SAND2011-0396 C

U.S. DEPARTMENT OF ENERGY | Nuclear Energy

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NEAMS Waste IPSC - Subcontinuum modeling

Recent progress in modeling glass performance

Overview of Upscaling from Atomistic to Continuum Models for Nuclear Waste Glass Dissolution

and

Making Models of Multicomponent Glass

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NNSA National Nuclear Security Administration

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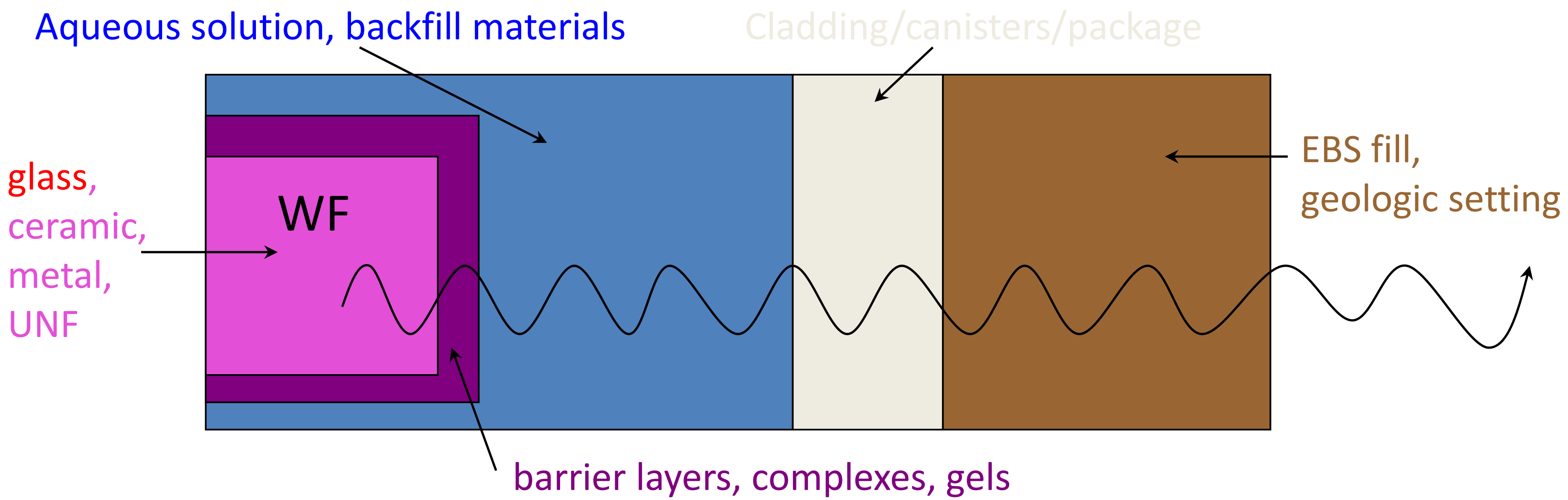
Waste-IPSC Challenge Milestone 2
Glass waste form and waste package

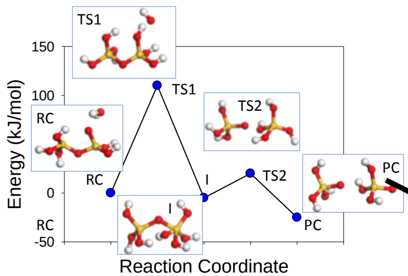


- Challenges

  Science - getting the chemistry right
  Upscaling - propagating mechanistic processes into collective behavior
  Time scale - extending defensible predictions to geological time scales

Upscaling: Glass dissolution gaps

Atomic/Quantum

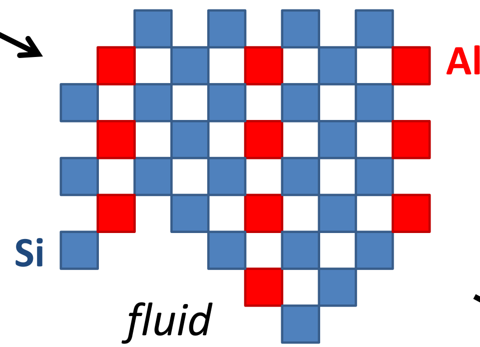


Ab initio (QM/DFT) calculations to determine bond-breaking energies

Gap 1

Stochastic Monte Carlo Modeling of the dissolution and re-precipitation of crystal units SiO_4 and AlO_4

"Mesoscale"

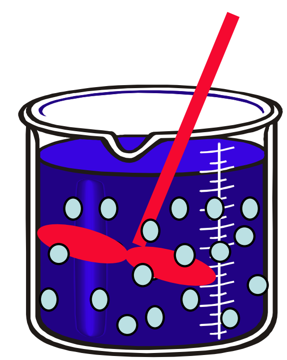


Constitutive equations developed to fit leach data from bulk experiments.

