	2.702	5.34×10^{-3}
Alkali Borosilicate Glasses	21	0.053	0.491	2.119	0.93×10^{-3}
Alkali Lime Silicate Glasses	32	0.672	0.334	3.856	7.98×10^{-3}
Alkali Aluminosilicate Glasses	28	0.679	0.536	3.667	8.08×10^{-3}

The V_{tot} was also regressed against compositions with LR_{Si} less than 28 g/m^2 , and the results of this analysis are shown in Table 4. The correlation for low-mass-loss samples taken from the entire database is much improved ($R = 0.79$), and the correlation for the sodium boroaluminosilicate glasses remains essentially unchanged. The standard errors for both subsets improve markedly. This indicates a fairly good capability for predicting mass losses for relatively low-mass-loss samples compared to the FEH model.

Thus, there is a fairly robust correlation between V_{tot} and Si release rates for sodium boroaluminosilicate glasses, and reasonably good correlations for alkali aluminosilicate and alkali lime silicate glasses. There is no correlation between V_{tot} and LR_{Si} for alkali borosilicate glasses, however, meaning that the role of various components in such compositions are not accounted for in the model. The variation in slopes of the regressions are somewhat smaller than seen for the FEH model.

5.3.3 Possible Improvements

In a recent revision of the SBS model, Feng et al. [218] have modified the treatment of Al_2O_3 , ZrO_2 , and B_2O_3 . Each mole of Al_2O_3 or ZrO_2 is taken to require one mole of alkali oxide to convert to a network former, and aluminum is given priority in the competition for alkalis. As an example, in a glass containing 15 mole% Na_2O , 10 mole% Al_2O_3 , and 10 mole% ZrO_2 , all Al atoms and 5 mol% of the Zr atoms would be converted into network formers. The remaining 5 mol% of ZrO_2 would be treated as intermediate. Boron can be

Fig. 9. Measured Release Rates vs. Release Rates Predicted by the Structural Bond Strength Model for All Glasses in the Reference Database (Appendix 5). The line indicates a perfect correlation.

converted into an intermediate cation by any alkalis that are not used to stabilize Al or Zr. Boron in excess of the remaining alkalis is converted into a network breaker. The model also has a provision for changing Fe^{3+} into a network former by a charge-balance mechanism, in which case it uses alkalis for this purpose before alkalis are assigned to Zr or B. These modifications result in a poorer correlation against the reference data set than for the original model, particularly for true borosilicate glasses. For those glasses, the correlation coefficient drops

Fig. 10. Measured Release Rates vs. Release Rates Predicted by the Structural Bond Strength Model for Sodium Boroaluminosilicate Glass Compositions (Appendix 5). The line indicates a perfect correlation.

essentially to zero. As with the original SBS model, boron itself may have an "intermediate" effect upon glass durability, but its effect upon alkali cations is quite pronounced, and therefore its negative impact on V_{tot} amounts to an overcorrection.

A more subtle but very important point is that while the values are calculated in terms of oxides, the relevant parameter varies with each oxygen atom in the oxide. This difference affects the normalization of mole fractions in an unpredictable way from one glass to

another. It may be better to compute V_{tot} on a single-oxygen basis for each oxide. This approach was not attempted for this review.

Like the FEH model, the SBS model predicts linearly varying durabilities across the $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ system, in contrast to observation [154], and makes a similar prediction for the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system. Furthermore, because so much weight is given to alkalis on one end of the scale and to SiO_2 on the other, the model's correlations with silicon losses for the very durable alkali lime silicate glasses are rather poor compared to all other models reviewed here. To address this problem, cation oxides could be elevated to "network former" status whenever a cation that produces a still greater enhancement to durability is missing from the composition: for example, CaO might be considered a network former in soda-lime silicate glasses, but an intermediate in alkali aluminosilicate glasses. In a pure borosilicate glass, B_2O_3 would be a network former, rather than a modifier, but this modified approach would take into account its tendency to form BO_3 species in low-silica glasses. This approach would obviously require a great deal of experimental work and, moreover, would increase the empirical nature of the model.

5.3.4 Predictive Utility of the SBS Model

As implemented in this study, the SBS model can provide an estimate for which sodium boroaluminosilicate glasses are likely to have very high mass losses, and is fairly good at predicting LR_{Si} for low-mass-loss samples. For these materials, the $2\sigma_x$ confidence interval for a predicted LR_{Si} of 10 g/m^2 is approximately $\pm 5 \text{ g/m}^2$. Provided that predicted mass losses are well below those of the reference EA glass, the SBS model may provide adequate predictive capability for process control at a vitrification facility, but as with the FEH model, it would be necessary to test all marginal compositions. As with the FEH model, the SBS model cannot predict which glasses are likely to form quench crystals or phase separate, and therefore may give erroneous (low) estimates of mass loss rates if either process occurs. The predictions of the SBS model are uncorrelated with measured LR_{Si} for alkali borosilicate glasses, and therefore compositions that fit this description should be avoided during waste glass production. Because the SBS correlations are obtained against short-term tests, there is no necessary correlation between the predicted durability rankings of the glasses and their rankings in long-term accelerated tests. Therefore, the model cannot be used to predict long-term durability.

5.4 Valence-Oxygen Model

The VO model was proposed to relate glass durability to the valence contribution of each cation in the glass [196]. The VO model assumes that each cation's contribution to the stability of a glass depends only upon its valence. This assumption arises from the observation that free energies of hydration for oxide species vary sympathetically (though not systematically) with the valence of the cation in the oxide [194]. Thus, the VO model is a hybrid of sorts between a predominantly thermodynamic model, such as the FEH model, and a purely structural model, such as the NBO model. The VO model has only seen significant application in analysis of the database of Geldart and Kindle [196] and the analysis of Abrajano et al. [197].

5.4.1 Formalism

The VO model assumes that each monovalent cation contributes a single "unstable" cation/oxygen bond. Cations (Z^+) with valences greater than +1 are taken to form Z "stable" bonds. The valence parameter, P , normalizes the number of moles of stable and unstable bonds to the number of oxygen atoms in the glass, O_{total} :

$$P = \frac{(UB + O_{\text{unstable}}) - (SB - O_{\text{stable}})}{O_{\text{total}}} \quad (17)$$

where UB represents the number of unstable bonds, SB represents the number of stable bonds, O_{stable} is the number of oxygen atoms in "stable" oxides, and O_{unstable} is the number of oxygen atoms in "unstable" oxides [196]. Unstable bonds are defined as those formed by alkali cations, and, as there is technically one NBO bond per alkali, UB is simply two times the total alkali oxide concentration. Unstable oxygens are those bonded to alkalis, and their concentration is equal to the total alkali oxide concentration. Stable bonds are used for everything else except B_2O_3 : for a stoichiometry M_xO_y , the number of stable bonds per molecule is y times the mole fraction of M_xO_y in the glass. The total number of oxygen is simply yX_i summed for all oxides M_xO_y , including the alkalis but excluding B_2O_3 . The value of P is then correlated with glass composition through an equation of the form of Eq. 7.

5.4.2 Testing the VO Model Using the Reference Database

Values of P have been calculated for all compositions listed in Appendix 5. The correlations between P and $\log(LR_{Si})$ are shown in Table 5 for the entire database and for the various subsets discussed above. As with the FEH and SBS models, the best fit is obtained for the sodium borosilicate subset ($R = 0.81$), and the worst fit for alkali borosilicates ($R = 0.42$), though the correlation with the latter is the best of any model considered in this review. Excluding alkali borosilicate glasses are excluded from the remainder of this analysis. The intercept of the line for the remaining subsets varies by a total of 0.5 log units, but the slope varies by approximately 30%, the largest variation of any model considered in this study. The variation in the intercept is similar to that seen for the SBS and FEH models, but the larger variation in the slope is unusual. The standard errors of the correlations are comparable to those of the SBS model for all data sets except the alkali borosilicate subset (for which the VO correlations are better), and the alkali lime silicates (for which the VO correlations are substantially worse). Figure 11 shows predicted LR_{Si} plotted against the measured value for the entire data set. The correlation is perceptibly better than for the FEH model, particularly for high-mass-loss samples.

Figure 12 compares predicted and measured LR_{Si} for the alkali borosilicate subset. The correlation is strong (Table 5) but is biased by high-mass-loss glasses that fall near the line. The scatter about the line for lower mass loss compositions and the separation between individual points are not as great as for the SBS model (Fig. 10). It is not surprising, then, that excluding high mass compositions worsens the fit (Table 5). P was also regressed against compositions with LR_{Si} less than 28 g/m², and the results of this analysis are shown in Table 5. The correlation for low-mass-loss samples taken from the entire database improves ($R = 0.74$), though not as much as seen for the SBS model. The correlation for sodium borosilicate glasses worsens considerably, though not as much as seen for the FEH model. This indicates a fairly good capability for predicting mass losses for general glass compositions with relatively low-mass-loss samples, but fairly poor capability when the compositions are confined to sodium borosilicate glasses.

Thus, there is a fairly good correlation between P and Si release rates for sodium borosilicate glasses taken as a whole, but this is the result largely of the capability of the model to predict high-mass-loss samples. When attention is confined to low-mass-loss samples, the model is somewhat better than the FEH model, but worse than the SBS model. There is a weak correlation between P and LR_{Si} for alkali borosilicate glasses, though it is questionable whether this correlation is strong enough to be described as "predictive capability." The variation in slopes of the regressions are larger than for any other model considered in this study.

Table 5. Valence Oxygen Model: Regression Coefficients and Statistics for Linear Correlation between P (Independent) and $\log(LR_{Si})$ (Dependent)

	No. of Observations	Correlation Coefficient	Standard Error	Intercept	Slope
All Glasses	165	0.657	0.379	2.194	0.960
All Glasses with $LR_{Si} \leq 28 \text{ g/m}^2$	120	0.743	0.180	1.715	0.651
Sodium Boroalumino- silicate Glasses	84	0.809	0.136	1.906	0.844
Sodium Boroalumino- silicate Glasses with $LR_{Si} \leq 28 \text{ g/m}^2$	79	0.656	0.112	0.719	0.652
Alkali Borosilicate Glasses	21	0.415	0.447	2.354	0.717
Alkali Lime Silicate Glasses	32	0.539	0.379	2.352	0.802
Alkali Aluminosilicate Glasses	28	0.807	0.431	2.329	1.115

5.4.3 Possible Improvements

The VO model has one of the best correlations of any of the models considered in this review, but it also has the weakest grounding in theory. If it were recast in terms of the solubilities of components in aqueous solutions, however, one would perform much the same computational manipulations but would instead arrange components in a hierarchy of solubility. Components that simply follow alkali cations out of the glass, as appears to be the case for B_2O_3 in multicomponent waste glasses, would be treated the same as B_2O_3 , but components that are nearly as soluble as alkali cations, such as P_2O_5 , would be treated as formers of unstable bonds. This approach would also permit prediction of differences in durabilities caused by different cations with the same valences, such as Na_2O , Li_2O , or K_2O . As presently construed, the VO model correctly predicts that substitution of CaO for Na_2O will enhance glass durability, but, like the FEH and SBS models, it predicts linearly varying (though increasing) durability as B_2O_3 is substituted for Na_2O on an equal oxygen basis. Therefore, it would also be necessary to incorporate some ranking of "instability" to account for behavior in simple systems. Like the SBS model, the empirical nature of the VO model makes it difficult to determine what its failings are and renders somewhat arbitrary any efforts to improve its predictions.

5.4.4 Predictive Utility of the VO Model

The VO model can provide an estimate of which sodium boroaluminosilicate glasses are likely to have very high mass losses, but is not as effective as the SBS model in predicting LR_{Si} for low-mass-loss samples. For these materials, the $2\sigma_x$ confidence interval for a

Fig. 11. Measured Release Rates vs. Release Rates Predicted by the Valence Oxygen Model for All Glasses in the Reference Database (Appendix 5). The line indicates a perfect correlation.

predicted LR_{Si} of 10 g/m^2 is approximately $\pm 7 \text{ g/m}^2$, only marginally better than the FEH model. Provided that predicted mass losses are well below those of the reference EA glass, this might prove sufficient for process control at a vitrification facility, but it would be necessary to test all marginal compositions. As with the FEH and SBS models, the VO model cannot predict which glasses are likely to form quench crystals or phase separate, and therefore may give erroneous (low) estimates of mass loss rates if either process occurs. The predictions of the VO model are weakly correlated with measured LR_{Si} for alkali borosilicate glasses, and therefore compositions that fit this description should be avoided during waste glass production. On the other hand, the

Fig. 12. Measured Release Rates vs. Release Rates Predicted by the Valence Oxygen Model for Sodium Boroaluminosilicate Glass Compositions (Appendix 5). The line indicates a perfect correlation.

assumptions of the model might have some use in improving the predictive capability of this or other models for such compositions. Because the VO correlations are obtained against short-term tests, there is no necessary correlation between the predicted durability rankings of the glasses and their rankings in long-term accelerated tests. Therefore, the model cannot be used to predict long-term durability.

5.5 Nonbridging Oxygen Model

The NBO model assumes that the concentration of NBO atoms is a measure of the openness or nonconnectivity of a glass. This model has not been used to correlate glass composition with durability, but rather to demonstrate how the FEH model is related to glass structure [194]. The number of NBO in glass has been related to glass durability [219] and more recently, to nuclear waste glass durability [194,196,220,221]. A direct relationship between the free energy of hydration of a glass and the average number of NBO atoms in a glass was noted by Jantzen and Plodinec [194].

5.5.1 Formalism

Jantzen and Plodinec [194] provide an algorithm for computing the number of NBO, denoted $n(\text{NBO})$:

$$n(\text{NBO}) = \frac{2(R_2\text{O} + \text{RO}) - 2(\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3) + 4(\text{RO}_2)}{\sum X_i} \quad (18)$$

where $R_2\text{O}$, RO , etc. denote the mole fractions of these components in the glass, and $\sum X_i$ is the sum of the mole fractions of all components. Each $R_2\text{O}$ or RO contributes two NBO to the total, but these are consumed, in effect, when Al^{3+} and Fe^{3+} use R^+ or R^{2+} for charge-balance. Tetravalent cations (other than silicon) contribute four NBO to the total [194,196]. Geldart and Kindle [196] include $6R_2\text{O}_3$ in the sum in the numerator, but the correlation between silicon release and $n(\text{NBO})$ thus obtained is much worse than in the original model [194], and this variation will not be considered further. It is also not clear what should be done if $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ exceeds the total alkali concentration—this problem is discussed in greater detail below. It is assumed that $n(\text{NBO})$ determined in this way can be regressed against $\ln(\text{LR}_i)$ obtained in short-term leach tests in an equation of the form of Eq. 7.

5.5.2 Testing the NBO Model Using the Reference Database

Values of $n(\text{NBO})$ have been calculated for all compositions listed in Appendix 5. The correlations between $n(\text{NBO})$ and $\log(\text{LR}_{Si})$ are shown in Table 6 for the entire database and for the various subsets discussed above. Unlike any other model considered in this study, the best fit is obtained not for the sodium boroaluminosilicate subset ($R = 0.64$) but for the alkali lime silicate subset ($R = 0.68$), for which only the SBS model provides a stronger correlation. As with the other models, the worst fit is obtained for the alkali borosilicates ($R = 0.01$), indicating no correlation between $n(\text{NBO})$ and LR_{Si} . Alkali borosilicate glasses are excluded from the remainder of this analysis. The intercept of the line varies by roughly 0.2 log units, and the slope varies by less than 20%, the smallest variations of any model considered in this study. Due to the relatively poor fits for all subsets except the alkali lime silicate subset, the standard errors of the correlations are significantly greater than for the other models in this review. Figure 13 shows the predicted LR_{Si} plotted the measured value for the entire data set. The correlation is noticeably worse than for any other model (Figs. 7, 9, and 11), particularly for intermediate-mass-loss samples. Figure 14 shows predicted vs. measured LR_{Si} for the alkali boroaluminosilicate subset. Intermediate-mass-loss glasses are more widely distributed along the line indicating a perfect correlation, but very few points lie on or quite close to the line.

