Glass dissolution: testing and modeling for long-term behavior

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Abstract

The basic concepts of thermodynamics and kinetics are discussed in relationship to glass dissolution testing. While it seems like these subjects are too basic to be discussed in a journal article, it is often the case that we forget these concepts when planning and designing dissolution tests and interpreting the results that come from these tests. The possible connection between the composition of the dissolving glass and its long-term behavior is discussed. Results from a preliminary study suggest that the aluminum content of a glass is important to its long-term behavior. The formation of a zeolite can cause the glass dissolution rate to increase under certain conditions that can be modeled. Results indicate that complex glasses can be modeled with a glass containing as little as six components. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

In this paper, I was requested by the organizing committee to cover testing and the connection between glass composition and the long-term testing of silicate-based glasses. To do this, I first cover some very basic principles that are, in my view, often overlooked in the dissolution testing of nuclear waste glasses. I will try to weave the discussion of basic thermodynamics and kinetics into the basis for testing. I follow this discussion with a discussion of the possible connection between the composition of glass and the long-term dissolution.

2. Basic concepts

When beginning tests or laying out a testing program, it is important to remember the difference between thermodynamics and kinetics. While it seems we ought not to confuse these two, we often do. Thermodynamics is a property of state and, as such, the thermodynamic values we obtain do not depend on the pathway we use

to get from one point to the other. If, experimentally, the thermodynamic values depend on the test (i.e., path), then there is either a difference in the starting or in the ending states.

In the discussion of kinetics, it is necessary to recognize that the net reactions described with thermodynamics are actually composed of many steps. Therefore, while the net reaction can be described as

$$A + B \rightarrow C,$$
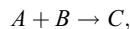
the reaction sequence may actually be composed of a sequence of steps in which

$$
\begin{aligned}
A + B &\rightarrow A \cdots B \\
A \cdots B &\rightarrow C.
\end{aligned}
$$

Therefore, the reaction of a 20 or more component glass with water may involve as many as 19 independent net reactions. Each of these net reactions may consist of several reaction steps. As the number of components in a system increases, the complexity increases even more rapidly. If we have to determine all of these reactions, our task would be daunting indeed. There is, however, hope and a way out of this apparently difficult situation.

Besides the path aspect of the kinetic problem, there is also a time aspect. Each step in the overall reaction has a time over which the ensemble of atoms/molecules reacts to yield a growing concentration of products. It is

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here where luck is often needed to be able to resolve such a complex kinetic problem as glass dissolution. Not all reactions proceed at the same rate. While there appears to be a dearth of reactions that occur during the dissolution of a glass, only a few may be rate-limiting. That is to say, the overall reaction depends very strongly on the rate at which these slow reactions proceed; the others are relatively fast. In the case of silicate-based glasses, we have observed over the past 20 years that one reaction involving H_4SiO_4 appears to be rate-limiting. Although I will allude to this later, there may be other species, notably aqueous species of Al, that may compete with the rate at which the reaction involving H_4SiO_4 proceeds or may under certain conditions participate in the same rate-limiting reaction with H_4SiO_4.

To sum up then, the net reactions that occur during the dissolution of a silicate glass can be described with thermodynamics. The number of these reactions becomes very large as the number of glass components increases. Each of these net reactions is composed of a number of reaction steps. While this appears to be a hopeless situation, there is at least one step in the dissolution of glass that appears to be the slowest and thus is rate-limiting, i.e., the rate of glass dissolution depends almost entirely on the rate associated with this one reaction step.

