DOE High-Level Waste Glass Corrosion Model and Its Implementation in Safety Analysis

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

NWTRB Questions

i. What are the recent improvements in DOE models for HLW glass corrosion? How are these improvements helpful to the DOE HLW geologic disposal program?

ii. How do the models take account of the important glass corrosion mechanisms and the range of environmental conditions expected for different repository host-rock types and near-field environments? How are environmental conditions such as dissolved organic matter and the presence of microbial life being investigated?

iii. How do the models take account of the wide range in DOE HLW glass compositions to be produced at the Waste Treatment and Immobilization Plant and the Defense Waste Processing Facility?

iv. How are the models and model parameters supported by experimental data, including the large database of glass dissolution experiments managed by DOE personnel?

v. What is DOE’s technical basis for using the results of short-term, small-scale tests on glass corrosion to support assessments of long-term glass performance in a repository?

vi. How are the process-level models of glass corrosion and radionuclide release integrated into repository performance assessments? How important is glass performance to the overall safety case for different repository designs?

NWTRB questions addressed

i. What are the recent improvements in DOE models for HLW glass corrosion? How are these improvements helpful to the DOE HLW geologic disposal program?

ii. How do the models take account of the important glass corrosion mechanisms and the range of environmental conditions expected for different repository host-rock types and near-field environments? How are environmental conditions such as dissolved organic matter and the presence of microbial life being investigated?

iii. How do the models take account of the wide range in DOE HLW glass compositions to be produced at the Waste Treatment and Immobilization Plant and the Defense Waste Processing Facility?

iv. How are the models and model parameters supported by experimental data, including the large database of glass dissolution experiments managed by DOE personnel?

v. What is DOE’s technical basis for using the results of short-term, small-scale tests on glass corrosion to support assessments of long-term glass performance in a repository?

vi. How are the process-level models of glass corrosion and radionuclide release integrated into repository performance assessments? How important is glass performance to the overall safety case for different repository designs?

Development of DOE Glass Degradation Model

- Developed using well-established mechanistically-based rate expression for borosilicate glass dissolution to limit radionuclide release.
  - Based on mineral dissolution kinetics (e.g., Lasaga 1983, Aagaard and Helgeson 1982)
  - Modified for application to borosilicate waste glasses (e.g., Grambow 1985)
- Dependencies of kinetic terms on glass composition, pH, and temperature were derived from short-term test data and confirmed by comparisons with literature data. Thermodynamic terms were based on long-term test data, but with limited mechanistic understanding of Stage 3.
- Current model represents dependencies on solution composition probabilistically by using bounding values extracted from tests representing extreme environmental conditions. Probability distribution represents uncertainty in whether Stage 3 behavior will occur.
- Model being developed represents effects of secondary phase nucleation and growth on glass dissolution rate (i.e., Stage 3) deterministically.
  - Based on mineral transformation theory (e.g., Nagy et al. 1991)
- Interfaces between improved model and DOE Generic Disposal System Analysis (GDSA) model are being developed as glass model is being completed.

BACKGROUND: Application to Glass

(based on B. Grambow 1985)

$$rate_G = k_0 \times 10^{\eta \cdot pH} \times \left[\exp\left(\frac{-E_a}{RT} \right) \right] \times \left[1 - \frac{Q}{K} \right] + k_{long}$$

$rate_G$ = glass dissolution rate (mass $area^{-1}$ $time^{-1}$)
η = empirical pH dependence (unitless)
Q = ion activity product (molar)
R = gas constant (kJ mol^{-1} K^{-1})
k_{long} = lower limit glass dissolution rate (mass $area^{-1}$ $time^{-1}$)

k_0 = intrinsic glass dissolution rate (mass $area^{-1}$ $time^{-1}$)
E_a = effective activation energy (kJ mol^{-1})
K = effective glass solubility product (molar)
T = temperature (K)
Q/K = effective saturation index

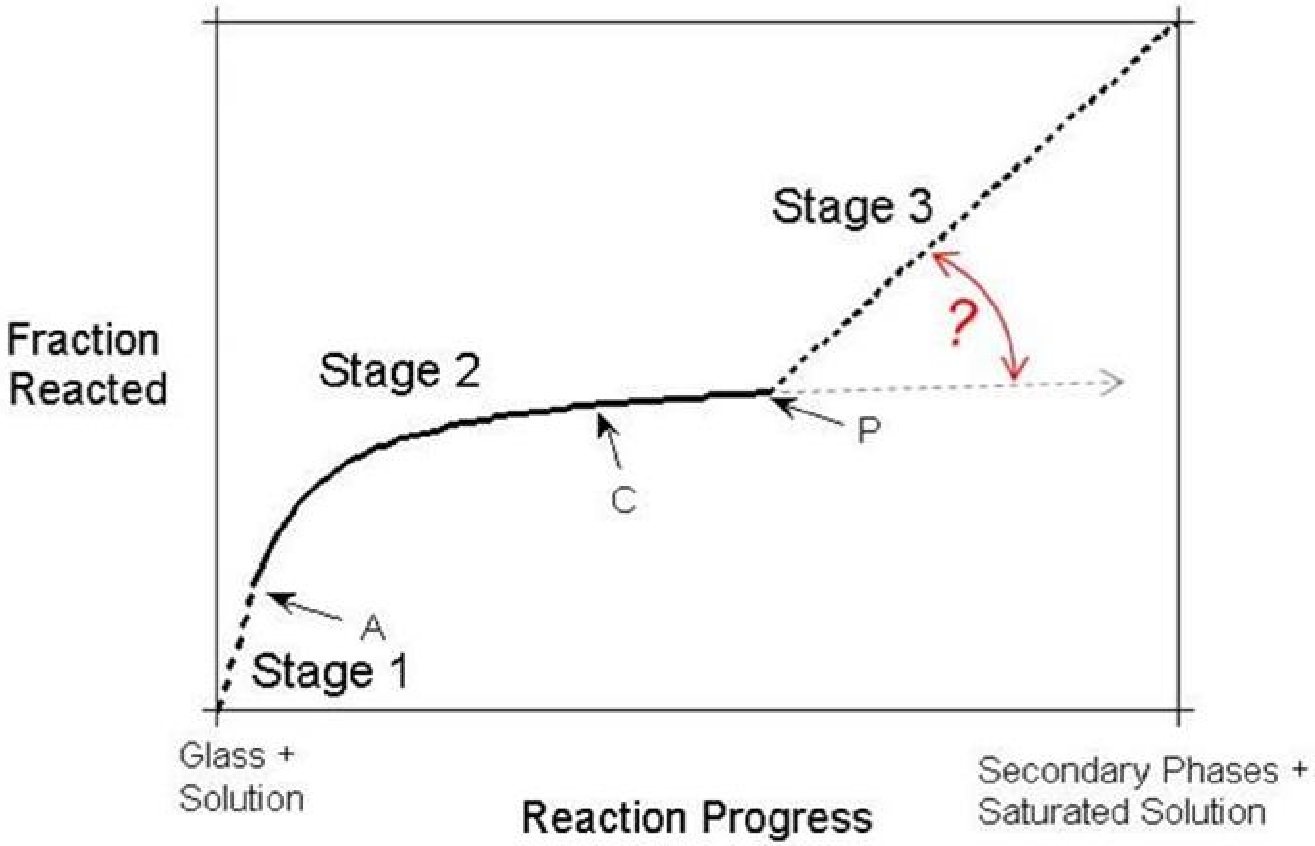
- The rate-limiting step for glass corrosion is hydrolysis of the $-OSi(OH)_3$ end member