The $n(\text{NBO})$ values were also regressed against compositions with LR_{Si} less than 28 g/m^2 , and the results of this analysis are shown in Table 6. The correlation for low-mass-loss samples taken from the entire database improves slightly ($R = 0.55$), but remains the worst of any of the models considered in this study. The correlation for sodium boroaluminosilicate glasses

Table 6. Nonbridging Oxygen Model: Regression Coefficients and Statistics for Linear Correlation between $n(\text{NBO})$ (Independent) and $\log(\text{LR}_{\text{Si}})$ (Dependent)

	No. of Observations	Correlation Coefficient	Standard Error	Intercept	Slope
All Glasses	165	0.504	0.434	0.475	1.512
All Glasses with $\text{LR}_{\text{Si}} \leq 28 \text{ g/m}^2$	120	0.550	0.224	0.553	0.986
Sodium Boroaluminosilicate Glasses	84	0.637	0.178	0.481	1.359
Sodium Boroaluminosilicate Glasses with $\text{LR}_{\text{Si}} \leq 28 \text{ g/m}^2$	79	0.681	0.109	0.630	0.998
Alkali Borosilicate Glasses	21	0.010	0.492	1.827	0.043
Alkali Lime Silicate Glasses	32	0.668	0.336	0.442	1.564
Alkali Aluminosilicate Glasses	28	0.419	0.663	0.321	1.401

improves somewhat, and in fact is much better than the FEH or VO models for this restricted range of compositions, but is still much poorer than the correlations obtained for the SBS model. The relatively large standard errors for both subsets are indicative of only a very modest predictive capability, though much better for the sodium boroaluminosilicate subset.

Thus, there is a modest correlation between $n(\text{NBO})$ and LR_{Si} for alkali lime silicate glasses and sodium boroaluminosilicate glasses, but the correlation obtained for the latter are the worst of any model considered in this study. When confined to low-mass-loss glasses, the correlation improves for alkali boroaluminosilicate glasses, but remains worse than the predictions of the SBS model. Therefore, $n(\text{NBO})$ is uncorrelated with LR_{Si} for alkali borosilicate glasses. The variations in the slopes and intercepts of the regressions are smaller than observed for any other model considered in this study. Because the NBO correlations are obtained against short-term tests, there is no necessary correlation between the predicted durability rankings of the glasses and their rankings in long-term accelerated tests. Therefore, the model cannot be used to predict long-term durability.

5.5.3 Possible Improvements

The NBO model treats all NBO equivalently, regardless of what cation creates them. As a consequence, the same durability is predicted for the glass composition $25\text{Na}_2\text{O} \cdot 75\text{SiO}_2$ as for $15\text{Na}_2\text{O} \cdot 10\text{CaO} \cdot 75\text{SiO}_2$, the archetype of the soda-lime silicate glass that is the mainstay of the durable container industry. Improving the model, then, would require making an explicit distinction between different "kinds" of NBO formed by different cations. Furthermore, because of the way $n(\text{NBO})$ is calculated, all Al^{3+} in a glass of the composition $\text{ZrO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$ would be charge-balanced, in effect, by zirconium: a very durable glass

Fig. 13. Measured Release Rates vs. Release Rates Predicted by the Nonbridging Oxygen Model for All Glasses in the Reference Database (Appendix 5). The line indicates a perfect correlation.

would be predicted, but the structural chemistry implications are nonsensical. More subtle effects, such as mixed alkali stabilization, probably cannot be accounted for at all. It is not evident how +3 cations that form NBO should be treated, including, perhaps, Fe_2O_3 or Al_2O_3 that is in excess of total alkali concentration. As mentioned above, including them in the calculations for the reference data set significantly worsened the correlation. These observations indicate that further development of the NBO model may not be fruitful.

It is also not at all clear that NBO always compromise durability. For example, $25Na_2O \cdot 75SiO_2$ glass and $15Na_2O \cdot 10CaO \cdot 75SiO_2$ glass have the same number of NBO, but as shown by Clark et al. [147], the Ca-bearing glass shows release rates nearly three orders of

Fig. 14. Measured Release Rates vs. Release Rates Predicted by the Nonbridging Oxygen Model for Sodium Boroaluminosilicate Glass Compositions (Appendix 5). The line indicates a perfect correlation.

magnitude lower. Another example is the finding by Feng et al. [222] that addition of modest amounts of ZrO_2 to WV205 glass increased its durability to a greater extent than addition of comparable amounts of SiO_2 . In this case, an increase in NBO resulted in a greater stabilization than an increase in BO. On the other hand, it is probably true that NBO formed by alkali cations are undesirable, and alkalis themselves are more readily leached than other components. Thus, one rather ironic improvement to the NBO model might be to consider alkali cations alone, or alkali cations that are not otherwise involved in charge-balance.

5.5.4 Predictive Utility of the NBO Model

The NBO model can provide a moderately accurate prediction of LR_{Si} for sodium boroaluminosilicate glasses, particularly for low-mass-loss samples, but the predictions are unlikely to be as accurate as those of the SBS model. For low-mass-loss sodium boroaluminosilicate glasses, the $2\sigma_x$ confidence interval for a predicted LR_{Si} of 10 g/m^2 is approximately $\pm 7 \text{ g/m}^2$, marginally better than the FEH model and essentially the same as the VO model. As with the other models considered in this review, provided that predicted mass losses are well below those of the reference EA glass, this capability might prove sufficient for process control at a vitrification facility, but marginal compositions would have to be tested. As with all other models considered in this review, the NBO model cannot predict which glasses are likely to form quench crystals or phase separate, and may give erroneous (low) estimates of mass loss rates if either process occurs. The predictions of the NBO model are uncorrelated with measured LR_{Si} for alkali borosilicate glasses, and therefore compositions that fit this description should be avoided during waste glass production.

5.6 PNL Composition Variability Study

The Composition Variability Study (CVS) is being developed at Pacific Northwest Laboratory (PNL) to aid in the development of nuclear waste glasses for the Hanford Waste Vitrification Plant (HWVP) waste that meet quality and processability requirements [198-200]. The CVS model is entirely empirical and simply correlates the weight-fraction of a component in a glass with a measure of durability, generally B loss in a 7-day PCT test [199]. A similar approach was used to develop compositions for vitrification of West Valley nuclear wastes [200]. The West Valley study will not be discussed in detail, since the methodologies and conclusions are the same as for the CVS. A recent report on the completion of Stage 1 of the CVS has been presented by Piepel et al. [223].

5.6.1 Formalism

The CVS model per se has no theoretical basis, but relies instead on the expectation that glass durabilities will vary smoothly and monotonically with the concentrations of particular components. It requires a substantial database of durability tests for different glass compositions, after which point an empirical correlation is developed between the weight fraction of component i and its effects upon glass durability. Glasses encompassing the range of compositions expected to be produced at the HWVP were tested for durability with MCC-1 and PCT tests [199, 201]. The test used to obtain normalized elemental release were 7-days PCT tests and 28-day MCC-1 tests. Changes in solution concentration of boron, silicon, sodium, and lithium were monitored, although normalized boron release was used to define the durability rankings of the glasses.

Data from all tests were regressed against the compositional parameters listed above using a first-order empirical mixture equation of the form

$$r = \exp\left(\sum_{i=1}^n a_i g_i\right) \quad (19)$$

where g_i is the mass fraction of i component in glass, a_i is the coefficient i component, and n ($=10$) is the number of components (SiO_2 , B_2O_3 , Na_2O , Li_2O , CaO , MgO , Fe_2O_3 , Al_2O_3 , ZrO_2 , and "Others," composed of oxides present in the glass at a level of 0.1 to 10 wt%). Normalized boron releases varied from 3 to 691 g/m^2 for MCC-1 tests and 0.07 to 21 g/m^2 per 7 days for PCT tests.

5.6.2 Analysis

Correlation coefficients (R^2) were 0.71 for MCC-1 test results and 0.78 for PCT test results. The range of glass compositions is comparable to that of the sodium boroaluminosilicate glass subset considered in this review, though smaller, and the range of compositions is better conditioned in a statistical sense than the data set considered in this study. It should be noted that R^2 for the SBS model against the sodium boroaluminosilicate glass data set is approximately 0.64, substantially less (and therefore indicative of a poorer fit) than obtained in the CVS study. This is a benefit of fitting a relatively large number of coefficients to a data set. Greater care was taken to characterize the condition of the samples and the errors in the analyses than is possible in this study, and a rigorous effort was made to analyze correlations between coefficients. The results are therefore indicative of rather high predictive capability.

What is still not certain is whether the coefficients can be used to predict behavior for intermediate compositions, or provide a reliable estimate of compositions that lie outside the envelope of unacceptable products. Stage II of the CVS study may clarify this issue. Because a fundamental premise of the CVS approach is that the reference database be statistically well-conditioned, no effort was made to apply the CVS fitted coefficients to the database in this study. However, a trial effort at fitting the sodium boroaluminosilicate data set with mole fractions of the nine oxide components listed above in an equation of the form Eq. 19 yielded a correlation coefficient of 0.86 ($R^2 = 0.74$), which is comparable to the values reported by Hrma et al. [199]. In particular, there were very strong positive correlation between LR_{Si} and the alkali concentrations of the glass, and strong negative correlation between LR_{Si} and the concentration of Al_2O_3 and ZrO_2 , as one would expect from the discussion in Sections 3 and 4. It is not clear, however, whether the actual values of the coefficients have any physical significance.

5.6.3 Predictive Utility of the CVS Model

As with other models that assume a direct relationship between the concentration of oxides and glass durability, intermediate components (e.g., NaAlO_2) that have a real, perceptible effect upon glass durability cannot be accounted for in the CVS model as presently designed. This means that the CVS cannot be interpolated into a subset of the database of glasses compositions being used to develop it (e.g., it cannot describe the strongly nonlinear composition/mass loss relationships seen in the Na_2O - B_2O_3 - SiO_2 system). Second-order terms (e.g., $\text{Al}_2\text{O}_3 \cdot \text{Na}_2\text{O}$) may account for some of this behavior but will have no possible physical interpretation. Unlike the models considered above, the CVS program includes an effort to specify compositions that are likely to crystallize or phase separate, but the model itself cannot predict whether this will occur *a priori* for a randomly selected glass.

The stated purpose of the CVS is to define the compositional envelope of acceptable products and also to set boundary conditions that define unacceptable products. In production, the CVS will be used to verify product consistency and to predict normalized release rates for waste glasses. So long as glasses remain within the compositional envelope ultimately determined to be acceptable by the CVS, the predictive capability of the model will be quite high, probably better than any of the models considered above. The CVS model is also potentially useful as a guide in waste glass development, provided that the only criterion for

durability is suitable performance in a 7-day PCT test or 28-day MCC-1 tests. As with the other models considered in this review, however, the CVS model has no long-term predictive capability. In particular, it provides no information about durability relationships outside the range of those measured for its database. Since it has no theoretical underpinnings, the CVS model relies exclusively on the strength of statistical correlations to make its predictions, but since these are better constrained than for the other models considered in this section, the anticipated uncertainty in predicted mass loss is expected to be less. Marginal compositions will still probably have to be tested, but the tolerances governing the decision to test a glass will likely be much smaller than for any other model analyzed in this review.

5.7 Thermodynamic Hydration Energy Reaction Model

The Thermodynamic Hydration Energy Reaction Model (THERMO) is an outgrowth of development and refinement of the FEH model (Section 5.2). It is being developed at Savannah River Laboratory (SRL) for use in process control during operation of the Defense Waste Processing Facility. A final report of the origins, development, and application of the model is not available at present, but a draft version was made available to be included in this review [224]. THERMO includes several applications that are beyond the scope of this study, including predictions of viscosity, glass transition temperature, phase formation, glass-glass phase separation, and conductivity. Emphasis here is placed on the role of THERMO in predicting the outcome of 7-day PCT tests during operation of the vitrification facility, and the ways in which it varies from the FEH model.

5.7.1 Formalism

At present it is not possible to determine the precise formalism of THERMO from the draft version made available for this review [224], but it is possible to describe the substance of the calculations that are to be performed. As with the FEH model (Section 5.2), THERMO estimates the hydration free energy of a glass as a sum of the hydration free energies of a chosen set of glass components. The list of components has been expanded considerably from those recommended for the FEH model, and the values themselves have been taken from standard compilations of hydration free energies. The reactions reflect the more probable case that an alkali silicate glass in prolonged contact with water in a glass-dominated test will increase the pH of the solution to the base regime, and therefore the reactions should be with H_2O or OH^- , not H^+ . Instead of requiring the final pH to perform a pH "correction," a means is now provided for estimating the impact of pH on the normalized release from the composition of the glass alone. These amendments address significant limitations raised in Section 5.2.3 about the FEH model.

The first step in the use of THERMO is to calculate a preliminary free energy of hydration, ΔG_p , using a formalism identical to that of the FEH model (Section 5.2.1), except that a revised hydration free energies are used instead of those listed in Table 2. In contrast with the FEH model, use of the values reported in the draft report of THERMO resulted in exothermic (spontaneous) estimated hydration free energies for all compositions in the reference database, thereby addressing another major concern raised in Section 5.2.3. If ΔG_p is more negative than -7.5 kCal/mol , then it is assumed that in a glass-dominated reaction the pH of the solution will rise to the point where the aqueous speciation of certain cations (weak acids) will change. This necessitates an additional term, ΔG_a , which accounts for the free energy change associated with the new speciation. Likewise, if ΔG_p is more negative than -9.5 kcal/mol , it is assumed that very high solution pH will be obtained, and a second term ΔG_a is added to account for the change in speciation of a number of additional cations and weak acids. The final estimated free energy of hydration, ΔG_f , is simply the sum of ΔG_a and ΔG_p . The ΔG_p term is used to correct for the inferred pH-dependence of glass corrosion. Since it is always exothermic, it always makes ΔG_f more negative, and therefore one would expect higher elemental releases than obtained from ΔG_p .

alone. This revision is in effect a pH correction for high-mass-loss glasses calculated in advance of experiment, and addresses a major concern regarding use of the pH correction for the FEH model (Section 5.2.1).

5.7.2 Analysis

In the draft report [224], values of ΔG_p and ΔG_f were regressed against 7-day PCT normalized release values for B, Li, Na, K, and Si for a set of glass compositions, most of which would be characterized as sodium boroaluminosilicate glasses in the present study (Section 5.0). The reported R^2 obtained for ΔG_p alone ranged from a minimum of 0.63 for K to a maximum of 0.84 for Na. The lower value obtained for K is attributed to the limited number of glass compositions used to obtain the correlation. Note that R^2 of 0.84 implies a $|R| \sim 0.92$, as compared to the value of 0.73 obtained for regression of the FEH model against the sodium boroaluminosilicate glass subset in this review (Section 5.2.2 and Table 3). When ΔG_a is included, the reported values of R^2 obtained for all elements except K exceed 0.9, with a maximum value of 0.96 ($R = 0.98$) obtained for LR_{Na} and LR_B . This is an exceptionally robust correlation, considerably exceeding the values reported in the CVS study [199, 200] (see Section 5.6). On the other hand, the range of glass compositions considered in the draft report is much less diverse than in the CVS study, so the strong correlation may in part be an artifact of a limited data set.

THERMO is intended for use in calculating normalized release of Li, Na, B, and Si in 7-day PCT tests [224], and therefore pH is likely to rise to a fairly high level within this period for most alkali boroaluminosilicate glasses. By contrast, in 28-day MCC-1 tests the pH may be far lower than would eventually be obtained as the solution approaches saturation, and therefore use of ΔG_a terms for MCC-1 tests is probably not justified. Using the method as described in the draft report [224], we were able to reproduce the reported value of ΔG_p for a test composition and for EA glass. However, the value of ΔG_f worked out for the test composition included two ΔG_a terms (e.g., corrections for ΔG_p of -9.5 kCal/mol) though ΔG_p is -5.9 kCal/mol, in contradiction to the method advocated in the text. Furthermore, though appropriate ΔG_p terms were included for EA glass, we were unable to reproduce the reported ΔG_f for the glass. When ΔG_p alone is regressed against the alkali boroaluminosilicate subset of the reference database, the value of R obtained is 0.72 ($R^2 = 0.52$), essentially the same as obtained for the FEH model. It may be that higher correlations are obtained for PCT tests because the least durable glass compositions very rapidly approach saturation, whereas the most durable glass compositions do not. This would serve to spread out the observed values for normalized release and might produce a higher correlation. For MCC-1 test results, and therefore as a statement about the inherent resistance of a glass composition to aqueous attack, the revised $\Delta_{hyd}G_i$ presented in THERMO do not appear to improve the predictive capability of ΔG_p as compared to $\Delta_{FEH}G$.

5.7.3 Predictive Utility of THERMO

Because a final report is not available, and because we were unable to reproduce the few reported values for ΔG_f discussed in the draft report, it is not appropriate to comment at present about the use of THERMO for process control. Very clearly, if the reported correlations with PCT test results are correct, then the predictions of THERMO are very good indeed, and high confidence can be placed in predicted values. On the other hand, because the range of compositions considered in obtaining the correlations was limited and because most of the experimental results reported represent duplicate analyses of a much smaller set of glasses, it is probably appropriate to test the strength of the correlation between THERMO and an external database of PCT test results. A good candidate might be the combined test results of the CVS study for stages 1 and 2, which represents a statistically well-conditioned database and a range of

glass compositions consistent with the compositional envelopes of proposed domestic waste glasses. As with all other models considered in this section, THERMO cannot predict durability rankings between different compositions in long-term, glass-dominated tests. This is because it cannot predict elemental releases for anything but 7-day PCT tests and cannot account for the identities of secondary crystalline phases formed during glass corrosion.