3. Glass dissolution

Thermodynamically, we have elected to describe the glass–water interaction as a net reaction in which glass dissolves totally (congruently) into water followed by precipitation of any phases that are at or over saturation. This is purely a thermodynamic description (i.e., glass plus water at the start and material dissolved in water and some precipitates at the end). This approach allows us to use thermodynamic codes to calculate the resulting solution concentration. However, the reaction of glass with water is not that simple and there are a host of paths that can take place as the glass dissolves and new solids form. If we highlight the dissolution step in which glass dissolves into water, we have observed that only one species seems to be involved in the rate-limiting step of dissolution – H_4SiO_4. Because there appears to be only one rate-limiting species, we can, from a kinetic point of view, adequately describe a silicate-based glass with a solid that involves only SiO_2. Therefore, we need only consider a solid whose equilibrium solubility is close to that which we observe in tests. This appears to be SiO_2 (am). So, we describe the net result of glass dissolution as a thermodynamic process to obtain the solids that form and the solution concentrations. We use kinetics and the thermodynamically calculated H_4SiO_4 concentration to calculate the rate at which the glass

dissolves. As the H_4SiO_4 concentration approaches the saturation concentration, the rate of reaction slows.

As indicated, involved in the overall process is the precipitation of mineral phases that result from the glass dissolution. These reactions have associated rate constants. We know that some solid phases form at very slow rates in laboratory experiments and in nature. So slow, in fact that they do not normally occur in a glass dissolution experiments. What this means experimentally is that reaction paths become altered relative to the one that would occur if all reactions occurred rapidly and chemical equilibrium was maintained as the system evolved. It appears to be just this point that we often forget when we run tests or combine tests of different varieties and then try to understand the experimental results.

4. Tests

Before nuclear waste glasses were investigated, the demand on the 'performance' of glass articles was not great. Bottles, glasses, windows, etc. were designed to last several years to several tens of years. The tests that were developed for these glasses fall into a class of tests known as service tests. The purpose of these tests was to compare the value one got for one glass with the value from another glass. A good glass was one that had survived for a long time; the value one got from a test of this glass was considered a good value. When nuclear waste glasses were first tested, we used whatever glass test was available. However, it soon became clear that these tests were inadequate for the task to which they were put.

While there were several tests available at the time, an effort was started at PNNL in 1979 to develop a set of standard tests that could be used to determine the thermodynamics and kinetics associated with the dissolution of glass. These tests were developed as part of the Materials Characterization Center (MCC) [1]. There were five tests developed (Table 1). Each had a specific purpose that is briefly described in Table 1. In one form or another, these tests are still around today. The tests had a lot of scrutiny during their development. Overseeing the activities of the MCC was a Materials Review Board, whose members comprised some of the best scientists in the country.

Also shown in Table 1 are three other types of tests, the most innovative of which is the pressurized unsaturated flow (PUF) test. This test is described elsewhere in this volume. The 'pulsed flow' test was developed early for the International Standards Organization [6], but was also meant to cover variants such as the test used primarily at Catholic University [7]. It can also cover the combination of tests that is also reported in this volume by the group at CEA in France [8]. The autoclave test

Table 1
Glass dissolution tests and conditions

Test	Conditions	Use/comments
MCC-1 [2]	Static. S/V usually 10 m^{-1}. Open to the atmosphere.	Used to compare waste forms. Nominally, this is a closed test. However, when performed with a Teflon® vessel, the solution equilibrates rapidly with the ambient atmosphere.
MCC-2 [2]	Static. High temperature, > 90°C. Closed.	The high-temperature version of MCC-1. This test is normally performed in a Teflon-lined, stainless steel vessel.
MCC-3 [2], PCT	Stirred with glass powder. Closed system. Open to the atmosphere in Teflon.	Used to accelerate the glass–water reaction. The MCC-3 was the predecessor of the PCT.
MCC-4 [2], SPFT [3,4]	Open, single-pass flow-through and atmosphere.	Used to determine the dissolution as a function of flow rate. Differs from the latest tests in that the specimen was a monolithic solid. Current versions at PNNL and LLNL use powder.
MCC-5 [2]	Open to both flow and atmosphere.	Used for forward dissolution rate measurements (high flow rate). Limited temperature variation because of the use of boiling water and reflux to obtain flow. This test has been superseded by the SPFT because of advances in equipment and test design.
PUF [9]	Open system to flow and atmosphere. Flow is unsaturated along the surfaces of the powdered specimen.	Use for accelerated alteration under open system conditions and for measurement of hydraulic properties measurements. This is a new test in which the unsaturated conditions of water flow in the strata of Yucca Mountain and Hanford soils are simulated.
Pulsed flow [7,6]	Open system with some percent of the leachant replaced with fresh leachant or the specimen removed and placed in fresh leachant. Open or closed to the atmosphere depending on the vessel construction.	Used for very low flow conditions and/or to obtain solution data with the same specimen. This test was originally developed as part of the ISO tests. A variant was developed at Catholic University by Barkatt et al. [7].
Vapor phase hydration [12]	Closed system. Only water vapor (saturated steam) is present. Monolithic specimen.	Used to accelerate alteration product formation. When run properly, the reaction is between the water that condenses on the surface of the specimen and the specimen.
Autoclave tests [5]	Covers a number of tests run usually at temperatures in excess of 100° C. Closed system usually in gold or other tube, but also in stainless steel or titanium vessels.	Used to determine equilibrium phase assemblages, kinetics of alteration, and solubility. Although mostly used in the geologic community, these tests were used in early test programs for waste isolation because of the initial high repository temperatures.

