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Upscaling Atomistic Mechanisms to Continuum Models For Nuclear Waste Glass
Dissolution
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Abstract - The aim of this report is to extend understanding and capability for linking atomistic understanding of glass corrosion mechanisms to continuum models of reaction and transport in the subsurface environment. The focus of this report is on aluminosilicate glass dissolution supported by studies on natural aluminosilicate minerals which exhibit similar corrosion properties. The ultimate objectives of this report and section three of the gap analysis report concurrently written for the NEAMS IPSC program (*Arguello et al. 2010, Nuclear Energy Advanced Modeling and Simulation (NEAMS) Waste Integrated Performance and Safety Codes (IPSC): FY10 Development and Integration*) are to discover the challenges in connecting atomistic scale information to continuum models. This report focuses predominantly on defining the gaps and potential links between scales for chemical processes.

INTRODUCTION

Glass waste forms have been evaluated for permanent disposal in radioactive waste disposal facilities (i.e., geologic repositories) in a number of countries. For example, the United States Department of Energy (US DOE) assessed a geologic repository at the Yucca Mountain site (US DOE, 2009) that included disposal of both spent nuclear fuel and high-level radioactive waste in an unsaturated fractured volcanic tuff characterized by oxidizing conditions. In addition, both the French “*Dossier 2005*” (ANDRA 2005) and the Swiss “*Project Opalinus Clay Safety Report*” (NAGRA 2002) evaluate disposal of spent nuclear fuel and high-level radioactive waste in a clay repository where conditions are anticipated to be water-saturated and chemically reducing, similar to approaches also being evaluated in Belgium and other countries.

Site selection and licensing of geologic repositories face a number of challenges including social and political opposition from potential host communities. Some of the scientific concerns for quantitatively assessing performance of long-term disposal of nuclear waste materials involve the complexity of reliably predicting interactions between the waste forms and the engineered and geologic systems over the very long time periods for which the waste must be isolated from the biosphere. Half-lives of some radionuclides extend to millions of years, requiring isolation for geologic time periods. Waste forms can generate substantial heat from radioactive decay, thermally driving chemical processes that modify the waste material. The waste-form degradation environment conditions are uncertain and variable, leading to complex coupled thermal-chemical-hydrological processes in the corrosion and eventual breach of a waste package containment and degradation of a waste form, the source term for release of the constituent radionuclides. Subsequent transport of radionuclides to the biosphere requires characterization of the geologic system.

Recently it was shown that the rate at which the waste degrades has a potential to improve estimated performance of repositories if the resulting waste-form lifetime is sufficiently long relative to the period

of performance (e.g., on the order of hundreds of thousands of years), and if the waste form effectively immobilizes key radionuclides in the proposed geologic setting (Swift et al., 2010). The relatively long duration of glass waste forms in the reference performance analysis of the French clay site (a few hundred thousand years – ANDRA, 2005) provides substantial delay to the peak releases to the biosphere of that system as shown by sensitivity analyses using constant glass degradation rates rather than rates that slow due to silica saturation in altering solution (Swift et al., 2010). Rates of glass waste form degradation used in the US DOE analyses of the unsaturated Yucca Mountain site reflect the far-from equilibrium glass dissolution rates that conservatively do not include any of the coupled chemical processes that can decrease those rates (US DOE, 2009).

Further understanding of the detailed mechanisms of glass corrosion would facilitate incorporation of more comprehensive and realistic representations of glass waste form behavior and provide further confidence in safety assessments of radioactive waste disposal. This report summarizes existing approaches and identifies a number of areas for further work focusing on topics that should advance the ability to upscale from molecular-scale approaches of glass behavior to models of glass degradation at the continuum-scale.

The rates of glass degradation observed from ancient glass artifacts are much slower than those observed in laboratory tests (Verney-Carron et al., 2010), similar to the slower degradation rates observed in nature for mineral degradation (White and Brantley, 2003; Ganor et al., 2005; Hellmann and Tisserand, 2006; Bryan et al., 2009). Studies of natural and synthetic glass dissolution rates show far-from equilibrium behavior can be compositionally dependent on Si content (Wolf-Boenisch et al., 2004) and Al content (Hamilton et al., 2001) of the glass. The slower degradation glass rates observed in the natural system result from a number of differences between those systems and glass studies in the laboratory including (a) dissolution mechanisms (Hamilton et al., 2001) and (b) glass reactive surface area (Wolf-Boenisch et al., 2004). Each of these aspects of the degradation are affected by the coupled feedback processes resulting during glass degradation due to formation of diffusion pathways through intermediate phases (e.g., gel layer), which may also develop to isolate fresh glass surfaces from contact with the bulk fluid (Cailleteau et al., 2008; Verney-Carron, 2010). Understanding the detailed mechanisms that lead to the disparity in rates between far-from equilibrium dissolution of glass measured in the laboratory and the fully-coupled degradation of glass observed in natural systems would provide insight into estimates of lifetimes for glass radioactive waste forms.

