



Effects of alteration product precipitation on glass dissolution



Denis M. Strachan*, James J. Neeway

Energy and Environment Directorate, Pacific Northwest National Laboratory, Richland, WA 99352, USA

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ABSTRACT

Understanding the mechanisms that control the durability of nuclear waste glass is paramount if reliable models are to be constructed so that the glass dissolution rate in a given geological repository can be calculated. Presently, it is agreed that (boro)silicate glasses dissolve in water at a rate dependent on the solution concentration of orthosilicic acid (H_4SiO_4) with higher $[\text{H}_4\text{SiO}_4]$ leading to lower dissolution rates. Once the reaction has slowed as a result of the buildup of H_4SiO_4 , another increase in the rate has been observed that corresponds to the precipitation of certain silica-bearing alteration products. However, it has also been observed that the concentration of silica-bearing solution species does not significantly decrease, indicating saturation, while other glass tracer elements concentrations continue to increase, indicating that the glass is still dissolving. In this study, we have used the Geochemist's Workbench code to investigate the relationship between glass dissolution rates and the precipitation rate of a representative zeolitic silica-bearing alteration product, analcime $[\text{Na}(\text{AlSi}_2\text{O}_6)\cdot\text{H}_2\text{O}]$. To simplify the calculations, we suppressed all alteration products except analcime, gibbsite ($\text{Al}(\text{OH})_3$), and amorphous silica. The pseudo-equilibrium-constant matrix for amorphous silica was substituted for the glass pseudo-equilibrium-constant matrix because it has been shown that silicate glasses act as a silica-only solid with respect to kinetic considerations. In this article, we present the results of our calculations of the glass dissolution rate at different values for the analcime precipitation rate constant and the effects of varying the glass dissolution rate constant at a constant analcime precipitation rate constant. From the simulations we conclude, firstly, that the rate of glass dissolution is dependent on the kinetics of formation of the zeolitic phase. Therefore, the kinetics of secondary phase formation is an important parameter that should be taken into account in future glass dissolution modeling efforts. Secondly, the results indicate that, in the absence of a gel layer, the glass dissolution rate controls the rate of analcime precipitation in the long term. The meaning of these results pertinent to long-term glass durability is discussed.

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1. Introduction

High-level radioactive waste is commonly incorporated into borosilicate glass because most of these glasses release radionuclides at rates (dissolution rates) sufficiently low to meet regulations, they are relatively easy to produce, and many of the elements present in nuclear waste can be incorporated into the vitreous matrix. Once placed in a geologic repository, the only credible natural way that radionuclides can reach the public is through contact with water (Birkholzer et al., 2012). Thus, the important chemical property of nuclear waste glass is the glass–water interaction. There are many experimental results that point to a dependence of the dissolution rate explicitly on the concentration of orthosilicic acid (H_4SiO_4) (Abratis et al., 2000a; Grambow, 1985a; Guittonneau et al., 2011; Jegou et al., 2000; Jollivet et al.,

2012; Pierce et al., 2008b). Because the durability of such glasses needs to be assured for periods up to a million years under a variety of repository conditions, these types of glasses have been extensively studied. Recently, Van Iseghem et al. (2009) discussed one of the initial attempts to arrive at an international consensus on the mechanisms that might be responsible for continued and low glass dissolution at long-periods. These mechanisms are based on chemical affinity (Icenhower et al., 2004; Pierce et al., 2008a), diffusion through a passivating layer (Frugier et al., 2008), ion exchange (McGrail et al., 2001b), and water diffusion (Grambow and Müller, 2001).

Because glass is a thermodynamically unstable phase with respect to more crystalline materials, it is universally agreed that glasses in contact with water will alter to more thermodynamically stable phases (alteration products). This slow alteration in water is kinetically controlled and related to the $[\text{H}_4\text{SiO}_4]$ as a rate-limiting species (Grambow, 1984a; Icenhower et al., 2005; McGrail et al., 2001a, 1997a). Because the rate-limiting species contains only

* Corresponding author.

E-mail address: Denis.Strachan@pnnl.gov (D.M. Strachan).

silica, the glass may be represented in kinetic calculations as a pure silica phase, chalcedony or $\text{SiO}_2(\text{am})$, but with different values for the equilibrium constants than the pure phase (Grambow, 1984a; Icenhower et al., 2005; McGrail et al., 2001a, 1997a). The formation of alteration phases has also been proposed as a mechanism that might control the dissolution rate at long time periods (Bates and Steindler, 1983; Jantzen et al., 2008; Strachan and Croak, 2000; Van Iseghem et al., 2009; Van Iseghem and Grambow, 1988). The formation of many alteration products at the glass surface, even those that have the potential to affect the $[\text{H}_4\text{SiO}_4]$, such as phyllosilicates, appears for the most part to have little demonstrable effect on the dissolution rate of the glass, i.e. as these phases appear in the alteration sequence, there is no apparent discontinuity in the dissolution rate that can be attributed to this event. However, this is not always the case as first demonstrated by Van Iseghem and Grambow (1988) and later observed experimentally, especially in vapor hydration tests (Ebert, 2012; Vienna et al., 2001) and under high reaction progress experiments (Ebert, 2012; Inagaki et al., 2006; Pierce et al., 2006). All of these experiments have shown that a sharp increase in glass corrosion rate is coincident with the formation of zeolitic phases, typically analcime [ideally $\text{Na}(\text{AlSi}_2\text{O}_6)\cdot\text{H}_2\text{O}$]. It has been hypothesized that analcime formation causes the glass dissolution rate to increase because $\text{SiO}_2(\text{am})$, the silica-only surrogate for glass, dissolves in favor of analcime formation (Strachan and Croak, 2000; Van Iseghem and Grambow, 1988). The calculations used to demonstrate this hypothesis were constrained to thermodynamic considerations, i.e. no kinetics was considered.