has been used for many years primarily in the geo-chemistry field of study.

The tests shown in Table 1 fall into two primary types – open and closed. An 'open' test is usually one in which transfer of fluid into and out of the test vessel is established. However, normally static tests such as the MCC-1 are also open with respect to the atmosphere when performed in Teflon®. McGrail [9] showed that the Teflon vessels normally used for this test allow CO_2 and O_2 gases to exchange across the Teflon. The rate at which this occurs is a function of the temperature of the test. At 90°C, equilibrium between the solution in the test vessel and the atmosphere is established quite readily.

All of these factors make it important to know which variables are being controlled and which are uncontrolled when a person selects a test and the test conditions. As an example, Grambow and Strachan [10] showed the pH that one measures depends on how the solutions are treated at the conclusion of the test. For the particular case of the MCC-1, for example, the vessel and leachate are quenched from 90°C to room temperature. This results in a solution that contains the inorganic carbon consistent with the solution in equilibrium with CO_2 (g) at 90°C in the ambient atmosphere. This point must be remembered when the solution is modeled with a geochemical code. It is also important to remember that this equilibrium is established when Teflon

is used as the test vessel material, but not when the material is stainless steel. At this point it is important to note that when a test is performed such that the test is closed with respect to the atmosphere, there is an atmosphere above the solution at the start of the test. While this may ultimately be determined to be a minor variation, it may be sufficient to cause a measurable difference in a test result. Hence, even these small variations should not be overlooked when trying to explain variations from test to test.

It is not within the scope of this paper to list all the possible variables that need to be considered when performing a test. The warning that should be clear is 'user beware'. Just as when one buys a used car, the fewer questions asked at the start of a test, the more surprises are sure to arise 'down the road'. The ability for a scientist or a critical reviewer of a scientist's work to explain the results depends strongly on understanding the test that is being performed and the variables that have been controlled. It is equally important to report accurately and completely the test conditions.

5. Tests needed for long-term behavior

Basically, this is a question of kinetics for the long-term rate of the glass and thermodynamics for the solids that form during dissolution (alteration products). To accelerate the formation of these alteration products, a vapor hydration test has been employed in the past [12]. This test is similar to that used by archeologists to date natural ancient glasses such as obsidian [11]. In this test, there are several uncontrolled parameters; parameters that change as the glass reacts. These include the amount of water that actually participates in the glass–water reaction, the concentration of species in the water, including the pH, the activity of the water at high reaction progress (amount of glass dissolved per unit volume of water), and the amount of water remaining as hydrous reaction products are formed (clays, metal hydroxides, etc.). These uncontrolled variables notwithstanding, the alteration phases that form on the surface of the test specimen appear to be the same as those that form during long-term testing with larger amounts of water present or on natural glasses over very long times [12]. The PUF test can also be used for this purpose [9] with the added advantage that the solutions associated with the formation of these phases are also collected. However, to date there is only one laboratory where the PUF test is being used.

