



# Adaptation of the GRAAL model of Glass Reactivity to accommodate non-linear diffusivity

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## ABSTRACT

The empirical GRAAL (Glass Reactivity with Allowance for the Alteration Layer) model, developed to capture the essential corrosion behavior of nuclear waste glasses, was modified in a simple manner by raising the unitless diffusion term by a power factor  $p$ . With values of  $p > 1.0$ , the diffusivity is a non-linear, power function of the altered layer thickness. The modified model, GRAALP, was used to fit the long-term alteration data for a series of sodium borosilicate glasses reported by Gin et al. J. Non-Cryst. Solids, 358 (2012) 2559 where glass alteration is dominated by growth of the hydrolysis layer. The optimal value for the parameter  $p$  was found to vary significantly and could be correlated with glass composition. A value of  $p = 3.0$  was found to be most suitable for the glasses containing both Ca and Al, while  $p = 2.6$  was more appropriate if Ce was present in the glass. For glasses without Ca, the optimal fit to the data followed the original GRAAL model with  $p = 1.0$ . In the absence of Al, glasses containing Ca and/or Zr were not as easily characterized. These findings point to a relationship between the residual alteration rate and glass composition. Elements present in the contacting solution may also play a similar role but for this data set only pure water was used. A power law dependence of diffusivity on local water content is proposed which can partially account for the formation of an altered layer with a relatively sharp interface with the pristine glass. The empirical models do not account for the removal of oxide species due to hydrolysis and the associated influx of water and this, in combination with a diffusivity dependent on local water content, may be required to understand the results of depth profiling studies.

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## 1. Introduction

Borosilicate glasses are one of the primary base materials being considered for use in the immobilization of nuclear waste materials [1,2]. These glasses have the necessary irradiation resistance and chemical durability required for low radionuclide release rates in repositories. Additionally, they provide desirable material properties needed for large-scale production. Within the borosilicate glass category, a variety of unique compositions have been selected by various countries to meet the specifics of their nuclear waste. It is important that the glass composition be related to the durability requirements of the chosen repository.

The durability of glass depends not only on the composition but also on the specifics of the repository groundwater: e.g., chemical composition, pH, temperature, and flow. An extensive body of

literature exists on the alteration of glasses under laboratory conditions such as that used in this study [3] and the recently compiled ALTGLASS database [4,5]. Interpreting this laboratory data, formulating glass, and assessing the performance of geological repositories require models of glass alteration that can account for the compositional and environmental factors noted above.

The interaction of glass with aqueous solutions exhibits three alteration behaviors, or stages [1]. Some authors have proposed more stages that are a finer division of the overall temporal behavior [6]. Stage I is an initial rapid dissolution that typically lasts a few to many hours depending on the glass and solution composition. In dilute conditions, the surface of the glass dissolves completely or congruently, releasing all elements within the glass simultaneously in the manner of most crystalline minerals. For this reason, an Åagaard-Helgeson (AH) like rate law, originally developed for minerals [7–9], is often part of the glass dissolution model despite the fact that the glass is thermodynamically unstable. However, glasses do not have a defined chemical equilibrium reaction for dissolution and an associated solubility equilibrium

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coefficient. For clarity, we use the terms “dissolved layer” and “dissolution” to denote the complete removal of glass material. The thickness of this layer is denoted by  $L_{diss}$ .

In Stage II, alteration becomes incongruent and a porous region between dissolved glass and pristine glass increases in thickness. This porous region is formed by diffusive transport of water, hydrolysis of oxygen bonds and diffusion of the products out of the glass and maintenance of electroneutrality by ion-exchange. Soluble elements, e.g. Na, Li, and B, are released nearly completely into solution while less soluble elements, e.g. Si and Al, are retained in full or in part. Depth profiling studies [10,11] have shown this porous region to be of near-uniform composition with a relatively sharp interface with the pristine glass. For example Gin et al. [11] showed, from atom probe tomography studies, this region to be approximately 20 nm thick with a transition region roughly 5 nm thick or less with each element having different profiles. They used the terms “porous gel” and “hydrated glass” to describe the outer region of near constant composition and the transition region to pristine glass, respectively. The term “passivating reactive inter-phase” (PRI) has also been applied to this zone [6]. More recently, Gin et al. [12] differentiated the alteration layer into three or more zones. We use the term “hydrolysis layer” to describe this entire region and do not differentiate this region into two or more distinct layers. The thickness of this layer is denoted by  $L_{hydr}$ .

Precipitation of some minerals may occur during Stage II, typically consisting of phyllosilicates or cryptocrystalline hydrated calcium silicate (CSH) phases like those observed in cements. Crystalline forms are often observed on the surface of the glass but are generally presumed to not influence mass transport between the hydrolysis layer and the contacting aqueous solution.