$$\equiv Si\text{-}O\text{-}Si(OH)_3 + H_2O \rightarrow \equiv Si\text{-}OH + H_4SiO_4$$

- The saturation index used to quantify the reaction affinity is the ratio of the activity of orthosilicic acid [$Q = a(H_4SiO_4)$] and the stability constant for the above reaction (K).
- The constant term k_{long} was included in the rate expression to prevent the calculated rate from becoming zero if the value of Q became equal to (or greater than) K in simulations over long durations.

Reaction Progress Plot

$$rate_G = k_0 \times 10^{\eta \cdot pH} \times \left[\exp\left(\frac{-E_a}{RT} \right) \right] \times \left[1 - \frac{Q}{K} \right] + k_{long}$$

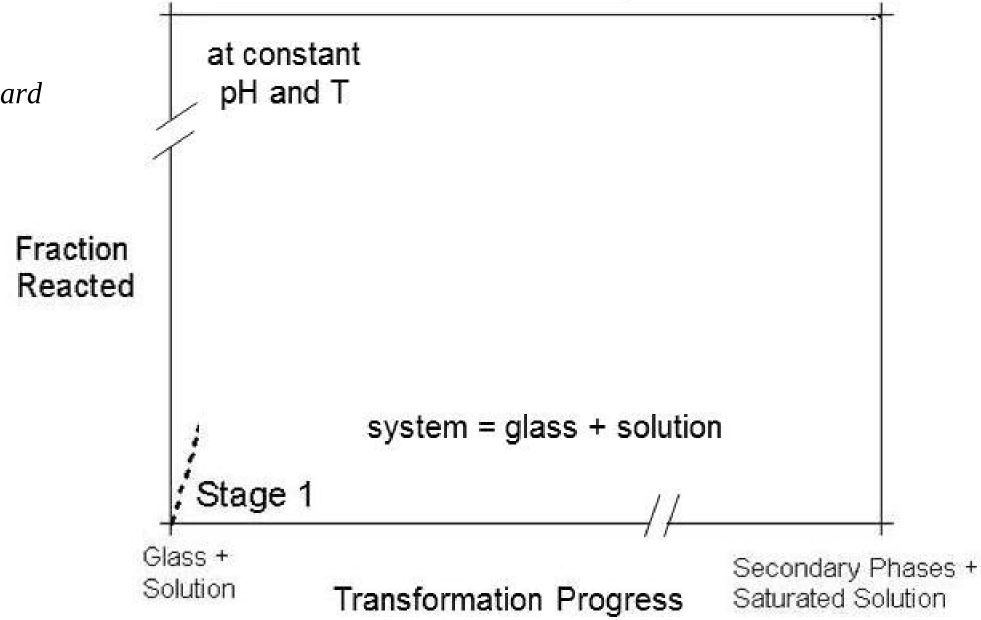


Relate Experimental Observations to Reaction Affinity Term: Stage 1

$$rate_G = \underbrace{k_0 \times 10^{\eta \cdot pH} \times \left[\exp\left(\frac{-E_a}{RT}\right)\right]}_{\text{kinetic rate coefficient}} \times \underbrace{\left[1-\frac{Q}{K}\right]_{\approx 1}}_{\text{reaction affinity}} + k_{long}$$

- Stage 1 rate is a rapid initial transient with no thermodynamic attenuation: system is as far from equilibrium as possible (affinity ≈ 1). Provides overall bounding forward rate $k_{forward}^{dis}$