2. Glass dissolution models

The above-mentioned studies involving the effects of precipitation on the dissolution rate of the glass involved only thermodynamic arguments. While there are kinetic models for glass dissolution (discussion to follow) there are no studies involving the kinetics both the dissolving glass and the precipitation or dissolution of the alteration phases. Here we will give a brief discussion of four models that have been developed to predict the glass dissolution rates observed in experimental studies.

2.1. The Grambow models

The dissolution models are, for the most part based on the kinetic model of Åagaard and Helgeson (1982). Grambow (1984a,b, 1985a, 1992) applied the transition state model to the dissolution of nuclear waste glasses. In his model, all effects on the dissolution of the glass were connected to other chemical reactions through the rate-limiting species H_4SiO_4 (orthosilicic acid). As the concentration of this species increased in solution, the dissolution rate slowed. The unfortunate part of this argument was that when the $[\text{H}_4\text{SiO}_4]$ reached saturation, the calculated rate fell to zero. To accommodate this inadequacy, a final and constant rate term was added to the rate equation. Later, Grambow and Müller (2001) determined that the final rate of glass dissolution was related to the diffusion of water into the glass matrix. Because the ingress of water into the glass resulted in changes to solution concentrations, equilibrium could never be achieved, which is consistent with observations.

2.2. The $r(t)$ model

The $r(t)$ model (Aertsens, 2006; Gin et al., 2001; Ribet et al., 2001; Ribet and Gin, 2004; Van Iseghem et al., 2009, 2003, 2001) also contains a first order rate law but with Si diffusion through the amorphous alteration layer considered to be rate limiting. Both

the forward and long-term dissolution rates are fixed parameters. The diffusion coefficient for silica in the amorphous alteration layer is the important fitting parameter to experimental results. That is, the process is viewed mainly as diffusive control.

2.3. The GRAAL model

Another model to describe the rate of glass dissolution was developed by scientists at the Commissariat à l'énergie atomique et aux énergies alternatives (CEA) in France. The model, known as GRAAL, is based on water diffusion through a passivating reactive interphase (PRI) (Frugier et al., 2009a, 2009b, 2008; Minet et al., 2010). The growth of the PRI is controlled by the solubility of this layer with respect to its constituent elements in solution. The dissolution of this rate-controlling entity is related to the silica concentration in solution relative to a saturation concentration. Secondary phases included in the model are allowed to appear once they reach solution saturation.

2.4. The STORM model

McGrail and coworkers at the Pacific Northwest National Laboratory (McGrail et al., 2001b; Shutthanandan et al., 2002, 2001) also used the Åagaard and Helgeson formulation. The first order dissolution rate mechanism was included in a chemical and transport code called STORM (Bacon and McGrail, 1998, 2003; McGrail et al., 2001a). Later, they performed experiments to highlight the role of ion exchange in the dissolution process. Results from their studies with D_2O and H_2O and solutions saturated with amorphous SiO_2 were used to come to the conclusion that ion exchange was a process that occurred independently of the matrix dissolution and at a fixed rate (McGrail et al., 2001b; Shutthanandan et al., 2002, 2001). No model for ion exchange was developed. However, a constant ion exchange would serve to keep equilibrium from being achieved and, hence, the dissolution rate would not decrease to zero, but to some constant rate.

2.5. Discussion of models

As noted above, all of these models discussed in this section use an *ad hoc* constant as a rate for the long-term, also known as a final rate. With glass being a thermodynamically unstable phase with respect to alteration products, the possibility exists that these alteration products can control the dissolution rate of the glass through the consumption of the rate-limiting species, in this case H_4SiO_4 . These models consider the diffusion of 'silica' or H_4SiO_4 through the gel layer. In the cases of the GRAAL and the $r(t)$ models, the gel layer or a part of the gel layer is considered protective with diffusion coefficients approximating solid state diffusion values, i.e. $\approx 10^{-22} \text{ m}^2/\text{s}$. These values seem unlikely since Bourg and Steefel (2012) have shown that diffusion in water-filled pores with dimensions of 1–4 nm occurs as if in bulk water.

While the kinetics of glass alteration is considered in the models discussed above, all of these models treat the precipitation of alteration products as thermodynamic, i.e. no kinetics consideration. Under conditions where alteration products form, conditions under which a gel layer forms or secondary alteration products reach saturation, these products accumulate on the surface of the glass and affect the dissolution rate as the concentration of the rate limiting species increases or decreases near the surface of the unreacted glass. The chemistry of the solution in this accumulating solid is a complex problem, as suggested by a number of authors including Gin et al. (2013b), Geisler et al. (2010) and Hellmann et al. (2012). Therefore, this discussion is not within the scope of this article. However, it is a combination of coupled chemical and transport processes, including ion exchange with alkali in the glass (Baucke,

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