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Implementing the Stage 3 Glass Degradation Model

William Ebert
Argonne National Laboratory
ebert@anl.gov 630/252-6103

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NWTRB questions addressed

May 15, 2017 pre-meeting briefing questions for DOE:

- Provide an overview of the compositions and projected quantities of existing and future HLW glass at the West Valley Demonstration Project, Savannah River Site, and the Hanford Site (including "German" glass logs).
  - How is the variability in DOE HLW glass composition taken account of in DOE's glass corrosion models?
  - How well are the glass corrosion model parameters supported by experimental data?
- What is the status of DOE R&D activities to understand and model the long-term performance of borosilicate HLW glass?
  - Which R&D activities are run or managed by the different DOE offices and programs [DOE-NE (including NEUP), DOE-EM, DOE Office of Science (if any)] and how are these activities integrated? What are the accomplishments?
  - A detailed plan for joint DOE-NE and DOE-EM R&D activities on glass corrosion initially was developed in 2011 (Ryan et al. 2011)1 that included experiments and modeling. What are the status and results of the tasks described in the plan?
  - How are the results of international R&D activities integrated with the results of DOE R&D?
- From DOE's perspective, what are the remaining technical uncertainties and gaps in data and understanding of the long-term performance of HLW glass? How is DOE addressing these uncertainties and gaps?
- How is DOE integrating process-level models of HLW glass corrosion and radionuclide release into generic repository performance assessments?
  - How is the DOE approach to HLW glass performance modeling different from that for the low-activity waste (LAW) glass to be disposed of at the Hanford Site Integrated Disposal Facility?
  - What lessons learned from LAW glass corrosion experiments and modeling can be applied to HLW glass?
- What is the technical basis for extrapolating the results of short-term, small-scale tests on glass corrosion to long-term glass waste form performance in a repository?

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Integration of Glass Degradation Model with Generic Disposal System Analysis (GDSA)

Contaminant transport is modeled using the reaction-advection-dispersion equation:

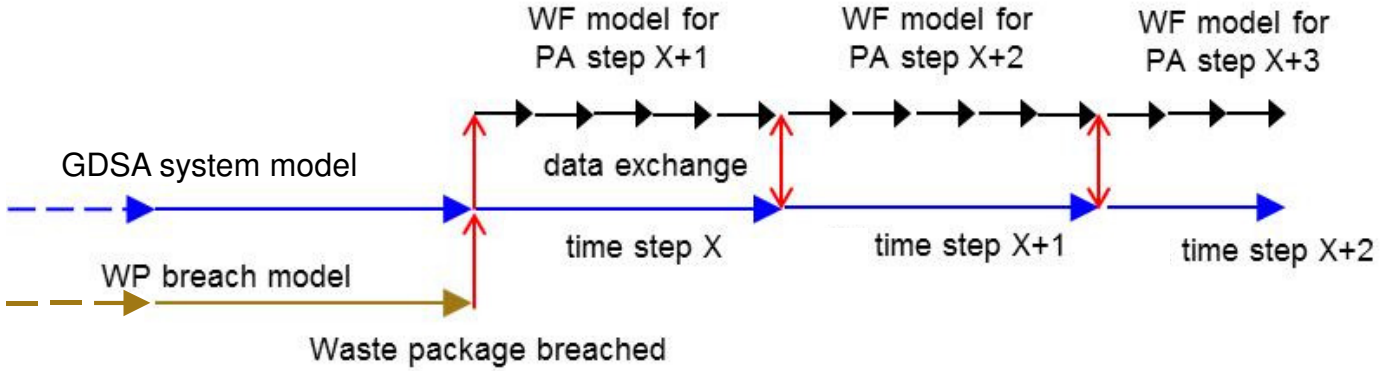
$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v_x\frac{\partial C}{\partial x} - \frac{\rho_b}{\theta}\left(\frac{\partial C_s}{\partial t}\right)_{\text{sorption}} + \sum_{k=1}^{N_c}\left(\frac{\partial C}{\partial t}\right)_{\text{reaction } k}$$

Different parameters for EBS, near field, and far field environments

C = contaminant concentration
D = dispersion coefficient
v_x = advective flow
θ = porosity of EBS
C_s = sorbed concentration
N_c = number of source/sink reactions
ρ_b = density of EBS
t = time

Glass degradation is treated as a source reaction that provides radionuclides (RN) from the breached glass waste package (WP) to the engineered barrier system (EBS).

