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Affinity Functions for Modeling Glass Dissolution Rates

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Introduction

Glass dissolution rates decrease dramatically as glasses approach "saturation" with respect to the leachate solution. This effect may lower the dissolution rate to 1/100 to 1/1000 of the unsaturated rate[1]. Although rate controls on glass dissolution are best understood for conditions far from saturation, most repository sites are chosen where water fluxes are minimal, and therefore the waste glass is most likely to dissolve under conditions close to saturation. Our understanding of controls on dissolution rates close to saturation, versus far from saturation, are therefore of greater significance for assessing release rates of radionuclides from repositories.

The key term in the rate expression used to predict glass dissolution rates close to saturation is the affinity term, which accounts for saturation effects on dissolution rates. The form of the affinity term and parameters used to model glass dissolution are clearly critical for accurate estimates of glass performance in a repository.

The concept of saturation with respect to glass dissolution is problematic because of the thermodynamically unstable nature of glass. Saturation implies similar rates of forward (dissolution) and back (precipitation) reactions, but glasses cannot precipitate from aqueous solutions; there can be no back reaction to form glass. However experiments have shown that glasses do exhibit saturation effects when dissolving, analogous to saturation effects observed for thermodynamically stable materials. Attempts to model the glass dissolution process have therefore employed theories and rate equations more commonly used to model dissolution of crystalline solids, as described below.

The Glass-Water Reaction

Glasses are unstable at low temperatures and react with water to partially dissolve and form crystalline and non-crystalline secondary solids. The most common alteration phases for high level borosilicate waste glasses reacted in dilute groundwaters are smectite clays and zeolites. These alteration phases rarely provide a diffusion barrier to further reaction. They tend to flake off and fall away from the glass-solution interface. Most experimental data on glass dissolution is therefore consistent with overall rate control by a surface reaction. The reaction rate is not controlled by diffusion through a surface layer, and secondary phases do not armor the glass from further attack. This concept is also consistent with results from closed-system tests in which even highly reacted glasses with surface alteration layers, when placed in fresh solutions, react at rates approaching their original rate when first placed in water (Chick and Pederson, 1984). Conversely, unreacted glasses placed in solutions which have been in previous contact with another glass of the

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[1] Glass corrosion modelers have developed a peculiar jargon to describe the phenomenology of glass dissolution. The rate of glass dissolution far from saturation at a relatively rapid pace is called the *forward rate*, whereas the rate close to "saturation" is called the *final* or *long-term* rate which takes place under *silica-saturated* conditions (see next section). The concept of slow dissolution at saturation gives rise to the term *residual affinity* which attempts to quantify the impact of the unstable thermodynamic nature of a glass and relate it to some enhancement in dissolution rate. Normal people trying to make sense of the glass dissolution literature will need to make the appropriate translation to their own terminology.

same composition, react at rates similar to those at which the original glass was reacting. Note that recent attempts to duplicate these results with more complex waste glasses have not been quite as diagnostic (Xing et al., 1994). In addition, in some cases, the rind of secondary phases may alter the local chemistry in the vicinity of the glass-solution contact, primarily through ion- exchange reactions with the clay and zeolite phases (Bates et al., 1991; Bunker, 1987).

The material present at the solution-glass interface is not unreacted glass. Typical waste glasses with significant alkali contents (10-30 cation mole %) undergo ion exchange to depths of 10-200nm (Oversby and Phinney, 1992; Bourcier et al., 1993). The glass structure hydrolyses to the extent that soluble elements such as alkalis and boron are quickly released (ion exchange rate>>Si-O breakage rate), but then the altered layer repolymerizes and partially dehydrates leaving a hydrous surface layer enriched in Si, Al, and other insoluble elements such as rare earths, Fe, Zr, and Ti (Bates et al., 1991). This was demonstrated for alkali borosilicate glasses which were dissolved in ^{17}O-enriched solutions. NMR spectroscopy showed that in addition to Si-^{17}OH groups, Si-^{17}O-Si groups were also present in the reacted glass surface layer (Bunker et al., 1988), indicating that dehydration repolymerization reactions were also taking place. It is the dissolution of this altered re-polymerized material which controls the overall rate of glass dissolution.