6.0 ACCOUNTING FOR COMPOSITION EFFECTS IN CORROSION MODELS

Glass compositional effects have been incorporated into mechanistic glass corrosion models. Such models are intended to predict glass corrosion rates over expected repository lifetimes. They are based on experimentally verified physical and chemical processes that take place during glass corrosion. Because they purport to incorporate the true reaction mechanism of the glass, they are intended to be credible indicators of long-term performance, an objective quite different from most of the models discussed in Section 5.

Mechanistic glass corrosion models [225-229] are based on a rate equation derived from macroscopic irreversible thermodynamics and transition state theory. This rate equation has the general form:

$$\frac{dn_i}{dt} = A \nu k_f \left(1 - \frac{Q}{K} \right) \quad (20)$$

where n is the number of moles of component i in the glass, t is time, A is the surface area of the glass, ν is a stoichiometric factor, k_f is the forward rate constant for glass dissolution, Q is the activity product for the dissolving solid (glass, an alteration layer, or silica, depending on the model), and K is a thermodynamic solubility product for the same solid. Glass composition can potentially impact Eq. 20 by affecting one of three factors: (1) the forward rate constant, k_f ; (2) the identities and quantities of secondary phases, which in turn affect the magnitude of the affinity term; and (3) the composition of the altered layer formed during corrosion, which also affects the magnitude of the affinity term. Therefore, explicit consideration of the ways in which glass composition affects glass reaction rates requires information about the rate-limiting reaction mechanism and its variation with environmental conditions.

In the glass dissolution model of Grambow [225], the affinity term $(1 - Q/K)$ is assumed to involve only silicic acid: Q is the concentration of silicic acid in solution, and K is a glass-composition-dependent parameter corresponding to "silica saturation" for the glass/water system. Glass composition effects have been represented in this model by using the FEH model (Section 5.1). Because the FEH model relates the thermodynamics of the glass to the kinetic reaction rate of the glass in an empirical way, there is no theoretically prescribed method to incorporate it into a mechanistic kinetic model for glass dissolution. It has been incorporated into the Grambow model in two ways: to modify the forward rate constant (k_f) and to modify the affinity term in the rate expression. The free energy of hydration has been used to estimate the effect of glass composition on the forward rate k_f by means of the expression:

$$k_f = X \exp \left(\frac{-E_a}{RT} \right) \exp \left(\frac{-\Delta G_r}{RT} \right) \quad (21)$$

where E_a is the activation energy for dissolution (determined experimentally), and ΔG_r is the free energy of hydration term for the glass dissolution reaction [225]. The value of ΔG_r for the glass is calculated as in Eq. 11. The free energy of hydration was expressed by Grambow as a function of the corrosion progress, though strictly speaking the free energy is defined only at equilibrium. We have therefore dropped the dependence of ΔG_r upon the reaction progress variable in Eq. 15. The factor $X \exp(-E_a/RT)$ accounts for the effect of temperature on the rate constant, and the factor $\exp(-\Delta G_r/RT)$ corrects the rate constant for the effect of glass composition. Correcting the rate constant in this way has been only partially successful for actual actual waste glass compositions. This correction has since been dropped from the Grambow model and been replaced with experimentally determined rate constants for specific glass compositions [230].

In the approach taken by Advocat et al. [226], the affinity term is related to the unaltered glass, whereas in the Lawrence Livermore National Laboratory (LLNL) model [227], the affinity term is determined by the composition of the hydrated surface layer of the reacted glass. In this approach, Q in Eq. 20 corresponds to the activity product for the corrosion reaction of the entire glass, and K is the equilibrium constant for glass corrosion calculated using the free energy of hydration calculations (Section 5.1). In both these approaches, a term is added to ΔG_r to account for mixing of the oxide components in the glass.

The LLNL model [226] assumes that the rate-limiting step in glass corrosion is the dissolution of the surface alkali-depleted hydrous layer. The thermodynamic properties of this layer are approximated by assuming it is a solid solution mixture of amorphous components [225], and ΔG_r is then computed for the alteration layer, rather than for the unreacted glass. The components are chosen to be amorphous rather than crystalline in order to be structurally and energetically similar to the amorphous surface alteration layer. Use of the layer composition to calculate K instead of the bulk glass composition [e.g., 228] results in better prediction of experimental glass dissolution rates, but the relationship between starting glass composition, layer composition, and the glass dissolution rate is complex. At present, the composition of the alteration layer is determined analytically from experimentally reacted glasses. The composition of the alteration layer is affected by both the glass composition and the solution composition, and as a result its ultimate composition cannot be predicted from the starting composition of the glass. Both groups [226,227] found that including all components in the Q and K terms did not improve the ability of the models to simulate experimental measurements. The quantity ΔG_r "predicts" that the glass never approaches saturation but continues to corrode at a constant rate, so that the affinity term has a value of one throughout the duration of the simulation. It is found experimentally, however, that corrosion rates decrease over time.

Although there is a gross correlation between glass dissolution rates and free energies of hydration [193,194,227], the discussion in Section 5.1 shows that this correlation is not sufficiently accurate to quantitatively model glass corrosion. Mechanistic models of glass dissolution that use ΔG_r to account for the effects of glass composition cannot be expected to reproduce the results of short-term experiments. At present, long-term predictions using the dissolution/precipitation model require that the relationship between glass composition and forward rate be derived empirically.

7.0 SUMMARY

The goal of this report has been review the state of knowledge regarding the effects that the composition of a waste glass has on its durability. Various tests that have been developed to test the durability of glasses and waste glasses were reviewed. It was shown that the tests that most accurately probe the resistance of a glass composition to chemical attack by water are those in which the glass components released to solution remain extremely dilute. (Otherwise, the buildup of corrosion products in solution results in a feedback between the evolving solution and the response of the glass to changes in solution chemistry, resulting in further evolution of the solution, etc.) These "solution-dominated" test conditions are best obtained by studying low-surface-area samples in a high volume of solution, such as in short-term MCC-1 tests, or better still in Soxhlet or flow-through tests conducted at moderately high flow rates. By extension, short-term tests designed to verify product consistency, such as the PCT, may not be appropriate for determining the compositional dependence of waste glass corrosion.

Because the results obtained in glass-dominated test procedures depend on the details of the experimental setup, the relationship between glass performance and composition is not necessarily revealed in such tests. On the other hand, "glass-dominated" tests such as long-term MCC-1 tests, PCT, and vapor hydration tests provide important information about the response of the glass to changes in the chemistry of the solution produced by the buildup of corrosion products in solution. This information is needed as input to long-term modeling of waste glass performance. Of particular importance is the identity, order of appearance, and quantity of secondary mineral phases produced when the solution becomes saturated in their components. This is because certain secondary crystalline phases are known to have an adverse impact on waste glass corrosion rate. The rate of release of radionuclides and RCRA metals is also needed to verify that release rates in the long term will meet current regulatory limits.

On an atomic level, the aqueous corrosion of a glass requires the destruction of cation-anion bonding arrangements in a glass and the formation of new bonding arrangements in an altered layer or in the solution. This suggests that a limiting factor in glass corrosion is the strength of local cation-anion bonds. Local atomic arrangements in borosilicate and aluminosilicate glasses were reviewed to identify the components that form the strongest cation-anion bonds in these glasses, and to show how sharing of oxygen atoms in the glass by different cations may enhance cation-anion bond strength. The strongest bonds are between oxygen and silicon atoms, followed by those between oxygen atoms and small trivalent cations that share the oxygen atoms with low-valence alkali or alkaline earth cations, followed by bonds between oxygen atoms and combinations of high-valence and low-valence cations that share the same oxygen atoms. When bond strengths depend on the presence of two or more different cations, small changes in glass composition may produce a very large change in durability as measured in solution-dominated durability tests, or variations in the rheologic properties of the melt from which the glass is formed.

This local atomic arrangement approach to the description of glass corrosion is successful in predicting the response of glasses to aqueous attack in solution-dominated tests. Simple glasses containing components involved in mutual bonding interactions will tend to be more durable than a glass containing a smaller number of components that are not involved in such interactions. Especially important examples in this regard are interactions between alkali cations and aluminum or boron, and between alkali cations and large, high-valence cations such as zirconium. Experimental observations of glass corrosion in simple glasses were also shown to have direct bearing on the interpretation of results of short-term, solution-dominated tests of candidate waste glasses. In particular, the addition of components whose chemistry is strongly coupled with the chemistry of alkali cations results in a marked enhancement to waste glass durability.

This information and a large database of solution-dominated test results for multi-component glasses were then used to evaluate the merits of four models that purport to explain the compositional dependence of glass durability. It was shown that thermodynamic approaches that rely on estimates of the free energy of dissolution (the free energy of hydration model) of a glass or on estimates of the average strength of cation-anion bonds (the structural bond strength model) are strongly correlated with measures of the release of glass components to solution; however, these models poorly predict the rate of corrosion for individual glasses. A structural model that treats alkali cations alone as the components that decrease glass durability (the valence oxygen model) was shown to describe the overall compositional dependence of glass corrosion at least as well as the thermodynamic approach, but again this model is a poor predictor of the performance of individual glasses. Finally, a very simple model of glass chemistry that estimates the number of nonbridging oxygen atoms in a glass (the nonbridging oxygen model) was shown to be a poor predictor of the compositional dependence of glass corrosion because it does not take into account the true complexity of bonding interactions in the glass.

The use of these and other models for predicting the long-term performance of waste glasses in repositories was also discussed. Short-term durability test results are generally incorporated into long-term corrosion models as measures of the forward rate of the corrosion process. Models that accurately predict forward corrosion rates might potentially be of use in these models. Most long-term corrosion models require empirical observations as input, such as the saturation concentrations of secondary crystalline phases, and, therefore, it has not been established how sensitively their predictions depend on knowledge of the forward rate.

The most important results of this review are as follows:

1. More experimental work is needed to isolate the roles of various cation and anion combinations in determining the response of glasses to aqueous attack. It is very important to (a) establish whether the addition to a glass of components that have low solubilities in aqueous solution will invariably increase glass durability and (b) identify which cations are most likely to form dependent relationships in their bonding interactions with oxygen atoms in glasses and waste glasses.
2. Thermodynamic and structural models of the compositional dependence of glass and waste glass durability should be modified to take better advantage of the known bonding arrangements in glasses. As an example, the free energy of hydration model would benefit from a more realistic set of glass components, and the structural bond strength model would benefit from use of glass components rather than simple oxides. Use of more realistic components would more accurately reflect the true bonding interactions in the glass and would reduce the magnitude of highly nonlinear thermodynamic mixing terms.
3. The predictive capabilities of the models reviewed in this study are probably not sufficient for use in predicting the long-term performance of waste glasses

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APPENDIX 1. Long-Term Corrosion of Glass under Vapor Unsaturated Conditions

It is essential to develop a means of modeling the long-term corrosion behavior of a glass in contact with water vapor, as these conditions are most germane to the unsaturated conditions in a geologic repository. LR_{Si} is used as the corrosion index in the database used to test the corrosion models (see Section 5), but other durability measures could have been used as well. No solution is recovered in vapor hydration tests, and therefore a different index is required to obtain correlations between vapor hydration test results and long-term glass performance. One possible measure is the thickness of a leached and partially hydrated "gel" layer on the glass surface, if one forms. Static hydrothermal experiments have shown that for some waste glasses, the release of glass components to solution occurs at the same time as the appearance and growth of a hydration layer.¹ The release of components to solution cannot be monitored in a vapor hydration test, but one does obtain an assemblage of secondary crystalline phases, and often one can measure the thickness of the hydration layer. The phase assemblage will vary from one composition to another, so the correlation of interest is between the thickness of the hydration layer and the rate of glass corrosion. The question is whether hydration layer thickness can be substituted for LR_{Si} in models such as the FEH model to predict the composition effect on vapor hydration durability.

The answer to this question depends on whether there is a simple relationship between LR_{Si} and layer thickness. LR_{Si} is a time-averaged measure of the rate at which Si is detached from the surface of the glass, via reactions such as

In this sense, the thickness of a hydration layer is a measure of the hydration of the network structure. Because network hydration simply represents a precursor to Si release,² one might surmise the existence of a simple relationship between hydration layer growth and LR_{Si} . On the other hand, diffusion and cation exchange reactions are generally thought to precede network hydration during reaction of some multicomponent glasses in liquid and vapor.² Under these conditions, for the depth of the hydration layer to provide quantitative information about the rate of glass corrosion, a steady state must be reached in which the rate of water migration into the glass is exactly balanced by the rate of release of components near the surface into solution. Both diffusion-controlled and network-hydration-controlled growth of hydrated layers may occur during vapor hydration depending on the composition of the glass and the duration of the test.

A more important impact on the rate of glass corrosion is the formation of secondary crystalline phases, as noted in Section 4.6.4. As an example, PNL 76-68 dissolves at a relatively high rate in static, hydrothermal tests, but shows very little reaction in vapor hydration tests

¹T. A. Abrajano and J. K. Bates, "Transport and Reaction Kinetics at the Glass:Solution Interface Region: Results of Repository-Oriented Leaching Experiments," Mater. Res. Soc. Symp. Proc. 84, 533-546 (1987).

²T. A. Abrajano, J. K. Bates, and J. J. Mazer, "Aqueous Corrosion of Natural and Nuclear Waste Glasses. II. Mechanisms of Vapor Phase Hydration of Nuclear Waste Glasses," J. Non-Cryst. Solids 108, 269-288 (1989).

because its composition is not amenable to the formation of secondary crystalline phases.² Secondary crystalline phases are "sinks" for glass components released from the surface of the corroding glass. If the rate at which glass components in solution are incorporated into growing secondary crystalline phases exceeds the rate of release of the components into solution, a situation will arise in which the formation of secondary phases controls the rate of glass corrosion.

The eventual appearance of secondary phases is likely for most high-level waste glass formulations, and the fine details of the order of appearance and relative proportions of the various phases will determine, to some extent, the rate of reaction of the glass. For this relationship to be general to all glasses, it must be established that for the conditions and time frame of interest a single, known mechanism is controlling the growth of hydration layers for all glass compositions considered. This requires that vapor hydration tests be performed for a suitably large range of glass compositions to establish the general validity of the single-reaction-mechanism assumption, or to identify the range of compositions through which a particular reaction mechanism is generally followed.

To predict when and under what circumstances secondary phases will form requires accurate, reliable thermodynamic data for the glass and for all secondary phases likely to form during vapor hydration. The objective of thermodynamic modeling is to map mass transfer in terms of chemical potential gradients. Models currently exist to calculate the activities of components in solution, but reliable, accurate thermodynamic data for key secondary crystalline phases must also be obtained. For the present purposes the following minerals are of interest: calcite, uranophane, weberite, analcime, tobermorite, gyrolite, saponite, nontronite, brannerite, birnessite, stevensite, lithium orthophosphate, and orthoclase. For these minerals, the following properties were sought:

- Standard state Gibbs free energy of formation, $\Delta_f G^\circ$;
- Heat capacity at constant pressure, $C_p(T)$, particularly for low temperatures (~5-360 K);
- Standard state enthalpy of formation, $\Delta_f H^\circ$;
- Integrated heat content, $H^\circ_T - H^\circ_{298}$, for a suitably large number of values of T ;
- Entropy as a function of T , $S^\circ(T)$;
- Solubility in aqueous solution; and
- Any other relevant thermodynamic properties, such as coefficient of thermal expansion, molar volume, density, etc.

A summary of the useful material found follows.

Calcite, CaCO_3

Complete thermodynamic data are available (see, for example, Robie et al.³).

Uranophane, $(\text{H}_3\text{O})_2\text{Ca}(\text{UO}_2)_2(\text{SiO}_4)_2 \cdot 3\text{H}_2\text{O}$

No thermodynamic data have been reported in the literature.

Weeksite, $\text{K}_2(\text{UO}_2)_2\text{Si}_6\text{O}_{15} \cdot 4\text{H}_2\text{O}$

No thermodynamic data have been reported in the literature.

Analcime, $\text{NaAlSi}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$

Complete thermodynamic properties have been reported by Johnson et al.⁴

Tobermorite, $\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$

Complete thermodynamic data have been obtained at ANL,⁵ but have not yet been published.