From a kinetics point of view, the data that are needed are related to the intrinsic properties of the glass and its response to the solution chemistry. As we currently understand the dissolution process, the parameters in the rate equation

$$r = r_0 10^{\eta \, \mathrm{pH}}[\exp(-E_a/\mathrm{RT})][1 - Q/K]$$

that are needed are the intrinsic rate constant (r_0), activation energy (E_a), pH response (η, the order of the reaction with respect to pH), and 'saturation' constant (K) [13]. Since Q cannot equal the saturation constant for a glass, r becomes constant in the long-term as Q becomes a constant and approaches K. These parameters are most easily obtained from a single-pass flow-through test (Table 1). The intrinsic rate of dissolution is an intrinsic property of the solid and, hence, is independent of the solution composition and temperature; it depends only on the composition of the solid. Experimental results to date suggest that there is not much variation in the value of the intrinsic rate over a wide variety of glass compositions. Similarly, the pH dependence of the rate-limiting step appears to be nearly independent of the glass composition. The value is about 0.4 for nuclear waste glass compositions [13,14]. The temperature dependence is often used as an indication of the type of rate-limiting step that is involved in the reaction. The activation energies are in the range of 70–90 kJ/mol. These values are too high to be associated with a diffusion-controlled process. The fact that the activation energies for glasses with a wide variety of compositions are within a rather small range of values indicates that the nature of the rate-limiting step is nearly independent of composition – even for glasses for which the Al^{3+} concentration has an effect on the measured forward rate. This effect needs to be further studied because it is pivotal to the understanding of the kinetic rate equation. Some of the spread in the values of the activation energy, perhaps for the other constants as well, may be the result of experimental error and the methodology by which the experiments are designed and performed.

Other possibilities that may limit the rate of dissolution are water diffusion, limited transport of H_4SiO_4 away from the glass, or the rate and type of alteration products that form on or near the glass. In the limit as the rate of the latter two go to zero, the rate at which water diffuses into the glass will limit the rate at which the glass decomposes. If research continues to show that, for most glasses, the rate-limiting step involves H_4SiO_4, then the rate at which H_4SiO_4 is transported or consumed will limit the rate at which the glass reacts. The transport of H_4SiO_4 takes place because there is a concentration gradient between the surface at which water is reacting with glass and other parts of the system. Transport can occur through the solution that exists in the clayey alteration products that often occur on the surface of the glass or through any over-pack material that occurs on or next to the glass surface. This layer can have a variety of transport properties with respect to H_4SiO_4. These layers may have sorption sites for H_4SiO_4 and, hence, may 'accelerate' the reaction (these sorption sites may be unsaturated because of

water flow). The rate of dissolution can increase as a result of phase formation because the phase that forms precipitates readily and with a commensurate decrease in the local H_4SiO_4 concentration and increase in dissolution (depicted in Fig. 1). I will return to this subject again in Section 5.1. However, the class of minerals that cause the glass dissolution to increase appears to be the zeolites. When one of these zeolites precipitates, the calculated concentration of H_4SiO_4 decreases while the total Si concentration (that which is measured in an ICP/MS for example) increases because the pH usually increases. Experimentally, zeolites are associated with accelerated glass dissolution.

Since we have a difficult time measuring the dissolution rate over reasonable experimental time frames (a rate different from zero is lost in the experimental errors of temperature control and analytical measurements), it is unlikely that we will be able to determine the alteration rate if diffusion of water into the glass is rate-limiting. It is experimentally very difficult to determine the precipitation rates for all the phases that might affect adversely the glass dissolution rate. However, if the approach is to determine if zeolites form and how 'long' at a given temperature it takes for these phases to form, then the vapor hydration test should be used. The relative goodness of a glass is subjective and qualitative when this test is used. As I will show below, zeolites form in all glasses containing alkali, silica, and alumina, but for some glasses zeolite formation causes the dissolution rate to increase. The difficult task in interpreting the results from the vapor hydration test comes when the test is used to rank several glasses and determine at what point is a glass 'good enough' to survive in a repository. Is a glass that completely alters in three days because zeolites form and increase the dissolution rate good enough or must it last three months or three years? I will not attempt to answer this here. However, glass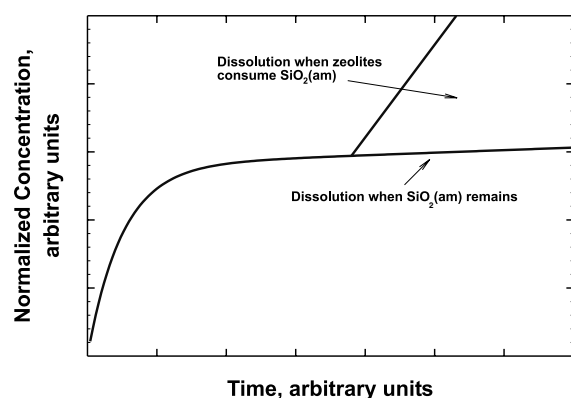es for which the dissolution rate does not increase when zeolites form are probably better in the sense that it is easier to convince the regulator and the public of the benefit of such a glass, all other things being equal.