The formation of secondary phases does have an important effect on glass dissolution rates in that they control the concentrations of dissolved elements such as aluminum and silicon. This is the reason that abrupt increases in measured dissolution rates observed in some tests correlate with the onset of precipitation of a secondary phase. Van Iseghem and Grambow (1988) showed that the precipitation of analcime after several weeks of reaction correlates with an abrupt increase in glass dissolution rate. Although the original interpretation is that analcime precipitation lowers Si concentration which causes the glass reaction rate to increase, more recent work suggests it may be due to decreased Al, or decreases in both Si and Al that enhance the rate. An even more dramatic example of this phenomena (Ebert et al., 1993) show glasses abruptly increasing in dissolution rates, after over 6 months of reaction, to rates 30 times or more higher and near their maximum rates observed in highly undersaturated solutions. In those tests the increase correlates with precipitation of the zeolite clinoptilolite.

Current Models of Glass Dissolution

Most current models for predicting borosilicate waste glass dissolution rates assume surface reaction control of dissolution rate, and that only the silica concentration of the solution affects the overall rate (Grambow, 1985). The process is therefore modeled using an affinity term written in terms of SiO_2(aq) only. The models assume glass dissolution rates are entirely a function of glass composition, temperature, pH, and solution silica concentration.

The models employ the transition state theory-based rate equation having the form:

$$r = r_+ \prod_i a_i^{-n} \left(1 - \exp(-A / \sigma RT\right) \qquad (1)$$

where r is the dissolution rate, r_+ is the rate constant, the activity product term refers to the effects of dissolved species *i* to some power -*n* on dissolution rate, A is the reaction affinity, R is the gas constant, σ is the ratio of the rate of destruction of activated complex to overall reaction rate, and T the temperature. Eqn. 1 is rearranged and simplified when applied to glass dissolution to:

$$r = r_+ a_{H+}^{-n} \left(1 - Q / K\right) \qquad (2)$$

where Q refers only to dissolved silica concentration and K is an empirically-determined silica saturation value for “glass saturation”.

Because glasses are thermodynamically unstable and equation 1 is derived for a solid that dissolves reversibly, a factor called the residual rate is sometimes added to equation 2 to account for observed slow long-term rates. This gave rise to the concept of “residual affinity” (Grambow and Strachan, 1984) and some attempts to provide a mechanistic basis to predicting long-term rates under near-saturation conditions (Petit et al., 1990; Advocat et al., 1990). These attempts have been unsuccessful. No mechanistically-based model for predicting long-term rates based only on dissolved silica concentration or silica diffusion through a surface alteration layer has been developed which is consistent with all experimental observations. As shown below, the effects of dissolved species such as Al greatly affect mineral dissolution rates, in some cases changing them by orders of magnitude, effects which would swamp the observed correlation of long-term glass dissolution rates with silica content, if the same mechanism affect glass dissolution and is not accounted for in the model.

In addition, the value of σ in equation 1 is assumed to be one. Analysis of the dissolution rate of a simple borosilicate glass as a function of silica concentration shown in Figure 1 shows that a value of $\sigma=0.1$ better fits the experimental data. This value is in the range of values of σ reported for kaolinite $Al_2Si_2O_5(OH)_4$ (Devidal et al., 1992) and amorphous silica (Jørgensen, 1968). This range of values of σ will clearly make a large difference in the calculated value of the dissolution rate close to saturation. Note however that the data from Bourcier et al. (1994) from which a value of $\sigma=0.1$ was obtained, could be reinterpreted in terms of the effects of increasing Al in solution, using an approach similar to the model of Oelkers and Schott described below.

Much recent experimental work on silicate mineral dissolution rates close to saturation are also inconsistent with simple affinity control following equation 2 (Nagy et al., 1991; Burch et al., 1993; Dove and Elston, 1992; Gin, 1996; Schott and Oelkers, 1995; Berger et al., 1994a; Berger et al., 1994b; Oelkers et al., 1994). In fact, only quartz dissolution has been successfully modeled with this approach. It is clear that the glass dissolution process is more complicated than any model based entirely on equation 2.

What Needs Improvement in the Current Models?

