Reaction Barriers for Glass Corrosion from First Principles Calculations

Fuel Cycle Research and Development

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SUMMARY

This report describes a set of barriers for modeling borosilicate glass dissolution developed from the first principles calculations and is intended to provide input for Model Integration for Engineered Materials Performance . It satisfies the Fuel Cycle Research and Development milestone M4FT-14AN0804013 in work package FT14AN080401.

The report’s objective is to document development of a set of the energy barriers of elementary reactions, including description of procedure for their derivation, mechanistic studies of reaction pathways and tabulated results.

The objectives outlined above require use of a range of subcontinuum modeling and code capabilities. The intent of the evaluation is to provide a basis for choosing methods that achieve an appropriate balance between rigor/accuracy and computational practicality for calculating reaction energy barriers and investigating potential reaction mechanisms. Such subcontinuum investigations are important for lending confidence to models used for long-term predictions. For example, such calculations provide an otherwise unavailable method for discriminating between potential reaction mechanisms and pathways that could control the long-term dissolution rate when the rates of the experimentally-observable dominant pathways decrease over time. Therefore, reaction barriers for elementary reaction steps involving different surface species and surface sites have been evaluated to parameterize reaction progress models.

The ultimate goal is the ability to identify and model mechanistic processes at the atomic scale that are important for waste glass dissolution, and thereby formulate rate law equations for dissolution and compute model parameters.

ACRONYMS

ANL	Argonne National Laboratory
DFT	Density Functional Theory
GGA	Generalized Gradient Approximation
KMC	Kinetic Monte Carlo
LDA	Local Density Approximation
MC	Monte Carlo
MD	Molecular Dynamics
PAW	Projector Augmented Wave (potentials)
PBE	Perdew-Burke-Ernzerhof (functional)
PRI	Passivating Reactive Interface
PW91	Perdew-Wang 91 (functional)
SNL	Sandia National Laboratory
TIP3P	US Ultrasoft (pseudopotentials)
VASP	Vienna Ab-initio Simulation Package

Reaction Barriers for Glass Dissolution from First Principles

1. INTRODUCTION

Subcontinuum methods can play a major role in modeling glass dissolution processes when properly used and interfaced with continuum scale models by applying appropriate upscaling procedures. This report provides a set of energy barriers calculated from first principles for borosilicate glass that can be used for kinetic modeling, e.g. using Kinetic Monte Carlo (KMC), to provide a first-principles basis for investigations of the affinity term used in the reaction affinity dissolution model. First-principles methods have been applied to calculate the energies and barriers for bond-breaking surface reactions involving Si-O and B-O bonds. This section provides an overview of the problem.

1.1. Modeling of Glass Dissolution

Degradation model for borosilicate glass waste forms is needed to provide uncertainty quantification of the source term in geological disposal models. The dissolution of borosilicate glass nuclear waste forms has been studied extensively for more than thirty years, yet a full understanding of the processes that will govern long-term glass dissolution following geological disposal remains elusive[1]. Some researchers believe that the long-term rate will be controlled by the residual dissolution affinity (i.e., free energy), while others believe that the long-term rate may be controlled by the mass transport rate through a thin protective restructured silicate layer that is formed on the surface of the corroding glass[Error! Bookmark not defined., 2, 3]. Incomplete understanding resulted in use of different rate laws to extrapolate the corrosion rate into the distant future[Error! Bookmark not defined.]. These rate laws are based either on a transition state theory chemical dissolution affinity rate law that was originally developed for silicate minerals[4] or on the rate of mass transport across the restructured silicate layer (referred to as the *Passivating Reactive Interface* layer) that is formed at the surface of the glass.[3] Another uncertainty is related to the role of secondary phase formation. Recent study suggests importance of interdiffusion coupled with hydrolysis reactions of the silicate network in determining the long-term dissolution rate.[5]

