



Monte Carlo simulations of the corrosion of aluminoborosilicate glasses



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ABSTRACT

Aluminum is one of the most common components included in nuclear waste glasses. Therefore, Monte Carlo (MC) simulations were carried out to investigate the influence of aluminum on the rate and mechanism of dissolution of sodium borosilicate glasses in static conditions. The glasses studied were in the compositional range $(70 - 2x)\% \text{SiO}_2$ $x\% \text{Al}_2\text{O}_3$ $15\% \text{B}_2\text{O}_3$ $(15 + x)\% \text{Na}_2\text{O}$, where $0 \leq x \leq 15\%$. The simulation results show that increasing amounts of aluminum in the pristine glasses slow down the initial rate of dissolution as determined from the rate of boron release. However, the extent of corrosion – as measured by the total amount of boron release – initially increases with addition of Al_2O_3 , up to 5 mol% Al_2O_3 , but subsequently decreases with further Al_2O_3 addition. The MC simulations reveal that this behavior is due to the interplay between two opposing mechanisms: (1) aluminum slows down the kinetics of hydrolysis/condensation reactions that drive the reorganization of the glass surface and eventual formation of a blocking layer; and (2) aluminum strengthens the glass thereby increasing the lifetime of the upper part of its surface and allowing for more rapid formation of a blocking layer. Additional MC simulations were performed whereby a process representing the formation of a secondary aluminosilicate phase was included. Secondary phase formation draws dissolved glass components out of the aqueous solution, thereby diminishing the rate of condensation and delaying the formation of a blocking layer. As a result, the extent of corrosion is found to increase continuously with increasing Al_2O_3 content, as observed experimentally. For $\text{Al}_2\text{O}_3 < 10$ mol%, the MC simulations also indicate that, because the secondary phase solubility eventually controls the aluminum content in the part of the altered layer in contact with the bulk aqueous solution, the dissolved aluminum and silicon concentrations at steady state are not dependent on the Al_2O_3 content of the pristine aluminoborosilicate glass.

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1. Introduction

Radioactive waste immobilization through vitrification and disposal in subsurface facilities or deep geologic formations is the favored strategy for long-term storage of high-level and low-activity nuclear wastes generated across the US Department of Energy's complex. The effectiveness and safety of this strategy, and thus its long-term impacts on public health and the environment, rely heavily upon our capacity to minimize the risks of radionuclide release into the biosphere, which, in turn, depends on our ability to predict the fate of glass waste forms over geological time scales. Therefore, a large and sustained effort has taken place, over the past three decades, to develop a robust scientific understanding of the chemical reactions that occur at the glass–water interface and a large amount of information on the relationship between the chemistry and corrosion behavior of nuclear waste glasses has been collected as a result [1–23].

Based on this body of work, glass dissolution in a static (non-renewed) solution is described as consisting of three stages: stage I – forward rate of dissolution in a relatively dilute solution; stage II – a decreasing rate of dissolution to a nearly constant (but non-zero) residual rate; and stage III – an abrupt renewal of dissolution at rates approaching that in Stage I. Stage I consists of the hydrolysis and dissolution of the glass network while protons from the aqueous solution exchange with network-modifying cations. When the concentration of dissolved components increases, the glass dissolution rate diminishes to the stage II-defining residual rate. With time, the solution becomes saturated and secondary phases (e.g., clay phases) begin to form. These processes can continue at a slow rate for very long time periods. Certain combinations of the glass composition and environmental conditions favor the formation of select secondary phases (e.g., zeolites) that are concurrent with an increase of the dissolution rate relative to the residual rate, which is designated as stage III.

In addition to experimental techniques, computer simulations, and in particular Monte Carlo (MC) models, have been employed to enhance our understanding of the interplay between composition, structure, and dissolution behavior in the dissolution stages

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mentioned above. Early Monte Carlo models by Aertsens and co-workers [24–29] considered two-component glasses and explicit diffusion via discretization on a lattice. One of the main insights that emerged from the work of Aertsens and co-workers [26] is the fact that the silica saturation concentration is not constant throughout the glass dissolution process, unlike what is assumed in the Grambow glass dissolution model [2]. Aertsens showed that the initial silica saturation concentration is that of the glass, whereas the final silica saturation is that of the gel that forms at the interface during corrosion. This finding resulted in a modification of the first order dissolution rate law proposed by Grambow for glass dissolution [8]. Monte Carlo simulations by Devreux and co-workers [12,30–37] have considered dissolution of glasses with up to five oxide components and have shown the formation of a dense layer, atop the altered layer, which blocks the aqueous glass corrosion. The formation of such a barrier layer was also obtained in the MC simulations of Aertsens [26]. In previous work [38], we employed a Monte Carlo model similar to that of Aertsens and co-workers and Devreux and co-workers to investigate the dissolution behavior of borosilicate glasses in dilute aqueous solutions, focusing on the effects of structural features such as non-bridging oxygens and boroxol rings. In a subsequent publication, we studied the dissolution of borosilicate glasses as equilibrium conditions are approached both in static and flow-through conditions [39]. The simulations revealed that dissolution followed different mechanisms as a function of flow rate in flow-through conditions. In particular, at low flow rates, water was able to occasionally break through the blocking layer observed in static conditions and resume corroding the glass, which led to a constant release of B in the effluent despite the formation of the blocking layer. The MC simulations also indicated that the linear rate law was applicable at high flow rates but that deviations occurred as near-equilibrium conditions with respect to amorphous silica were approached.