Gyrolite, $\text{Na}(\text{Ca},\text{Mg},\text{Fe})_{16}(\text{Si},\text{Al})_{24}\text{O}_{60}(\text{OH})_7 \cdot 15\text{H}_2\text{O}$

No experimental data have been reported.

Saponite, $(\text{Ca}_{1/2},\text{Na})_{0.3}(\text{Mg},\text{Fe}^{2+})_3(\text{Si},\text{Al})_4\text{O}_{10}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$

Sarazin and Michard⁶ have calculated the Gibbs free energy of formation $\Delta_f G^\circ$ "on the basis of chemical analyses." The lack of experimental details renders the value of $\Delta_f G^\circ$ suspect. No additional thermodynamic data are available.

Nontronite, $\text{Na}_{0.3}(\text{Fe}^{3+})_2(\text{Si},\text{Al})_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$

A limited set of thermodynamic data is available for this smectite. Sarazin and Michard⁶ calculated $\Delta_f G^\circ$ "on the basis of chemical analyses." As with saponite, this value of $\Delta_f G^\circ$ is considered suspect. Tardy et al.⁷ calculated $\Delta_f G^\circ$ of nontronite from a study of the silicification of goethite. The value obtained is judged to be more reliable than the value reported by Sarazin and Michard. Horvath⁸ has determined the enthalpy of dehydroxylation of nontronite, but no basic thermodynamic property values can be deduced from this work.

³R. A. Robie, B. S. Hemingway, and J. R. Fischer, "Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 bar (10^5 Pascals) Pressure and at Higher Temperatures," U.S. Geol. Surv. Bull. 1452 (1979).

⁴G. K. Johnson, H. E. Flotow, P. A. G. O'Hare, and W. S. Wise, Am. Mineral. 67, 736 (1982).

⁵G. K. Johnson, Argonne National Laboratory, personal communication (1994).

⁶G. Sarazin and G. Michard, R. Acad. Sci. Ser. D285, 487 (1977).

⁷Y. Tardy, J. J. Trescases, and B. Fritz, C. R. Acad. Sci. Ser. D278, 1665 (1974).

⁸I. Horvath, Rev. Chim. Mineral. 17, 509 (1980).

Brannerite, (U,Ca,Y,Ce)(Ti,Fe)₂O₆

Mocala and Navrotsky⁹ have studied the energetics of brannerite-type solid solutions. It does not appear possible to deduce $\Delta_f H^\circ$ of "real" brannerite from this work.

Birnessite, Na₄Mn₁₄O₂₇•9H₂O

From considerations of fields of stability of several related Mn-bearing minerals, Parc et al.¹⁰ have estimated $\Delta_f G^\circ$ of birnessite to lie between -4439 and -4389 kJ/mol. This result is not considered very reliable because of a number of estimates and assumptions made in the analysis.

Stevensite, (Ca_{1/2})_{0.3}Mg₃Si₄O₁₀(OH)₂

No thermodynamic data have been reported in the literature.

Lithium Orthophosphate, Li₃PO₄

In the NBS tables of thermodynamic values,¹¹ $\Delta_f H^\circ = -2095$ kJ/mol. From the number of significant figures quoted, this is judged to be a reliable value.

Orthoclase, KAlSi₃O₈

The low-temperature heat capacity of orthoclase was measured from 5 to 300 K by Kirkina et al.¹² and the integrated heat content and standard entropy have been deduced from these values. Enthalpies and free energies of formation are reported by Robie et al.³ These data are considered to be very reliable.

⁹K. Mocala and A. Navrotsky, J. Solid State Chem. 74, 224 (1988).

¹⁰S. Parc, D. Nahon, Y. Tardy, and P. Viellard, Am. Mineral. 74, 466 (1989).

¹¹D. D. Wagman et al., J. Phys. Chem. Ref. Data 11, Suppl. No. 2 (1982).

¹²E. B. Kurkina, V. M. Kadoshnikov, and V. E. Yachmenev, Geokhim. 1987, 151 (1987).

APPENDIX 2. Effects of Network-Modifying Cations on the Coordination States of Oxygen Atoms in Silicate Glasses

The purpose of this Appendix is to calculate the effect of the addition of a cation oxide M_xO_y on the coordination numbers of oxygen atoms. A simple reference case is the addition of an alkali oxide (M_2O) to pure liquid SiO_2 , producing a liquid with the composition $xM_2O \cdot (1-x)SiO_2$. Each cation-anion bond requires an anion-cation bond, so the sum of cation coordination numbers equals the sum of anion coordination numbers. This can be used to compute the average coordination number of an oxygen atom, $n_{ave}(O)$, in the liquid:

$$n_{ave}(O) = \frac{2x(n_{ave}(M)) + (1-x)(n_{ave}(Si))}{x + 2(1-x)} = \frac{4 + x(2n_{ave}(M) - 4)}{2 - x} \quad (2.1)$$

where a coordination number of 4 for Si^{4+} is assumed (note that if $x = 0$, $n_{ave}(O) = 2$, as required). Using a coordination number of 4 for alkalis in M_2O (Li, Na^{13,14}; K, Rb, Cs¹⁵), and $x = 0.5$ as trial values, the projected value of $n_{ave}(O)$ is 4.0. Coordination numbers of 6 have been measured for Na^+ in alkali silicate glasses,³ which means that in such glasses $n_{ave}(O) \sim 5.3$.

This result can be generalized for a cation of valence z . The stoichiometry of an oxide can be written in terms of a single oxygen atom as $M_{2/z}O$, where z is the formal valence of M , in which case $n_{ave}(O)$ is written

$$n_{ave}(O) = \frac{[4 + 2x(n_{ave}(M)) / z - 4]}{2 - x} \quad (2.2)$$

From Eq. 2.2, it follows that when $n_{ave}(M)$ is greater than z , then $n_{ave}(O)$ will be greater than 2.0, its value in $v-SiO_2$. This is more often the case than not for cations of valence +4 or less. Thus, a general result of the addition of low-valence, electropositive cations to a silicate melt is that many of the oxygen atoms will coordinate with three or more cations, and only one of these will be Si^{4+} . This contrasts with the two-fold coordinated oxygen ions invoked in the continuous random network model, showing that it does not apply to multicomponent glasses.

We can now consider the distribution of bonds over oxygen atoms. Assume that in $xM_{2/z}O \cdot (1-x)SiO_2$ all oxygen atoms are BO bonded to two silicon atoms (denoted Si-O-Si) or bonded to one Si atom and one or more M atoms (denoted M-O-Si). (A third kind of oxygen bonded only to M atoms, is introduced below.) Each formula unit, $M_{2/z}O$, creates two M-O-Si, for a total of $2x$ in the liquid. Since the total number of O atoms is $2 - x$, the number of O atoms in Si-O-Si species is simply $2 - 3x$. As the $M_{2/z}O$ concentration increases, the number of Si-O-Si bonds decreases until $x = 2/3$, at which point all Si-O-Si bonds are consumed to form M-O-Si bonds. From this it follows that whenever $x < 2/3$, at least some of the oxygen will be involved

¹³J. W. Mellor, *Supplement to Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. II, Suppl. II, John Wiley & Sons Inc., New York (1961).

¹⁴J. W. Mellor, *Supplement to Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. II, Suppl. III, John Wiley & Sons Inc., New York (1963).

¹⁵X. Xue and J. F. Stebbins, "²³Na NMR Chemical Shifts and Local Na Coordination Environments in Silicate Crystals, Melts and Glasses," *Phys. Chem. Minerals* **20**, 297-307 (1993).

in Si-O-Si bonding arrangements. The glass-forming regions of most binary and more complicated silicate glasses are bounded on the low-SiO₂ end by $x \sim 0.5-0.6$, which means that a substantial fraction of oxygen atoms in nearly all silicate glasses are BO.

Oxygen atoms in M-O-Si species are termed nonbridging oxygen, or NBO. In the limit that M cations coordinate solely with NBO, one can use the following method to obtain an average NBO coordination number, $n_{ave}(NBO)$. The number of NBO is $2x$, and the number of BO is $2 - 3x$; therefore, the average coordination number of all oxygen expressed in terms of NBO and BO is

$$n_{ave}(O) = \frac{2x(n_{ave}(NBO)) + (2 - 3x)(n_{ave}(BO))}{2 - x} \quad (2.3)$$

Assuming $n_{ave}(BO) = 2.0$, then,

$$n_{ave}(NBO) = \frac{(2 - x)n_{ave}(O) - 2(2 - 3x)}{2x} \quad (2.4)$$

As determined in Eq. 2.4, $n_{ave}(NBO)$ is the maximum number of NBO in a binary silicate liquid. (The extension of this equation to a multicomponent liquid is trivial and will not be addressed.) Considering again the case in which an alkali cation is four-fold coordinated by oxygen in $0.5M_2O \cdot 0.5SiO_2$ glass, $n_{ave}(NBO) = 5.0$. Since one of the five cations would be silicon, the remaining 4 are M^{2+} cations.

APPENDIX 3. Compositions of Glasses Referenced in Section 4

This appendix is a compilation of glass compositions referred to in Section 4.0. Its purpose is to aid the reader in following the discussion in the text. A description of the tables and the sections in which they are discussed follows.

- Table 1. Compositions of Selected Domestic and Foreign Candidate Waste Glasses (Section 4.1). Compositions are expressed in terms of oxide components on a mole basis. All oxides present at a level of at least 0.1 mol% in at least one glass are shown, though additional elements appear in some listings. At the bottom of the table are shown the average concentration of each oxide in the glasses in which it occurs, the average concentration taken over all 29 glasses (whether present or not), the median concentration (a better indicator of central tendency), the minimum and maximum values, and the number of glasses in which the oxide is reported as a constituent.
- Table 2. Compositions of Glasses Discussed in the Study of Nogues et al. [172] (Section 4.6.1). The glass M7 is also analyzed by Advocat et al. [171].
- Table 3. Compositions of Glasses Studied by Hermansson et al. [176] (Section 4.6.1). Glasses ABS 39, ABS 41, and ABS 118 also appear in Table 1. Part (a) gives the bulk oxide constituents; part (b), the composition of the waste component.
- Table 4. Glass Compositions (mol%) from the Study of Van Iseghem et al. [179] (Section 4.6.1).
- Table 5. Compositions of Glasses Discussed in the Study of Tovenia et al. [181] Section 4.6.2). The composition of R7T7 is also given by Advocat et al. [171].
- Table 6. Compositions of Glasses Discussed by McGrail et al. [182] (Section 4.6.2). A complete listing of oxides for glass 76-68 presented by McVay and Buckwalter [183] is shown in Table 7 (note that the major oxide compositions of 768 and 3008 differ between these two studies).
- Table 7. Compositions of Glasses Discussed by McVay and Buckwalter [183] (Section 4.6.2). PNL 7668 and 3008 are also discussed by McGrail et al. [182].

Table 1. Compositions of selected candidate waste glasses (mol%).

Glass	SiO ₂	B ₂ O ₃	Na ₂ O	Li ₂ O	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	TiO ₂	ZnO	ZrO ₂	BaO	MnO ₂	MoO ₃
HW-39-1	56.74	9.16	11.15	8.45	2.80	4.62	3.44	1.32			0.32	0.04	0.15	0.14
SRL 131A	51.15	9.73	13.69	7.05	2.25	5.57	1.16	2.28	0.57	0.02	0.13	0.07	1.96	
SRL 165A	58.09	6.41	11.56	9.24	2.64	4.85	1.91	1.15	0.12	0.03	0.35	0.03	2.60	
SRL 202A	55.15	7.75	9.74	9.58	2.55	4.84	1.45	2.22	0.77	0.02	0.05	0.10	1.72	0.02
SRL 211	48.30	7.68	16.71	6.98	2.44	6.13	6.22					0.15	3.02	
WVCM-47	51.30	12.56	10.83	4.92	5.71	5.53	0.77	2.39	0.90		0.17	0.02	1.09	0.01
WVCM-50	48.38	12.94	11.59	5.45	7.10	5.48	1.07	1.44	0.77	0.03	0.24	0.09	1.02	0.02
WVCM-70, Ref-6	48.62	13.20	9.20	8.85	4.19	5.37	0.61	1.57	0.71	0.02	0.76	0.07	0.83	0.02
WV205	51.75	9.84	12.20	7.13	2.23	5.08	0.75	2.22	0.86		1.73	0.27	1.34	
PNL 76-68	52.59	9.03	17.87		0.33	4.99	2.83		2.82	4.32	0.99	0.25	0.03	0.97
GP 98/12	57.98	9.39	16.79		0.93	0.04	4.75	4.88	2.70		0.53	0.12	0.16	0.40
UK 209	53.95	10.18	8.53	8.51	3.19	1.09		10.02		0.31	0.74	0.16		0.78
UK 189	44.78	20.36	8.03	8.00	3.20	1.09		10.02		0.32	0.73	0.16		0.78
C 31/3	46.84	4.82	4.34	2.66	8.17	0.75	5.55	2.89	2.84	4.86	2.71	7.82	0.32	1.33
B 1/3	37.80	7.46	4.97	6.51	10.18	0.77	5.79	2.41	4.63	3.59	2.14	8.20	0.32	1.33
VG 98/3	49.10	10.61	25.31		0.83	0.31	2.92	0.70	3.11		1.34	0.29	0.32	1.06
SON 58	55.86	21.01	11.68		0.76	0.29					1.96	0.50		0.16
SON 64	56.76	19.13	14.62		1.20	2.46					1.15	0.29		0.95
SON 64/G3	56.35	19.03	14.21		0.15	2.83					1.22	0.31		1.06
SON 68 18 17 L1C2A2Z1	52.47	13.96	11.03	4.59	3.34	1.26	4.99			2.13	1.49	0.28	0.59	0.82
SAN 60	46.49	15.71	11.08	10.77	11.42	0.13	4.02				0.08	0.02		0.07
SM 58 LW 11	58.70	10.94	8.31	7.76	0.71	0.45	4.24	3.15	3.45		0.57	0.26	0.13	0.51
ABS 29	57.47	15.16	10.07	6.67	1.63	0.25				4.90	0.69	0.20	0.59	0.75
ABS 41	58.31	15.39	10.22	6.76	1.65	1.27				2.48	0.70	0.20	0.60	0.76
ABS 39	57.09	19.40	14.72		2.15	2.52					0.73	0.21	0.63	0.80
ABS 118	52.45	13.93	11.06	4.64	3.33	1.26	4.94			2.13	1.47	0.26	0.77	0.98
JSS-A	52.19	14.37	10.97	4.58	3.32	1.26	4.97			2.15	1.48	0.27	0.57	0.82
JW-D	54.86	18.14	12.39	4.25	1.33	1.51	2.27				1.58	0.28	0.20	0.82
GC-12/9B	52.35	13.10	9.96	7.75	2.80	2.23	3.04	2.53	4.36		1.11		0.03	
average(when present)	52.55	12.77	11.82	6.87	3.19	2.56	3.22	3.20	2.04	1.82	0.97	0.75	0.83	0.64
average (all glasses)	52.55	12.77	11.82	5.21	3.19	2.56	2.33	1.77	0.99	0.94	0.94	0.72	0.66	0.53
median	52.47	12.94	11.08	7.01	2.55	1.51	3.04	2.34	1.80	2.13	0.75	0.21	0.59	0.78
minimum	37.80	4.82	4.34	2.66	0.15	0.04	0.61	0.70	0.12	0.02	0.05	0.02	0.03	0.01
maximum	58.70	21.01	25.31	10.77	11.42	6.13	6.22	10.02	4.63	4.90	2.71	8.20	3.02	1.33
occurrence (%)	100%	100%	100%	76%	100%	100%	72%	55%	48%	52%	97%	97%	79%	83%

Table 1. (cont.)