Glass degradation model provides the mass of each RN that is available for transport during the next GDSA model time step. GDSA system model provides boundary conditions, e.g., liquid flux/volume, used to calculate the fractions of glass that corrode during next degradation time steps. GDSA system model tracks and updates RN source masses and pore water volume and composition.



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Activities to Develop Implementation of Glass Degradation Model

- Objectives of PNNL model implementation activities (Rieke and Kerisit 2015):
  - Develop Fortran code for glass degradation model to integrate with PFLOTRAN code used for GDSA system model
  - Develop input/output interfaces between glass degradation model and GDSA transport model for data exchanges
  - Exercise coupled model
- Objectives of ANL model implementation activities:
  - Demonstrate glass model can be directly incorporated into GDSA system model
  - Measure sensitivities of Stage 3 model output to model parameter values and time step duration using GeoChemist's Workbench
  - Match precision of Stage 3 model to sensitivity of GDSA transport model as limited by parent model time steps
  - Minimize calculations required to provide radionuclide source terms discernable to precision of GDSA
  - Identify set of glass model parameter values to be retained between GDSA time steps
  - Identify remaining issues

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Representing Residual and Stage 3 Rates in Glass Degradation Model

$$rate_3 = \frac{k_{forward}^{dis}\, k_{forward}^{pptn}}{\left(k_{forward}^{dis} + k_{forward}^{pptn}\right)}\left(1 - \exp\left(\frac{\Delta G_{r\ dis} + \Delta G_{r\ pptn}}{RT}\right)\right)$$

(for small deviations from equilibrium)

Most measured Stage 3 rates are constant and reaction affinity for coupled reactions is constant (ZBV model), so coupled kinetic term must be constant.

Based on test results, changes in surface areas don't have measureable effect on measured Stage 3 rates.

Assume constant Stage 3 rate persists until glass is completely dissolved.

Simplify rate equations and measure empirical dependence of coupled rates on pH and T:

Stage 3 $rate_3 = fn$(T, pH) *TBD*

Residual $rate_{RR} = fn$(T, pH) *TBD*

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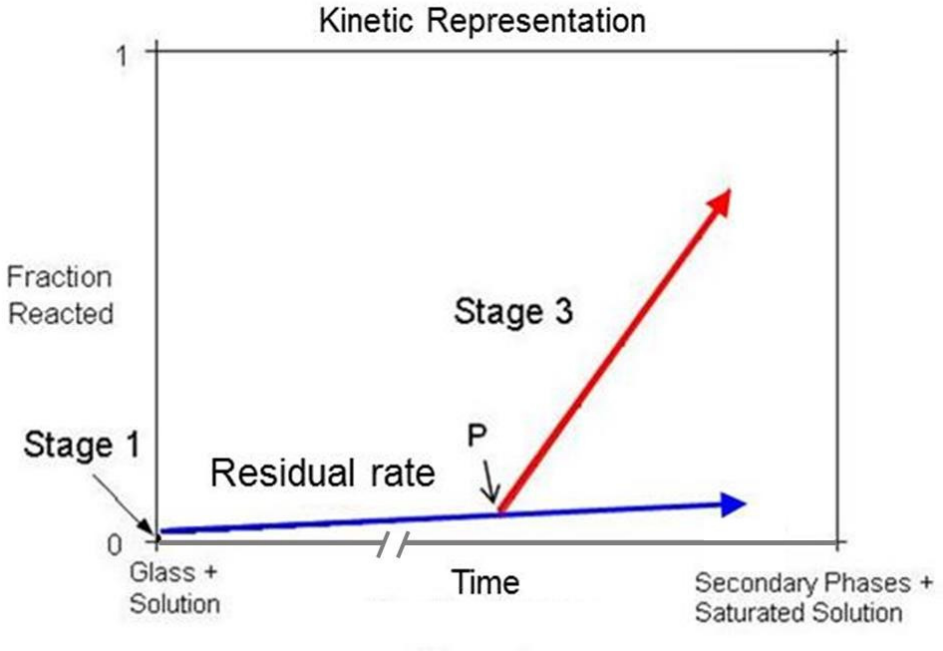
Proposed Implementation of Glass Degradation Model