5.1. Dependence of the long-term rate on glass composition

The following material is taken in part from a journal article that Teresa Croak and I just published [15]. In this article, we show that the formation of zeolites and the effect on the long-term rate is a very sensitive function of the Al content of the glass. To do this, we started with a simple six-component glass as representative of all boro-aluminosilicate glasses. We further assumed that the zeolite analcime $[Na(AlSi_2O_6) \cdot H_2O]$ is representative of all zeolites, that the rate-limiting step in the dissolution mechanism involves H_4SiO_4 (glass is adequately represented by SiO_2 (am)), and that, for this initial exercise, we can ignore ion exchange. The second assumption means that when SiO_2 (am) precipitates the glass is at 'final rate' (the horizontal part of the dissolution curve depicted in Fig. 1) and any alteration phase that forms and causes SiO_2 (am) to dissolve causes the glass to dissolve rapidly (the positive slope part of the curve at the right in Fig. 1).

To introduce the methodology, we reproduce a figure from Van Iseghem and Grambow [16] (Fig. 2). In Fig. 2, the reaction of a series of glasses (different SiO_2 contents and $Si + Al = 55$ cation%) with water is shown. As a glass with 45 cation% Si and 10 cation% Al dissolves in water, there are no alteration phases calculated to precipitate until about 10^{-3} mol of glass have dissolved in a litre of water. As more glass dissolves into solution, first SiO_2 (am) precipitates followed by the zeolite analcime. Because there is insufficient aluminum in the glass, the

Fig. 1. A general schematic for glass dissolution showing the potential effects of zeolite precipitation on dissolution.
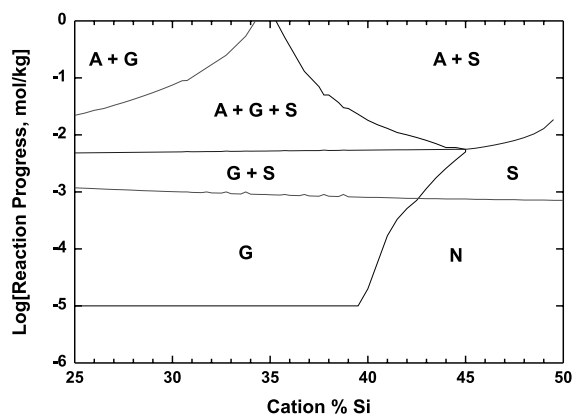