One fruitful path to achieving understanding of dissolution processes is likely to be through modeling and experiments designed to study the surface processes at the molecular level.[6] Examples of calculations of reaction barriers relevant to dissolution processes in minerals and glasses at the density functional theory (DFT) level of theory have been numerous and provided valuable information for development of reaction mechanisms[7,8,9,10,11,12]. It is desirable to gain further insights by applying first-principles methods to realistic glass models. At the same time, it is recognized that investigation of surface processes involved in the dissolution rate of glass is particularly difficult because there is no ordered surface structure and because the surfaces may reorganize extensively as they interact with water during the dissolution process.[Error! Bookmark not

defined. Thus, only a few quantum chemical studies addressed hydrolysis in sodium borosilicate glasses. Monte Carlo simulations of glass dissolution[13, 14] gained valuable insights on relationships between the composition and dissolution rates and mechanisms of nuclear waste glasses. Commonly, the rates for different reaction steps are postulated in these simulations, e.g. B release is assumed to be instantaneous once in contact with the bulk aqueous solution. First-principles calculations of hydrolysis reactions can determine energies and barriers for hydrolysis reactions on the surface to achieve understanding of rate-limiting steps and build better models for determining long-term dissolution rate.

Our previous work using first-principles methods has addressed some aspects of the dissolution model. Work on crystalline analogs has been performed to develop experimentally validated constitutive models for the forward dissolution rates. This work established subcontinuum models for the pH dependence of the dissolution rates and provided comparison to experimental data.[15] It was also demonstrated that for acidic conditions suggest that the pH-dependence of the dissolution rate for pH > 2 is controlled primarily by the impingement rate of protons at the mineral surface and can be well described by a Langmuir model as controlling the proton coverage. The other work has addressed pH dependence of B-O bond dissociation and suggested explanation for change in glass dissolution mechanism with pH.[16] In addition, our earlier report FCRD-WAST-2012-000280 provided detailed description of modeling procedures and some tabulated results.

Here we report calculated reaction barriers and reaction energies for dissolution reactions on protonated, neutral and deprotonated sites on sodium borosilicate glass surfaces for different configurations involving Si-O and B-O bonds. The results can provide useful insights in understanding surface reactions and forward rates in the more complex waste glass systems.

1.2 Scope and Objectives

The purpose of this report is to provide results for using first-principles modeling of barriers and energies for elementary reactions to provide energetic parameters needed to model atomistic chemical processes and upscaling the results of those simulations (and their associated accuracies and uncertainties) into constitutive relations. The borosilicate glass structure used in these calculations contains Na, B and Si. The structure is derived from the molecular dynamics models. The particular emphasis is placed on calculations of reaction barriers for breaking Si-O bonds.

This report is intended to meet milestone the Fuel Cycle Research and Development milestone M4FT-14AN0804013 in work package FT14AN080401.

2. MODELING APPROACHES

This section provides description of computational methods used to obtain reaction barriers on glass surfaces provided in the subsequent sections. Primarily, first-principles computational methods used are based on DFT. One of the main advantages of first-principles compared to empirical based modeling is the capability to rigorously take into account events beyond the limits of experimental measurements, such as contributions of slow reaction pathways that could dominate the effective rates at long time scales. Direct atomistic modeling of a glass surface in contact with solution at a given pH and temperature is not always feasible. Therefore, the use of first-principles methods requires judicious choice of approximations that are suitable for specific applications.

All the calculations were done within the framework of the density functional theory (DFT) as implemented in the VASP program.[17] Periodic boundary conditions are applied, which makes it possible to take into account geometry constraints during reactions. In a periodic model, the boundary conditions are satisfied for bulk crystals by virtue of Bloch theorem. Application of periodic boundary conditions to surfaces requires an additional approximation, a slab model. The PBE exchange-correlation functional form was used. The plane-wave basis set and the PAW potentials were used. The energy cutoff for plane waves was 400 eV. Transition states along the reaction pathways were located using the Climbing Image Nudged Elastic Band algorithm.[18]