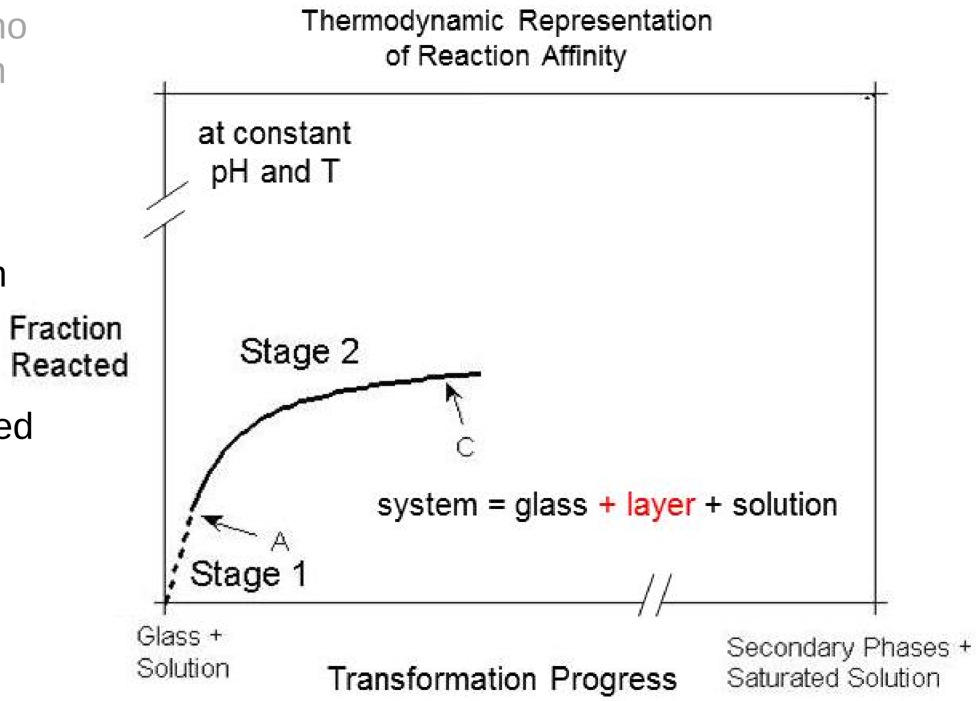
Thermodynamic Representation of Reaction Affinity



Relate Experimental Observations to Reaction Affinity Term: Stage 2

$$rate_G = \underbrace{k_0\times 10^{\eta\cdot pH}\times\left[\exp\left(\frac{-E_a}{RT}\right)\right]}_{\text{rate coefficient}}\times\underbrace{\left[1-\frac{Q}{K}\right]_{\to 0}}_{\text{reaction affinity}}+k_{long}$$

- Stage 1 rate (➝A) is a rapid initial transient with no thermodynamic attenuation: system is as far from equilibrium as possible (affinity ≈ 1). Provides overall bounding upper rate.
- Stage 2 rate (A➝C) slows due to solution feed-back constraints: system approaching equilibrium (affinity ➝ 0). Lower bound to rate = **k_{long}**.
- Mass transport through layer impacts time required for transformation to progress.

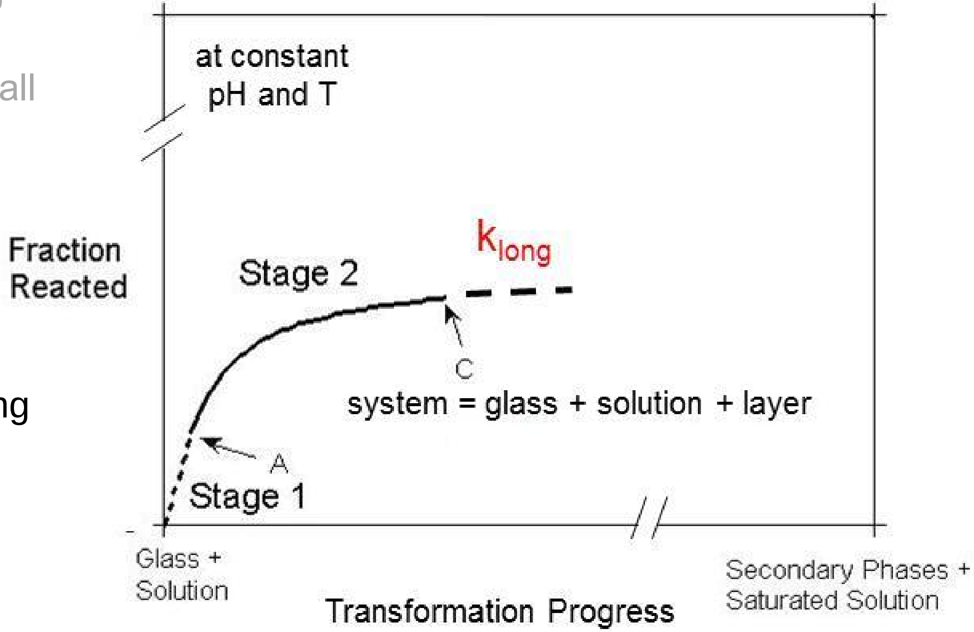

Thermodynamic Representation of Reaction Affinity

Relate Experimental Observations to Reaction Affinity Term: Residual Rate

$$rate_G = \underbrace{k_0 \times 10^{\eta \cdot pH} \times \left[\exp\left(\frac{-E_a}{RT}\right)\right]}_{\text{rate coefficient}} \times \underbrace{\left[1 - \frac{Q}{K}\right]}_{\text{reaction affinity}} + \underset{\approx 0}{k_{long}}$$

- Stage 1 rate (→A) is a rapid initial transient with no thermodynamic attenuation: system is as far from equilibrium as possible (affinity ≈ 1). Provides overall bounding upper rate.
- Stage 2 rate (A→C) slows due to solution feed-back constraints: system approaching equilibrium (affinity → 0).
- Nearly constant residual rate (k_{long}) observed very near to equilibrium (affinity near 0) persisted for long test durations. Controlling process is uncertain.