Continuum

$$r = k \prod_{i=1,i\neq k}^{i} \left[\frac{K_i \left(\frac{a_{H^+}^{v_i}}{a_{M_i}^{v_i}} \right)^s}{\left(1 + K_i \left(\frac{a_{H^+}^{v_i}}{a_{M_i}^{v_i}} \right) \right)^s} \right]$$

Gap 2



Gap 1

❖No consensus on how activation energies for bond-breaking should be modeled in QM/DFT calculations

❖Not clear how to go from the energy of breaking one bond to dissolving "crystal units"

Gap 2

❖Mesoscale models are used to test dissolution scenarios – not completely predictive.

❖Not clear how to link mesoscale models directly to continuum models or develop new constitutive equations from them.

Gap 3

❖Aluminosilicate crystal dissolution → Nuclear Waste Glass Dissolution

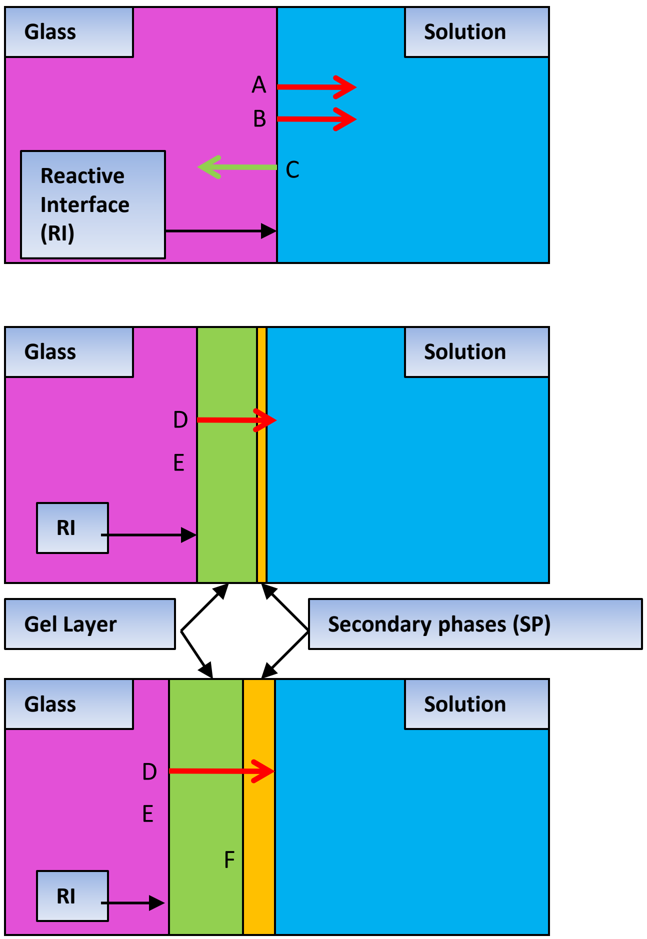
Upscaling strategy - incremental *validated* complexity