The description of the procedure to obtain models of the glass structure is provided in [16]. For borosilicate glass calculations, the surface Na^+ ions were substituted with protons in considering the fast ion-exchange effect near surface in contact of water. These surfaces are then used to explore reaction pathways for water reactions with neutral, protonated and deprotonated sites of constituting network formers Si and B. A typical supercell has about ~120 atoms and a vacuum of 15 Å in the z direction of the supercell. All the barrier calculations are done for charge-neutral systems. In case of protonation, either a charge-compensating H (overall charge balanced) or an extra H is introduced. In case of deprotonation, an extra OH is introduced. Effectively, after reaching the self-consistency of electron distribution, H and OH species become H^+ and OH^-, respectively. The charges of H^+ and OH^- are compensated by the complementary OH- and H+, respectively, on the other side of the slab.

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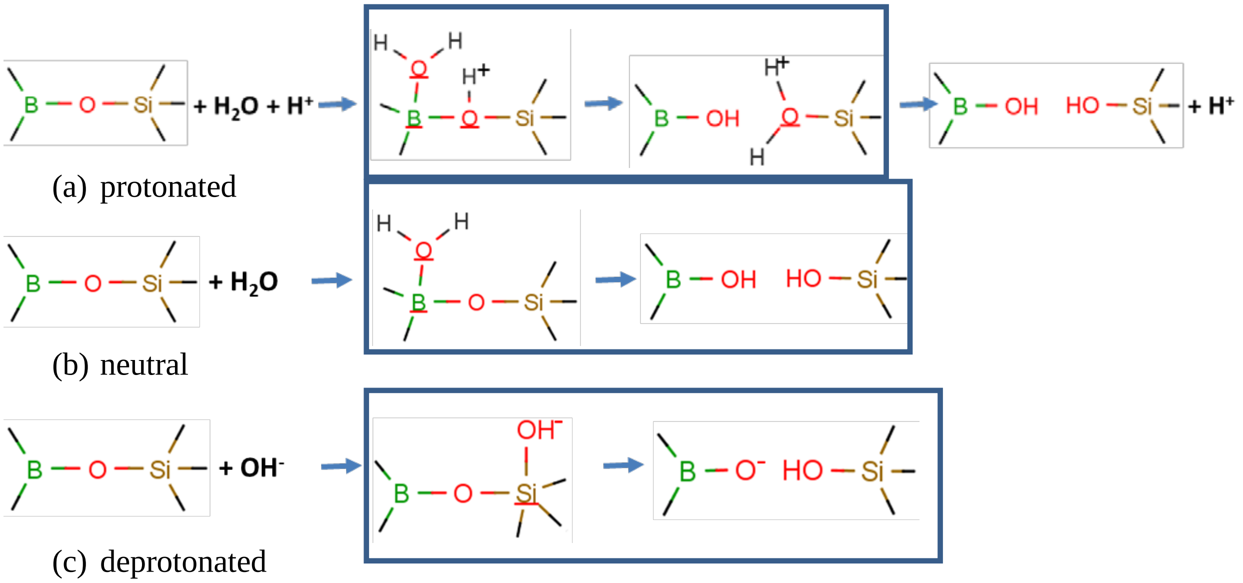
3. REACTION ENERGIES AND BARRIERS IN BOROSILICATE GLASS

This section describes calculated reaction barriers and reaction energies for dissolution reactions on protonated, neutral and deprotonated sites on sodium borosilicate glass for different configurations involving B-O bonds. While the results are summarized for a simple sodium borosilicate glass, it can be generalized for the more complex waste glass systems.

3.1 Reaction Barriers for Hydrolysis of B-O Bonds on Glass Surface

Reaction energies and barriers for hydrolysis reaction in sodium borosilicate glass were calculated for deprotonated, neutral and protonated sites for various Q configurations of B and Si atoms. The results for reaction energies/barriers are summarized in Table VI. Schematic of hydrolysis reactions is given in Fig.I (B-O-B) and Fig. II (B-O-Si). In cases when multiple pathways were investigated, only the pathway with the lowest barrier is given in Table VI.