Thermodynamic Representation of Reaction Affinity



Relate Experimental Observations to Reaction Affinity Term: Stage 3

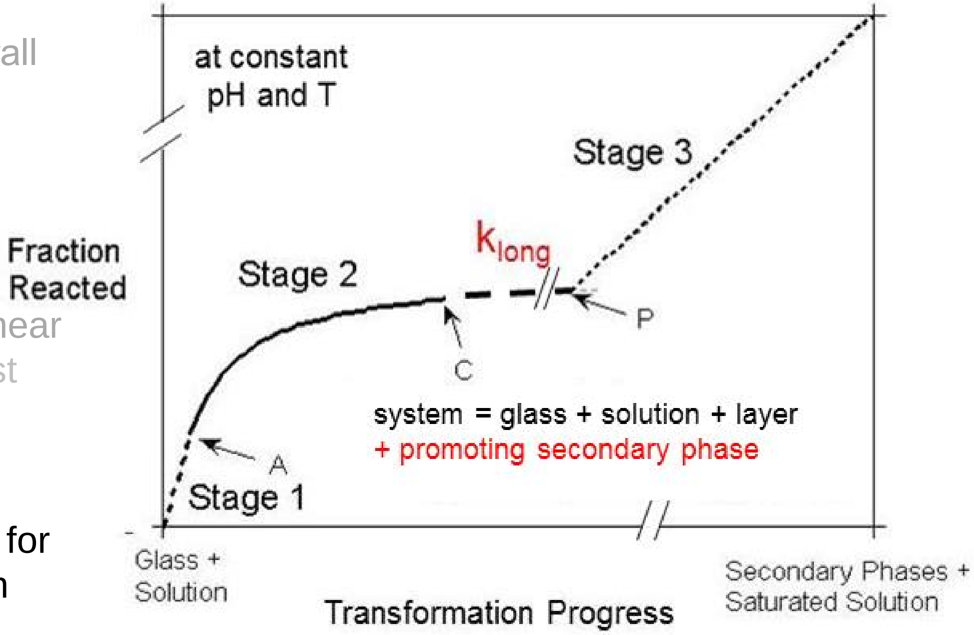
$$rate_G = \underbrace{k_0 \times 10^{\eta \cdot pH} \times \left[\exp\left(\frac{-E_a}{RT} \right) \right]}_{\text{rate coefficient}} \times \underbrace{\left[1 \overset{?}{-} \frac{Q}{K} \right]}_{\text{reaction affinity}} + k_{long}$$

Form of affinity term changes

constant > 0

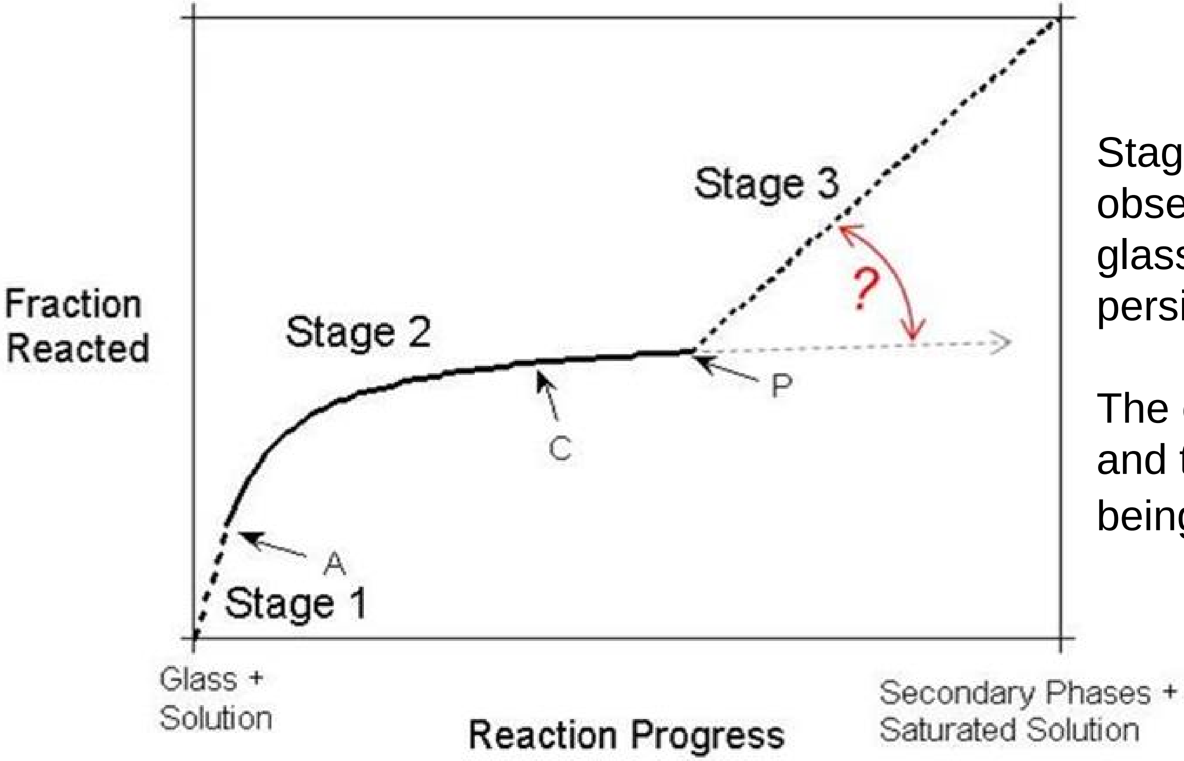
- Stage 1 rate (→A) is a rapid initial transient with no thermodynamic attenuation: system is as far from equilibrium as possible (affinity ≈ 1). Provides overall bounding upper rate.
- Stage 2 rate (A→C) slows due to solution feed-back constraints: system approaching equilibrium (affinity → 0).
- Nearly constant residual rate (***k**$_{long}$*) attained very near to equilibrium (affinity near 0) persisted for long test durations.
- Higher Stage 3 rate triggered (at P) if secondary phases form that establish a new equilibrium state for system (reaction affinity for new system > reaction affinity for original system at residual rate). Test results indicate affinity term is constant in Stage 3.

