Preliminary Simulation of the Corrosion Rate of Archaeological Glass

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# *Preliminary Simulation of the Corrosion Rate of Archaeological Glass*

## Fuel Cycle Research & Development

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# APPENDIX E
# FCT DOCUMENT COVER SHEET [1]

| | |
|---|---|
| Name/Title of Deliverable/Milestone/Revision No. | Preliminary Simulation of the Corrosion Rate of Archaeological Glass |
| Work Package Title and Number | Waste Form Degradation Modeling - LBNL FT-14LB080403 |
| Work Package WBS Number | 1.02.08.04 |
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| Quality Rigor Level for Deliverable/Milestone[2] | ☐ QRL-3 | ☐ QRL-2 | ☐ QRL-1<br>☐ Nuclear Data | ☒ Lab/Participant QA Program (no additional FCT QA requirements) |

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# ACRONYMS

| | |
|---|---|
| BSE | Backscattered Electron |
| EPMA | Electron Probe Micro-Analysis |
| KμC | Kinetic Micro-Continuum |
| PRI | Passive Reactive Interface |
| SEM | Scanning Electron Microscopy |
| TST | Transition State Theory |
| XRF | X-Ray Fluorescence Analysis |

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# 1. INTRODUCTION

A long-standing problem in the analysis of nuclear waste glass corrosion rates is the short term time scales associated with laboratory studies. While this problem has been rectified to some extent by the recent publication of a study of a nuclear waste borosilicate glass SON68 leached in a granitic environment for 25 years (Guittonneau et al., 2011; Gin et al., 2011; Gin et al., 2013), there is still a need to validate corrosion models over longer time scales. One approach that has been taken is to study archaeological glasses, particularly where the environment within which they existed can be well constrained over time. One such study has been presented by Verney-Carron et al. (2008), who focused on an 1800 year old archaeological glass recovered from the seafloor of the Mediterranean in 2003. While this glass is not the robust borosilicate glass planned for use in the geological repository environment (as is the case with SON68), it has been demonstrated that many of the naturally occurring and archaeological glasses can be described with models that are similar to those used for nuclear glass (Verney-Carron et al., 2008).

In this study, we make use of a micro-continuum modeling approach described briefly below (the Kinetic-Microscopic-Continuum Model or KμC model) to capture the spatial distribution and identity of reaction products developing over time as a result of the archaeological glass corrosion, while also matching the time scales of alteration where possible. Since the glass blocks sat on the Mediterranean seafloor for 1800 years, the physical and chemical boundary conditions are largely constant. We focus on a fracture within the glass block identified by Verney-Carron et al. (2008) and simulate it as a 1D system, with a fixed concentration (Dirichlet) boundary corresponding to the interior of the fracture. This kind of boundary condition can be justified where the rate of replenishment of fluid in the fracture, whether due to flow or diffusion, is rapid compared to the time scales for glass corrosion (Steefel and Lichner, 1994).

# 2. SUMMARY OF ARCHAEOLOGICAL GLASS STUDY

The results of the ancient Roman archaeological glass study are presented in Verney-Carron et al. (2008), with additional material provided in Verney-Carron et al. (2010). Fractured archaeological glass blocks altered 1800 years in seawater were investigated because of their morphological analogy with vitrified nuclear waste. Both are fractured due to rapid cooling after they were melted. Second, the archaeological materials have been altered for 1800 years in a known and stable environment, that of seawater at 1ºC. The blocks weighing few kilograms each were collected in 2003 from a shipwreck in the Mediterranean Sea (Figure 1). They lay on the seafloor at a depth of 56 m; some of them were partially buried. Several blocks weighing between 0.5 and 10 kg were retrieved, dried and stored at ambient temperature. The drying caused microcracks in the alteration layers and separation of the different layers but these effects did not hinder observations and analyses. The samples have been archaeologically dated to the end of the 2nd century AD or the beginning of the 3rd century AD (Foy et al., 2005; Fontaine and Foy, 2007).