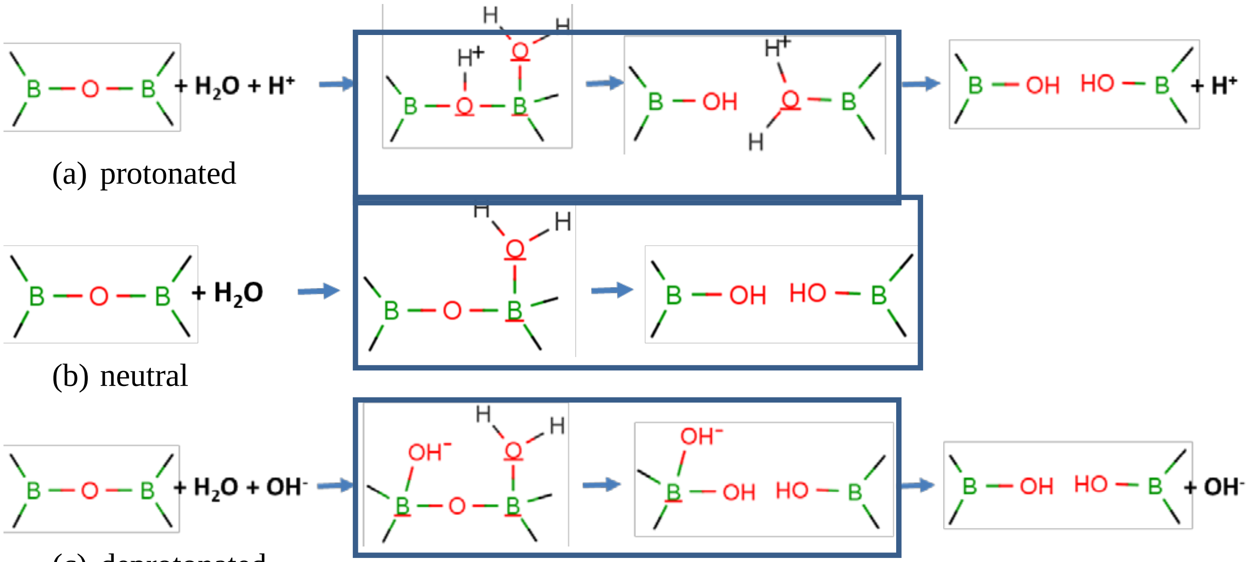


(a) protonated

(b) neutral

(c) deprotonated

Figure I: Schematic illustration of the hydrolysis reactions at the ^{3}B-O-Si bridge under (a) acidic (protonated), (b) neutral, and (c) basic (deprotonated) conditions. Boxes illustrate reaction steps calculated using DFT.



(a) protonated

(b) neutral

(c) deprotonated

Figure II: Schematic illustration of the hydrolysis reactions at the ^{3}B-O-^{3}B bridges under (a) acidic (protonated), (b) neutral, and (c) basic (deprotonated) conditions. Boxes illustrate reaction steps calculated using DFT.

Table I. Calculated activation barriers E_a and reaction energies E_{rxn} (in kJ/mol) for dissolution reactions at borosilicate glass surface.

	E_a (kJ/mol)			E_{rxn} (kJ/mol)		
	Protonated	Neutral	Deprotonated	Protonated	Neutral	Deprotonated
$^3B(Q^1)$-O-$^3B(Q^3)$	23	102	39	-228	-67	-168
$^3B(Q^2)$-O-$^3B(Q^2)$	18	129	145	-53	-3	42
$^3B(Q^2)$-O-$^3B(Q^3)$	53	98	115	-5	47	73
$^3B(Q^3)$-O-$^4B(Q^4)$	60	113	-	48	-21	-
$^3B(Q^2)$-O-Si(Q^3)	60	106	108	-1	48	45
$^3B(Q^2)$-O-Si(Q^4)	80	102	120	-70	1	64
$^4B(Q^4)$-O-Si(Q^2)	72	151	-	17	20	-

It was found that ^{4}B is easily coverted into ^{3}B in the presence of proton near the B-O bond. For ^{3}B reactions, reaction barriers are low (≤ ~50 kJ/mol) under acidic conditions.