Glass	K2O	NiO	CeO2	Nd2O3	P2O5	Cs2O	RuO2	SrO	Cr2O3	ThO2	La2O3	U3O8	PdO	Pr2O3
HW-39-1		0.53	0.08	0.10		0.05	0.05	0.06	0.57		0.10			0.02
SRL 131A	2.88	1.17						0.01	0.06		0.00	0.23		
SRL 165A	0.13	0.75						0.07				0.07		
SRL 202A	2.67	0.74						0.02	0.04	0.07		0.16		
SRL 211	0.04	1.53	0.35	0.19				0.24	0.00					
WVCM-47	0.99	0.27	0.03	0.03	1.28	0.02		0.02	0.10	0.99	0.01	0.05		0.01
WVCM-50	1.25	0.30	0.31	0.03	1.28	0.02		0.01	0.07	0.98	0.01	0.05		0.01
WVCM-70, Ref-6	3.78	0.24	0.07	0.03	0.60	0.02	0.04	0.01	0.07	0.96	0.01	0.05	0.02	0.01
WV205	2.55	0.64	0.06		1.21	0.02			0.10					
PNL 76-68		0.25	0.44	0.90	0.36	0.22	0.43		0.24		0.11			
GP 98/12		0.08	0.16	0.07	0.20	0.05	0.25	0.15	0.02		0.02	0.02	0.17	0.02
UK 209		0.31	0.37	0.34	0.10	0.17	0.33	0.20	0.23		0.09		0.23	0.08
UK 189		0.31	0.37	0.34	0.11	0.17	0.32	0.20	0.23		0.09		0.22	0.08
C 31/3		0.25	0.62	0.58		0.49	0.56	0.46	0.22		0.16	0.04	0.07	0.15
B 1/3		0.26	0.62	0.58		0.49	0.32	0.46	0.23		0.16	0.05	0.05	0.15
VG 98/3		0.20	0.64	0.45	0.30	0.34	0.56	0.34	0.11		0.13	0.10	0.36	0.12
SON 58		1.13	0.93	0.68	0.33	0.49	1.08	0.49	0.10		0.46	0.33	0.61	0.21
SON 64		0.23	0.54	0.40		0.29	0.34	0.29	0.20	0.12	0.13	0.04	0.20	0.12
SON 64/G3		0.21	0.58	0.42	0.22	0.31	0.37	0.10	0.25		0.14	0.08	0.21	0.13
SON 68 18 17 L1C2A2Z1		0.69	0.37	0.33	0.14	0.32		0.23	0.23	0.09	0.19	0.04		0.09
SAN 60			0.04	0.01				0.03			0.04			0.02
SM 58 LW 11		0.09	0.23	0.39										
ABS 29		0.33	0.29	0.24		0.21		0.17			0.14	0.13		0.08
ABS 41		0.33	0.29	0.24		0.21		0.17			0.15	0.13		0.08
ABS 39		0.35	0.31	0.25		0.22		0.18			0.15	0.14		0.08
ABS 118		0.80	0.38	0.31	0.15	0.27		0.22	0.23		0.19	0.07		0.10
JSS-A		0.69	0.37	0.33	0.23	0.35		0.22	0.23	0.04	0.19	0.04		0.09
JW-D		0.30	0.56	0.33		0.24		0.22			0.11			0.10
GC-12/9B	0.01	0.07		0.15				0.06	0.05			0.38		
average(when present)	1.59	0.47	0.36	0.31	0.46	0.23	0.39	0.18	0.16	0.46	0.12	0.11	0.21	0.08
average (all glasses)	0.49	0.45	0.31	0.27	0.22	0.17	0.16	0.16	0.12	0.11	0.10	0.08	0.07	0.06
median	1.25	0.31	0.37	0.33	0.27	0.22	0.33	0.17	0.16	0.12	0.13	0.07	0.21	0.08
minimum	0.01	0.07	0.03	0.01	0.10	0.02	0.04	0.01	0.00	0.04	0.00	0.02	0.02	0.01
maximum	3.78	1.53	0.93	0.90	1.28	0.49	1.08	0.49	0.57	0.99	0.46	0.38	0.61	0.21
occurrence (%)	31%	97%	86%	86%	48%	76%	41%	90%	76%	24%	79%	69%	34%	72%

Table 1. (cont.)

Glass	Gd2O3	TeO2	Y2O3	Tc2O3	CuO	Sm2O3	CoO	As2O3	Ag2O
HW-39-1			0.01		0.08	0.01			
SRL 131A				0.01	0.02				
SRL 165A									
SRL 202A				0.01	0.34				
SRL 211					0.00				
WVCM-47			0.01			0.01			
WVCM-50			0.01		0.04				
WVCM-70, Ref-6			0.01		0.03	0.01	0.02		
WV205									
PNL 76-68	0.01								
GP 98/12		0.04	0.02			0.01			
UK 209			0.05						
UK 189			0.05						
C 31/3		0.13	0.12					0.20	
B 1/3		0.13	0.12					0.16	
VG 98/3	0.01	0.11	0.10			0.10			
SON 58	0.02	0.24	0.13	0.21		0.13			0.01
SON 64	0.01	0.14	0.07	0.12		0.08			0.01
SON 64/G3	1.25	0.15	0.08	0.13		0.08			0.01
SON 68 18 17 L1C2A2Z1		0.10	0.06				0.11		0.01
SAN 60				0.04					
SM 58 LW 11							0.09		
ABS 29			0.04						
ABS 41			0.04						
ABS 39			0.05						
ABS 118			0.06						
JSS-A		0.10	0.06				0.11		0.01
JW-D	0.01	0.10	0.06			0.06	0.11		0.10
GC-12/9B									
average(when present)	0.22	0.12	0.06	0.09	0.08	0.05	0.09	0.18	0.02
average (all glasses)	0.05	0.04	0.04	0.02	0.02	0.02	0.02	0.01	0.00
median	0.01	0.12	0.05	0.08	0.03	0.06	0.11	0.18	0.01
minimum	0.01	0.04	0.01	0.01	0.00	0.01	0.02	0.16	0.01
maximum	1.25	0.24	0.13	0.21	0.34	0.13	0.11	0.20	0.10
occurrence (%)	21%	34%	69%	21%	21%	31%	17%	7%	21%

Table 2. Glass compositions (wt%) from the study of Nogues et al. [172].

Glass	SiO ₂	Al ₂ O ₃	Na ₂ O	B ₂ O ₃	Fe ₂ O ₃	CaO	MgO	MoO ₃	Li ₂ O	Simulated Waste
M1	47.6		12.4	18.6	6.4			2.5		15.0
M2	42.7	8.6	14.2	17.8	4.0			2.1		12.7
M3	51.1	4.1	13.2	13.6	1.6	4.1	3.5	1.6		10.9
M4	45.6	4.9	8.8	22.0	2.8			2.6		15.9
M5	50.0	3.0	12.5	14.4	3.0	2.0		1.7	2.0	12.2
M6	48.4	2.0	11.3	18.5	3.0	3.8		1.7		12.2
M7	46.1	5.0	12.5	14.2	3.0	4.1		1.7	2.0	12.2

Table 3.a. Glass compositions (wt%) from the study of Hermansson et al. [176].

Glass	SiO ₂	Na ₂ O	B ₂ O ₃	Fe ₂ O ₃	Al ₂ O ₃	UO ₂	ZnO	Li ₂ O	CaO	P ₂ O ₅	Cr ₂ O ₃	NiO	ZrO ₂	Waste
EXP 1	54.0	9.9	16.7	3.1	2.6	1.6	3.1							9.0
EXP 2	52.2	12.6	16.1	3.0	2.5	1.6	3.0							9.0
EXP 3	54.0	9.9	16.7	3.1	2.6	1.6		3.1						9.0
EXP 4	46.3	12.5	18.5	5.5	3.0	1.7	3.0							9.0
EXP 5	51.5	12.9	16.1	5.7	3.1	1.7								9.0
EXP 6	51.2	12.9	19.1	3.0	3.1	1.7								9.0
EXP 7	48.5	9.9	19.1	5.7	3.1	1.7		3.0						9.0
ABS 39	48.5	12.9	19.1	5.7	3.1	1.7								9.0
ABS 41	52.2	9.6	16.1	3.0	2.5	1.6	3.0	3.0						9.0
ABS 118	45.5	9.9	14.0	2.9	4.9	0.9	2.5	2.0	4.0	0.3	0.5	0.4	1.0	11.3

Table 3.b. Waste composition (wt%) from the study of Hermansson et al. [176].

Cs ₂ O	SrO	BaO	Y ₂ O ₃	ZrO ₂	MoO ₃	MnO ₂	NiO	Ag ₂ O	SnO	Sb ₂ O ₃	La ₂ O ₃	Nd ₂ O ₃	Pr ₂ O ₃	Ce ₂ O ₃	CdO
9.78	2.89	5.11	1.67	14.22	18.11	8.56	4.11	0.12	0.19	0.04	7.89	13.44	4.22	8.33	0.29

Table 4. Glass compositions (mol%) from the study of van Iseghem et al. [179].

Glass	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Fe ₂ O ₂	Na ₂ O	K ₂ O	MgO	CaO	BaO	MoO ₃	Cr ₂ O ₃	CuO	NiO	TiO ₂
WG 119	66		10		6	6	6	6						
WG 122	66			10	6	6	6	6						
WG 123	66	5		5	6	6	6	6						
WG 124	70	2		6	4	1	5	5	2	1	1	1	1	1

Table 5. Glass compositions from the study of Tovená et al. [181]. Ro is initial rate. (FP+act)ox is oxides of fission products and actinides.

Glass	SiO ₂	Al ₂ O ₃	B ₂ O ₃	Na ₂ O	Fe ₂ O ₃	CaO	Li ₂ O	(FP+act)ox	Other	Ro (g/m ² /d)
R7T7 (0.710)	41.78	5.08	12.89	10.64	3.71	3.71	1.82	15.56	4.81	5.12
R7T7 (0.739)	43.51	5.00	13.41	10.28	3.34	3.86	1.90	14.11	4.59	4.03
R7T7 (0.755)	44.47	4.95	13.71	10.07	3.13	3.95	1.94	13.28	4.50	3.55
R7T7 (0.819)	48.22	4.78	14.87	9.27	2.31	4.28	2.10	10.10	4.07	3.50
R7T7 (0.872)	51.30	4.63	15.82	8.61	1.64	4.56	2.24	7.43	3.77	3.00
R7T7 (0.932)	54.81	4.47	16.90	7.86	0.88	4.87	2.39	4.42	3.40	3.02
1	69.35	3.00	2.00	19.00				6.65		5.09
2	65.55	3.00	2.00	19.00				10.45		3.47
3	66.00	3.00	2.00	14.25				14.25		4.60
4	63.48	6.00	2.00	18.40				10.12		4.38
5	64.40	6.00	2.00	13.80				13.80		4.27
6	59.34	12.00	2.00	17.20				9.46		5.23
7	51.60	12.00	2.00	21.50				12.90		3.70
8	64.97	3.00	8.00	17.80				6.23		2.03
9	61.41	3.00	8.00	17.80				7.79		2.21
10	62.30	3.00	8.00	13.35				13.35		1.55
11	59.34	6.00	8.00	17.20				9.46		1.56
12	55.90	6.00	8.00	17.20				12.90		2.06
13	55.20	12.00	8.00	16.00				8.80		1.30
14	47.20	12.00	8.00	24.00				8.80		2.05
15	48.00	12.00	8.00	12.00	2.40			20.00		1.60
16	52.70		9.80	19.70	4.20			15.40		8.03
17	49.60		9.60	10.80	5.30			25.80		2.78
18	43.20	1.80	18.40	9.40	2.80			21.90		5.80
19	45.60	4.90	22.00	8.80	4.50			15.90		3.94
20	51.60		19.10	15.30	6.40			9.50		14.90
21	47.60		18.60	12.40	5.60			15.00		16.65
22	46.70		18.60	15.20	6.45			13.90		18.94
23	45.20		15.00	19.60	6.90			13.80		27.00
24	40.40		20.70	18.40		5.10		13.60		68.00
25	54.13		13.56	13.19		4.10		10.86		11.70
26	51.13	4.00	13.56	13.19				10.86		1.70

Table 6. Compositions of glasses from the study of McGrail et al. [182].

Oxide	No. 1	No. 2	No. 3	No. 5	3008	No. 6	No. 7	No. 8	7668
SiO ₂	76.0	73.0	68.0	59.0	43.5	57.0	54.0	52.0	42.3
B ₂ O ₃	10.0	10.0	10.0	10.0	11.2	10.0	10.0	10.0	9.0
Na ₂ O	14.0	14.0	14.0	14.0	15.4	14.0	14.0	14.0	14.2
CaO		3.0	3.0	3.0	2.9	3.0	3.0	3.0	2.2
ZnO			5.0	5.0	5.2	5.0	5.0	5.0	3.3
Fe ₂ O ₃				9.0	12.1	9.0	9.0	9.0	9.2
ZrO ₂						2.0	2.0	2.0	1.8
TiO ₂					4.8		3.0	3.0	3.0
MoO ₃								2.0	1.9
NiO					2.4				0.2
Cr ₂ O ₃					0.5				0.4
La ₂ O ₃									4.1
Nd ₂ O ₃									1.4
Ce ₂ O ₃									1.1
Other*									5.9

* See Table 7.

Table 7. Compositions of glasses from the study of McVay and Buckwalter [183].

Oxide	7668	3007	3008	Oxide	7668	3007	3008
SiO ₂	41.1	41.4	43.5	Rh ₂ O ₃	0.2		
B ₂ O ₃	10.4	10.7	11.2	Ag ₂ O	trace		
P ₂ O ₅	0.7	0.7		TeO ₂	0.3	0.4	
Na ₂ O	13.0	12.5	15.4	La ₂ O ₃	0.7		
K ₂ O	0.2	0.2		CeO ₂	1.2	1.0	
Rb ₂ O	0.1			Pr ₆ O ₁₁	0.6		
Cs ₂ O	0.8	0.8		Nd ₂ O ₃	3.2		
BaO	0.5			Sm ₂ O ₃	0.2		
CaO	2.2	2.4	2.9	Eu ₂ O ₃	0.1		
SrO	0.4	0.9		Gd ₂ O ₃	0.1		
MoO ₃	1.8	2.5		Fe ₂ O ₃	8.5	11.9	12.1
ZrO ₂	1.5	1.7		Cr ₂ O ₃	0.4	0.6	0.5
Y ₂ O ₃	0.1			NiO	0.2	0.3	2.4
RuO ₂	0.6	1.3		ZnO	5.2	5.7	5.7
PdO	0.5			TiO ₂	3.0	3.1	4.8
CdO	0.1						
Total					97.9	98.1	98.5

APPENDIX 4. A Primer on Linear Correlation

Linear correlation is used to obtain linear relationships between normalized elemental release and the indices obtained from the various models discussed in Section 5. It is not necessary to understand all of the mathematics by which linear correlations are obtained, but it is important to recognize the strengths and limitations of the approach.

Linear correlation is a form of least-squares regression in which the uncertainties for all points are assumed to be the same. In least-squares regression, one minimizes the merit function χ^2 :

$$\chi^2 = \sum_{i=1}^n \left(\frac{y_i - y}{\sigma_i} \right)^2 \quad (4.1)$$

where y_i is the measured value of one of the n data points, y is the predicted value, and σ_i is the uncertainty in y_i . In linear correlation one sets all $\sigma_i = 1$, in which case χ^2 is referred to as the predicted error sum of squares. The goodness of fit is usually expressed in terms of the dimensionless correlation coefficient R

$$R^2 = 1 - \frac{\sum_{i=1}^n (y_i - y)^2}{\sum_{i=1}^n (y_i - \bar{y})^2} \quad (4.2)$$

where y_i is the i -th measured value, y is the predicted value, and $\bar{y}$ is the average of the n values of y_i . R is positive for a positive correlation (slope) and negative for a negative correlation (slope). In the limit of a perfect linear correlation, the numerator in Eq. 4.2 goes to zero and $R = R^2 = 1$. In the limit that the model is completely uncorrelated with the data, the predicted value y will oscillate randomly about the average, and the R will go to zero. Though it is usually R that is reported, R^2 is the more significant statistic, as it is proportional to the percentage of the trend in the data that is accounted for by the correlation.

Goodness of fit is more often expressed in terms of R , and any variation in R is regarded as significant. This is probably true when R is already large (i.e., the correlation explains most of the trend in the data), but is less significant when R is relatively small, mainly because relatively little of the data is accounted for by the correlation. It is not possible to establish a general rule between the value of R and the validity of a model because errors that might bias the result are explicitly ignored. To this end, it is useful to consider another measure of the goodness of fit, the standard error of the correlation, σ_x

$$\sigma_x = \sqrt{\frac{\sum_{i=1}^n (y_i - y)^2}{N - 1}} \quad (4.3)$$

where N is the number of degrees of freedom (for regression of a single parameter through n points, $N = n - 1$). The standard error provides an estimate of the range of measured values about the predicted values. It is, in effect, the sample standard deviation of the distribution of

measured values about the line representing a perfect correlation, and therefore approximately 67% of measured values will lie within one standard error of the line representing a perfect correlation. Since the model indices are regressed against $\log(LR_i)$, the standard error represents a difference in log units, and therefore can be quite substantial in linear terms.