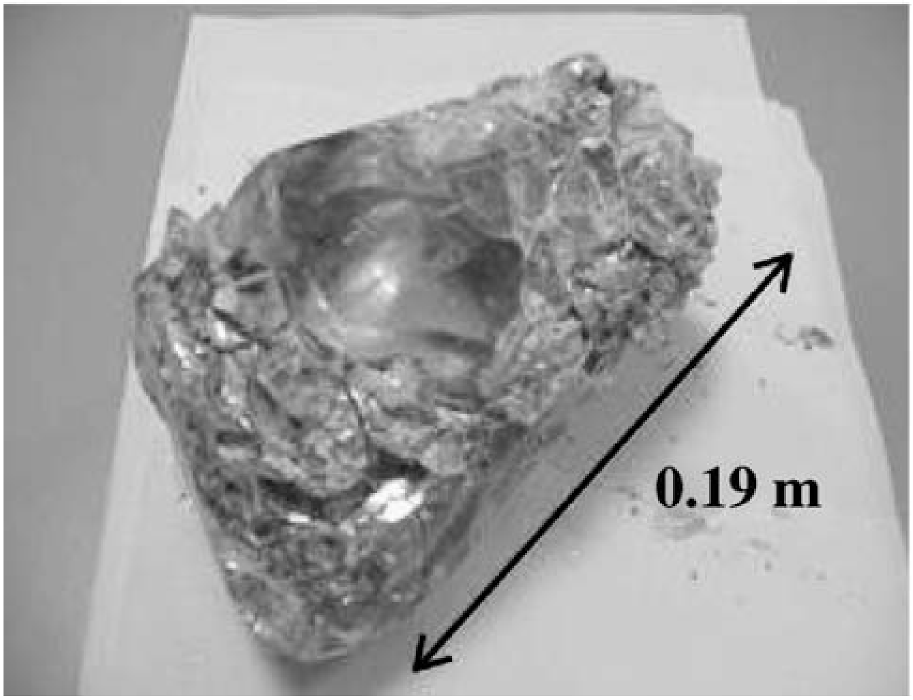

Figure 1: Photograph of the archaeological glass block (Verney-Carron et al., 2008).

Three different alteration products (a sodium-depleted layer, Mg-smectite, and carbonate) develop in the larger external fractures that were open to seawater. Geometric parameters such as the glass surface area/solution volume ratio and transport parameters (renewal of the alteration solution) strongly affected the glass dissolution kinetics. The precipitation of secondary phases resulted in sealing of the cracks. External cracks in direct contact with renewed seawater were altered at the highest rates, while internal cracks altered much more slowly, presumably due to the more closed system conditions.

The composition of the pristine archaeological glass was determined by several different methods (Verney-Carron et al., 2008). The composition based on X-ray Fluorescence analysis (XRF) is presented in Table 1. The mineralogy of the alteration products were determined by X-ray diffraction methods (Verney-Carron et al., 2008). Scanning Electron Microscopy (SEM) in Backscattered Electron (BSE) mode was used to image the fractures and cracks within the archaeological block, while Electron Probe Micro-Analysis (EPMA) was used to carry out oxide concentration analyses perpendicular to the fractures (Figure 2).

Table 1: Chemical composition of the pristine archaeological glass (Verney-Carron et al., 2008).

| **Oxide** | **Weight % by XRF** |
|---|---|
| $SiO_2$ | 70.70 |
| $Na_2O$ | 19.52 |
| $Al_2O_3$ | 1.78 |
| CaO | 4.94 |
| $Fe_2O_3$ | 0.30 |
| $K_2O$ | 0.38 |
| MgO | 0.38 |
| $Sb_2O_3$ | 0.83 |
| $SO_3$ | 0.26 |
| Cl | 1.00 |
| Total | 100.16 |