1
- Establish initial solution composition by treating Stage 1 as instantaneous dissolution of *TBD* -thick layer of glass when breached package fills to *TBD* threshold level initiating reaction.
- Partition elements (including radionuclides) between solution and gel by using residual rate partition functions. *(from ALTGLASS)*.
- Equilibrate in-package solution and calculate pH.

2
- Dissolve aliquant of glass during *TBD* WF time step at residual rate = fn(T, pH). *being measured*.
- Partition elements and calculate pH.
- Check for Stage 3 trigger based on threshold solution composition P = fn(T, Al, Si, pH). *being measured*.
- If Stage 3 is not triggered, return to Stage 2 loop.

3
- If Stage 3 is triggered, impose Stage 3 rate = fn(T, pH) for next WF time step. *being measured*
- Partition elements to evolve solution composition by using Stage 3 partition functions. *(from ALTGLASS)*
- Return to Stage 3 loop.



Ebert and Jerden (2016).

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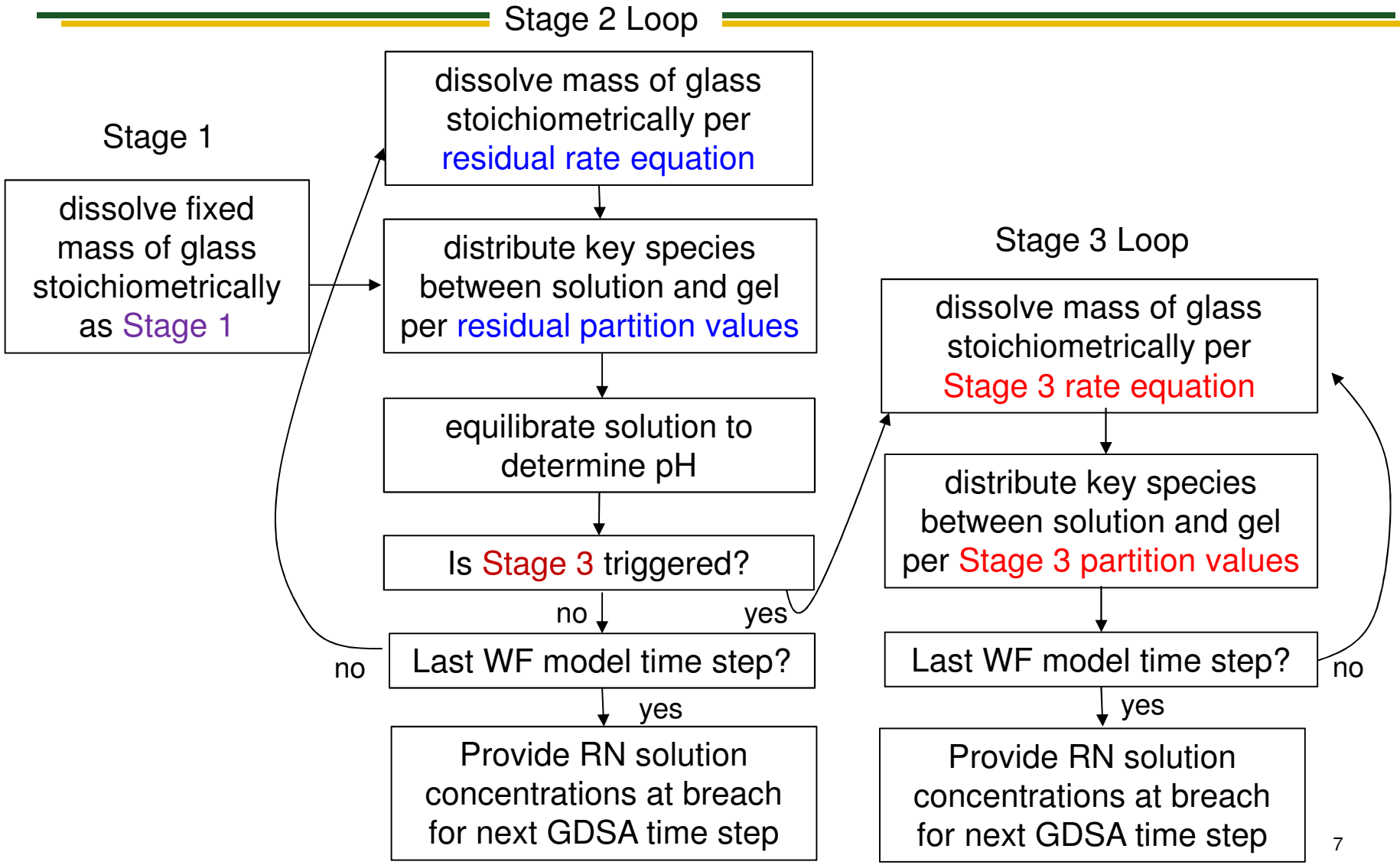
Proposed Flow Diagram of Glass Degradation Model Calculations