A significant limitation to least-squares regression for real data is that the predicted error sum of squares is much larger for points far from the predicted value than for points close to the predicted value. For this reason, least-squares regression in general, and linear correlation in particular, are generally quite sensitive to data that lie far from a predicted trend. As a result, when one plots the difference between the measured and predicted values, $y_i - y$, against the measured value y_i , there is often a trend in the data that does not look at all random. An alternative method for identifying a linear correlation known as robust estimation uses the median value of the ordinate (y_i values) and minimizes $|y_i - y|$ rather than $(y_i - y)^2$. It is less susceptible to outliers than least-squares regression, but $|y_i - y|$ does not correspond to any normal statistic obtained in least-squares regression. It is still possible to calculate a value of χ^2 , but with the caveat that all errors in measurement are assumed to be equal and normally distributed. Because this assumption seems ill-founded for the database used in this analysis, robust estimation was not employed in this review.

APPENDIX 5. Reference Data Base Used to Test Models of the Composition Dependence of Glass Corrosion

This appendix presents the compositions of glasses used to test the free energy of hydration, structural bond strength, valence oxygen, and nonbridging oxygen models of glass corrosion kinetics. The compositions were taken from the compilation of Geldart and Kindle [196] but have been converted from wt% to mol%, oxide basis. In addition to the mol % of each oxide component, the number of moles of the oxides in 100 g of glass are also presented. Glasses are listed in order of increasing normalized silicon loss in a 28-day MCC-1 test. Solution pH at 28 days is also provided. The glasses have been subdivided into four categories: sodium boroaluminosilicate, alkali borosilicate, alkali lime silicates, and alkali aluminosilicates. The criteria used in these categories and the tables in which the compositions are found follow.

- Table 1. Compositions and MCC-1 Test Results of Sodium Boroaluminosilicate Glasses, Defined as Containing at Least 3 mol% Al_2O_3 , B_2O_3 , and Na_2O . Compositions in mol%.

- Table 2. Compositions and MCC-1 Test Results of Alkali Borosilicate Glasses, Defined as Containing at Least 3 mol% B_2O_3 and Alkali Oxide, but Less than 1 mol% Al_2O_3 . Compositions in mol%.

- Table 3. Compositions and MCC-1 Test Results of Alkali Lime Silicate Glasses, Defined as Containing at Least 5 mol% CaO and at Least 10 mol% Alkali Oxides, but Less than 3 mol% Al_2O_3 or B_2O_3 . Compositions in mol%.

- Table 4. Glasses and MCC-1 Test Results Containing at Least 3 mol% Al_2O_3 and Alkali Oxides, but Less than 1 mol% B_2O_3 . These are referred to as alkali aluminosilicates. Compositions in mol%.

Table 1. Sodium Boroaluminosilicate Glasses (mol%)

Glass	SiO ₂	B ₂ O ₃	Na ₂ O	Li ₂ O	Al ₂ O ₃	Fe ₂ O ₃	FeO	CaO	MgO	TiO ₂	ZrO ₂	BaO	MnO	K ₂ O	NiO	P ₂ O ₅
25-64	64.49	10.77	16.32		7.93			0.48								
M3	58.75	13.44	14.69		2.74	0.45	0.28	5.05	0.59	1.34	0.18	0.25	0.74		0.42	
51-66	67.03	9.85	15.60		3.67	1.97		0.63			0.04			0.01	0.11	0.47
M2	52.03	18.71	16.78		6.18	1.20	0.72				1.07	0.31	0.92		0.51	
165AL	57.53	8.07	9.01	8.80	6.55	2.39	1.44	1.66	1.41	0.05	0.56		1.34		0.86	
HWVS7	61.18	8.96	7.81	7.99	5.21	1.99		3.43	1.40		0.39	0.06			0.67	0.01
SRL165 AL	57.42	8.05	8.99	8.78	6.54	2.38	1.43	1.66	1.41	0.05	0.56	0.07	1.34		0.86	0.06
41-63	60.73	9.40	17.63		8.27	2.53		1.44								
JAP GB7	59.76	9.55	9.81	4.66	3.40	3.21	1.93	1.49	0.13	0.03	1.23	0.80	0.24	0.76	1.21	
M5	57.59	14.33	13.96	4.64	2.03	0.83	0.50	2.47			0.64	0.28	0.84		0.46	
4-44	51.69	7.71	21.24		6.04	3.27		7.40			0.08			0.02	0.24	1.00
HWVS12	57.25	9.46	7.91	7.65	5.67	6.44		3.47	2.00							
JAP G2	54.64	9.75	9.75	7.54	4.73	3.09	1.86	2.50	0.12	0.02	1.23	0.33	0.27	1.59	0.48	
54-72	37.41	18.35	19.14		7.67			17.44								
HWVS6	57.01	9.59	8.13	8.21	5.68	6.18		3.40	1.20		0.12	0.02			0.20	
21-36	66.52	4.90	17.49		1.90	2.18		5.01			0.06			0.02	0.18	0.75
U3O8_1	57.36	9.21	11.47	8.29	2.82	4.53		3.40	1.33	0.02	0.30	0.04			0.52	0.01
HWCR2	57.13	9.11	10.93	8.47	2.91	4.62		3.36	1.48		0.36	0.04			0.52	0.01
40-47	52.09	9.10	22.27		3.30	4.05		9.18								
U3O8_2	57.39	9.23	11.41	8.25	2.79	4.47		3.40	1.40	0.02	0.33	0.04			0.51	0.01
HWMAS4	57.09	9.07	6.56	6.34	2.82	4.61		3.28	1.29	0.03	0.37	0.05		7.13	0.54	0.10
HWMAS5	56.25	9.40	9.75		2.89	4.86		3.65	1.34	0.03	0.34	0.04		10.08	0.53	0.10
hwvs8	53.95	8.81	17.57	7.64	5.31	2.08		3.26	1.26							
HWCR0	57.69	9.28	10.97	8.53	2.91	4.67		3.37	1.49		0.32	0.04			0.53	0.01
HWCR134	57.26	9.23	10.91	8.52	2.94	4.65		3.38	1.46		0.32	0.04			0.52	0.01
HWCR1	57.72	9.24	10.76	8.36	2.93	4.67		3.37	1.46		0.32	0.04			0.52	0.01
U3O8_3	57.72	9.15	11.15	8.13	2.64	4.16		3.41	1.56	0.03	0.33	0.03			0.48	
HWCR5	57.68	9.22	10.97	8.63	2.92	4.67		3.35	1.49		0.31	0.04			0.53	0.01
UK209	55.02	9.74	8.30	8.54	3.19	4.57			8.80		0.65	0.15			0.28	
U3O8_5	58.24	9.29	10.79	8.40	2.15	3.50		3.45	1.31	0.03	0.25	0.03			0.42	
HWMAS1	56.68	9.32	18.92		3.01	4.68		3.58	1.32	0.03	0.40	0.05		0.62	0.53	0.10
U3O8_4	57.59	9.20	11.21	8.13	2.49	3.76		3.36	1.72	0.03	0.27	0.04			0.44	
ZR6A	55.65	8.95	11.51	8.11	3.60	5.90		3.21	1.37			0.05			0.68	0.01
zr1a	57.88	9.42	10.90	8.87	2.53	4.27		3.47	1.41			0.04			0.49	
ZR8A	55.48	8.72	11.58	8.32	3.52	6.01		3.32	1.28			0.06			0.67	0.01
HWVS10	57.66	9.06	12.21	8.44	2.08	3.53		3.31	1.56		0.39	0.06			0.69	0.01
165MM	57.06	6.46	11.74	10.75	2.46	3.30	1.98	1.67	1.11		0.36		2.38		0.65	

Table 1. Sodium Boroaluminosilicate Glasses (cont.).

Glass	Nd2O3	Cs2O	ThO2	Cr2O3	UO2	SrO	PbO	Sb2O3	Si loss (28d)	pH	moles/100g
25-64									4.0	8.5	1.55
M3	0.80	0.26							4.2	8.4	1.50
51-66	0.01	0.01	0.33	0.12	0.10	0.04			6.7	9.4	1.50
M2	0.98	0.32				0.26			7.8	8.5	1.41
165AL				0.08	0.21	0.03			7.8	8.9	1.53
HWVS7	0.06	0.05		0.72		0.08			8.2	9.0	1.51
SRL165 AL				0.08	0.21	0.03	0.08		8.6	9.0	1.53
41-63									9.0	9.0	1.49
JAP GB7	1.30	0.01		0.22		0.25			9.1	7.8	1.39
M5	0.89	0.30				0.23			9.2	9.1	1.50
4-44	0.03	0.03	0.70	0.25	0.22	0.08			9.5	9.4	1.42
HWVS12	0.15								9.8	9.5	1.49
JAP G2	1.30	0.25		0.21	0.05	0.29			9.9	7.8	1.39
54-72									10.0	9.8	1.55
HWVS6	0.02	0.01		0.20		0.03			10.0	9.0	1.47
21-36	0.02	0.02	0.53	0.19	0.17	0.06			10.9	9.5	1.51
U3O8_1	0.08	0.04		0.53		0.05			11.1	9.6	1.51
HWCR2	0.10	0.04		0.87		0.05			11.4	9.7	1.51
40-47									11.6	10.0	1.51
U3O8_2	0.09	0.04		0.51	0.05	0.05			11.9	9.6	1.48
HWMAS4	0.09	0.04		0.55		0.05			12.0	9.0	1.43
HWMAS5	0.09	0.04		0.57		0.06			12.0	9.1	1.39
hwvs8	0.13								12.0	9.7	1.53
HWCR0	0.10	0.04				0.05			12.1	9.7	1.51
HWCR134	0.10	0.04		0.58		0.05			12.2	9.7	1.51
HWCR1	0.09	0.03		0.43		0.05			12.2	9.7	1.51
U3O8_3	0.08	0.04		0.50	0.54	0.05			12.3	9.4	1.49
HWCR5	0.10	0.04				0.05			12.4	9.7	1.50
UK209	0.32	0.11		0.15		0.19			12.6	9.4	1.60
U3O8_5	0.07	0.03		0.42	1.59	0.04			12.7	9.5	1.44
HWMAS1	0.09	0.04		0.59		0.05			12.8	9.1	1.43
U3O8_4	0.08	0.03		0.45	1.16	0.05			13.0	9.4	1.48
ZR6A	0.12	0.05		0.73		0.07			13.0	9.7	1.44
zr1a	0.08	0.04		0.54		0.05			13.0	9.7	1.51
ZR8A	0.12	0.05		0.78		0.07			13.0	9.7	1.45
HWVS10	0.12	0.05		0.74		0.08			13.2	9.5	1.51
165MM						0.06			13.2	8.5	1.59

Table 1. Sodium Boroaluminosilicate Glasses (cont.)

Glass	SiO ₂	B ₂ O ₃	Na ₂ O	Li ₂ O	Al ₂ O ₃	Fe ₂ O ₃	FeO	CaO	MgO	TiO ₂	ZrO ₂	BaO	MnO	K ₂ O	NiO	P ₂ O ₅
SRL131 AL	51.89	9.45	10.42	8.53	7.14	2.75	1.65	2.18	2.92	0.07	0.29		1.49		0.88	
SRL165 TDS	55.33	8.25	9.30	9.26	3.79	4.09	2.46	2.07	1.54		0.37		2.05		1.08	
HWVS5	57.97	9.33	12.00	8.07	2.04	3.65		3.34	1.40		0.41	0.06			0.70	0.01
SRL131 AL	51.89	9.45	10.42	8.53	7.14	2.75	1.65	2.18	2.92	0.07	0.29		1.49		0.88	
U3O8_6	57.99	9.31	10.95	8.42	1.96	3.16		3.52	1.37	0.03	0.24	0.03			0.37	
HWVS2	57.57	9.42	12.09	8.29	2.03	3.60		3.32	1.48		0.41	0.06			0.70	0.01
8-62	61.12	10.74	17.95		3.76	4.94		1.49								
SRL165 TDS	55.33	8.25	9.30	9.26	3.79	4.09	2.46	2.07	1.54		0.37		2.05		1.08	
SRL-165NR	57.66	6.90	11.86	11.40	3.23	4.56		1.17	1.26		0.83	0.05		0.06	0.77	0.01
52-42	48.94	6.31	19.57		2.39	2.70		18.01			0.07			0.02	0.19	0.78
HWVS11	56.77	8.46	17.61	7.68	3.28	1.98		3.00	1.20							
zr2a	60.40	9.93	10.54	9.13	1.68	2.70		3.51	1.32			0.02			0.31	
ZR9A	60.55	9.76	10.65	9.14	1.56	2.74		3.51	1.32			0.02			0.31	
AH11	53.87	11.51	7.28	8.59	2.91	3.72	2.23	1.00	2.12	1.09			2.47	2.27	0.88	
165 BLACK	56.50	6.70	10.27	11.05	2.82	2.21	4.37	1.98	1.09		0.35		1.50		0.85	
AH7	53.73	11.01	10.15	7.24	2.94	3.76	2.26	1.01	1.07	1.10			2.50	2.30	0.89	
AH10	57.34	7.10	7.18	9.89	2.87	3.67	2.20	0.99	2.09	1.07			2.44	2.24	0.86	
AH9	55.49	8.77	10.08	7.91	2.92	3.74	2.24	1.01	1.09	1.09			2.48	2.28	0.88	
AH165	56.21	6.73	10.71	10.97	2.72	3.62	2.17	0.97	1.16	1.06	0.38		2.40		0.85	
AH5	57.24	6.57	10.01	8.56	2.90	3.71	2.23	1.00	1.06	1.08			2.46	2.26	0.87	
131AT 50%	41.70	7.66	12.87	6.92	4.00	8.27	4.97	2.59	1.80	0.45	0.15		5.68		2.82	
SRLS2	53.00	13.79	15.09		3.38	4.26	2.56	1.93	1.23		0.39		3.45		0.92	
AH2	47.94	12.86	12.24	8.68	2.94	3.81	2.28	1.01	1.07	1.10	0.35		2.49	2.29	0.89	
SRL131 TDS	49.77	11.01	9.93	7.14	7.13	3.78	2.27	1.83	2.40	0.61	0.26		2.33		0.87	0.01
80-46	53.25	5.91	20.90		2.62	9.30		5.70			0.07			0.02	0.21	0.87
AH1	52.05	8.18	12.50	9.70	2.71	3.71	2.23	1.55	1.03	1.04	0.33		1.88	2.23	0.82	
131AT 30%	46.61	9.44	14.08	8.53	2.11	4.37	2.62	1.37	3.61	0.56	0.18		2.99		3.47	
SRL 168A	52.09	11.24	10.70	9.24	3.09	3.88	2.34	1.83	1.17		0.37		3.15		0.90	
AH6	51.56	8.40	12.07	9.99	2.90	3.71	2.23	1.00	1.06	1.08	0.35		2.46	2.26	0.87	
AH3	53.88	9.45	11.26	6.98	2.73	3.74	2.25	1.56	2.08	1.05			1.90	2.25	0.83	
AH8	53.45	9.71	10.79	7.20	2.93	3.74	2.25	1.01	2.13	1.09			2.48	2.28	0.88	
AH15	49.86	9.11	10.43	6.56	3.73	4.82	2.89	2.12	1.94	1.13			3.86	2.35	1.14	
SRL 168B	52.12	11.24	10.70	9.25	3.09	3.88	2.34	1.77	1.17		0.37		3.15		0.90	
AH13	53.52	6.27	9.75	7.82	3.72	4.80	2.88	2.11	0.97	1.12	0.32		3.20	2.34	1.13	
AH131	49.12	10.04	14.49	9.07	2.76	3.68	2.21	0.99	2.36	1.67	0.19		2.44		0.87	
AH14	48.48	7.97	11.67	9.16	3.73	4.81	2.89	2.12	0.98	1.12	0.32		3.21	2.35	1.14	
AH12	45.16	12.06	11.83	7.94	3.78	4.88	2.92	2.15	0.99	1.14	0.32		3.25	2.38	1.15	

Table 1. Sodium Boroaluminosilicate Glasses (cont.)