Although our current simple models can predict glass dissolution rates reasonably well in dilute weakly alkaline solutions typical of groundwaters in repositories, the models fail badly under conditions which deviate significantly from those in the site-specific tests where rate measurements were made. Recent experimental data for glasses (Gin, 1996; Berger et al., 1994b; Bourcier et al., 1992) as well as analogous aluminosilicate minerals (Devidal et al., 1992; Oelkers et al., 1994; Berger et al., 1994a; Burch et al., 1993) show rate dependencies which cannot be explained entirely by changing silica concentrations, or even as functions of reaction affinity. Numerous papers show the importance of species other than dissolved silica affecting the dissolution rates of silicate minerals. Alkalis such as sodium and dissolved lead increase the rate of quartz dissolution (Dove and Elston, 1992; Berger et al., 1994a). Aluminum dramatically affects dissolution rates of borosilicate waste glass (Gin, 1996) kaolinite (Devidal et al., 1992) and albite (Oelkers et al., 1994). Flow-through tests of simulated radioactive waste glasses and simple analog composition glasses (Bourcier et al., 1992) show that dissolved aluminum decreases glass dissolution rates, with the effect larger at lower pHs (Figure 2). In the same tests, dissolved silica lowers glass dissolution rates above pH 7, but has little effect below pH 7. Dissolved Mg and Ca had no effect at any pH tested when present at 2.5 mmolal concentrations. Clearly the effects of other dissolved species need to be included in the glass dissolution model.