CONTINUUM-SCALE GLASS AND MINERAL DISSOLUTION MODELS

There are many different expressions that have been used to fit silica and aluminosilicate dissolution data from leach tests in the laboratory. Many of these expressions rely on transition state theory (TST), where the activation energy associated with a complex mechanism defines the rate-limiting step in the dissolution process. Transition state theory (TST) is generally considered to be appropriate only for elementary reactions. However, it is argued that if a complex mechanism is rate-limited by a single elementary reaction, then TST may be usefully applied to the overall reaction (Oelkers et al., 1994; Oelkers, 2001).

Different dissolution behaviors, as defined by observed changes in solution composition with time, are observed under far-from-equilibrium and under near-equilibrium conditions. These different behaviors have often been fit with different rate expressions; partly because historically, the experimental data used to define the rate law does not extend over the entire range of geochemical conditions. For nuclear glass waste form dissolution, these are the types of rate laws that have been implemented in the past. According to a presentation earlier this year (J. Vienna, *pers. comm.*), there are six different glass dissolution rate laws used in the nuclear waste glass dissolution community, that are all based on transition state theory.

Other investigators have focused on the concept that crystal dissolution and growth mechanisms should bear some relationship to each other, and have developed crystal dissolution models based on Burton Cabrera Frank (BCF) crystal growth theory (e.g., Dove et al., 2005). In general, the dissolution of a crystal can be thought of as the sum of (1) horizontal movement of atomic-scale steps defining incomplete surface layers (step retreat), and (2) removal of atoms by 2D or pit nucleation in the material. Regardless of the type of pit, when dissolution occurs near equilibrium, pits are unlikely to form. From small to large undersaturation, dissolution steps are more likely to nucleate at crystal edges, at dislocation etch pits, at impurity etch pits, at point defects, and at perfect surfaces respectively because both the rates of reaction at these sites differ and the relative number of these sites varies as a function of undersaturation.

Lasaga and Lutge (2001) introduced a model for dissolution based on the propagation of stepwaves from etch pits. Experimental data (Vertical Scanning Interferometry [VSI]) suggested that although etch pits form, the entire crystal surface dissolves. Observations suggest that stepwaves emanating from etch pits combine to lower the entire crystal surface. The evolution of stepwaves can be quantified with this equation:

$$v(r) = v_{step} \left(1 - \frac{1 - e^{-\frac{\sigma v}{r k T} e^{-\frac{u(r)v}{k T}}}}{1 - e^{-\frac{\Delta G}{k T}}} \right) \quad (1)$$

where v_{step} is the velocity of a series of straight steps, $v(r)$ is the velocity of dissolution stepwaves at a distance r from the dislocation defect, $u(r)$ is the strain field of dislocation defects, v is the molecular volume, k is the Boltzmann's constant, r is the radius of a circular dissolution step, σ is the surface free energy.

The overall dissolution rate is written as:

$$Rate = v_{\infty} (1 - e^{\Delta G/kT}) \tanh \left[\frac{1}{2x_s f(r_{pit})} \right] f(r_{pit}) \quad (2)$$

where the modifying function $f(r_{pit})$ comes from Eqn. (1) above, and x_s is a surface diffusion distance expressed in molecular units. Using this expression, the dissolution rate approaches a simple linear rate or TST-like equation far from equilibrium, and exhibits a nonlinear decrease near equilibrium (Lasaga and Lutge, 2003). This equation can be tested with detailed kinetic models such as MC methods (see below). In these methods, σ , $u(r)$, and x_s are known exactly. The only adjustable parameter is the dissolution rate at infinite dilution (the "dissolution plateau").

Much more has been done to incorporate atomistic data into continuum models for silicate and aluminosilicate minerals than for glasses, because of a strong desire by the geochemical community to understand silicate weathering in the natural environment. For over twenty years, geochemists have recognized that reactions occurring at the mineral-water or rock-water interfaces are critical to field scale processes (Hochella and White, 1990). Figure 1 provides an illustration of the spatial and time scales that are significant in geological systems, and the types of modeling that can prove useful to understanding each scale.

Figure 2 illustrates the time dependent alteration rate and extent of glass corrosion over time. First, dissolution occurs rapidly, and Si and Na concentrations increase in solution. During the next stage, a silica gel layer forms at the glass surface, and the rate of glass dissolution becomes, in part, transport limited by diffusion of aqueous species into and out of the gel. Then, a steady state is achieved within the gel and the overall corrosion rate is controlled by the coupled processes that occur within this multi-phase system. The precipitation of secondary phases, such as clay minerals, can lead to a new time period of rapidly changing solution compositions, as the solution re-equilibrates with the new solids present in the

system. Understanding long-term glass corrosion and developing models to predict this corrosion with different glass compositions, waste streams, and under different environmental conditions is critical to the development of new high-level waste forms and repository systems. The majority of this report addresses fundamental glass dissolution questions.

Although the dissolution of aluminosilicate minerals and glass has been studied for decades now, not as much attention has been devoted to the impact of mixing nuclear waste into the glass. Grambow (2006) points out that commercial high-level waste (HLW) immobilized in the glass is composed of over 30 different nuclear fission and activation products, as well as minor actinides generated by neutron capture reactions. A number of these radionuclides have long half-lives, creating the need for long-term isolation. Radionuclides like $^{137}\text{Cs}/^{137\text{m}}\text{Ba}$ and ^{241}Am remain important heat sources for hundreds to thousands of years. The blocks of glass crack during cooling resulting in surface areas as much as 50 times greater than the external surface area.