Under neutral conditions, reaction barriers are around 100-110 kJ/mol and not sensitive to the Q value. These values are lower than comparable values for Si-O bonds, suggesting that B dissolution is faster than Si, in general agreement with experimental observations. In contrast to results for Si-O bonds, deprotonation under basic condition does not help to reduce the reaction barriers for B-O bonds.

3.2 Reaction Barriers for Hydrolysis of Si-O Bonds on Glass Surface

Reaction energies and barriers for hydrolysis reaction of Si-O-Si bridges in sodium borosilicate glass were calculated for deprotonated, neutral and protonated sites for various Q configurations Si atoms. The results for reaction energies/barriers are summarized in Tables II-IV. The geometries are given in Fig. III-V.

Table II. Reaction barriers and energies for bond breaking at protonated Si(Q_n)-O-Si(Q_m) bridge (kJ/mol).

	Ea	Erxn
Si(Q^1)-O-Si(Q^3)	85.9	-36.7
Si(Q^2)-O-Si(Q^3)	68.5	-56.9
Si(Q^2)-O-Si(Q^4)	135.1	-50.2
Si(Q^3)-O-Si(Q^2)	99.4	-1.0
Si(Q^3)-O-Si(Q^3)	127.4	98.4
Si(Q^4)-O-Si(Q^3)	129.3	97.4

In this case, we calculate reaction barriers to be lower for lower Q values, consistently with the general trends in previous studies. Reaction energies are negative for low Q values and positive for high Q values, which was also the case in orthoclase simulations. In general, we do not observe much lower reaction barriers for Si-O bond dissociation in glass than in orthoclase.

Figure III: Optimized initial, transition and final state geometries along the hydrolysis reaction pathway at the Si-O-Si bridges under acidic (protonated) conditions.