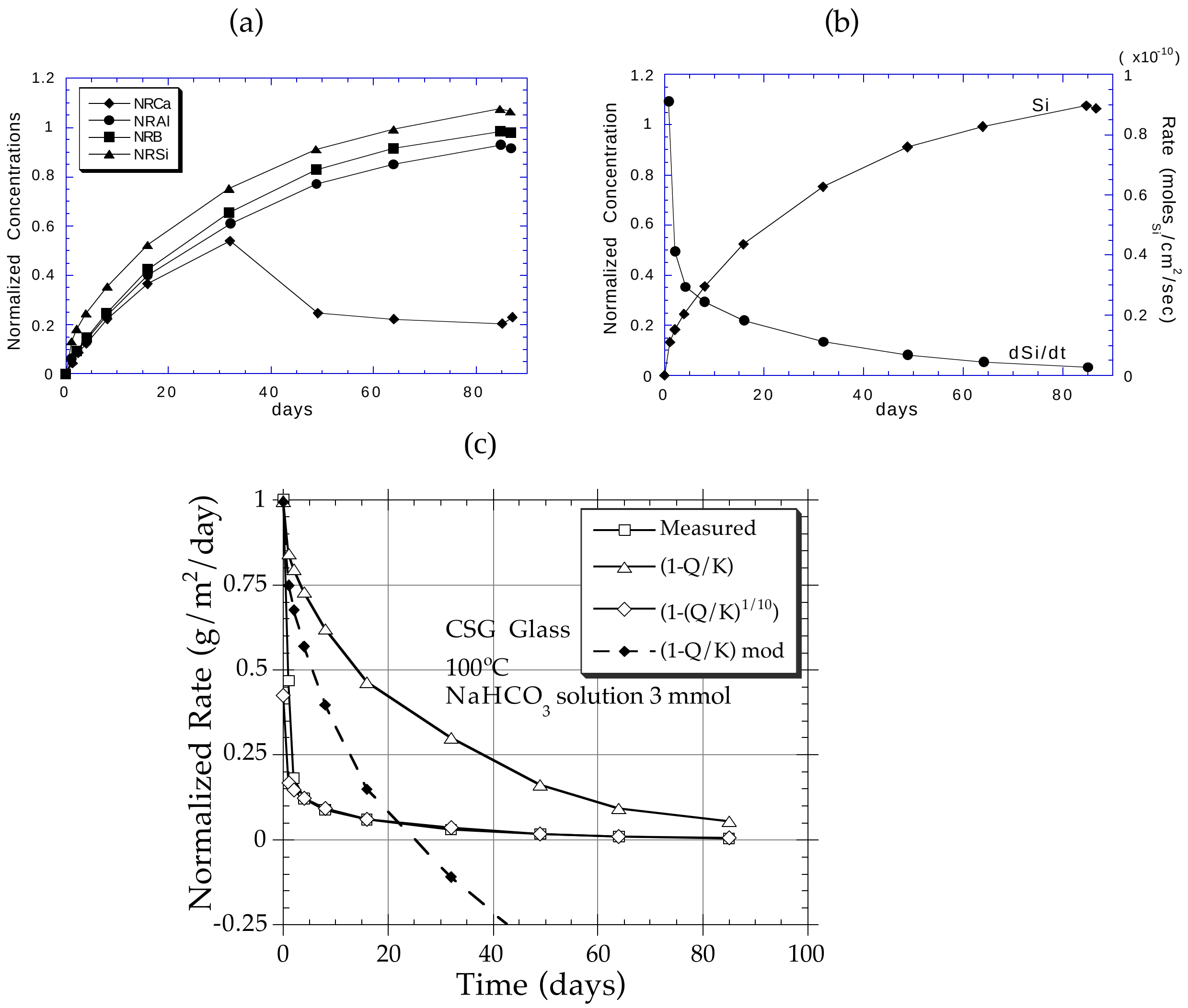

Figure 1. Experimental data for simple SRL-165 glass analog (Na_2O 19 mol%, CaO 7 mol%, B_2O_3 8 mol%, Al_2O_3 7 mol%, SiO_2 59 mol%) dissolving in 3 mmol $NaHCO_3$ solution at 100^{o}C in closed system. Plot (a) shows release data for all elements, (b) shows rate of silica release from slope of silica curve in (a) after release data corrected for pH effect on rate constant and solution volume changes due to sampling. Plot (c) shows attempted fit to data using various affinity functions where both σ and K were allowed to vary. Best fit is obtained when σ=0.1 (n=10) and log K is -3.1 (data are open boxes, calculated values are open diamonds). Open triangles show curve for σ=1.

For glasses, some observed deviations from simple rate control by SiO_2(aq) were explained by assuming rate control by silica concentrations at the glass-water contact inside a surface gel layer (Grambow, 1987). Silica diffusion through this gel layer controls the silica concentration at the contact, and the silica concentration at the contact controls the glass dissolution rate. By combining this mechanism with the rate law of equation 2, Grambow was able to explain observed maxima in flow-through glass dissolution tests and regress physically reasonable values for the diffusion constant for SiO_2 in this gel layer. But even with this added term, the model still cannot predict results of recent experiments, in particular, experiments which show significant effects of dissolved aluminum (Gin, 1996).

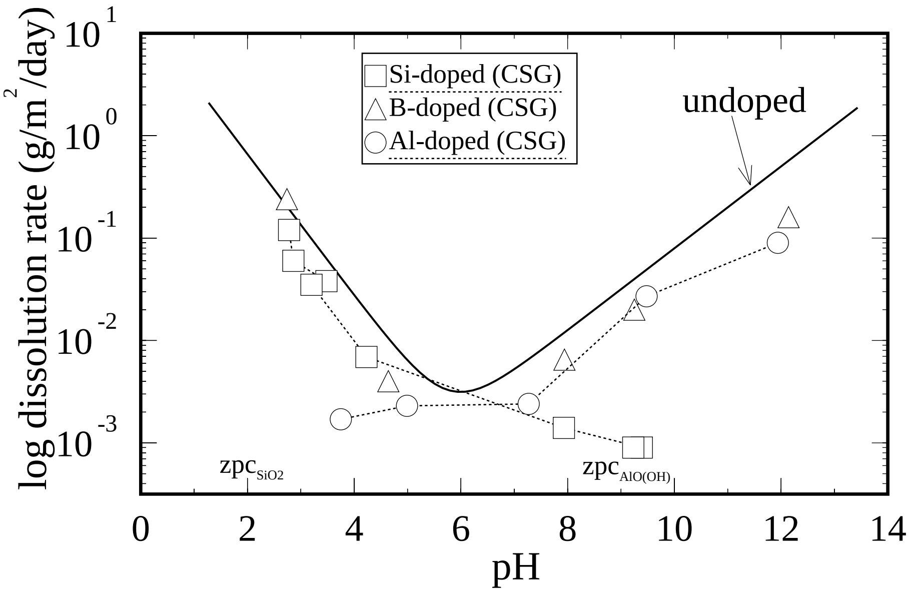

Figure 2. Dissolution rates of CSG glass measured in flow-through reactors in pH buffer solutions doped with 2.5mM $Al(ClO_4)_4$, 2.5mM $B(OH)_3$, and 2.5mM K_2SiO_3. V-shaped line is regression to data for CSG glass in undoped buffers. Dissolution rates are decreased by dissolved Si at high pHs, and rates are lowered due to the presence of dissolved Al at low pHs (Bourcier et al., 1992).