To evaluate the impact of cracks internal to the glass structure on dissolution rates, Verney-Carron et al. (2010) coupled glass alteration models with diffusive transport in solution. The coupled model was used to simulate alteration within a fractured block of Roman glass that has been altered for 1800 years. External cracks in direct contact with seawater were more altered than internal cracks (by 1 to 2 orders of magnitude) because of the strong coupling between alteration chemistry and transport in the cracks. The archeological block has a surface area developed by cracks that is 86 times greater than the geometric surface. However, according to the model, only the external cracks alter at a constant rate. The internal crack network which is responsible for most of the reactive surface area is altered at a rate that decreases over time. Over longer time periods the discrepancy between the alteration kinetics of the external and internal cracks should increase and the contribution of the internal cracks to the overall alteration should decrease. At present nuclear glass models used for performance assessment assume that the amount of altered glass will remain proportional to the initial surface of the glass blocks (including cracks) until complete alteration is reached (Gin et al., 2005). Based on Verney-Carron et al. (2010) this assumption probably overestimates the true extent of alteration.

New waste streams are being proposed that would be generated by recycled nuclear fuel (Weber et al., 2009). These waste streams include (1) the fission product ^{99}Tc , (2) heat-generating isotopes ^{137}Cs and ^{90}Sr ; (3) lanthanides; (4) minor actinides; (5) the remaining fission products; (6) the volatile radionuclides ^3H , ^{129}I , ^{14}C , Xe and Kr ; and (7) the undissolved solids from fuel dissolution. Based on years of radiation-effects research on nuclear waste forms, only radiation effects from actinides and the fission products Cs and Sr are expected to be of major concern. Because of desired high waste loading, Cs/Sr waste forms will be subject to significant self-heating (up to 1000°C) and high ionization and transmutation rates. The cumulative ionization dose projected for Cs/Sr waste forms is higher than in commercial HLW glass. At these doses and temperatures, many materials undergo decomposition, phase separation and bubble formation. Developing predictive models and validating such an approach will require a fundamental understanding of ionization effects and the coupling of electronic excitations to atomic dynamics. However, the intent is to allow for waste form cooling prior to enclosure in the nuclear waste repository (Weber et al., 2009).

In actinide-bearing waste forms, helium atoms formed from α -particles must be accommodated. For high actinide loadings, the He concentrations can become quite high ($>1\%$) and difficult to accommodate within both glass and ceramic structures. In glass waste forms, at the ambient temperature expected over the decay times for actinides, the effects of α -decay are generally small. There are small changes in stored energy, structure and volume with decay, but for the most part glasses generally do not exhibit significant changes in chemical durability.

KEY GAPS AT THE ATOMIC AND MOLECULAR SCALES

Surface Site Hydroxylation and Charge

For all interfacial reactions involving water and the hydroxylation of oxides including aluminosilicates, the protonation scheme and specific surface site charges as a function of pH on a mineral or glass surface remains uncertain. At the continuum scale, surface protonation is determined by fitting potentiometric titration data over a wide pH range using one of many available Stern-Gouy-Chapman models. Two of these models are briefly described here. The continuum-based triple-layer model (TLM) developed by Hayes and Leckie (1987) assumes one generic type of surface site for a single-metal oxide material, and does not distinguish the surface sites based on connectivity of the sites (i.e., Q^1 , Q^2 , Q^3) on the surface. It also assumes that the surface sites have three possible charges (+1, 0, -1). The electric potential and charge distribution from the surface into bulk solution is described by equations originally developed for a parallel-plate capacitor combined with a Poisson-Boltzmann distribution. Another continuum-based model for the material surface is the MUSIC model of Hiemstra et al. (1989). One of the main differences between the MUSIC model and the TLM is that the MUSIC model accounts for different types of surface sites based on connectivity to the bulk material and assigns partial charges to the surface sites according to site connectivity and bond length. These models have evolved considerably to examine different mineral-water interactions by numerous investigators since the late 1980s (e.g., Hiemstra et al., 1996; Hiemstra and van Riemsdijk, 2006; Sahai and Sverjensky, 1997a, b; Sverjensky, 2001, 2003; Venema et al., 1998). In addition, quantum calculations have been used to refine bond lengths at a material surface and surface site charges (e.g., Bickmore et al., 2004). Some studies (Bickmore et al., 2006) suggest that a static picture of the surface protonation scheme is inappropriate because the protonation of one surface site will impact the acidity of neighboring surface sites. Both of these models have sufficient parameters to fit potentiometric titration data successfully. For the purposes of fitting bulk experimental data, both types of models are successful.

At the nanometer scale, it is clear from numerous classical molecular dynamics studies that the structure of water on crystal surfaces is strongly influenced by the protonation scheme chosen for the initial simulation cell. On crystal surfaces, the structure of the first two-three layers of water also reflects the orderly distribution of atoms defining the crystal structure (e.g., . The water structure on glass surfaces compared to crystal surfaces has never been compared. The structure of water on a glass surface must reflect the greater disorder of the surface, potentially creating preferential pathways for surface attack. This topic has never been investigated.