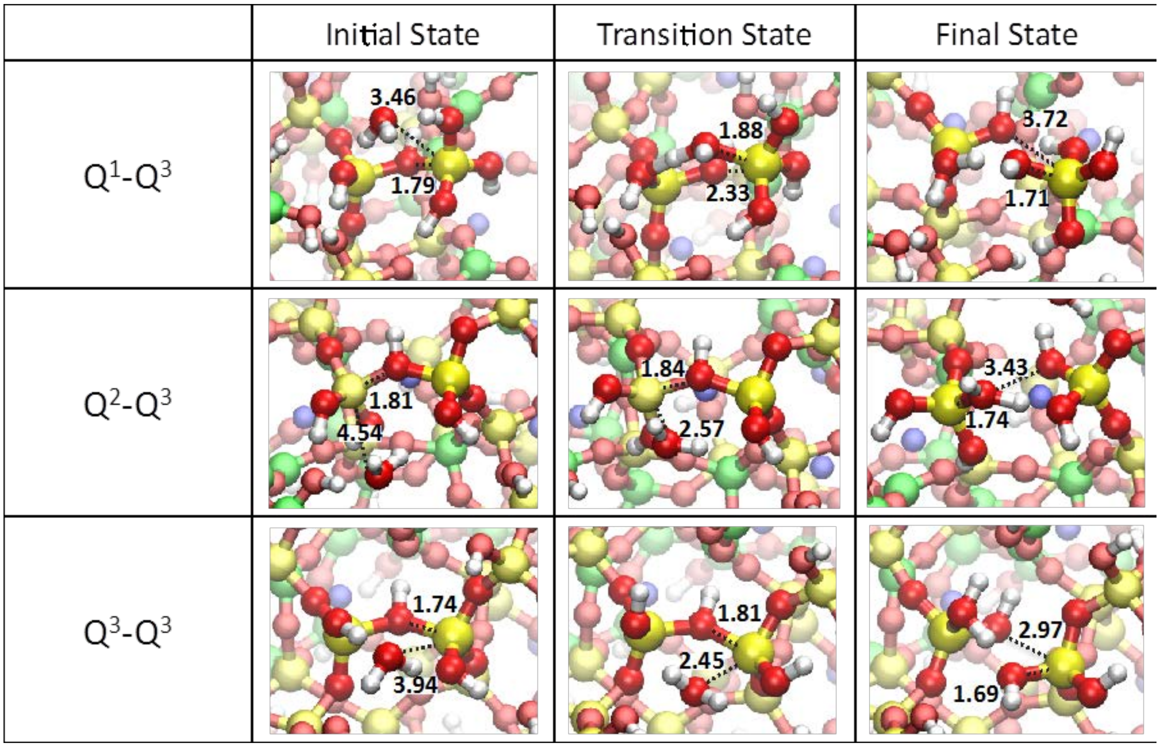


Table III. Reaction barriers and energies for Si-O-Si bond breaking (kJ/mol) in neutral case

Reaction Barriers	Q^1	Q^2	Q^3	Q^4
Q^1		170.8	158.2	243.1
Q^2		151.5	166.9	205.5
Q^3	214.2	190.1	214.2	250.8
Q^4		248.0	272.1	
Reaction Energies	**Q^1**	**Q^2**	**Q^3**	**Q^4**
Q^1		81.0	94.6	-1.9
Q^2	32.8	63.7	178.5	74.3
Q^3		70.4	92.6	0.0
Q^4		81.0	94.6	-1.9

As in the other studies by us and others, the barriers are much higher compared with either protonated or deprotonated case.

Figure IV: Optimized initial, transition and final state geometries along the hydrolysis reaction pathway at the Si-O-Si bridges under neutral conditions.