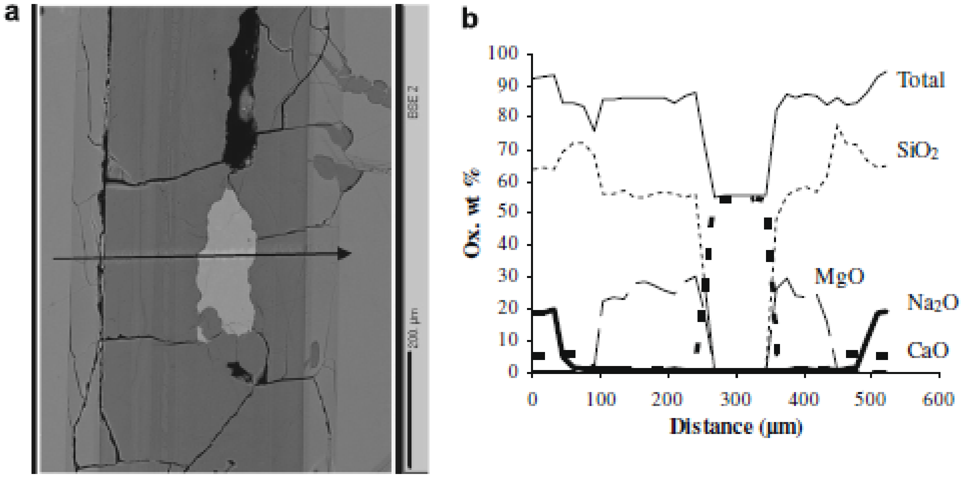

Figure 2: (a) Scanning Electron Microscopy (SEM) photograph using Backscattered Electron Microscopy (BSE) of a crack in archaeological glass and (b) Electron Probe Micro-Analysis (EPMA) cross section perpendicular to the crack (Verney-Carron et al., 2008).

## 3. KINETIC-MICROSCOPIC-CONTINUUM MODEL (KµC)

A new Kinetic Micro-Continuum (KµC) model for glass corrosion has been developed that avoids *a priori* assumptions about rate-limiting steps in the overall corrosion process. The KµC model provides a flexible approach in which individual parameters and processes are tunable, but in every case coupled within an overall dynamic framework. The KµC model may currently be run with either a single glass composition, which requires initially congruent dissolution, or it may be run with one or more glass end-member compositions that show differing thermodynamic and kinetic behavior. Since the single glass composition can be used to model overall incongruent reaction by incorporating rapid re-precipitation and/or ripening reactions, it is the preferred approach. The model currently includes the following processes

- Diffusion of water through the pristine glass and its alteration products;
- Ion exchange between water and the cations in the glass;
- Kinetically controlled hydrolysis reactions resulting in breaking of glass network bonds (Si, B, Al,…). The rate may be described by either a linear or a nonlinear TST law with an affinity control supplied by a specific phase (e.g., amorphous silica), or with an irreversible rate law with no affinity control. In either case, far from equilibrium dependencies of the rate on other dissolved (e.g., pH, Al, silica) or sorbed species can be included;
- Multicomponent diffusion of ions through the glass corrosion products;
- Precipitation reactions for amorphous and/or crystalline phases of variable composition that are kinetically and thermodynamically controlled;
- Kinetically controlled ripening and/or densification reactions that can reduce the porosity and/or pore connectivity (and thus the diffusivity) of the corrosion products;
- Kinetically and thermodynamically controlled formation of new crystalline phases (e.g., smectite, zeolite), with possible consequences for the transport properties of the corrosion layer;
- Flow and diffusion in the aqueous phase adjacent to the glass surface.

The KμC model incorporates the possibility of diffusion-limited glass corrosion by considering explicitly the kinetically-controlled densification of either (1) a residual silica-rich glass network in which other important components (e.g., the cations and network former boron) have been leached, or (2) a newly precipitated silica-rich gel layer. However, in contrast to the GRAAL model (Frugier et al., 2008; Cailleteau et al., 2008), a diffusion-limited corrosion rate is not assumed *a priori* in the KμC model. Whether a passivating layer (i.e., defined as the *Passivating Reactive Interface* (PRI) by Frugier et al., 2008) forms in the KμC model depends on the relative rates of (1) silica recrystallization and densification, (2) leaching of the glass constituents, and (3) dissolution and/or recrystallization of the corrosion products.

The dissolution rate of the glass in the KμC model is not artificially limited by the approach to amorphous silica saturation (e.g., Grambow, 2006), although this formulation can be used if needed. Thus, non-zero corrosion rates are allowed under conditions of silica saturation. Since the KμC model is formulated with an explicit treatment of multicomponent diffusion, kinetically-controlled mineral dissolution and precipitation, and glass corrosion, it can take into account the possibility that local chemical conditions within the nano- and micropores in the reaction products (i.e., the silica gel layer) may differ from conditions in the bulk solution adjacent to the corroding glass. In the absence of a reaction layer that limits diffusive transport to the pristine glass surface, silica saturation may not occur and the long-term rate of glass corrosion may remain high. In this case, the reduction in rate due to silica will be largely due to the ambient silica concentrations in the groundwater.