Geisler et al. [13,14] and Hellmann et al. [15] proposed that the altered layer is formed by a series of precipitation steps where the precipitate materials are sourced by dissolution at a thin interfacial film of water on pristine glass. The GRAAL (Glass Reactivity with Allowance for the Alteration Layer) model focuses on diffusive transport of water with hydrolysis to account for the formation of the altered layer. In the development of the GRAAL model, Minet et al. [16] suggested that part of the porous gel layer may be formed on the surface of the glass as a conformal coating that cannot be physically distinguished from the rest of the altered glass. It is often assumed to be part of the “gel” layer. The important characteristic of this material is that it has no impact on the diffusion of water or soluble species into or out of the underlying glass altered layer. This is obvious if the material does not form a conformal coating, but not particularly clear if it does cover the surface of the glass.

To address this issue, Valle et al. [17] determined the isotopic Si exchange profiles for SON68 in contact with flowing solutions. These solutions remained undersaturated with respect to amorphous silica. Significant isotopic exchange was observed in their “gel” layer. While hydrolysis and condensation reactions occurred, no net deposition of silica by precipitation should have occurred. In related studies, but using solutions saturated with respect to amorphous silica, Gin et al. [10] found little exchange with the solution. The authors suggest this layer has undergone structural evolution through a “re-polymerization” process. It is not clear if this involves formation of mobile silicate species or rather a process of partial bond breakage and reformation. The minimal degree of isotopic exchange suggests that much of the original glass matrix is retained in the gel but has undergone significant reorganization including the formation of nanometer sized pores in which diffusion approaches that of bulk water [18] [19–21]. The effective diffusivity in this porous material will also depend upon the pore volume.

In Stage III, certain zeolitic minerals are observed to precipitate on any exposed surface, resulting in a sudden and significant

resumption of the glass dissolution rate. This mineral formation is thought to be controlled by the kinetics of nucleation followed by rapid growth [1,22–26]. Nucleation, whether homogeneous or heterogeneous, rarely shows a reproducible time dependence in most industrial and geochemical environments, except under highly controlled laboratory conditions. Thus, it is difficult to relate zeolite nucleation to solution composition [27–30].

GRAAL is an empirical model of glass alteration that successfully reproduces much of the glass alteration behavior discussed. GRAAL was originally developed by workers at the French Alternative Energies and Atomic Energy Commission (CEA) [6,16,31]. Some modifications to the model have been advanced by the French team, including rate and diffusion terms dependent on pH and temperature [31]. In the most recent modifications, the gel layer composition is modeled as a solid solution with a set of bounding mineral phases chosen to account for the experimental data [32–34]. The model presupposes two fronts that move into the glass with velocities dependent on solution conditions. The two velocities describe the rate of complete dissolution of glass and the rate of formation of an altered layer. Originally, the thickness of the altered layer was interpreted to be that of the PRI and did not include the overlying gel zone.

In the present work, we show that GRAAL does not explain certain data trends in a series of borosilicate glass compositions [3]. For this reason, we propose a simple modification involving a power factor parameter that resolves this issue. Further, we show that the optimal value of the power factor changes with differences in the composition of the glass and that glasses with similar compositions can be grouped and fitted with a common power factor. This raises the possibility of modeling the dependence of glass alteration rate on the pristine glass composition. Finally, we suggest the new power factor is physically associated with the non-linear dependence of water diffusion through the hydrolysis region extending from bounding aqueous solution to pristine glass.

## 2. Modified GRAAL model

### 2.1. The solution mass balance equation

For any system in which a glass or mineral is reacting, the elemental analysis of the solution concentration can be described by a solution mass balance equation (SMBE), which accounts for all in-flux and out-flux phenomena within the experimental chamber. For a well-stirred system with continuous flow through of fresh solution, the SMBE can be written as

$$\frac{dC_i^{sol}}{dt} = \frac{S_0}{V} J_i - \frac{F_v}{V} (C_i^{sol} - C_i^{in}) - \frac{dC_i^{min}}{dt}. \quad (1)$$

The elemental concentrations are those in the experimental chamber solution,  $C_i^{sol}$ , inlet source solution,  $C_i^{in}$ , and captured as precipitate,  $C_i^{min}$ . The three right-hand terms represent, respectively, 1) the flux of each element,  $J_i$ , from the glass source with a total initial surface area,  $S_0$ , diluted into the solution volume,  $V$ , 2) the dilution of each element due to solution flow,  $F_v$ , in and out of the experimental container, and 3) the removal of each element involved in the precipitation of secondary mineral phases.

Each of these terms may influence the solution composition which may, in turn, influence the rates for each of the terms. In general, for time-dependent quiescent or flow experiments, a model for the flux term as well as the mineral precipitation term must be specified. For this discussion, the glass alteration model will be the GRAAL model and/or our modifications of the model to account for non-linear diffusion within the hydrolysis layer. For the series of data discussed here, the data were taken under quiescent,

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