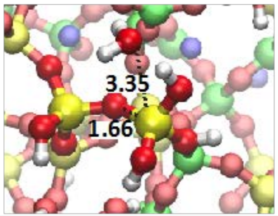
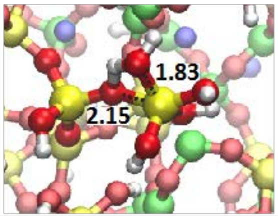
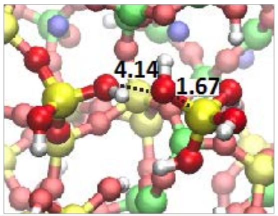
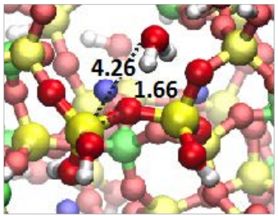
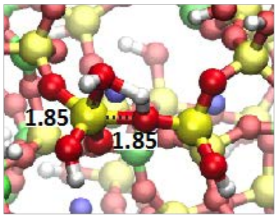
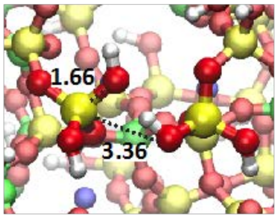
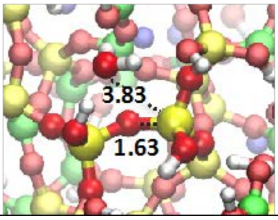
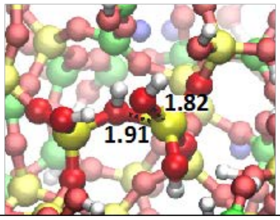
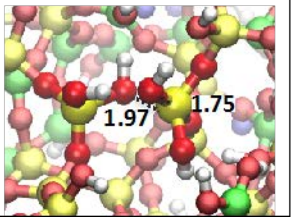
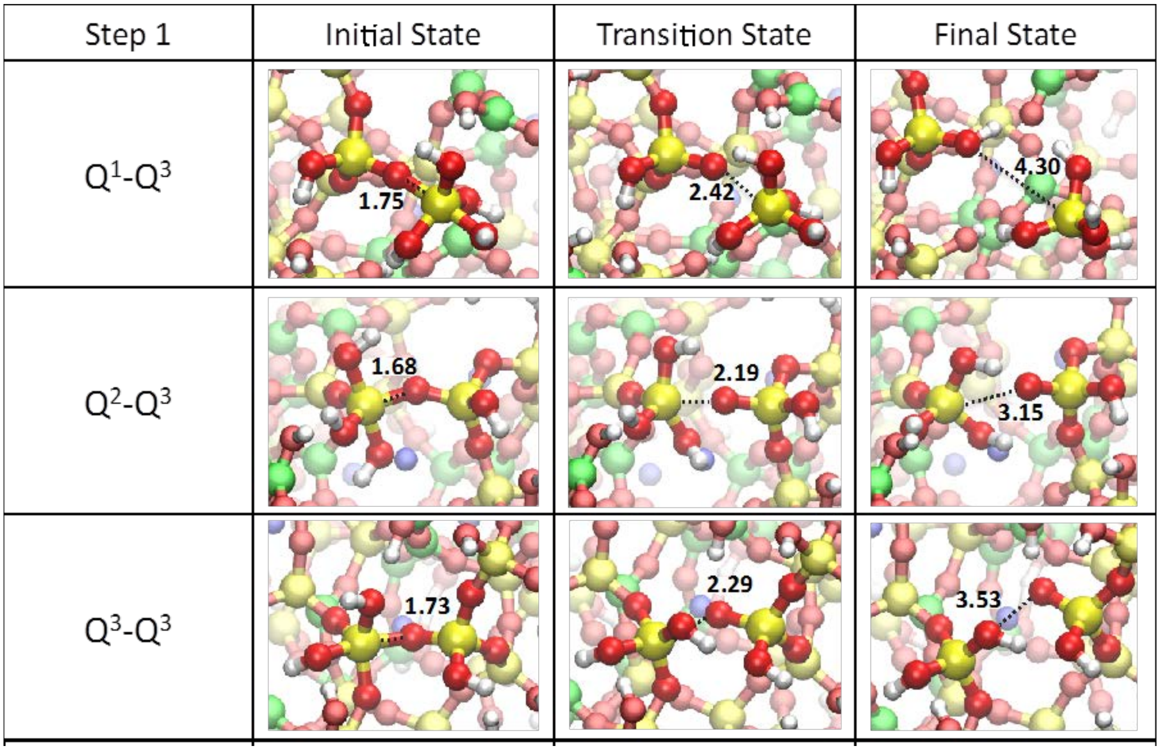
	Initial State	Transition State	Final State
Q^1-Q^3			
Q^2-Q^3			
Q^3-Q^3			

Table III. Reaction barriers and energies for Si-O-Si bond breaking (kJ/mol) in basic (deprotonated) case.

	E_a	E_{rxn}
Si(Q^1)-O-Si(Q^3)	28.0	-63.7
Si(Q^2)-O-Si(Q^3)	55.0	14.5
Si(Q^2)-O-Si(Q^4)	29.9	-83.9
Si(Q^3)-O-Si(Q^2)	53.1	29.9
Si(Q^3)-O-Si(Q^3)	59.8	33.8

The barriers are calculated for the Si-O bond dissociation starting with five-coordinated intermediate. The barriers in deprotonated case are lower than in the neutral case.

Figure V. Optimized initial, transition and final state geometries along the hydrolysis reaction pathway at the Si-O-Si bridges under acidic (protonated) conditions.



4. CONCLUSIONS AND RECOMMENDATIONS

This report provides a set of energy barriers for silica hydrolysis reactions developed from the first principles calculations that can be used for modeling borosilicate glass dissolution.

Calculations of elementary reactions steps need to be followed by Kinetic Monte Carlo simulations of glass dissolution. Subsequent sensitivity analysis needs to be used to determine rate-limiting steps. These simulations will provide a connection between glass structure/composition and the dissolution rate in order to form a basis for investigations of the affinity term used in the reaction affinity model.