Glasses Versus Crystalline silicates

Many similarities and parallels between the dissolution behavior of silicate glasses and silicate minerals suggest that recent developments in surface complexation models for crystalline silicates can be applied to silicate glasses as well. Figure 3 shows dissolution rates vs. pH for albite glass vs. albite mineral at 70^{o}C. For both crystalline albite and albite glass, the pH dependence of the rate is identical. However, the glass dissolves 2-3 orders of magnitude faster than the mineral. As noted above, the dissolving solid which is rate limiting for glass-water reactions is an alkali-depleted partially re-polymerized hydrous material. A similar type of material exists on the surface of dissolving minerals such as albite, where several surface techniques have consistently shown a sodium-depleted partially hydrated layer at the albite-water interface (Hellmann et al., 1990; Casey et al., 1988). The observed layer thickness for albite at near-neutral pHs is 1-90 nm whereas for typical borosilicate waste glasses it is thicker, 10-200 nm. Similar hydrous layers are likely present on other reacting silicate minerals, or, if they are not observed, it is likely the same mechanisms are operating with both glasses and minerals but at different rates (Petit et al., 1989). Therefore for both glasses and minerals, the water contacts an alkali-depleted partially hydrated surface where the rate limiting hydrolysis reaction takes place. For all these reasons, it is clear that the basic framework for understanding dissolution rate control for both silicate glasses and silicate minerals is the same.

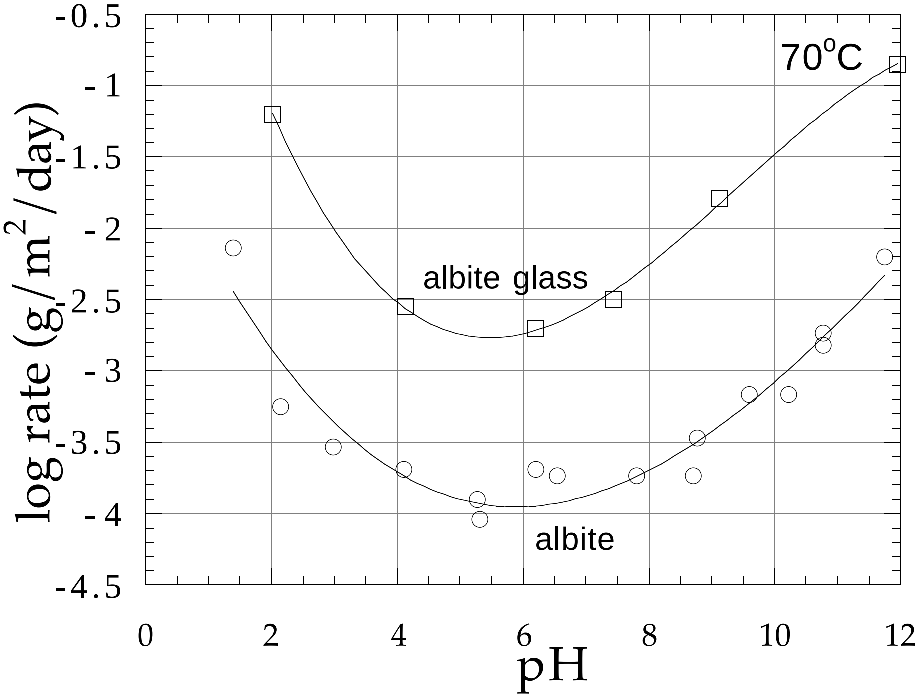

Figure 3. Comparison of dissolution rates of crystalline albite vs. albite glass in flow-through reactor at 70C (unpub. data).