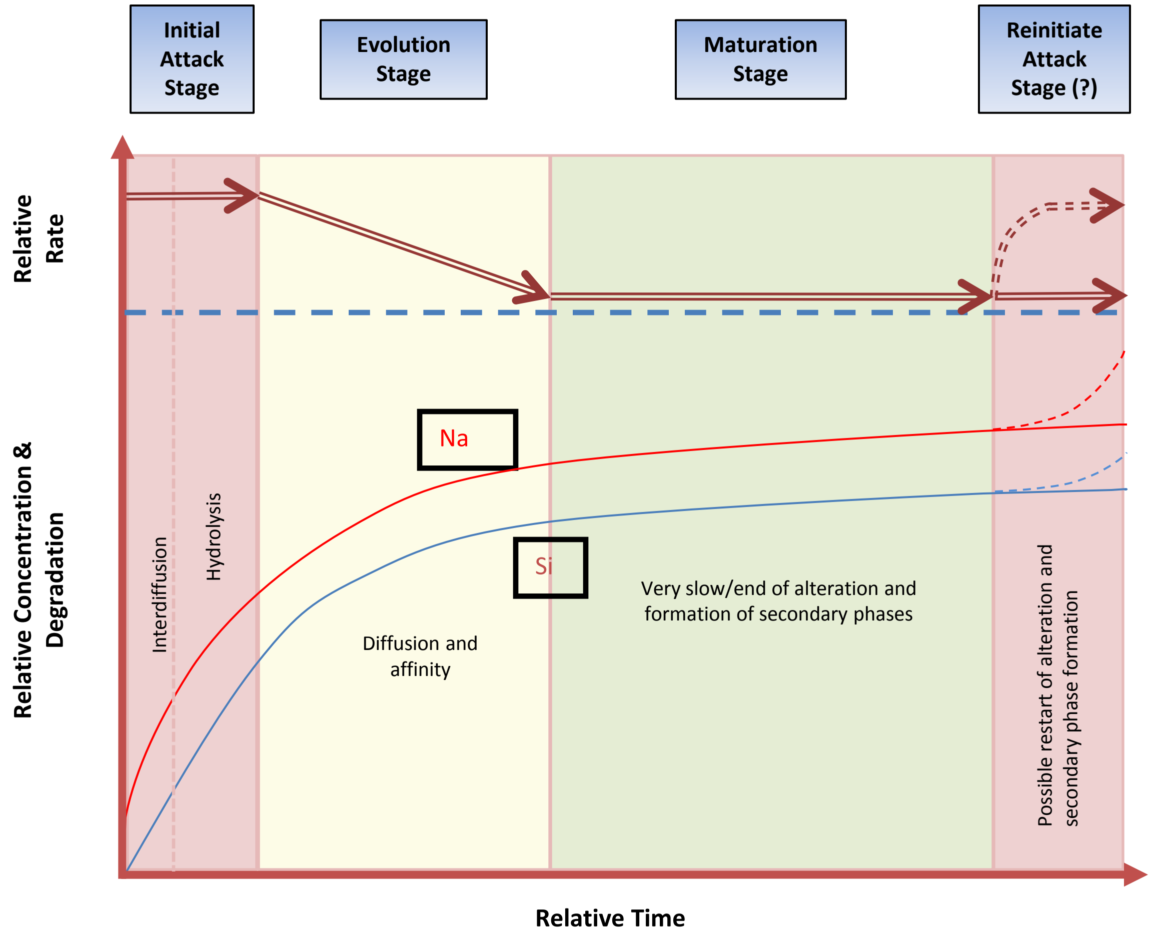
- Start with feldspar/orthoclase … (Zapol, ANL)
  - Simple crystalline structure - well controlled model system
  - Good experimental characterization - validate key elements of upscaling
  - Unconvoluted test of individual unit processes
- **… add amorphous character**
  - **Glass introduces structural complexity, statistical behavior**
  - **Similar chemistry, test-verify/validate another element of upscaling**
- **… add multicomponent**
  - **Test-verify/validate another element of upscaling**
- … add conformational complexity
  - Bulk/surface/gel … cracking, porosity contributions to surface area,
  - Test-verify/validate conformational models
- … connect to downscaling continuum models (Steefel & Bourg, LBNL)
- … develop/refine constitutive models for continuum scale dissolution

Upscaling strategy - downscaling, too

- Start with corroded archeological/geological glass … (Steefel)…
  - Natural or archeological analogs of long-term corrosion of glass
- … formulate reactive transport model to reproduce observed behavior
  - Reactive transport models for millimeter-scale simulations
  - Discover and test formulations that describe long-term evolution
  - Interim stage: phenomenological constitutive models
- … associated elements of model with underlying chemical processes
  - TST interpretation in terms of activations barriers: reaction/diffusion
  - Postulate a chemical interpretation to reactive transport model
- … use lower scale methods (e.g., MD) to test formulation and parameters
  - Bulk/surface/gel … cracking, porosity contributions to surface area,
  - Test-verify/validate downscaled model
- … connect to upscaling subcontinuum models
  - Mature stage: refined subcontinuum-based constitutive models
- … develop/refine constitutive models for continuum scale dissolution