5. REFERENCES

1 P. Van Iseghem, M. Aertsens, S. Gin, D. Deneele, B. Grambow, P. McGrail, D. Strachan, and G. Wicks, “A Critical Evaluation of the Dissolution Mechanisms of High Level Waste Glasses in Conditions of Relevance for Geological Disposal” European Commission, 5th Euratom Framework Programme 1998-2002, Contract NO. FIKW-CT-2001-20140, Final Report 2001-11-01 to 2004-10-31.

2 W. H. Casey, H. R. Westrich, J. F. Banfield, G. Ferruzzi, and G. W. Arnold. “Leaching and Reconstructing at the Surface of Dissolving Chain-Silicate Minerals”, *Nature*, 366, 1993.

3 P. Frugier, S. Gin, Y. Minet, T. Chave, B. Bonin, N. Godon, E. E. Lartigue, P. Jollivet, A. Ayral, S. De Windt, and G. Santarini. “SON68 Nuclear Glass Dissolution Kinetics: Current State of Knowledge and Basis of the New GRAAL Model”, Journal of Nuclear Materials, 380, pp 8-21, 2008.

4 P. Aagaard and H.C. Helgeson, “Thermodynamic and kinetic constraints on reaction rates among minerals and aqueous solutions: I. Theoretical considerations”, *American Journal of Science* **282** (1982), pp. 237–285

5 S. Gin, J.V. Ryan, D.K. Schreiber, J. Neeway, M. Cabié, “Contribution of atom-probe tomography to a better understanding of glass alteration mechanisms: Application to a nuclear glass specimen altered 25 years in a granitic environment”, *Chemical Geology*, 349–350, (2013), 99-109.

6 Lasaga, A. C. *Kinetic Theory in the Earth Sciences* 728 (Princeton Univ.Press, 1998).

7 M. H. Du and A. Kolchin and H. P. Cheng, “Water-silica surface interactions: A combined quantum-classical molecular dynamic study of energetics and reaction pathways”, *J. Chem. Phys.* 119 6418, 2003.

8 Y. Ma A. S. Foster and R. M. Nieminen, “Reactions and clustering of water with silica surface”, *J. Chem. Phys.* 122144709, 2005.

9 Xiao, Y.; Lasaga, A. Geochim. Cosmochim. Acta 1994, 58, 5379; Xiao, Y.; Lasaga, A. Geochim. Cosmochim. Acta 1996, 60, 2283.

10 Gibbs, G. V. Am. Mineral. 1982, 67, 421; Gibbs, G. V.; D'Arco, P.; Boisen, M. B., Jr. J. Phys. Chem. 1987, 91, 5347.

11 Lasaga, A.; Gibbs, G. V. Am. J. Sci. 1990, 290, 263.

12 Strandh, H.; Pettersson, L. G. M.; Sjöberg, L.; Wahlgren, U. *Geochim. Cosmochim. Acta* 1997, 61, 2577.

13 C. Cailleteau, F. Angeli, F. Devreux, S. Gin, J. Jestin, P. Jollivet, O. Spalla, *Nat. Mater.*

7 (2008) 978–983.

14 S. Kerisit, E.M. Pierce, *Journal of Non-Crystalline Solids* **358** (2012) 1324–1332.

15 P. Fenter, P. Zapol, H. He, N. Sturchio, On the Variation of Dissolution Rates at the Orthoclase (001) Surface with pH and Temperature, Geochim. Cosmochim. Acta, 2014, DOI: 10.1016/j.gca.2014.06.019

16 P. Zapol, H. He, K. D. Kwon and L. J. Criscenti, First-Principles Study of Hydrolysis Reaction Barriers in a Sodium Borosilicate Glass, International Journal of Applied Glass Science, 4, 395–407 (2013)

17 Kresse, G. and J. Furthmuller,Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, Physical Review B 1996, **54**(16): 11169-11186.

18 Henkelman, G. and H. Jonsson, Improved tangent estimate in the nudged elastic band method for finding minimum energy paths and saddle points. J. Chem. Phys., 2000, **113**(22): 9978-9985.