Fig. 2. Stability fields of potential alteration products modified after Fig. 6 from Van Iseghem and Grambow [16] (A = analcime; G = gibbsite; S = amorphous silica, and N = no phases present).
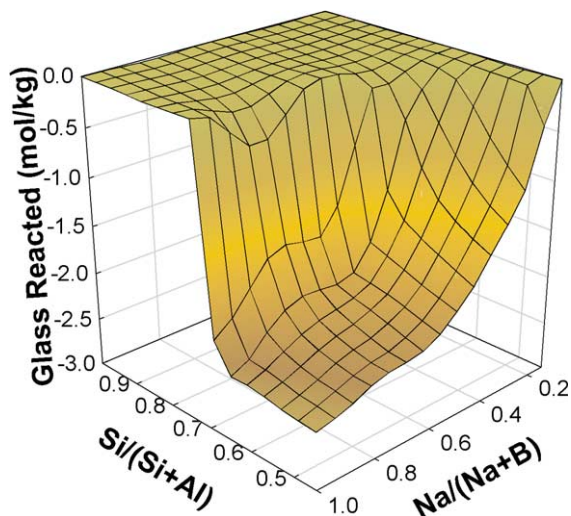
Fig. 3. Upper surface of the amorphous silica stability with respect to analcime. The case plotted is for 10% silica sorption; Si + Al is 55 cation%, Na + B is 35 cation%, and Ca and Li are 5 cation%.
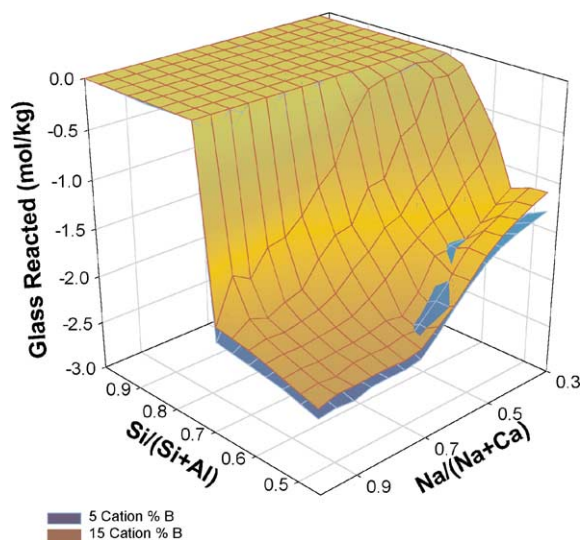

Fig. 4. Upper surface of the amorphous silica stability with respect to analcime. The plot is the same as Fig. 3; only plotted on the composition surface are the composition locations of various waste glasses, a few of which are labeled.
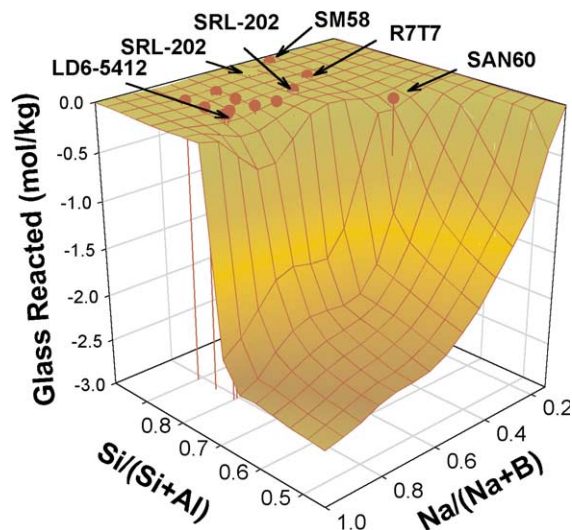

Fig. 5. Fig. 3 showing the positions on the Si/(Si + Al)–Na/(Na + B) plane of several proposed nuclear waste glass compositions.

mass of analcime that can precipitate is insufficient to consume all of the precipitated SiO₂ (am), but the total mass of SiO₂ (am) is decreased when analcime precipitates. [1] Since SiO₂ (am) is the surrogate for glass, the presence of SiO₂ (am) means that glass remains a viable phase even in the presence of analcime and, hence, the dissolution rate remains low (horizontal part of the curve in Fig. 1).

The situation is different when the glass contains 35 cation% SiO₂ and 20 cation% Al. The first phase to precipitate is gibbsite [Al(OH)₃] followed by SiO₂ (am) as glass dissolves in water. As more glass dissolves, analcime precipitates and consumes SiO₂ (am). When sufficient glass dissolves, sufficient mass of analcime precipitates that all of SiO₂ (am) is consumed and what remain are analcime and Al(OH)₃. From a thermodynamic point of view, the absence of SiO₂ (am) suggests that the glass should disappear. What this means kinetically, however, is that dissolution rate of the glass should increase dramatically – the glass becomes, in terms of this argument, unstable.