In this work, we aim to investigate the effects of including aluminum in borosilicate glasses. The influence of aluminum on the corrosion of borosilicate glasses has been studied experimentally for a range of dissolution conditions. Trotignon et al. [40] compared the rate of dissolution based on B release of a borosilicate glass with that of a glass with 4 mol% Al_2O_3 in static conditions and at a surface-to-volume (S/V) ratio of 100 m^{-1} and found the aluminoborosilicate glass to dissolve six times slower than the borosilicate glass. Gin et al. [41] also found that adding Al to a sodium borosilicate glass reduced its initial dissolution rate. Abratis et al. [42,43] studied the effect of dissolved Al and Si on the rate of dissolution of a complex borosilicate glass (i.e., magnox glass composition). They concluded that the effect of dissolved Al was more significant than that of Si, thus reinforcing the previously drawn conclusion that Al slows down the kinetics of dissolution. A study by Van Iseghem et al. [44] on the long-term corrosion of aluminoborosilicate glasses of varying Al content indicated that, although Al appeared to affect the short-term dissolution, the eventual extent of corrosion was comparable for all the aluminoborosilicate glasses. More recently, Ledieu et al. [45] studied borosilicate glasses with increasing Al_2O_3 content of up to 10 mol% in static conditions and at $S/V = 100 \text{ m}^{-1}$. Again, they found that the presence of Al slowed down the kinetics of dissolution; however, they noted that the final extent of corrosion increased with increasing Al content. They attributed this effect to the formation of a secondary phase and the fact that slowing down the kinetics of dissolution retards the formation of the passivation layer. Although they could not detect any secondary phases by X-ray diffraction and transmission electron microscopy, Ledieu et al. [45] observed an increase in dissolved Si and Al and a reduced extent of corrosion based on B release when the aqueous solution contained an excess of ethylene-diamine-tetraacetic acid (EDTA), a strong Al complexing agent. Both observations are consistent with the formation of secondary aluminosilicate phases. Therefore, they concluded that secondary phases were in the form of either poorly crystalline or amorphous phases. Crystalline secondary phases have been

observed from the alteration of borosilicate waste glasses containing aluminum such as the formation of phyllosilicates from the alteration of R7T7 [46], SON68 [47], and AVM10 [48]. The formation of secondary phases represents a challenge for Monte Carlo simulations and has thus generally been ignored in such models. Consequently, MC simulation studies of the influence of minor oxides on borosilicate glass dissolution [12,36,37] have mostly focused on elements such as Zr, which do not form silicate secondary phases as readily as Al. In this work, we investigate the effect of adding increasing amounts of Al_2O_3 to borosilicate glasses and use a simple model to represent the net effect of secondary phase formation and gain insights into the elementary glass–water interfacial processes that give rise to the experimental observations discussed above.

2. Computational methods

All the calculations were carried out with a parallel Monte Carlo computer program developed for the purposes of this work. The Monte Carlo model was described in detail in previous publications [38,39]. The core algorithm of our Monte Carlo model is based on the glass dissolution model of Devreux, Barbois and co-workers [32–34,36].

In the MC model, the glass framework is mapped onto a cubic lattice wherein each lattice site represents a network-former cation (e.g. Si, Al, or B) and its first oxygen coordination shell, and two connections are removed at each lattice site to represent the fourfold connectivity of the network-former cations. Network-modifier cations (e.g. Na) are placed in interstitial positions. When a site is dissolved, it is considered to be replaced by water. Connections between nearest-neighbor sites represent X–O–X linkages, where X is a network-former cation and O is oxygen. The contacting (bulk) aqueous solution can either be considered infinite to mimic a single-pass flow-through test conducted under dilute conditions or have a fixed number of water sites calculated to obtain a desired surface-area-to-volume ratio.

Each simulation step of the MC algorithm comprises five stages: (1) a dissolution evaluation and execution stage, in which each surface site is evaluated for dissolution using dissolution probabilities determined using the approach described below; (2) a glass connectivity evaluation stage, in which the new glass configuration is evaluated to determine whether clusters of lattice sites not connected to the main glass matrix are present and therefore should also be dissolved; (3) a condensation stage, in which glass components can deposit back at surface sites; (4) a liquid connectivity evaluation stage, in which, in an analogous way to the glass connectivity evaluation stage, the connectivity of the water sites is evaluated to determine the water sites that are part of the bulk aqueous solution and those that belong to closed pores (we note that the current implementation of the MC algorithm only allows dissolution and condensation processes to occur at glass surface sites in contact with the bulk aqueous solution and not inside closed pores); and finally, (5) a coordination evaluation stage, in which the coordination of each site in the final glass configuration is recalculated.

Four elements were considered in this work: boron, silicon, aluminum, and sodium. Boron atoms are considered to dissolve instantaneously once in contact with the bulk aqueous solution; therefore, their dissolution probability is set to 1. In addition, boron is considered fully soluble, and therefore cannot condense back on the glass surface. For silicon, dissolution probabilities w_1 , w_2 , and w_3 are used for sites with one, two, or three connections to nearest-neighbor silicon sites. Silicon atoms can deposit back at surface sites with probability $w_r = w_{c-Si}c_{Si}$, where w_{c-Si} is the silicon condensation probability and c_{Si} is the silicon concentration in the aqueous solution (in atoms per aqueous site). The MC program also includes aluminum, and therefore Si and Al can find themselves in a number of possible bonding environments. To minimize the number of parameters used to describe all possible bonding environments, we employed the formulation introduced

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