Thermodynamic Representation of Reaction Affinity



Reaction Progress Plot

$$rate_G = k_0 \times 10^{\eta \cdot pH} \times \left[\exp\left(\frac{-E_a}{RT} \right) \right] \times \left[1 - \frac{Q}{K} \right] + k_{long}$$



Stage 3 behavior has not been observed in tests with all waste glasses, for which the low rate persists.

The conditions triggering Stage 3 and the form of affinity term are being identified and quantified.

NWTRB questions addressed

i. What are the recent improvements in DOE models for HLW glass corrosion? How are these improvements helpful to the DOE HLW geologic disposal program?

ii. How do the models take account of the important glass corrosion mechanisms and the range of environmental conditions expected for different repository host-rock types and near-field environments? How are environmental conditions such as dissolved organic matter and the presence of microbial life being investigated?

iii. How do the models take account of the wide range in DOE HLW glass compositions to be produced at the Waste Treatment and Immobilization Plant and the Defense Waste Processing Facility?

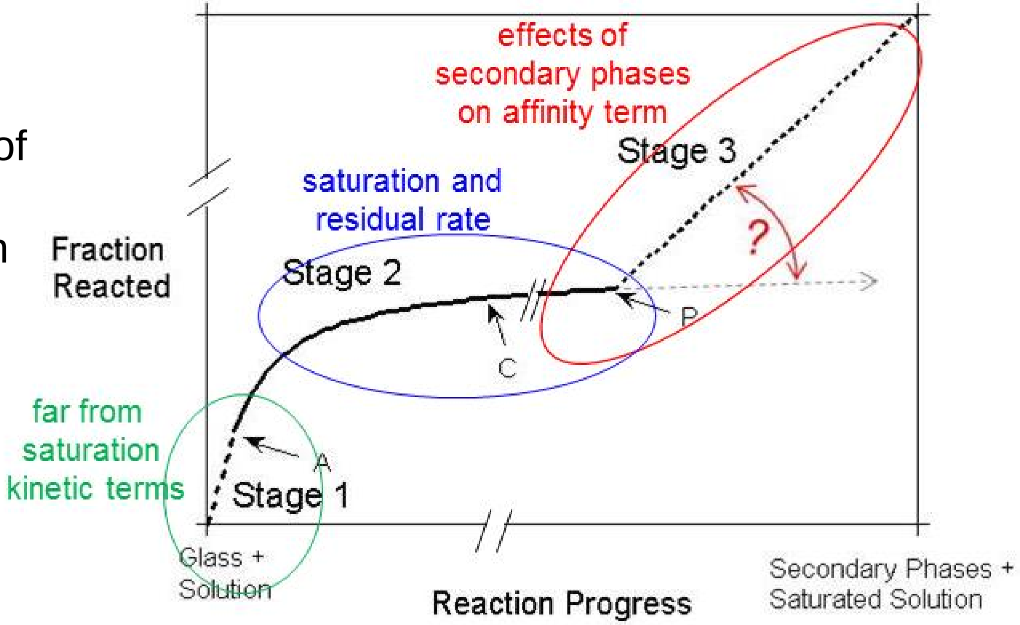
iv. How are the models and model parameters supported by experimental data, including the large database of glass dissolution experiments managed by DOE personnel?

v. What is DOE’s technical basis for using the results of short-term, small-scale tests on glass corrosion to support assessments of long-term glass performance in a repository?

vi. How are the process-level models of glass corrosion and radionuclide release integrated into repository performance assessments? How important is glass performance to the overall safety case for different repository designs?

Parameterizing Rate Equation

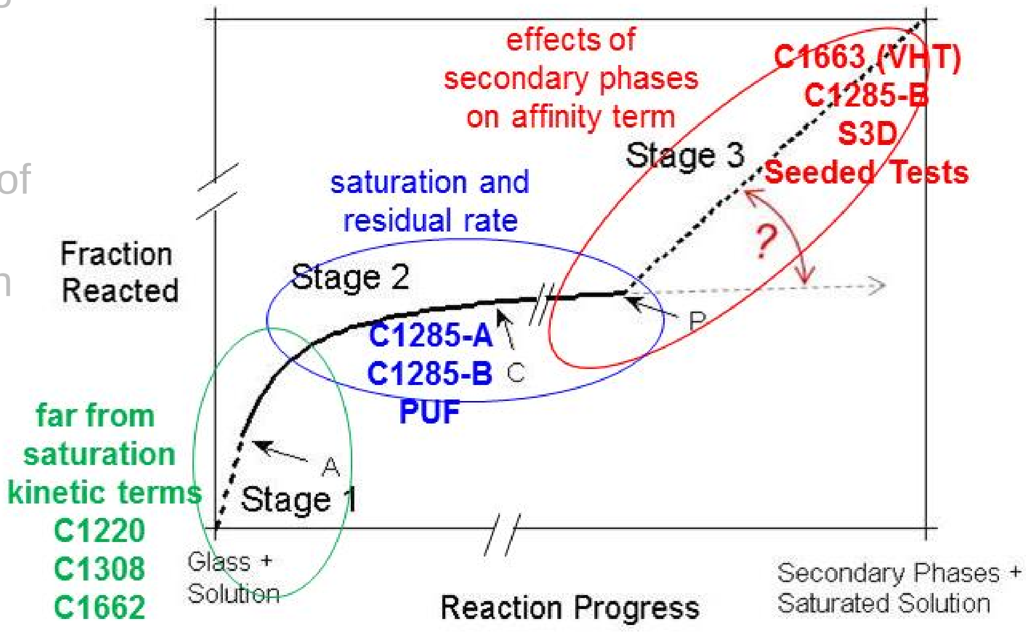
- Different test methods are used to highlight different aspects of corrosion behavior.
- Different test conditions are used to generate fluids having different degrees of saturation that result in different reaction affinities and different extents of reaction progress within laboratory time-frame.