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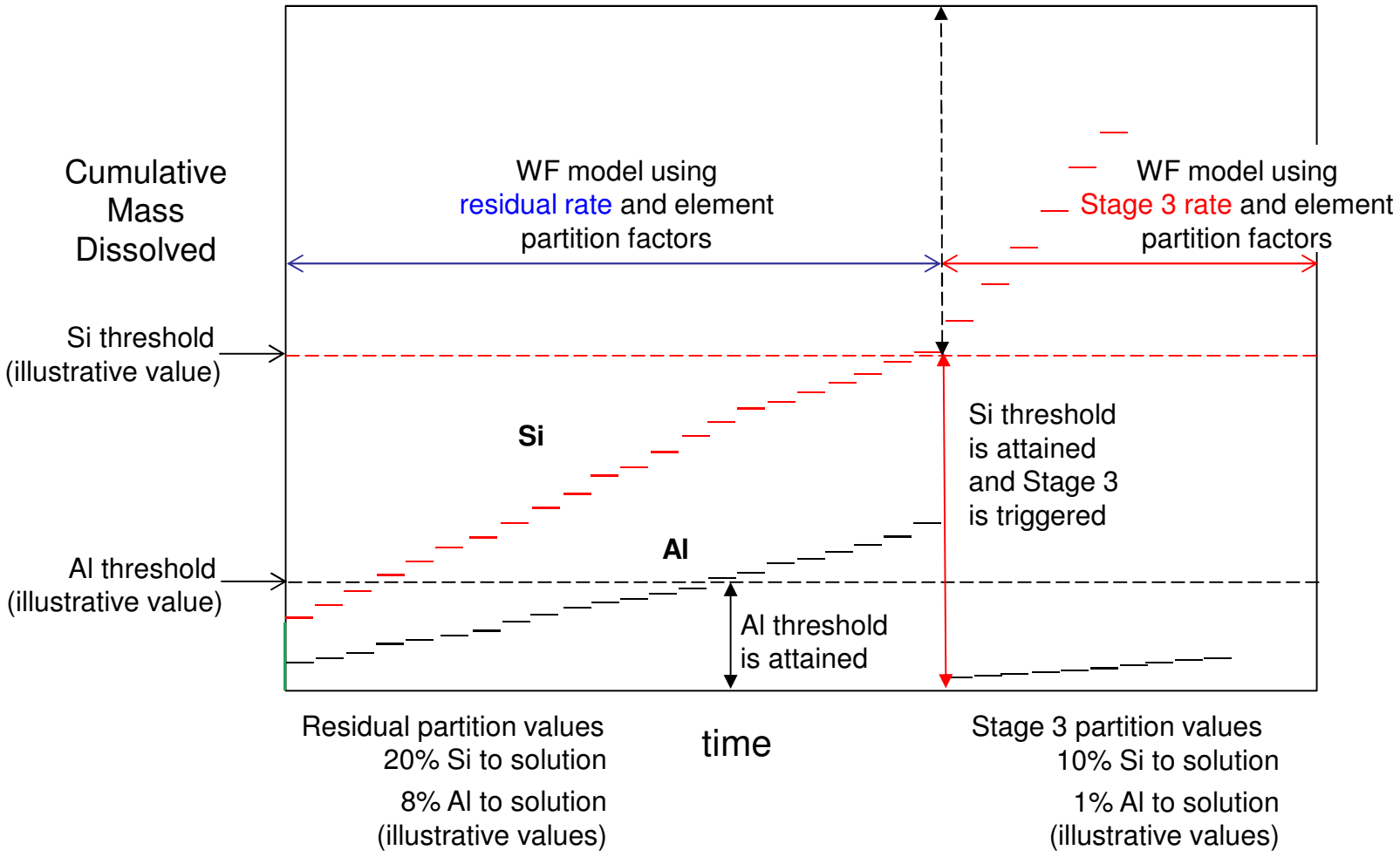
Schematic Illustration of Approach Developed for Modeling Stage 3 Trigger