At the electronic scale, Nangia and Garrison (2008) and Morrow et al. (2009) systematically calculated the activation energy for the hydrolysis of Si-O and Al-O bonds for protonated, neutral, and deprotonated species from quantum mechanical calculations on small silicate and aluminosilicate clusters, using a constrained optimization approach. Nangia and Garrison (2008) combined these activation energy barriers with concentrations for the different surface species determined for quartz using the TLM model of Hayes and Leckie (1987) to calculate dissolution rates ($\text{mol m}^{-2} \text{s}^{-1}$) for the 2-12 pH range at 298 K, using the following expression:

$$r = k_{\equiv\text{SiOH}_2^+} \theta_{\equiv\text{SiOH}_2^+} \rho + k_{\equiv\text{SiOH}} \theta_{\equiv\text{SiOH}} \rho + k_{\equiv\text{SiO}^-} \theta_{\equiv\text{SiO}^-} \rho \quad (3)$$

where $\theta_{\equiv\text{SiOH}_2^+}$, $\theta_{\equiv\text{SiOH}}$, and $\theta_{\equiv\text{SiO}^-}$ are the fraction of the protonated surface sites, and ρ is the molar surface density of reactive sites. This approach represents a valuable advance in incorporating atomistic data into a continuum rate law expression. However, pulling the surface site concentrations from the TLM model, suggests that we are still not completely capable of building a continuum model from atomistic data only.

Leung et al. (2009) used *ab initio* molecular dynamics to investigate the protonation of silanol groups (SiOH) on silica surfaces and compared the results to surface titration data measured by Ong et al. (1992) using surface-sensitive second harmonic generation (SHG) spectroscopy. This study successfully reproduced the pK_a 's reported by Ong et al. (1992). However, the more acidic pK_a reported by Ong et al. (1992) has not yet been generally adopted or accepted by the scientific community. The use of *ab initio* molecular dynamics, surface-sensitive SHG (Eisenthal, 2006) and sum frequency vibrational spectroscopy (Shen and Ostroverkhov, 2006) techniques to determine surface-site acidities is still relatively new and has not been conducted with nuclear waste glasses in mind.

In summary, to date, there is still much work to be done to understand the proton and charge distributions at a solid-water interface. Assumptions need to be made before further investigations of solid-water interactions can be made. Despite this underlying gap, advances in using models to understand interfacial reactions have been made.

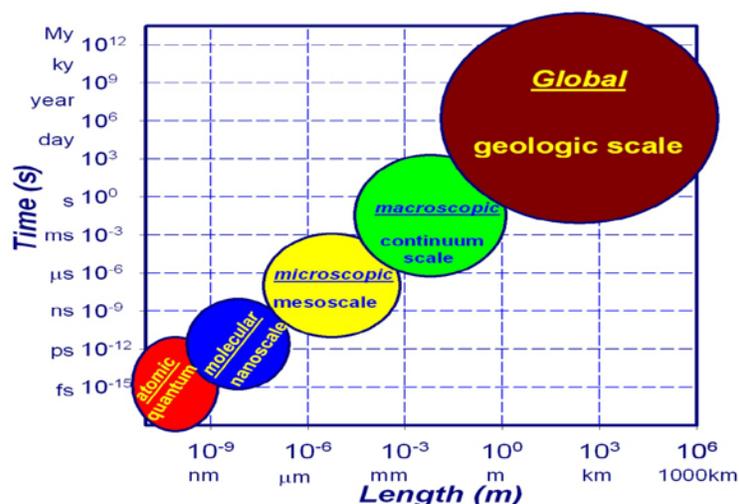


Figure 1. Time and length scales of geochemical modeling. *The nanostructure of minerals, their interaction with fluids, and reactions on their surfaces are poorly understood and difficult to study. Molecular-scale understanding of these phenomena is crucial to understanding and prediction of geochemical processes on a much larger scale. Computer modeling can provide fundamental understanding of the structure, energetic, dynamics, reaction mechanisms, etc. with atomic and molecular scale resolution. From Kalinichev (pers. comm.) “Molecular Modeling applied to Environmental Geochemistry”, ACS-PRF Summer School, 2004.*

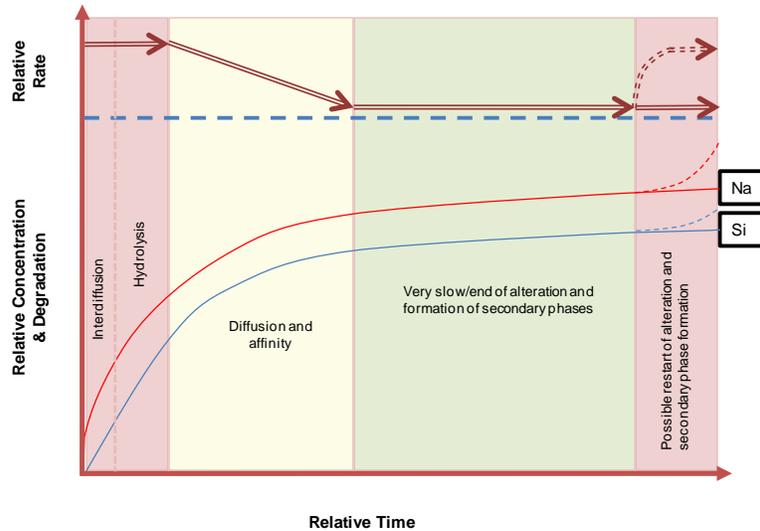


Figure 2. Time dependent alteration rate and extent for glass degradation.