# 4. MODEL SETUP FOR SIMULATION OF 1800 YEAR ARCHAEOLOGICAL GLASS

We focus on a single fracture within the glass block studied by Verney-Carron et al. (2008) and simulate it as a 1D system, with a fixed concentration (Dirichlet) boundary corresponding to the interior of the fracture (Figure 2). The assumption here is that the rate of replenishment of the fluid in the fracture is much more rapid than the rate of diffusion into and out of the glass block. We discretize the system with 100 equally spaced 5 micron grid cells and run the simulation to 1800 years. The chemical system consists of $H^+$, $SiO_2(aq)$, $Na^+$, $HCO_3^-$, $Al^{3+}$, $Ca^{2+}$, $K^+$, $Mg^{2+}$, $Fe^{3+}$, and $Cl^-$. In addition, we consider 42 secondary species (complexes) formed from the ten primary (or component) species listed above. We consider the following solids or minerals: pristine archaeological glass, hydrated archaeological glass, amorphous silica, calcite, hematite, cristobalite, smectite (Mg-saponite), analcime, brucite, and gibbsite. The glass corrosion is simulated using an affinity term based on amorphous silica (Grambow, 2006). Kinetic reaction rates are used for all of the minerals. A diffusivity in the glass of $5 \times 10^{-16}$ $m^2/s$ is assumed for the simulations.

# 5. DISCUSSION

Preliminary results for the 1D diffusion-reaction simulations are shown in Figure 3. The pristine glass corrodes as a result of the diffusion of water into the glass matrix, forming hydrated glass as a reaction product.

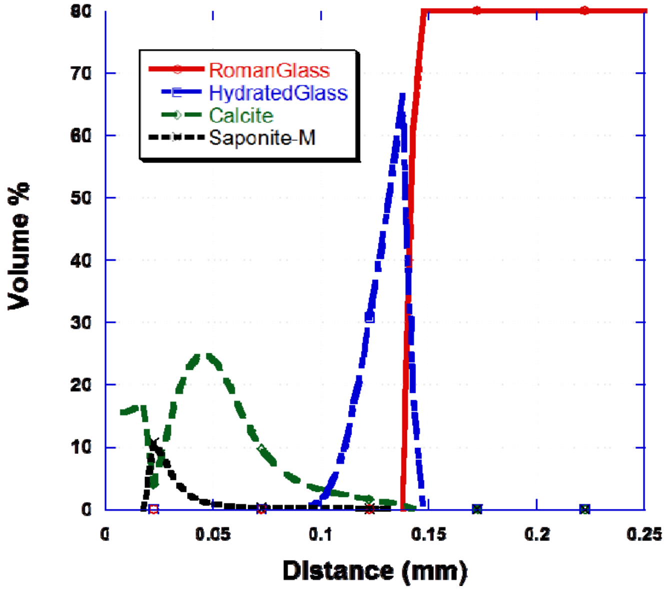

Figure 3: Simulation results after 1800 years for corroding archaeological (Roman) glass in seawater. The pristine glass corrodes as a result of the diffusion of water into the glass matrix, forming hydrated glass. The hydrated glass then corrodes following an affinity or Transition State Theory (TST) rate law linked to the solubility of amorphous silica. Calcite and smectite (Mg-saponite) form over time, in agreement with the observations reported in Verney-Carron et al. (2008).

The pristine glass corrodes as a result of the diffusion of water into the glass matrix, forming hydrated glass as a reaction product. The hydrated glass then corrodes following an affinity or Transition State Theory (TST) rate law that is linked to the solubility of amorphous silica (Grambow, 2006). Calcite and smectite (Mg-saponite) form over time, in agreement with the observations reported in Verney-Carron et al. (2008). The formation of smectite (saponite) reduces the silica concentration in the pore space close to the corroding glass, thus accelerating the rate as a result of the TST rate law used. However, a larger effect potentially comes from the change in physical properties, especially diffusivity, when the silica gel converts to a crystalline phase. This may be relevant to the increase in corrosion rate observed in some experimental studies that is associated with the formation of secondary silicate phases (especially smectite). Since the silica gel does not densify in the simulations, there is no tendency to form a Passivating Reactive Interface (PRI) as described by Cailleteau et al. (2008).

## 6. SUMMARY

Although preliminary, the 1D micro-continuum reactive transport simulations suggest that the corrosion rate of ancient archaeological glasses like that described from the Mediterranean Sea by Verney-Carron et al. (2008) can be simulated. Most importantly, the model captures the approximate mineralogical zoning, as well as the identity of the newly formed secondary phase smectite. This may be important in future studies, since the formation of new secondary silicate phases appears to be associated with an increase in the glass corrosion rate relative to the "residual" rate (Verney-Carron et al., 2008; Verney-Carron et al., 2010; Gin et al., 2011).

## 7. ACKNOWLEDGEMENTS

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