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Illustrative Rates at 90 ℃ used for Model Implementation Study

Modelled system: Total mass glass = 16,260 kg
Total surface area glass = 175.6 m^2
Free volume in waste package = 6.36 m^3

Dissolve 16,260 kg glass into 6.36 m^3 seepage water at 90 ℃ (2.557 kg/L).
Neglect seepage water flow and loss of mass as glass dissolves for initial analyses.

Use time-steps of 10, 100, and 1000 years.

Stage 1 instantaneous release = 0.03 g glass L^{-1}

Residual rate at 90 ℃ = 0.012 g L^{-1} y^{-1}

Stage 3 rate at 90 ℃ = 0.73 g L^{-1} y^{-1}

Compare solution composition to Stage 3 trigger values:

$Al(OH)_4^-$ = 4E-5 M
$NaHSiO_3$ + $HSiO_3^-$ = 3E-3 or 8E-3 M
pH = calculated; separate pH or Na thresholds were not used

Objective is to develop method for implementing glass degradation model in GDSA
Rates and partition values are illustrative and represent Modified PCT conditions

Ebert and Jerden (2016).

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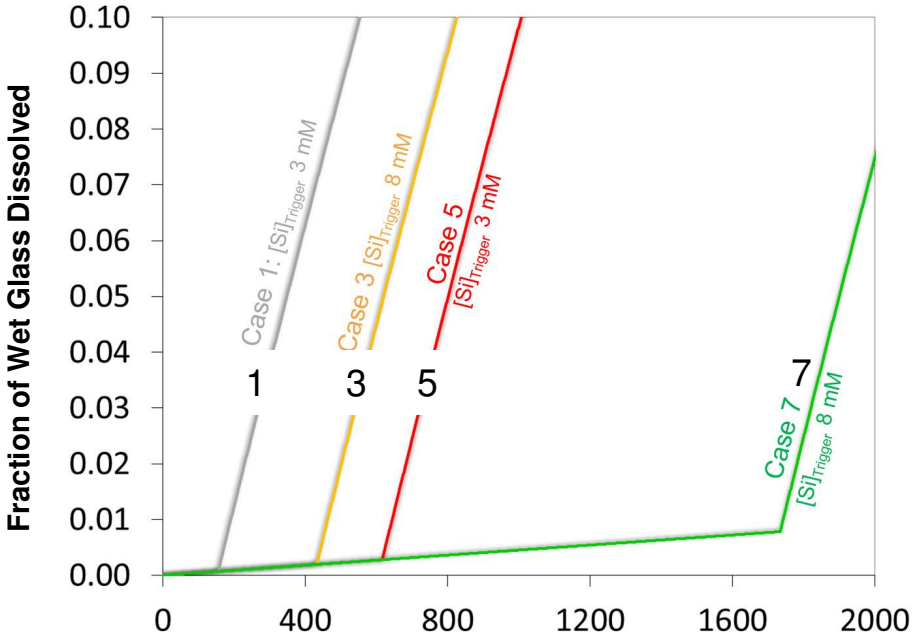
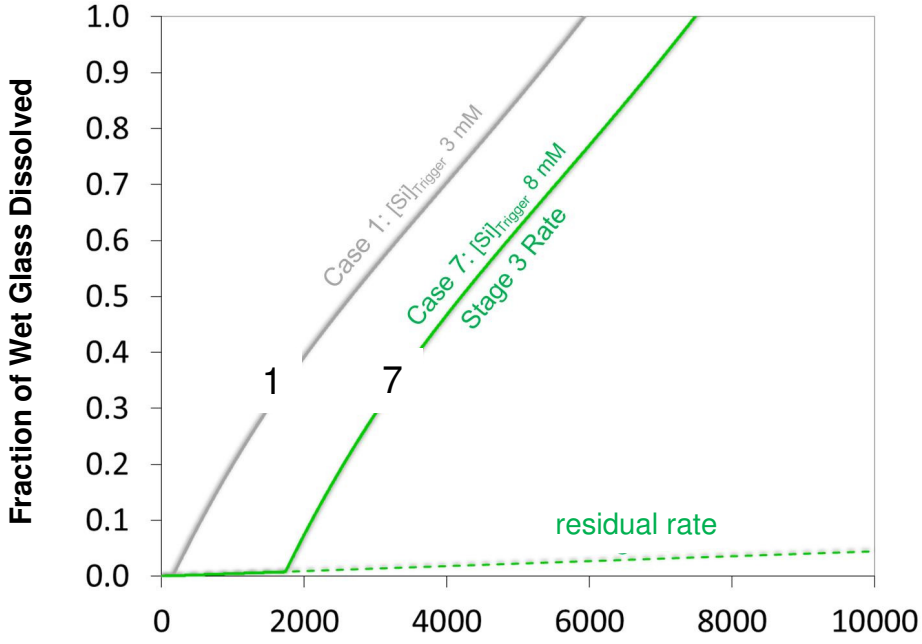
Relative Effects of Residual Partition Fractions and [Al] and [Si] Thresholds on Degradation



10-y time step



100-y time step

Illustrative values

	residual rate partition fraction			threshold concentration, M	
Case	**Si to gel**	**Al to gel**	**Na to gel**	**Si**	**Al**
1	0.80	0.89	0.10	3E-3	4E-5
3	0.80	0.89	0.10	8E-3	4E-5
5	0.95	0.99	0.40	3E-3	4E-5
7	0.95	0.99	0.40	8E-3	4E-5

Ebert and Jerden (2016).