Reaction Path Selection

Quantum mechanical modeling can be used to examine *postulated* reaction mechanisms using constrained optimization methods. A number of algorithms exist (e.g., linear and quadratic synchronous transit, (Halgren and Lipscomb, 1997) internal reaction coordinate (Schlegel, 1987), eigenvector following, (Cerjan and Miller, 1981), synchronous transit quasi-Newton (Peng and Schlegel, 1994)) that potentially can predict reaction pathways, but with most geochemical reactions involving more than a few atoms, experimental data and chemical insight are usually more reliable at estimating in initial reaction step (Kubicki, 2008). Using quantum mechanical calculations, Kubicki et al. (1996) found that the protonation of a terminal oxygen on a Q^3Si or Q^3Al cluster shortened the remaining three cation-oxygen bonds. This result contrasted with previously proposed mechanisms that suggested this protonation might be the first step in aluminosilicate dissolution mechanisms. In sum, the prediction of reaction pathways is still an area that should be regarded with skepticism.

Impact of Crystal or Glass Surface Structure and Solvation

Ab initio cluster calculations have been used to calculate the activation energies of bond-breaking and bond-making in aluminosilicate materials. Because these calculations only involve a small number of atoms, the results apply to both glass and crystal structures. There are differences in the approaches currently used that are worthy of consideration. These differences are largely conceptual. For example, Pelmenchikov et al. (2000) uses cluster calculations to calculate activation energies for breaking β -cristobalite bonds. They maintain the β -cristobalite structure during hydrolysis, thereby calculating higher activation energies than if the cluster was fully-relaxed or partially-relaxed to mimic surface relaxation on a material surface. Criscenti et al. (2005, 2006) and Nangia and Garrison (2008) use fully relaxed clusters to calculate the activation energy barriers associated with breaking an $Si-O_{br}-Si$ bond. These calculations predict lower activation energy barriers associated with silica dissolution. Kubicki (2008) and Felipe et al. (2003) emphasize the need to include several explicit water molecules in the calculations, because the reaction path changes with the addition of these molecules. In addition, the activation energies for hydrolysis again decrease. If cluster calculations are going to be used to develop a

database of activation energies associated with glass dissolution then a consistent methodology needs to be selected with an understanding of the corresponding uncertainty is necessary.

Nuclear Waste Glass Compositions

It should be mentioned here that less research has been done at the quantum molecular scale to evaluate the effect of elements such as boron and zirconium on glass dissolution rates. Aertsens and Ghaleb (2001) proposed that *ab initio* cluster calculations for nuclear waste glass dissolution could be used to provide (1) a better understanding and modeling of effects of solution composition (including pH) on the glass dissolution rate, (2) more accurate estimates of the activation energy for glass dissolution, or (3) a better understanding of the mixed alkali effect. They also suggested that these types of calculations might be useful in waste package design – i.e., determining what to put in the waste package.

Aertsens and Ghaleb (2001) also point out that the structure of the gel that forms between the dissolving glass and aqueous solution can be studied through *ab initio* calculations. They suggested that the pores in the gel may be considered as the hole of a ring formed by glass formers. Using *ab initio* calculations, Tossell and Saggi-Szabo (1997) showed that in these rings, Si – Al – Si – Al was more stable than Si – Si – Al – Al (Loewenstein rule). However, the incorporation of a proton or Ca^{2+} made the Si – Si – Al – Al configuration more stable. Similar calculations were executed for boron instead of aluminum. For the dissolution of Na^+ -aluminosilicate glasses, their calculations show that the reaction of H_2O with $\text{Si}_2\text{Al}_2\text{O}_{12}\text{Na}_2$, which can be considered as a simulation of ion exchange, does not lead to the hydrolysis of the Si-O-Al bond. Instead, the water molecule sits near the Na^+ .

Even less research at this scale has been done to determine where the actual waste elements will reside within the glass and how their release from the glass matrix will occur.

KEY GAPS AT THE MESOSCALE

Mesoscale in this report is defined as the scale that is observable in an atomic force microscope (AFM) or by vertical scanning interferometry (VSI) that can both be used to watch how the surface topology changes as the material dissolves *in situ*. Stochastic Monte Carlo (MC) simulations have been used to investigate processes at this scale, primarily for the dissolution of natural silica (quartz) and aluminosilicate (feldspar) minerals. Nonetheless, the approaches used, the issues addressed, and many of the calculated results are directly applicable to amorphous silica and aluminosilicate glass dissolution.