Dissolution Models for Silicate Minerals

Recent work in developing a mechanistic understanding of silicate mineral dissolution has generated dissolution models with specific provisions for the effects of adsorbed surface species on activated complex]. From their data on albite dissolution kinetics, Schott and Oelkers (1995) have proposed a model for aluminosilicate mineral dissolution which includes a functional dependency of dissolved Al on dissolution rates of both silicate and aluminosilicate minerals. They propose that the dissolution rate for most silicate minerals is rate limited by a silica-rich precursor complex. The dissolution rate is proportional to its concentration. An increase in Al in solution increases the number of Al-rich complexes on the surface of aluminosilicate minerals, and thereby lowers the dissolution rate by decreasing the concentration of the silica-rich precursors. Their rate equation which incorporates this effect can successfully predict a wide variety of data from several silicate and aluminosilicate minerals.

A similar modeling approach was developed previously by (Berger et al., 1994a) for quartz dissolution in solutions containing dissolved lead and sodium. They proposed a surface complexation model in which changes in dissolution rates are caused by changes induced in the surface structure due to ionic adsorption. Inner sphere complexes generally decrease rate, outer sphere ionic complexes do the opposite, but both effects change in magnitude in response to pH and reaction affinity. The effects become less significant close to saturation because of competition between electrolyte and silica adsorption on the surface.

It is clear that at this point in time, no comprehensive and generally accepted model exists which explains the existing dissolution data for silicates. But the models which have been proposed are converging on a modified rate law formulation which includes the effects of adsorbed species and accounts for their effects on some rate limiting precursor complex. Future experimental studies on glass dissolution should focus on experiments which are explicitly designed to test these models (i.e. Gin, 1996 and Berger et al., 1994b).

Experimental Issues

A common problem with experiments designed to measure rates close to saturation is that the rates are small and therefore difficult to measure. Using stirred reactors to make these measurements, the preferred method, means having to compare small differences in large measured concentrations of species. The resolution is thus poor. Closed system tests are generally not suitable because alteration phases precipitate and render the experiment uninterpretable.

A new light interferometry technique first developed by Tsukamoto and Sunagawa of Tohoku University in Japan, may potentially improve resolution by 1-2 log units (Ian MacInnis, pers. com) and allow rate measurements in systems where conventional techniques are ineffective. The technique uses interference of white light to directly measure the rate of retreat of a dissolving mineral or glass surface with respect to some reference surface. For glasses, an inert rod of platinum or some other inert material can be placed inside the glass during fabrication, or an inert material vapor deposited on the glass surface. The interferometer measures distances relative to that surface. Resolution of the instrument is on the order of Angstroms/minute which translates into dissolution rates of minerals on the order of 10^{-12} moles/cm^2/sec. The technique also eliminates the need for soluble indicator species (such as Li or B in glass) and also allows measurements to be made in systems where secondary phases are precipitating. For borosilicate waste glass dissolution tests this will almost always be the case because they contain many insoluble elements such as Fe^{3+}, Ti, Zr, and others.

Conclusions

Interpretations of experimental data on the dissolution behavior of silicate glasses and silicate minerals indicate the following:

1. Simple affinity control (Eqn 2) does not explain the observed dissolution rate data for silicate minerals or glasses

2. Dissolution rates can be significantly modified by dissolved cations even under conditions far from saturation where the affinity term is near unity.

3. The effects of dissolved species such as Al and Si on the dissolution rate vary with pH, temperature, and saturation state

4. As temperature is increased, the effect of both pH and temperature on glass and mineral dissolution rates decrease, which strongly suggests a switch in rate control from surface reaction-based (affinity control) to diffusion control (Guy and Schott, 1989; Berger et al., 1994b; Vernaz et al., 1988; Petit et al., 1989) which is also consistent with the relative magnitudes of their activation energies (E_a diff< $E_a$affinity).

Borosilicate glass dissolution models need to be upgraded to account for these recent experimental observations. Most important of these are the effects of dissolved species which can sorb on the glass surface and either increase or decrease the dissolution rate. The glass model should be based on current dissolution models for aluminosilicate minerals which are based on a modified transition state theory rate equation which specifically accounts for the existence and stoichiometry of a rate-limiting precursor complex. The effects of ionic strength and both inner and outer sphere surface complexes must be accounted for before we will be able to predict glass dissolution rates under repository conditions.

However, the model for glass dissolution must eventually feed into waste form performance assessment codes. These codes do not generally calculate values for all the parameters which will be needed by any rigorous glass dissolution submodel. We will need some way to simplify these complex models into something which can be coupled to the performance assessment codes.

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