Solution-mediated transformation of glass to thermodynamically stable secondary phases

Different Test Methods Used to Highlight Different Stages of Glass Degradation

- Different test methods are used to highlight different aspects of corrosion behavior.
- Different test conditions are used to generate fluids having different degrees of saturation that result in different reaction affinities and different extents of reaction progress within laboratory time-frame.
  - Different glass surface area-to-solution volume (S/V) ratios are used to achieve solution concentrations that maintain far from saturation conditions or accelerate reaction progress to approach saturation.
  - Static, dynamic, or various semi-dynamic conditions are used to control solution evolution, evaluate mass transport, etc.
  - Leachant compositions are used to impose various pH, high dissolved silica or aluminum concentrations, etc.
  - Elevated temperatures used to accelerate process rates and reaction progress.
  - Mineral seeds are added to eliminate nucleation delays to Stage 3 trigger.
  - etc.



Solution-mediated transformation of glass to thermodynamically stable secondary phases

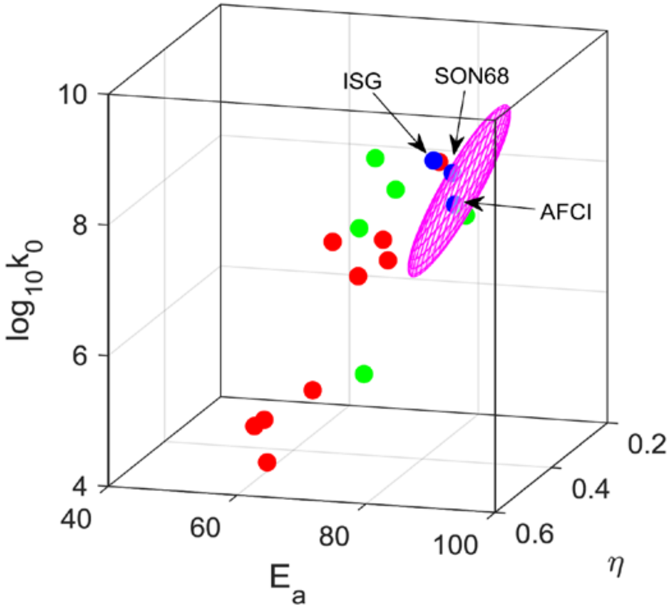
Use Far from Saturation Conditions to Quantify Dependence of Rate on pH and Temperature

$$rate_G = k_0 \times 10^{\eta \cdot pH} \times \left[\exp\left(\frac{-E_a}{RT} \right) \right] \times \left[1 - \frac{Q}{K} \right] + k_{long}$$

- Determined representative values for rate constant (k_o), temperature (E_a), and pH (η) dependence parameters
  - Used data from short-term ASTM C1220 or ASTM C1662 tests in which value of (1-Q/K) remains near 1 and k_{long} is negligible, so that

$$rate_G = k_0 \times 10^{\eta \cdot pH} \times \left[\exp\left(\frac{-E_a}{RT} \right) \right]$$

  - Conducted series of tests at constant pH and temperature (and constant k_0)
  - Extracted parameter values of k_0, η, and E_a based on boron release rate
  - Dependencies extracted for different glasses showed small variance in values



Neeway et al. (2017)

NWTRB questions addressed

i. What are the recent improvements in DOE models for HLW glass corrosion? How are these improvements helpful to the DOE HLW geologic disposal program?

ii. How do the models take account of the important glass corrosion mechanisms and the range of environmental conditions expected for different repository host-rock types and near-field environments? How are environmental conditions such as dissolved organic matter and the presence of microbial life being investigated?

iii. How do the models take account of the wide range in DOE HLW glass compositions to be produced at the Waste Treatment and Immobilization Plant and the Defense Waste Processing Facility?

iv. How are the models and model parameters supported by experimental data, including the large database of glass dissolution experiments managed by DOE personnel?

v. What is DOE’s technical basis for using the results of short-term, small-scale tests on glass corrosion to support assessments of long-term glass performance in a repository?

vi. How are the process-level models of glass corrosion and radionuclide release integrated into repository performance assessments? How important is glass performance to the overall safety case for different repository designs?

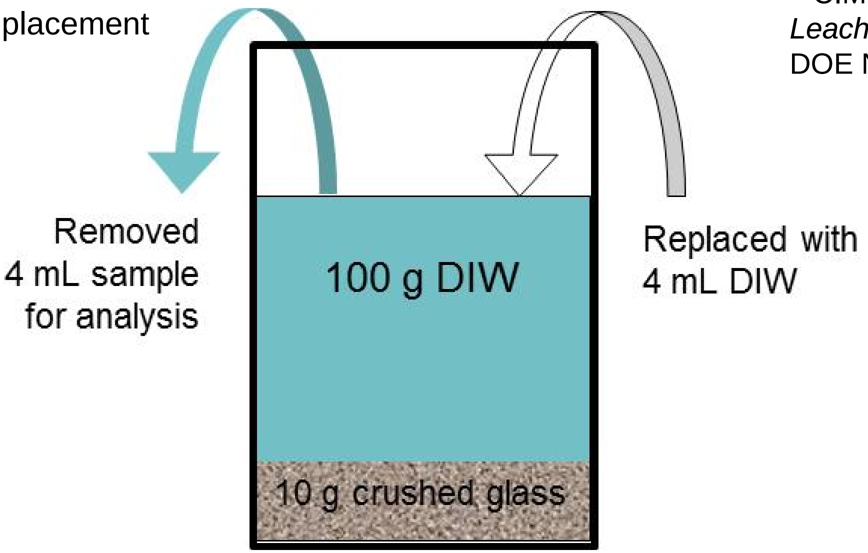
Modified PCT-B: Partial Replacement

Long-term tests were conducted at the Catholic University of America Vitreous State Laboratory (VSL) with 127 surrogate ILAW Glasses* and 10 HLW Glasses**