Nangia and Garrison (2009) developed an MC algorithm to study the interplay between dissolution and precipitation reactions for quartz (SiO_2). The goal of the research was to understand how the local arrangement of reactive sites and surface topology impacted dissolution. Two possible mechanisms were tested for dissolution at neutral pH conditions. The mechanism that reproduced the experimentally-observed steady-state dissolution of the quartz-water system was defined is depicted in Figure 3. In this approach, only one Si-O_{br}-Si bond is hydrolyzed at each MC step. Various simulations using this approach all lead to the same Q^0 (H_4SiO_4) fraction in solution and the Q^4 bulk species fraction attained a nearly constant value. The amount of silicic acid in solution at steady-state depends on the number of initial Q^1 sites.

The MC approach used by Nangia and Garrison (2009) combines Reactive MC (RxMC; Smith and Triska, 1994; Johnson et al., 1994) for incorporating reactions and configurational bias MC (CBMC; Siepmann and Frenkel, 1992) to allow for the interchange of bulky surface groups with several water groups. To describe reactions where bonds are broken and formed, it is impossible to use an MC method that preserves the identity of the molecules in the system. RxMC conserves the number of atoms in a

system and not the identity of individual molecules. For the silica-water system, the forward dissolution leads to the consumption of one water molecule per formation of an aqueous silicic acid molecule in bulk water, and the back precipitation reaction leads to the formation of water and the bridging of the free silicic acid back onto the mineral surface or polymerization in solution. The CBMC technique provides an approach to carry out simulations of systems that involve components with very dissimilar densities and molecular structures.

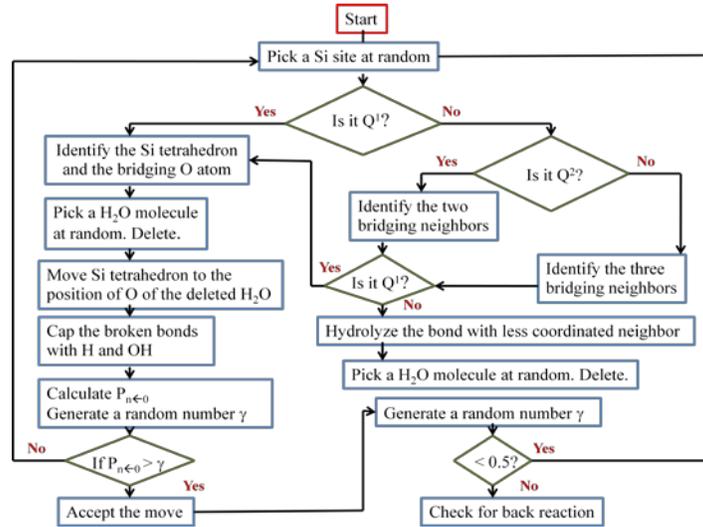


Figure 3. Flowchart for steps involved in the stepwise dissolution algorithm. (after Nangia and Garrison, 2009).

Lasaga and Luttge (2003, 2004a) introduced a general Monte Carlo (MC) kinetic model for crystal dissolution that explicitly tracks all the various atoms in the crystal structure as part of the reaction mechanism. The model uses a probabilistic approach to describe bond breaking and formation at a crystal surface. It is built from both *elementary reactions*, i.e., bond-breaking and forming, and *basic reactions*, i.e., dissolution of surface units, adsorption and incorporation of solution units, and the mobility of units at the crystal surface. In Lasaga and Luttge (2004a), the theory is developed in detail for a crystal with a simple AB structure (e.g., halite), then, in Lasaga and Luttge (2004b), the theory is developed for the dissolution of an A₃B structure that is a cubic analogue for the more complex feldspar tetrahedral structure. In later papers, the theory is expanded to model the feldspar solid solution series.

Lasaga and Luttge (2004a) define a *basic reaction* as the removal of a tetrahedral Si or Al group or unit from a feldspar structure. The basic reaction is a summation of their elementary reactions, and the probability of the basic reaction is a convolution of the probabilities of the elementary reactions that contribute to it. This stochastic approach corresponds to the theory of dissolution that stems from Burton Cabrera Frank (BCF) crystal growth theory (e.g., Dove et al., 2005), rather than transition state theory. A significant difference between the MC and the TST approach describing dissolution is that the activation energy for the overall *basic dissolution reaction* of a unit with n bonds, E_{act}^n does not reflect the activation energies needed to break individual bonds, n , and the energy difference between an original bond and a broken bond

$$E_{act}^n = n\Delta E \quad (4)$$

This is also true of the stochastic MC approach used by Nangia and Garrison (2009) for quartz. The activation energy barriers for individual bond-breaking and making are not considered in the overall basic dissolution model.

Lasaga and Luttge (2005) successfully reproduced the solubility product for albite ($\text{NaAlSi}_3\text{O}_8$), a continuum-scale property, from stochastic MC calculations that investigated how the solubility product arises from the coupling that occurs between the concentration in solution and the distribution of surface sites. Continuing with this model, Zhang and Luttge (2007) examined the role of (Al, Si) disorder on the kinetics of albite dissolution. Two different dissolution mechanisms – multilayer leaching and single-layer retreat – were tested. The results suggest that the effect of (Al, Si) disorder on albite dissolution rate is mechanism dependent. Zhang and Luttge (2008) showed that inhibition of Si atoms in solution governs the kinetic effects of feldspar dissolution relatively close to equilibrium, while the inhibition of Al atoms in solution controls the kinetic effects at far-from-equilibrium conditions. The stochastic approach also suggests the appearance of an alteration silica-rich gel layer on the aluminosilicate surface as dissolution progresses. These simulation results are all consistent with experimental observations.