If we now want to understand the effect of glass composition on the dissolution of glass with respect to the other components of glass, we must convert to a multi-dimensional picture. Since three dimensions are easier to depict, we need to add another axis to Fig. 2. This means that the lines in Fig. 2 become surfaces in a

three-dimensional graph. If all the lines in Fig. 2 were plotted as surfaces in a three-dimensional graph, it would be very difficult to understand. However, we realize that the important surface is the one where SiO₂ (am) disappears or the line in Fig. 2 that defines the points at which analcime consumes the last amount of SiO₂ (am) – the boundary between analcime–Al(OH)₃–SiO₂ (am) region and the Al(OH)₃–analcime region. For

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[1] Recall that from a thermodynamic argument, the mass of a given phase in the system is not a factor in establishing equilibrium.

the discussion here, it is this surface that defines where the dissolution rate should increase – an effect that would be good to avoid for reliability in a repository. So the surfaces that will be shown in the following graphs represent the upper stability surface for SiO_2 (am) or the point at which the dissolution rate for the glass should increase. Therefore, high values of reaction progress (the amount of glass dissolved in solution) represent better glass compositions (more glass must dissolve to reach the upper stability of SiO2 (am)) than lower values.

Fig. 3 shows the effect of glass composition on the upper stability of SiO_2 (am). It should be noted that the flat surface at log (reaction progress) = 0 is an artifact of the calculation. When 1 mole of glass is allowed to dissolve per litre of water, the calculated ionic strength becomes high enough to become problematic for Debye–Huckel activity coefficient calculations. Therefore, the calculations were only performed for reaction progress values up to 1 mol/kg [log (reaction progress) = 0]. The results shown in Fig. 3 are from calculations for glasses containing Si + Al equals 55 cation%, Na + Li equals 35 cation%, and both Ca and B equal 5 cation%. The precipitous drop in the amount of glass that needs to dissolve to reach the upper stability of SiO_2 (am) depends strongly on the aluminum content of the glass (recall the discussion above). This means that adjustments of very small concentrations of aluminum (0.25 mass%, perhaps) can have a profound effect on the amount of glass that needs to dissolve to reach the point at which the glass dissolution rate increases.

The effects of other elements in the glass have only minor effects on the amount of glass that must dissolve in solution to form sufficient analcime (zeolite) to consume SiO_2 (am). In the example shown in Fig. 3, there needs to be sufficient Na for forming analcime, but the 'steepness' of the effect is much less than that observed for aluminum. In Fig. 4, the effect of the boron on the dissolution of glass is shown. The two surfaces (5 and 15 cation%) are nearly coincident. The glasses with 15 cation% are unlikely to be used because the concentration of B_2O_3 in these glasses is very high and the chemical durability would be low. However, the insensitivity of the boron concentration in the glass on the upper stability of SiO_2 (am) is adequately illustrated. In these glasses, the variation in the glass composition is plotted as the Si/(Si + Al) and the Na/(Na + Ca), where (Na + Ca) = 30 cation%.

To show the comparison of the calculations to actual glasses, selected simulated waste glasses were reduced to six components and 'mapped' onto the plot shown in Fig. 3. The details of how this was done are discussed in our journal article [15]. The results are shown in Fig. 5. The differences discussed by Van Iseghem and Grambow [16] for SAN 60 and SM 58 are reproduced here. The glass LD6-5412 [17] is known to be very reactive and analcime causes accelerated dissolution at small reaction

progress. However, other glasses, such as SRL 202, are known to react to form analcime, which in turn causes the dissolution rate to accelerate, and are shown here to require much higher reaction progress for the acceleration to be manifested. These apparent discrepancies are probably the result of the initial character of this study. More study is obviously needed. Also, as noted above a more complete description of this work is described by Strachan and Croak [15].