-100 +200 mesh crushed glass
10 g glass/100 g demineralized water
steel reaction vessel
90 °C
partial solution replacement
7 d through 19 y

*Papathanassiu et al. (2011). *ILAW Glass Testing for Disposal at IDF: Phase 1 Testing*. VSL-11R2270-1, Rev. A.

**C.M. Jantzen et al. (2013). *SRNL Modeling Accelerated Leach Testing of Glass (ALTGLASS)*.
DOE NE report FCRD-SWF-2013-000339



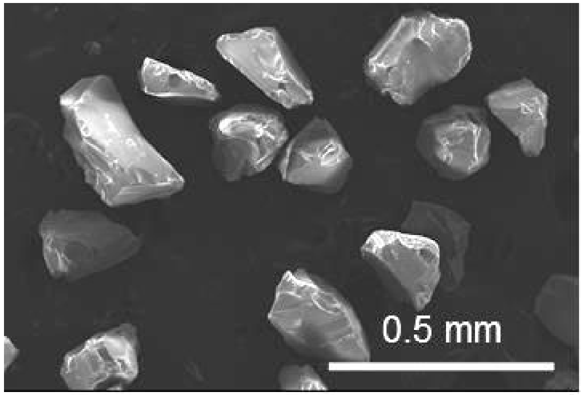
Removed
4 mL sample
for analysis

100 g DIW

10 g crushed glass

Replaced with
4 mL DIW

ALTGLASS database also includes results of standard PCT-B tests.

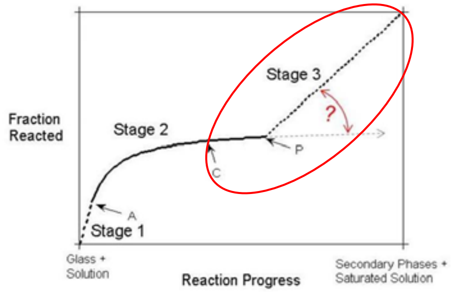


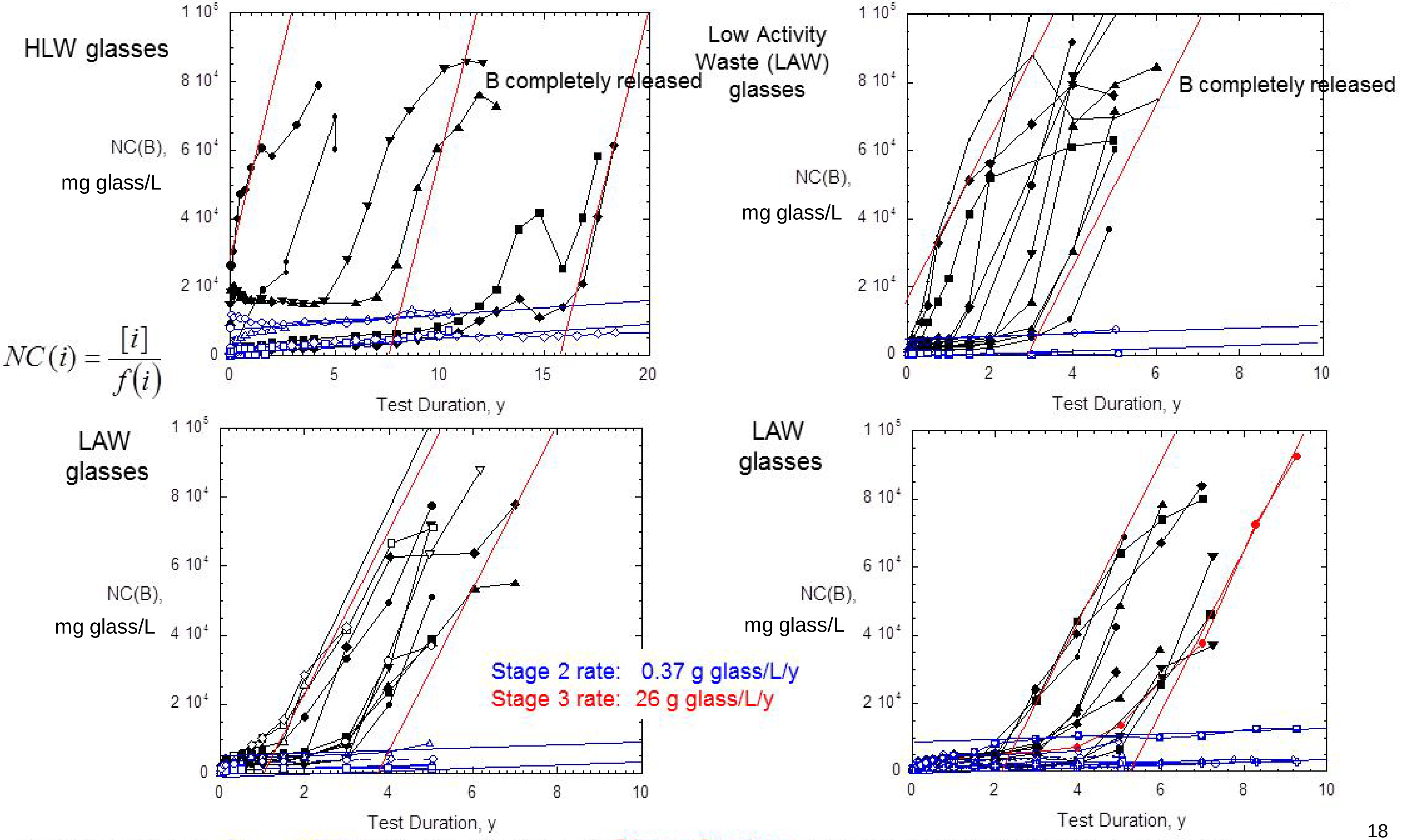
SEM image of crushed glass

$$rate_G = k_0 \times 10^{\eta \cdot pH} \times \left[\exp\left(\frac{-E_a}{RT} \right) \right] \boxed{\times \left[1 - \frac{Q}{K} \right]} + k_{long}$$