In Zhang and Luttge (2009), the more rapid dissolution of Ca-rich feldspars relative to Na, K-rich feldspars is examined. This more rapid dissolution has been attributed to two possible mechanisms: (1) the preferential leaching of Al deep within the feldspar, or (2) preferential dissolution of Al only in the top feldspar layers and the precipitation of an amorphous silica surface layer. Using stochastic MC simulations, the two different mechanisms were tested over the entire range of compositions in plagioclase solid solution series. The simulations suggest that an interfacial dissolution-reprecipitation mechanism governs the dissolution of plagioclase feldspars.

The stochastic MC methods and simulations discussed above demonstrate that these methods can be used to test different dissolution scenarios and describe the non-stoichiometric dissolution behavior of aluminosilicate minerals (i.e., feldspars). The computations are performed largely based on a series of conceptual rules. Zhang and Luttge (2007) incorporated activation energies for Si-O_{br}-Si and Al-O_{br}-Si bond breaking based on *ab initio* and DFT cluster calculations into the MC model. The energies chosen are the same for all Si-O_{br}-Si regardless of the Si connectivity (i.e., Q¹, Q², Q³).

Nangia and Garrison (2010) also have started to develop a kinetic MC approach to study the overall rate of dissolution and identify the intermediate species that make significant contributions to the dissolution process. In this approach, the master equation for the system is constructed from the rate equations of constituent reaction pathways. These equations result in a collection of coupled differential equations that are solved to obtain the time-propagation of the entire system. The solution of these equations gives the concentration of chemically active species as a function of time. This approach of using rate constants for a suite of possible dissolution and precipitation reactions has fewer approximations and assumptions about the system than the stochastic MC approaches.

These techniques have not yet been implemented for glass dissolution studies, but could provide a very useful way to incorporate a data base of activation energies for bond breaking between different glass components and introduce actinides and radionuclides into the glass structure. The use of stochastic and kinetic MC approaches to study aluminosilicate dissolution is relatively new. The stochastic MC approach has been used successfully to model the dissolution of several different feldspar minerals. In each study, several different scenarios are tested and compared to experimental results. It would be useful to evaluate these scenarios for aluminosilicate glasses of different compositions, and extend this approach to multicomponent nuclear waste glasses. To my knowledge, Nangia and Garrison (2010) are the first to start developing a kinetic MC approach to study silica dissolution processes. These MC approaches look very promising for bridging the atomistic and continuum scales, particularly because they can be used to reproduce both near- and far-from equilibrium dissolution and the start of gel layer formation on an

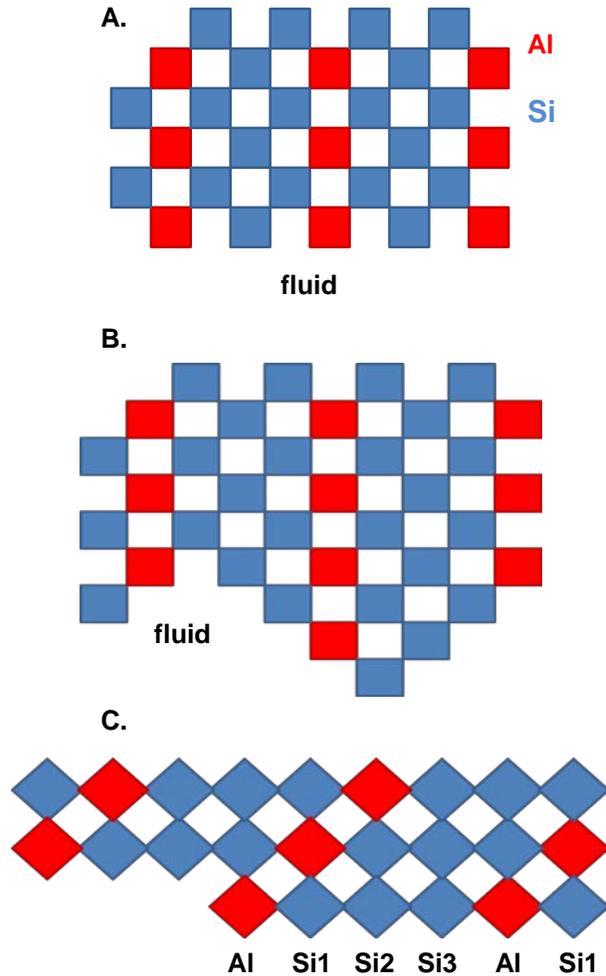


Figure 4. Simplified model of a dissolving feldspar surface. (A) The four coordinated framework is displayed in two dimensions. The AlSi_3 stoichiometry is representative of the feldspar series. The reactive surface shown consists of all Q^2 sites requiring two new bonds to attach a new unit. (B) Surface in (A) after reaction with a fluid. The reactive sites grow (or dissolve) quickly to produce new surfaces. (C) A diagonal face of the model crystal which grows or dissolves in an orderly step-controlled fashion. An Al kink site is shown. Note the different kink sites produced by the removal of the Al kink atom and subsequent Si atoms along the step. These kink sites are labeled Al, Si₁, Si₂, and Si₃ (after Lasaga and Lutge, 2005).

aluminosilicate surface. One area of research to consider is how far this approach can be used to describe gel layer formation and whether it can be extended to include calculations of gel layer porosity. It should be pointed out however, that the MC methods are used to test different conceptual models for dissolution and then compared against experimental data. Therefore, the predictive capabilities of the approach strongly depend on the validity of the embedded conceptual model. Nonetheless, these approaches look very promising for investigating multicomponent nuclear waste form dissolution processes.