Glass	Nd2O3	Cs2O	ThO2	Cr2O3	UO2	SrO	PbO	Sb2O3	Si loss (28d)	pH	moles/100g
SRL131 AL				0.09	0.24	0.03			13.3	9.0	1.54
SRL165 TDS				0.09	0.28	0.04			13.5	9.6	1.56
HWVS5	0.11	0.05		0.79		0.08			13.5	9.6	1.49
SRL131 AL				0.09	0.24	0.03			13.7	8.8	1.54
U3O8_6	0.06	0.03		0.39	2.14	0.04			13.9	9.4	1.43
HWVS2	0.13	0.06		0.76		0.07			13.9	9.5	1.49
8-62									13.9	9.2	1.47
SRL165 TDS				0.09	0.28	0.04			14.3	8.9	1.56
SRL-165NR	0.12			0.06		0.02	0.03		14.3	10.0	1.48
52-42	0.02	0.02	0.55	0.20	0.17	0.06			14.5	10.5	1.50
HWVS11				0.02					14.6	10.2	1.61
zr2a	0.05	0.02		0.33		0.03			15.0	9.7	1.58
ZR9A	0.05	0.02		0.33		0.03			15.0	9.8	1.58
AH11		0.01				0.03			15.0	8.8	1.50
165 BLACK					0.25	0.05			15.3	9.5	1.57
AH7		0.01				0.03			15.5	8.4	1.48
AH10		0.01				0.03			15.6	8.8	1.52
AH9						0.03			15.6	8.6	1.49
AH165		0.01				0.03			15.7	9.4	1.54
AH5		0.01				0.03			15.7	8.4	1.50
131AT 50%	0.11								16.0	9.4	1.38
SRLS2									16.2	9.0	1.46
AH2		0.01				0.03			16.8	8.2	1.48
SRL131 TDS				0.08	0.53	0.03			16.8	9.9	1.48
80-46	0.02	0.02	0.61	0.22	0.19	0.07			17.0	10.0	1.34
AH1		0.02				0.03			17.1	8.8	1.52
131AT 30%	0.07								17.2	9.5	1.57
SRL 168A									18.6	8.2	1.54
AH6		0.01				0.03			18.7	9.0	1.50
AH3		0.02				0.03			18.8	8.9	1.51
AH8		0.01				0.03			18.9	8.8	1.49
AH15		0.02				0.04			19.5	8.9	1.44
SRL 168B									19.6	9.4	1.54
AH13		0.02				0.04			19.8	8.9	1.45
AH131	0.07	0.01				0.03			20.2	9.6	1.51
AH14		0.02				0.04			20.2	9.1	1.45
AH12		0.02				0.04			20.8	8.9	1.43

Table 1. Sodium Boroaluminosilicate Glasses (cont.)

Glass	SiO ₂	B ₂ O ₃	Na ₂ O	Li ₂ O	Al ₂ O ₃	Fe ₂ O ₃	FeO	CaO	MgO	TiO ₂	ZrO ₂	BaO	MnO	K ₂ O	NiO	P ₂ O ₅
60-20	45.24	25.16	14.06		6.18	9.04		0.32								
AH4	56.81	6.51	10.59	8.79	2.70	3.70	2.22	1.55	1.14	1.04			1.87	2.22	0.82	
SRLS17	54.98	6.11	10.82	11.23	3.15	3.96	2.38	1.80	1.14		0.36		3.22		0.86	
SRL131 FE	41.05	11.97	16.37	9.30	2.38	5.42	3.25	1.42	2.27	0.68	0.28		3.22		1.95	
SRL165 FE	49.88	10.48	15.10	8.32	1.59	4.70	2.81	1.31	1.38	0.63	0.28		2.28		1.08	
SRLS12	43.22	10.35	3.38	18.09	4.85	6.09	3.66	2.77	0.94		0.29		4.94		1.42	
SRL131 FE	41.05	11.97	16.37	9.30	2.38	5.42	3.25	1.42	2.27	0.68	0.28		3.22		1.95	
22-27	38.00	18.29	29.96		5.21			8.54								
2-38	48.07	20.13	19.21		2.21	2.56		5.65			0.07			0.02	0.20	0.81
55-27	37.16	18.10	31.49		5.15			8.10								
70-55	39.60	19.24	33.90		3.00	3.96		0.30								

Table 1. Sodium Boroaluminosilicate Glasses (cont.)

Glass	Nd ₂ O ₃	Cs ₂ O	ThO ₂	Cr ₂ O ₃	UO ₂	SrO	PbO	Sb ₂ O ₃	Si loss (28d)	pH	moles/100g
60-20									20.9	8.9	1.35
AH4		0.02				0.03			21.4	8.9	1.52
SRLS17									22.5	10.0	1.56
SRL131 FE				0.11	0.29	0.05			23.8	9.2	1.45
SRL165 FE		0.03		0.09		0.04			24.6	9.1	1.58
SRLS12									25.0	9.8	1.53
SRL131 FE				0.11	0.29	0.05			42.0	10.0	1.45
22-27									56.0	11.8	1.56
2-38	0.02	0.02	0.57	0.21	0.18	0.06			70.9	9.5	1.46
55-27									97.3	12.2	1.56
70-55									122.6	11.8	1.48

Table 2. Alkali Borosilicate Glasses (mol%)

Glass	SiO ₂	B ₂ O ₃	Na ₂ O	Li ₂ O	Al ₂ O ₃	Fe ₂ O ₃	FeO	CaO	MgO	TiO ₂	ZrO ₂	BaO	MnO	K ₂ O	NiO	P ₂ O ₅
16-58	43.39	7.20	20.52		0.69	9.29		18.90								
FRIT S12	53.42	15.37	2.59	26.86					1.33		0.43					
12-65	67.02	11.28	16.67		0.51	4.52										
103-83	53.25	12.83	21.87		0.20			11.86								
HWVS4	62.33	9.32	7.98	8.51		6.24		3.32	1.36		0.16	0.02			0.29	
HWVS15	59.35	9.78	8.52	8.38		4.88		3.67	1.55		0.70	0.10			1.20	0.01
88-91	55.02	5.45	18.83		0.31	1.03		17.35			0.06			0.02	0.18	0.75
HWVS14	58.85	9.59	8.44	8.52		5.69		3.68	1.59		0.69	0.10			1.19	0.01
FRIT S2	62.05	17.85	18.05						1.54		0.50					
X	65.22	8.70	16.08		0.16	0.09		9.67	0.08							
FRIT211	56.77	9.33	19.45	8.62				5.84								
FRIT165	64.58	8.20	11.97	13.37					1.42		0.46					
FRIT153	65.21	8.40	12.74	8.81					2.90	1.46	0.47					
HWVS13	54.60	8.90	18.20	7.86		6.17		3.14	1.13							
FRIT S17	63.77	7.75	12.36	14.25					1.41		0.46					
17-21	44.31	11.51	34.20		0.57	9.13		0.28								
83-8	60.93	17.41	21.12		0.27			0.28								
FRIT 165	64.58	8.20	11.97	13.37					1.42		0.46					
FRIT 168A	58.62	14.07	11.88	11.89	0.73	0.13		0.71	1.43		0.40				0.14	
FRIT 131	56.06	12.28	16.61	11.10					2.89	0.73	0.24					
FRIT 168	60.01	14.20	12.20	11.68					1.44		0.47					

Table 2. Alkali Borosilicate Glasses (cont.).

Glass	Nd2O3	Cs2O	ThO2	Cr2O3	UO2	SrO	PbO	Sb2O3	Si loss (28d)	pH	moles/100g
16-58									11.4	10.6	1.43
FRIT S12									15.8	9.5	1.87
12-65									28.2	9.3	1.51
103-83									29.6	10.2	1.63
HWVS4	0.15	0.01		0.31					33.9	9.8	1.50
HWVS15	0.27	0.10		1.37		0.12			33.9	10.1	1.44
88-91	0.02	0.02	0.53	0.19	0.17	0.06			34.2	10.6	1.56
HWVS14	0.13	0.09		1.31		0.13			34.5	10.1	1.45
FRIT S2									38.6	9.5	1.61
X									43.5	9.7	1.61
FRIT211									50.2	10.3	1.71
FRIT165									62.7	9.9	1.75
FRIT153									79.0	9.6	1.71
HWVS13									82.6	11.0	1.53
FRIT S17									154.4	10.5	1.76
17-21									159.2	11.7	1.41
83-8									198.9	10.2	1.61
FRIT 165									215.5	10.5	1.75
FRIT 168A									308.4	10.4	1.68
FRIT 131	0.09								555.0	11.1	1.72
FRIT 168									560.4	11.5	1.72

Table 3. Alkali Lime Silicate Glasses (mol%)

Glass	SiO ₂	B ₂ O ₃	Na ₂ O	Li ₂ O	Al ₂ O ₃	Fe ₂ O ₃	FeO	CaO	MgO	TiO ₂	ZrO ₂	BaO	MnO	K ₂ O	NiO	P ₂ O ₅
WINDOW	70.00		13.32		0.29			13.88	2.51							
DGH	76.13		11.71	0.09	1.65	0.14		7.24	2.31					0.65	0.01	
642ACTUAL	74.35	0.03	11.51	0.09	1.70	0.19		10.19	0.92	0.05		0.01	0.32	0.50	0.02	0.06
635ACTUAL	67.06		13.96	0.04	1.91	0.07		12.84	1.00	0.01	0.01		0.43	2.55	0.02	0.02
SCU	75.43		2.22	0.04	0.81	0.28		11.52	2.11	0.17	0.12	0.08	0.02	6.89	0.16	
DGW	62.55		1.83	0.05	1.93	0.68		20.94	4.65				0.61	6.71	0.01	
AAX	69.46	0.05	17.21		1.63	0.23		8.69	1.46				0.30	0.66		
EZI	65.43		17.28		1.64	0.75		11.77	1.58	0.01			0.87	0.65	0.02	
57-7	71.70		13.67		0.75	8.66		5.21								
EZT	66.26		16.40	0.09	1.40	0.41		9.41	3.74				1.02	1.28		
EZA	48.99		19.87	0.18	2.56	0.06		21.51	2.69					4.13		
JQR	59.89		1.49	0.09	1.20	0.45		18.77	4.03	0.01			0.83	12.73		0.47
53-52	65.28		12.63		0.41	2.27		17.26			0.07			0.02	0.20	0.81
AY	66.54		13.03		0.79	0.45		13.81	3.32				0.80	1.22		
EZB	51.66		9.93	0.27	1.91	0.06		13.68	11.89				0.01	10.14	0.02	
1824ACT	71.26	0.11	9.72	0.09	0.79	0.21		7.99	7.85	0.05	0.01		0.26	1.54	0.02	0.05
19AE	75.56		3.46	0.09	0.15	0.08		12.55	0.08					8.01	0.02	
1825 ACT	71.83	0.06	10.74	0.04	0.67	0.26		7.38	7.20	0.03			0.35	1.39		0.04
EZC	54.26		4.40		1.37			7.29	16.00					15.98		
GPX-DUP	69.11		19.15	0.13	0.14	0.10		11.24	0.09					0.02	0.01	
EFS148	57.30		0.10		2.45	0.16		29.55	0.08				0.18	9.92		
ESF150	54.52		9.06		2.49	0.11		23.09	9.68		0.10			0.94		
96-76	60.18		25.73		0.19			13.90								
ESF77-33	49.91		21.56		2.48	0.96		24.82	0.08	0.08		0.08	0.04			
EFS149	60.89		0.10		2.65			24.70	0.08	0.16			1.63	9.78		
ESF147	52.28		0.10		2.40			34.62	0.08	0.40	0.05			10.00		
ESF159	46.59				2.43	0.04		39.59	0.11	0.40			0.90	9.79		
74-12	54.37		29.42		0.22			15.99								
GPX	69.11		19.15	0.13	0.14	0.10		11.24	0.09					0.02	0.01	
ESF158	46.77		0.11		2.46			33.40	0.10				0.09	16.94	0.09	
ESF144	49.59		0.11		2.61	0.90		25.10	0.07	0.09		0.09	0.05	21.40		
10-30	41.44		32.61		0.46	7.17		18.33								

Table 3. Alkali Lime Silicate Glasses (cont.).

Glass	Nd2O3	Cs2O	ThO2	Cr2O3	UO2	SrO	PbO	Sb2O3	Si loss (28d)	pH	moles/100g
WINDOW									3.6	7.8	1.68
DGH								0.06	9.7	9.6	1.64
642ACTUAL				0.01		0.04	0.01		11.3	9.9	1.64
635ACTUAL				0.01		0.07	0.01		12.0	9.8	1.65
SCU						0.15			12.3	10.0	1.62
DGW				0.01		0.01	0.03		12.7	10.0	1.58
AAX								0.32	14.0	9.4	1.61
EZI				0.01		0.01	0.01		14.3	10.0	1.58
57-7									16.0	9.5	1.45
EZT									16.1	9.6	1.66
EZA								0.02	18.5	10.5	1.62
JQR						0.03			20.6	9.9	1.54
53-52	0.02	0.02	0.57	0.21	0.18	0.06			21.7	10.2	1.54
AY						0.03			22.3	9.8	1.67
EZB								0.43	25.2	10.7	1.59
1824ACT				0.01		0.03	0.02		27.7	9.6	1.62
19AE									28.2	10.1	1.59
1825 ACT							0.01		28.9	9.5	1.66
EZC								0.70	34.0	11.0	1.58
GPX-DUP									52.6	9.9	1.68
EFS148							0.26		62.9	9.3	1.56
ESF150									77.2	10.2	1.69
96-76									79.8	11.7	1.66
ESF77-33									84.0	9.8	1.62
EFS149									94.2	10.2	1.55
ESF147						0.06			95.3	9.8	1.55
ESF159							0.14		97.0	10.6	1.57
74-12									99.7	12.5	1.66
GPX									105.1	11.3	1.68
ESF158							0.04		109.0	10.6	1.52
ESF144									163.2	10.8	1.46
10-30									345.7	13.0	1.49

Table 4. Alkali Aluminosilicate Glasses (mol%)

Glass	SiO ₂	B ₂ O ₃	Na ₂ O	Li ₂ O	Al ₂ O ₃	Fe ₂ O ₃	FeO	CaO	MgO	TiO ₂	ZrO ₂	BaO	MnO	K ₂ O	NiO	P ₂ O ₅
BGC-50	62.72		9.95		8.06	2.97	1.78	6.72	4.25	2.57						0.97
CORNING	79.06		4.57		7.63		1.30	3.09	2.97	0.15				1.24		
SPODUMENE GLASS	73.26	0.03	0.17	9.24	14.11	0.09		0.67	0.06	1.21	0.82				0.32	
A&T	76.53	0.06	1.82	0.05	7.94		5.08	2.91	3.17	0.65	0.02		0.12	1.65		
CORNING	79.06		4.57		7.63		1.30	3.09	2.97	0.15				1.24		
GQQ	47.97	0.05	0.15	0.29	7.71		5.17	6.23	31.39	0.84			0.05		0.04	
DQF	77.45		6.23	0.09	7.92	1.59		5.13	1.11	0.01	0.01		0.05	0.34	0.02	
GQN	71.60		0.62	0.03	7.99		4.71	6.54	6.94	0.80			0.04	0.66	0.02	
RRL2-3134	68.33		3.42		8.84		9.42	4.48	0.96	2.21			0.24	1.69		0.43
9-3	73.24		13.60		5.61	7.56										
DQH	67.23		1.72	0.05	11.67	3.30		10.35	4.84	0.01			0.11	0.70	0.01	
39-59	63.96		7.62		8.20	1.82		16.47			0.06			0.02	0.18	0.72
P-16F	57.79		5.20		10.29	0.61	1.35	18.02	5.22	0.09	0.12			1.29		
69-16	50.10		14.63		6.26	9.09		19.92								
85-16	50.49		14.42		6.15	8.89		20.05								
73-1	60.73		17.36		5.03			16.87								
31-1	61.97		16.60		4.94			16.49								
P-40	63.28		11.03		3.82	4.64	2.79	8.78	1.36				2.78		0.82	
P-3	55.48	2.92	17.49		5.58	2.29	4.53	5.56		2.54			2.20		1.18	
P-1	58.22		19.42		8.00	1.72	3.44	6.20					2.07		0.54	
87-86	44.04		30.32		5.19	1.93		16.50			0.06			0.02	0.19	0.76
SRLS15	51.42		6.19	17.81	4.78	5.99	3.60	2.73	0.93		0.29		4.87		1.40	
6-71	39.17		32.06		7.99	2.89		17.90								
67-75	45.17		36.23		9.26	9.08		0.25								
86-68	64.77		27.47		7.65			0.11								
36-19	49.08		34.95		6.39	9.23		0.34								
27-2	64.24		30.36		5.16			0.24								
72-2	63.22		31.26		5.15			0.37								

Table 4. Alkali Aluminosilicate Glasses (cont.).