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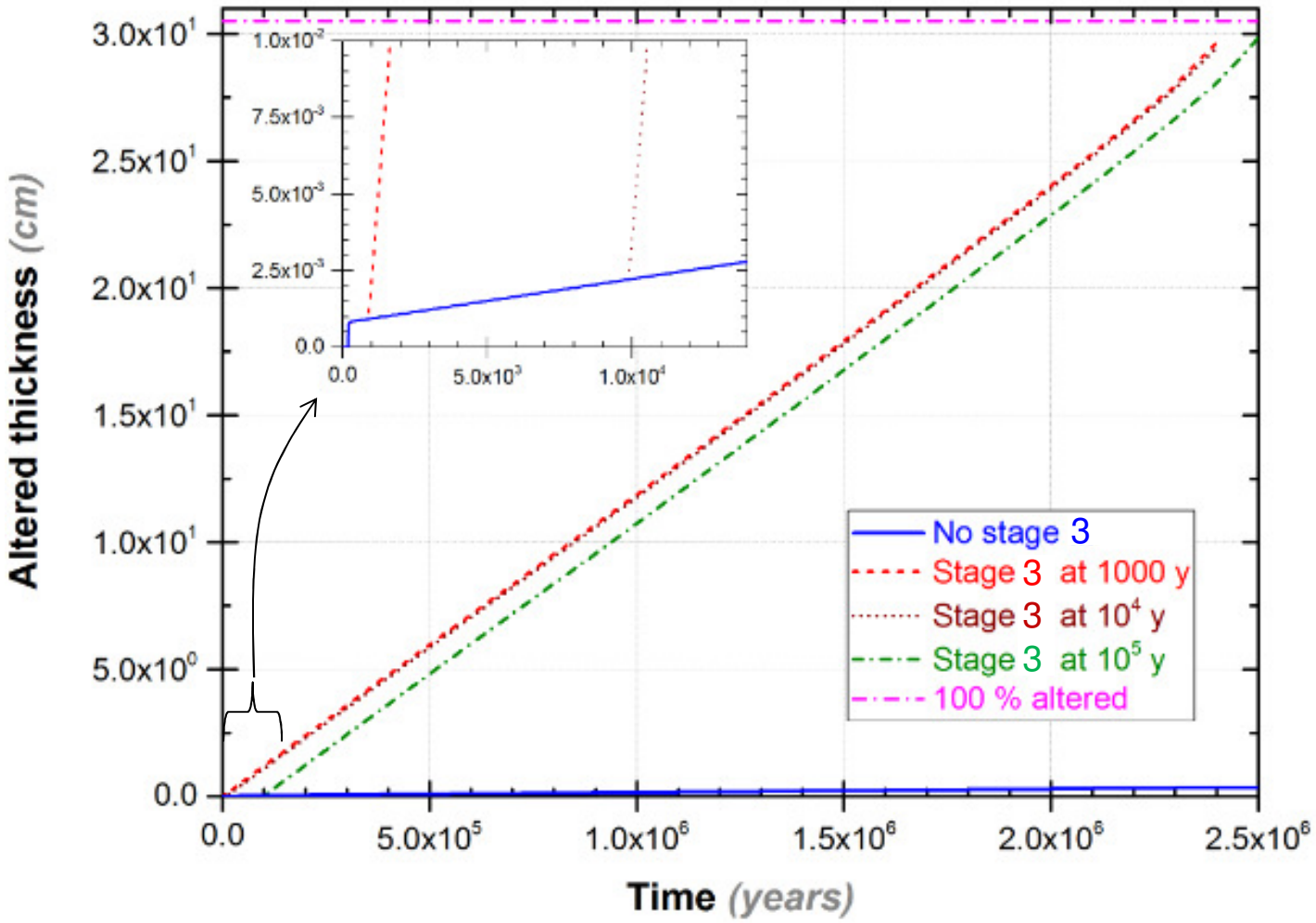
Model Calculations at 40 ℃ with Imposed Stage 3 Trigger Points



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Conclusions

- **Glass model can be implemented in GDSA PFLOTRAN system model**
- **Glass model results replicate experimental observations (qualitatively)**
- **Both the partitioning of elements into solution and gel and the threshold values for triggering Stage 3 rate have a significant effect on calculated extent of glass degradation**
- **Experimental work in progress to**
  - measure pH and temperature dependencies of residual and Stage 3 rates
  - identify key species affecting Stage 3 trigger
  - determine appropriate threshold concentrations for key species
  - determine appropriate partition fractions for key species

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Summary Response to Board Questions

- How is DOE integrating process-level models of HLW glass corrosion and radionuclide release into generic repository performance assessments?

Glass degradation model for GDSA is being developed for direct implementation as a nested sub-model that would be fully coupled into PFLOTRAN representation of the glass source term. The glass degradation model used in GDSA could have time steps shorter than the GDSA time step as needed for fidelity to the degradation process and GDSA would track the appropriate system components. Developing improved model based on scientific understanding.

References

- Ebert, W.L., and Jerden, J.L. Jr. (2016). Implementation of the ANL Stage 3 Glass Dissolution Model. DOE NE report FCRD-MRWFD-2016-000296.
- Rieke, P.C. and Kerisit, S.N. (2015). Modeling Tool Enhancement. DOE NE report FCRD-MRWFD-2015-000252.

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Acknowledgements

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