KEY GAPS IN COUPLED AND CONTINUUM SCALE PROCESSES

Reactive-transport models for the subsurface environment, such as CRUNCH (Steeffel and Maher, 2009) typically have two major parts: a thermodynamic geochemical model that handles equilibrium or kinetic reactions between aqueous species, solids (e.g., mineral precipitation and dissolution) and solid surfaces (e.g., adsorption of contaminants to mineral surfaces). One issue that has been raised repeatedly is that glass is not a thermodynamically stable phase, and therefore selecting an appropriate solubility product or chemical affinity to describe “glass equilibrium” in these reactive-transport models has been handled in various ways in the literature. Most approaches have focused solely on the silica content of the glass (or the gel), but development of an approach that accounts for variable glass composition might provide a more coherent framework for upscaling studies. Because there can be correlations between the rates of reactions and the free energy of overall reactions, it may be possible to define the chemical affinity terms relative to a standard set of overall reaction products that represent the stable assemblage of the glass composition, as opposed to a nonexistent glass–solution equilibrium condition.

On the other hand, because the glass is metastable, it might be possible to treat the glass outside the conventional framework of geochemical speciation and solubility codes. In this scenario, the glass would be a source term that introduces an influent solution that changes as a function of glass dissolution. Information regarding the chemical affinity of silica and other glass components in solution would be fed back to the “glass” module where new influent information would be calculated for the next timestep.

Another issue that has not been addressed is the transport of aqueous species through the gel layer at the glass surface. Explicit atomistic models can be used to investigate the diffusion of aqueous species, particularly silica within the gel layer. Classical molecular dynamics can be used to investigate the diffusion of species in the layers of structured water near solid surfaces and through different size pores, as well as the “jumping rate” of a species; that is, the frequency with which a molecule (e.g., H_4SiO_4) attaches and detaches from the surface. These results can be used to constrain the transport parameters in continuum models that are presently fitted parameters in these models. Reproducing silica diffusion explicitly would allow the physical properties of the gel layer (e.g., porosity, tortuosity) to be more fully evaluated from the progression in the experiments. However, experiments that can characterize the porosity and tortuosity of the gel layer and provide ranges of pore size and continuity through the gel layer will be required to link the atomistic scale models to the gel structure.

Reactions at the glass surface and diffusion through the gel layers will affect the aqueous solution compositions within the gel layer and will evolve to be different from the bulk solution composition. A number of studies have considered the changes in dissolved silica but this should be expanded to include full water compositions. Explicitly evaluating the changes in solution composition in the gel would be facilitated by a pore-scale reactive transport approach that included the major dissolved constituents.

In addition to the changes in solution composition at the glass surface, the reactive surface area of both the glass and the gel layer may change with time. Experiments coupled with computational studies are required to investigate how to define this surface area and how it changes through time. The effective surface area may also increase dramatically as cracks in the glass surface nucleate and grow through time. Prior to being introduced to the repository setting, the nuclear waste glass forms may undergo expansion during heating due to radioactive decay. Subsequent cooling could generate cracks that propagate into the waste form structure. The formation of these cracks would not be accounted for through an analysis of changes in surface roughness at a single glass–water interface. At the continuum level, crack propagation theory is being modified to address non-linear material behavior at the tip of the crack (Grossman, 2010). At the molecular scale, models of cracks in silicon demonstrate that the atomic-scale progress of a crack occurs in jumps followed by static periods of atomic restructuring (Grossman, 2010). These advances in

continuum and subcontinuum understanding present an opportunity for a coherent upscaling study for crack development.

Through analysis of fracture alteration in archeological glass and reaction-transport modeling, Verney-Carron et al. (2010) demonstrated that glass alteration at internal cracks will decrease over time, and that the majority of glass alteration occurs on external surfaces. It was concluded that the coupled glass alteration provided a negative feedback on the transport of constituents through fracture pathways. The physical and chemical processes leading to decreased transport rates along cracks represents another area that may be amenable to upscaling analysis from subcontinuum to continuum scale models. Additionally, developing general constraints on the integrated result of these field scale coupled processes (the occlusion of glass reactive interface surface area and additional crack growth) would address one of the major areas for upscaling from continuum models to field scale models. This is one of the key study areas for making the connection between continuum models and performance assessment models that represent the system response on the larger scale. Explicitly evaluating these integrated changes to the total glass surface area in the field would be facilitated by a continuum-scale reactive transport approach applied at the tens of centimeters to meter scale.

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