Glass	Nd2O3	Cs2O	ThO2	Cr2O3	UO2	SrO	PbO	Sb2O3	Si loss (28d)	pH	moles/100g
BGC-50									0.8	7.2	1.46
CORNING									1.7	4.7	1.57
SPODUMENE GLASS					0.01				1.9	8.3	1.50
A&T									1.9	6.5	1.51
CORNING									2.3	8.3	1.57
GQQ				0.01			0.09		2.6	7.8	1.68
DQF				0.01		0.01	0.02		3.4	8.6	1.55
GQN				0.01			0.04		3.6	8.2	1.60
RRL2-3134									4.0	8.3	1.45
9-3									5.0	8.8	1.42
DQH				0.01					5.1	8.6	1.52
39-59	0.02	0.02	0.51	0.18	0.16	0.05			5.6	9.3	1.48
P-16F						0.02			5.8	8.5	1.54
69-16									7.2	10.1	1.40
85-16									7.6	8.8	1.41
73-1									7.9	10.2	1.62
31-1									8.7	10.3	1.62
P-40	0.14	0.02		0.13	0.33	0.07			9.7	8.0	1.46
P-3					0.24				11.2	9.8	1.48
P-1					0.38				11.5	10.0	1.50
87-86	0.02	0.02	0.53	0.19	0.17	0.06			11.6	11.2	1.50
SRLS15									18.7	10.0	1.55
6-71									24.5	12.2	1.51
67-75									61.0	11.9	1.36
86-68									68.7	12.4	1.57
36-19									76.3	12.0	1.38
27-2									704.1	12.7	1.59
72-2									812.8	12.7	1.59

APPENDIX 6. Thermodynamics of Mixing of Silicate Glasses

This appendix addresses the structural chemistry and durability relationships of critical subsystems of vitreous waste glasses. First, it is necessary to decide precisely which components are "critical" and representative of the structural chemistry of the very much more complicated compositions typical of waste glasses. Ellison and Navrotsky¹⁶ have suggested that the most important components are those that, when added to a glass or varied in concentration within a series of glasses, produce the largest and most exothermic enthalpy or free energy of mixing. An example of great relevance in waste glass chemistry is the substitution of a component such as NaAlO_2 for SiO_2 in a simple silicate glass, which results in a large and exothermic enthalpy of mixing. Enthalpies of mixing measure the change in bond character as a function of the mixing parameter and therefore directly reflect the relative stabilities of bonding arrangements in an intermediate composition relative to either end-member. Therefore, large exothermic enthalpies of mixing mean that any intermediate composition has energetically more favorable bonding arrangements than either end-member. It should be noted, however, that a large, exothermic enthalpy or free energy of mixing produced by the addition of a component will only enhance waste glass durability in the limit that the partial enthalpy (free energy) of hydration of the component is relatively small or, ideally, endothermic. This has bearing upon the FEH model, discussed in more detail in Section 5.1.

Enthalpies of mixing are occasionally quite small. One reason for this is that there is very little difference in bond character between two components (e.g., mixing of two large alkali cations), and mixing is driven by entropy. Another, more important reason is that the glass or its precursor liquid may be a mechanical mixture of two phases, in which case compositional variations may simply change the relative proportions of the two phases. In the limit that the mixing parameter is parallel to a tie-line of a phase-separated field, enthalpies and free energies of mixing will be identically zero. This subtle and important point is also discussed in the context of the FEH model (Section 5.1) and SBS model (Section 5.2).

A glass or liquid is considered a continuous phase because a small variation in composition at fixed temperature and pressure (T and P), in general, does not result in the formation of a new phase. This is not generally true of crystals except in the case of solid solutions, which are true continuous phases within the limits of their mixing components, for which the considerations in this appendix apply. The mixing components in a crystalline solid solution are simply the end-member crystals, but for liquids and glass-forming systems, the choice of end-member components is somewhat arbitrary and is dictated mostly by the type of information desired. For example, if one generally obtains concentrations in terms of oxides, then oxide components might be the simplest mixing model; if one has theoretical or empirical evidence that a certain composition is manifestly more stable than any other, it might be a viable component by itself, regardless of what the other components are. This discussion will focus on mixing in the fictive binary liquids in the A-B system in equilibrium at constant T and P. Under these conditions, the thermodynamic state of the system is completely described by the molar Gibbs free energy, $\bar{G}_{A-B}$.

¹⁶A. J. G. Ellison and A. Navrotsky, "Thermochemistry and Structure of Model Waste Glass Compositions," *Mater. Res. Soc. Symp. Proc.* **176**, 193-207 (1990).

One can obtain a mechanical mixture of liquids A and B by placing each in contact with a constant T-P reservoir but separating them by a barrier that is impermeable to mass transfer. The molar free energy of this system is the weighted contribution of the end-members, e.g.,

$$\Delta G_{A-B} = X_A \bar{G}_A + X_B \bar{G}_B \quad (6.1)$$

where X_A and X_B are the mole fractions of A and B. When the barrier is removed, A and B will mix. If they form a single, homogeneous phase, then at all compositions it has a unique, well-defined molar free energy as well. By definition the free energy of the homogeneous mixture is more negative than the mechanical mixture; thus,

$$\Delta_{\text{mix}} G = \Delta G_{A-B} - (X_A \bar{G}_A + X_B \bar{G}_B) \quad (6.2)$$

where $\Delta_{\text{mix}} G$ represents the deviation of the free energy of the mixture from a mechanical mixture of the end-members.

The parameter $\Delta_{\text{mix}} G$ itself is a combination of the enthalpy of mixing, $\Delta_{\text{mix}} H$, and the entropy of mixing, $\Delta_{\text{mix}} S$:

$$\Delta_{\text{mix}} G = \Delta_{\text{mix}} H - T \Delta_{\text{mix}} S \quad (6.3)$$

From the Second Law, $\Delta_{\text{mix}} S$ is positive, so the only means by which $\Delta_{\text{mix}} G$ can be positive is if $\Delta_{\text{mix}} H$ is both positive and exceeds $\Delta_{\text{mix}} S$. Since $\Delta_{\text{mix}} H$ is often only weakly dependent on temperature, there is generally some (high) temperature at which $\Delta_{\text{mix}} G$ is negative even if $\Delta_{\text{mix}} H$ is positive. In effect, $\Delta_{\text{mix}} H$ lumps together all contributions from the changes in chemical bonds resulting from a chemical mixing process. When these interactions are favorable, $\Delta_{\text{mix}} H$ will be negative, and $\Delta_{\text{mix}} G$ must be everywhere negative as well. When they are unfavorable, $\Delta_{\text{mix}} H$ may be positive, and there may be a temperature at which $\Delta_{\text{mix}} G$ changes sign from negative to positive. When this temperature is greater than the melting temperature of crystalline A or B (or any intermediate crystal), the result is a region in composition space where two liquids coexist with each other at the same T and P, like oil and water. Alternatively, $\Delta_{\text{mix}} H$ may be positive, but so small that $\Delta_{\text{mix}} G$ is positive at all temperatures above the solidus of the A-B system. In this case, there exists a metastable two-liquid field below the solidus, which is only accessed when there is a barrier to nucleation, such as a rapid change in temperature or a high nucleus-liquid interfacial tension. An example of a metastable two-liquid field of considerable importance to waste-form development exists in the B_2O_3 -rich region of the Na_2O - B_2O_3 - SiO_2 ternary system, as discussed in Section 3.2.2 and indicated in Fig. 3.

A schematic representation of a $\Delta \bar{G}_{A-B}$ surface at fixed T (1300 K) and P is shown in Fig. 6.1. Each point along the surface represents the free energy of a liquid with that particular composition. A tangent line is shown intersecting the surface at composition X. The points at which the tangent line intersects the A and B axes are defined as the chemical potentials of A and B, $\mu_A(T,P)$ and $\mu_B(T,P)$, respectively:

$$\mu_A(T,P) = \frac{dG_{A-B}}{dX_A} \quad \text{and} \quad \mu_B(T,P) = \frac{dG_{A-B}}{dX_B} \quad (6.4)$$

Fig. 6.1. A Schematic Representation of the Molar Free Energy of the A-B System, $\bar{G}_{A-B}$, Plotted Against the Mole Fraction of B. The end-members are assumed to mix ideally. The solid curve is the free energy surface. The dashed line connecting the end-members is the mechanical mixing line. The solid line tangent to the free energy surface at composition X identifies the chemical potentials of A and B, μ_A and μ_B , respectively, in this composition. End-member molar free energies were arbitrarily chosen. The reference temperature is 1300 K.

When $X_B = 1$, $\mu_A(T,P) = \mu_A^0(T,P) = \bar{G}_A$, and likewise $\mu_B^0(T,P) = \bar{G}_B$. In the limit that A and B mix as discrete molecules with no chemical interactions, the difference in the chemical potential of A in its pure liquid compared to the A-B binary liquid is written

$$\mu_A(T,P) = \mu_A^0(T,P) + RT \ln(X_A) \quad (6.5)$$

The value of X_A must vary between 0 and 1, and therefore in this limit $\mu_A(T,P) \leq \mu_A^0(T,P)$. This is referred to as ideal mixing. Combining Eqs. 6.2 and 6.5,

$$\Delta_{\text{mix}}G = X_A RT \ln(X_A) + X_B RT \ln(X_B) \quad (6.6)$$

When a third, ideally mixing component C is added to liquids in the A-B system, the mole fractions of A and B are reduced, and thus the free energy of the liquid is reduced as well. Figure 6.2 shows $\Delta_{\text{mix}}G$ for ternary A-B-C liquids (1300 K) as a function of the mole fraction of C projected onto the A-B binary system. Two effects can be seen. First, the chemical potentials of the end-members must decrease with increasing C, as each represents not pure A or B, but rather binary A-C and B-C liquids. Second, $\Delta_{\text{mix}}G$ at all points decreases substantially from $X_C = 0.0$ to $X_C = 0.05$, but by proportionally smaller amounts as X_C increases from 0.05 to 0.1, and so on. The minimum in $\Delta_{\text{mix}}G$ occurs at the composition where $X_A = X_B = X_C = 0.33$.

In real liquids, ideal mixing does not occur because of Van der Waals interactions, magnetic interactions, chemical bonding, etc., and the discrepancy between ideal mixing and observed mixing behaviors of A (or B) is expressed in terms of the chemical activity a_A , and in particular in terms of the activity coefficient γ_A

$$\mu_A(T,P) = \mu_A^0(T,P) + RT \ln(a_A) = \mu_A^0(T,P) + RT [\ln(X_A) + RT \ln(\gamma_A)] \quad (6.7)$$

When $\gamma_A > 1$, use of X_A results in an underestimate of the true chemical potential of A; that is, the mixture behaves more as if it were pure A than otherwise. This is a hallmark of unfavorable chemical interactions and is referred to as a positive deviation from ideality. On the other hand, when $\gamma_A < 1$, use of X_A in Eq. 6.2 results in an overestimate of the chemical potential of A; that is, A has very favorable chemical interactions in the A-B liquid. Figure 6.3 compares $\Delta_{\text{mix}}G$ for A-B binary liquids and liquids with 10 mol% C for values of γ_C of 1.0 (ideal mixing), 10.0 (large positive deviation from ideality), and 0.1 (large negative deviation from ideality). The positive deviation from ideality actually raises the free energy of the mixed system to a value greater than that of the A-B binary alone, though $\Delta_{\text{mix}}G$ is still everywhere negative. The negative deviation from ideality, however, decreases $\Delta_{\text{mix}}G$ such that the minimum lies well below the absolute minimum in the A-B-C system when all components mix ideally (Fig. 6.2).

Chemical reactions proceed so as to decrease the free energy of the system, which means that on average the chemical potentials of the components in the system are reduced as well. In some cases particular components may have much stronger (favorable or unfavorable) interactions with each other than with the remainder of the liquid, and thus their chemical potentials will play a substantial role in determining the overall free energy change of the reaction. Moreover, the chemical potentials of some components may be so high that a new phase forms, perhaps a crystal or a second liquid. Thus, it is difficult to predict in advance what effect the addition of a component might have on the free energy of the system. With these caveats in mind, it is still worthwhile to make some generalizations about the effects of adding components to homogeneous, well-mixed silicate liquids. First, as demonstrated in Fig. 6.2, the first few mole percent of an oxide added to a liquid has a larger absolute effect upon the free energy of the system than subsequent additions. Second, an oxide added in low concentrations

Fig. 6.2. The Free Energy of Mixing of the A-B-C System as a Function of the Addition of C Projected onto the A-B Binary. All components are assumed to mix ideally. The reference temperature is 1300 K. The molar free energy decreases with increased C concentration.

Fig. 6.3. The Free Energy of Mixing of the A-B-C System as a Function of the Activity Coefficient of C, γ_C , Projected onto the A-B Binary. Values for the activity coefficient are 1.0 (ideal mixing), 10.0 (positive deviation from ideality), and 0.1 (negative deviation from ideality). The reference temperature is 1300 K. The molar free energy increases for $\gamma_C > 1.0$ and decreases for $\gamma_C < 1.0$.

to a silicate liquid will very often dissolve completely into the liquid at a temperature far below its own melting temperature. This is because its chemical potential in the liquid is so much lower than its chemical potential in its pure solid. Third, as suggested by Fig. 6.3, the addition of a component with very favorable chemical interactions with other components in the liquid will in turn stabilize the liquid with respect to crystallization. Components that play this role are sometimes referred to in the glass literature as "fluxes" and include alkali oxides and B_2O_3 . Fourth, as implied by Fig. 6.2, a component with very unfavorable interactions with the other components in the liquid may increase $\Delta_{\text{mix}}G$ (relative to the original liquid) so much that immiscibility results. In multicomponent liquids, however, it is more common for an "incompatible" component to induce nucleation of a crystalline phase in which it is a principal constituent. Examples of this include ZrO_2 , TiO_2 , and other large, tetravalent cations,^{17,18} the thermodynamics of which have been discussed elsewhere.¹⁹ Finally, when two components have very strong, favorable interactions with one another, but less favorable interactions with other components in the liquid, they may stabilize a crystalline phase in which they are both principal components. A well-known example is RPO_4 , monazite, where R is a lanthanide cation.^{20,21,22} These factors are important in the design of waste glasses to accommodate high levels of waste loading.

The attack of a glass by deionized water is very clearly a reaction driven by the differences in the chemical potentials of the glass components and pure water. These gradients are reduced by the movement of water into the glass and the movement of glass components into the water. From the discussion thus far, the resistance of a waste glass to aqueous attack, particularly by deionized water, can be increased by at least two complementary strategies. First, a component can be added to the waste glass that has very negative deviations from ideality in the waste glass, but near ideal or positive deviations from ideality in water. This sharply lowers the free energy of the waste glass relative to deionized water, particularly for the component in question. Second, one can add many components to the waste glass, regardless of how they behave in water, because each will serve to reduce the chemical potential gradients between the waste glass and water. Most waste streams contain many oxide components, and so to a significant degree the waste itself can serve in this role.

The trick, then, is to identify components which mix with the base components of waste glasses with substantial negative and positive deviations from ideality. The former are used to stabilize the waste glass, while concentrations of the latter are minimized (where possible) to avoid destabilizing the waste glass. Then one adds as many favorable mixing components as possible to the waste glass so as to reduce the free energy of the waste glass overall. It is important to recognize that while thermodynamics points out the direction in which reactions will proceed, it provides absolutely no information about the mechanism, nor does it provide any

¹⁷E. B. Watson, "Zircon Saturation in Felsic Liquids: Experimental Results and Applications to Trace Element Geochemistry," *Contrib. Mineral. Petrol.* **70**, 407-419 (1979).

¹⁸J. E. Dickinson Jr. and P. C. Hess, "Rutile Solubility and Titanium Coordination in Silicate Melts," *Geochim. Cosmochim. Acta* **49**, 2289-2296 (1985).

¹⁹A. J. Ellison and P. C. Hess, "Solution Behavior of +4 Cations in High-Silica Melts: Petrologic and Geochemical Implications," *Contrib. Mineral. Petrol.* **94**, 343-351 (1986).

²⁰J.-M. Montel, "Experimental Determination of the Solubility of Ce-Monazite in SiO_2 - Al_2O_3 - K_2O - Na_2O Melts at 800°C, 2 kbar, under H_2O -Saturated Conditions," *Geology* **14**, 659-662 (1986).

²¹R. P. Rapp, F. J. Ryerson, and C. F. Miller, "Experimental Evidence Bearing on the Stability of Monazite During Curstal Anatexis," *Geophys. Res. Lett.* **14**, 307-310 (1987).

²²A. J. G. Ellison and P. C. Hess, "Peraluminous and Peralkaline Effects upon 'Monazite' Solubility in High-Silica Liquids," *EOS, Trans. Am. Geophys. Union* **69**, 498 (1988).

direct information about the rates at which various reactions will occur. In addition, as noted by Pauling,²³ the free energies of formation of simple oxides from the elements account for all but about 5% of the free energy of formation of a multicomponent oxide from the elements, and all of the physics and chemistry of multicomponent materials is contained in that 5%. Uncertainties that are introduced by neglecting mixing processes can therefore have a dramatic impact upon the interpretation one obtains from using thermodynamic data for oxides.

²³L. Pauling, "The Principles Concerning the Structure of Complex Ionic Crystals," J. Amer. Chem. Soc. 51, 1010-1026 (1929).