Anatomy of glass dissolution





A – rate of alkali surface release
B – rate of Si, Al surface detachment (tends to be limiting)
C – rate of H_2O diffusion into glass

D – rate of silica diffusion through the gel (± SP) layer (at least partially limiting). Other constituents mass transport rates may also be important.
E – the aqueous composition at the RI is not the same as the Solution (aqueous silica concentration especially) and the surface area of the RI may be reduced by glass-gel contact area.
F – the gel and secondary phase layers may be acting as a mantle, in part isolating the fresh glass from the Solution.

Amorphous and Multicomponent Character of Nuclear Waste Glass

First approach tested: Vyas et al. (2006)

Developed by scientists at Corning and Accelyrs to study surfaces of sodium silicate and alkaline earth based aluminoborosilicate (ABES).

Computations and experiments proceeded more or less *hand in hand*. The computational tools allowed/predicted judgments to be made as to which hypotheses were most valid and which should be done next.

Approach to Constructing Multicomponent Glass and Glass Surfaces

Approach to Creating Glass Surfaces

Select fragments to use to create glass

↓

Fragments packed into periodic cell using MC algorithm

↓

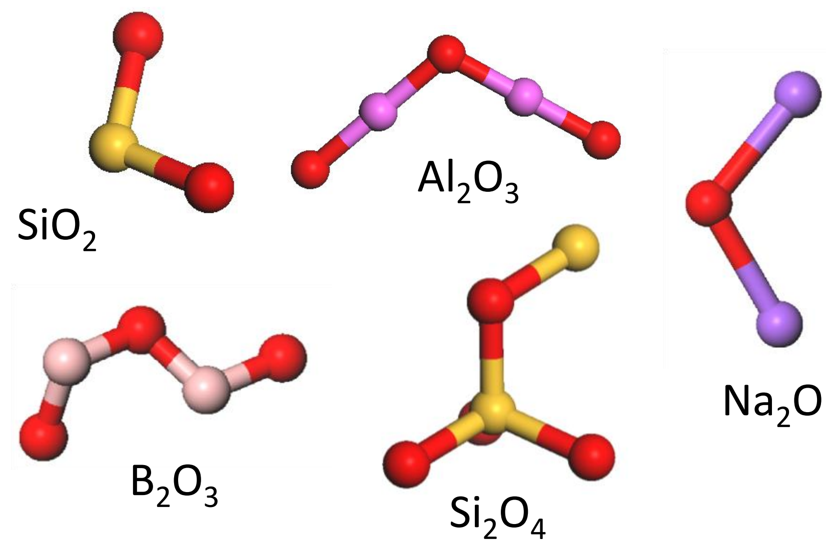
Quenched MD approach to optimize glass structure
7000K → 300K

↓

Create glass surface and anneal
600K → 300K

Vyas et al. (2006)
Materials Studio Amorphous Cell Module, Accelyrs

Fragments



• *Fragments are charge neutral.*
• *Glass compositions are based on mole % of each fragment.*

This approach will allow for constructing and comparing a suite of glasses of different compositions.

Considerations in Modeling Multicomponent Amorphous Glass Surfaces

- Amorphous Nature –
  - Is sampling size adequate to account for all surface conditions?
  - How many samples of the surface should be considered to have a statistically valid representation of the surface?
- Force Field Selection –
  - Charge distribution on ions
    - CVFF-aug (formal charges used for atoms)
    - CLAYFF – (partial charges used for framework atoms and full charges for non-framework ions).
    - Other force fields (e.g., Teter – $Na^{0.6}$-$O^{-1.2}$)
    - Dissolution – charges on surface sites, protonation of surface sites, removal of ions into solution
  - Bulk and surface structure
    - Compare to spectroscopic data available (NMR, IR, etc.).
    - Ring structures, NBOs vs. BOs.
- Quenching Technique
  - Incremental from 7000K to 300K
  - Cycling between high and low temperatures
  - Quenching/annealing of both bulk glass and surface glass