6. Conclusions

I have discussed three topics – testing, thermodynamics and kinetics, and the potential effect of glass composition on long-term dissolution. It is important to know when beginning a test what questions are being asked and if the questions are thermodynamic or kinetic in nature. Of course, one could argue that the questions need to be formulated first and the tests selected that will yield the answers. This, however, appears to happen infrequently with glass dissolution studies. All too frequently, a test or sequence of tests is performed and the user is left with results that need to be explained, such is the case for the sequence of static and flow tests described by others in this volume. I cannot stress enough the need to understand the test or test sequence sufficiently to know what the results are likely to mean and, when faced with unexpected results, to examine the test or test sequence to determine how test conditions or sequence of conditions influenced the outcome of the test. These concepts seem far too basic to be written in a formal journal article, but the overwhelming evidence suggests that they do need to be emphasized.

Although it is also a very basic subject, the role of a kinetic mechanism needs to be emphasized. The reaction of a multi-component glass with water is a complex reaction involving many chemical reactions. In any such system, there are fast and slow reactions. In the case of glass, we are fortunate to have one reaction of all these reactions that appears to be rate-limiting. Since this rate-limiting reaction appears to depend on the H_4SiO_4 activity, a useful construct is to consider a rate-limiting reaction that involves only Si in the reactants and products. Hence, Grambow [18] proposed that the reaction involve the dissolution of SiO_2 (am) or chalcedony. That is, these solids were stand-in solids for the glass so that thermodynamic calculations could be made. As we learn more about the reaction mechanism for glass, it is possible that we discover other species to participate in the rate-limiting reaction or that under certain conditions another reaction in the kinetic mechanism becomes slow. This seems to be the case for aluminum-containing species [9,19].

Thermodynamics are a state function and as such describe only the starting and end states for the reactants and products. Therefore, to apply thermodynamics to a kinetic problem such as the dissolution of glass in water is sure to get one into scientific difficulties. Models that are thermodynamics-based, such as the hydration free energy approach [20], cannot reliably be used to describe the rate at which a glass reacts with water. Thermodynamics can reliably be used to describe a kinetic problem if the thermodynamics of the starting state (glass), all intermediate reactants/products such as activated complexes, and all products are known. All of these are rarely known and the quest to understand all of them would be a formidable task indeed.

Two tests are recommended for determining the long-term dissolution of glass. The single-pass flow-through test (Table 1), when used properly, yields parameters that are needed for the existing model of glass dissolution. These are the intrinsic dissolution rate, activation energy, pH dependence, and the equilibrium constant for the SiO_2 dissolution reaction. The vapor phase hydration test yields the solid phases that are likely to form in the long-term when the dissolution of glass dominates the composition of the solution in contact with the glass. This appears to hold even for a dynamic test like the PUF test (Table 1).

Lastly, I proposed a model to determine the effect of glass composition on the long-term dissolution of the glass. In this model, we rely on the case that there is one rate-limiting species, H_4SiO_4, and that the formation of zeolites is deleterious to the dissolution of glass. Our calculations [15] show, as did the calculations by Van Iseghem and Grambow [16], that H_4SiO_4 is consumed when zeolites form. To replenish the H_4SiO_4 some SiO_2 (am) must dissolve. When there is insufficient SiO_2 in the glass relative to the amount of Al_2O_3, SiO_2 (am) cannot coexist with the zeolite (in our calculations we used analcime) and the H_4SiO_4 concentration decreases. This situation causes the glass to dissolve more rapidly. This model is very preliminary, but does indicate the sensitivity of the long-term dissolution on the amount of aluminum in the glass.

Determination of the long-term rate must be treated carefully. I hope my views are interpreted as a careful treatment of the subject. The long-term rate may come in a variety of forms that depend on the glass composition, the conditions under which the glass is stored, and the conditions that may result from climatic and geologic changes. It is the latter that cause me to choose the word 'calculate' rather than 'prediction' when talking about the rate of glass dissolution. To 'predict' the rate connotes that the person doing the predicting can forecast the conditions under which the glass will be stored, including the changes to the incoming water caused by the other waste packages in the repository. This is an impossible task. What is possible with a good

(semi-quantitative?) understanding of the rate law for glass dissolution is to calculate the dissolution of the glass under various supposed conditions. Even this ability falls short of what is needed. However, having stated this, our ability to calculate and demonstrate that we understand the dissolution rate gives confidence to the regulator and the public that glass does or does not have an impact on our ability to safely dispose nuclear waste.

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