and Stage 3 rate

Long-term Modified PCT-B (primarily VSL data in ALTGLASS)





$$NC(i) = \frac{[i]}{f(i)}$$

Stage 2 rate: 0.37 g glass/L/y

Stage 3 rate: 26 g glass/L/y

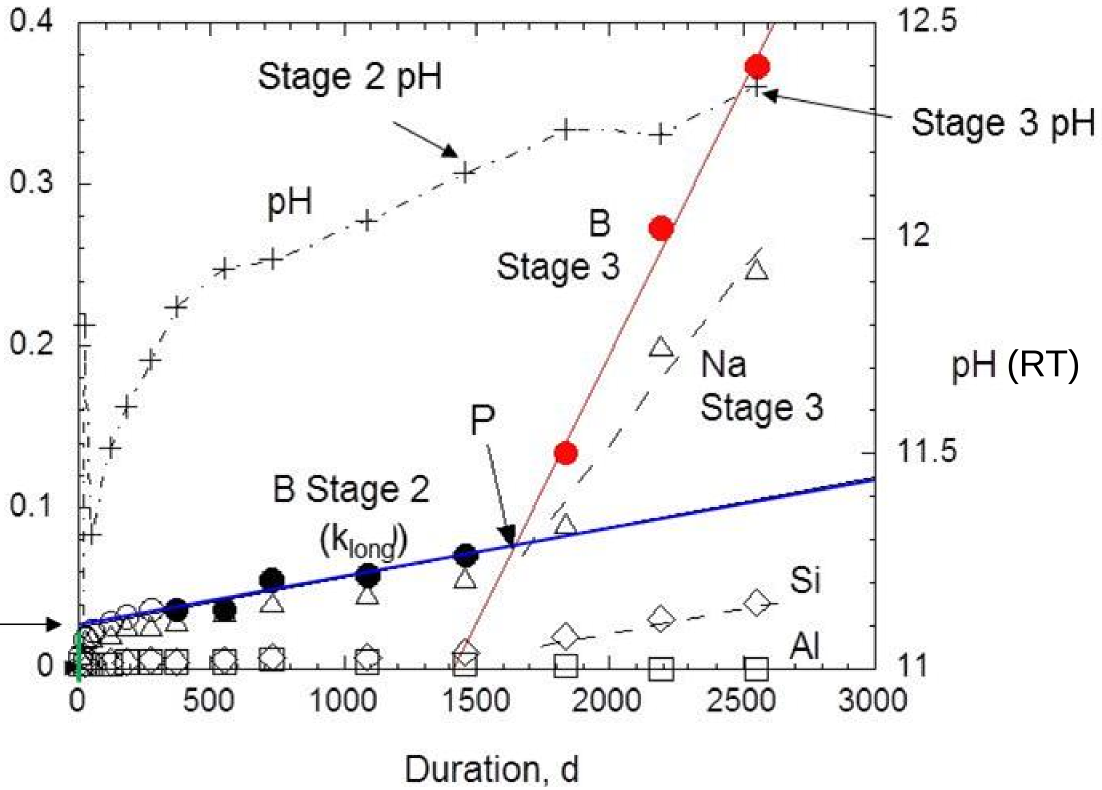
Blue lines show k_{long} rates and red lines show Stage 3 rates are about the same for all glasses.

Extracting Rates from PCT-B Results

Modified PCT
LAW glass LAWA88
demineralized water
~2000 m^{-1}
90 °C
(VSL)

fractional mass loss

$$\frac{\text{mass } i \text{ in solution}}{\text{initial mass } i \text{ in glass}}$$

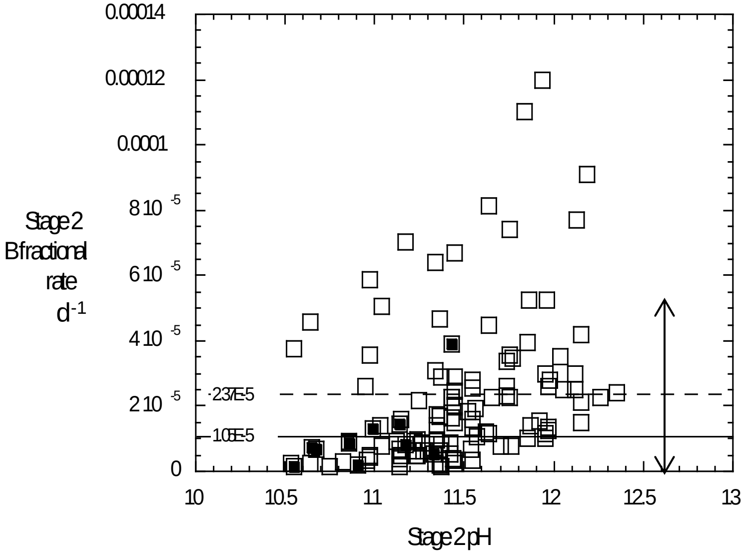


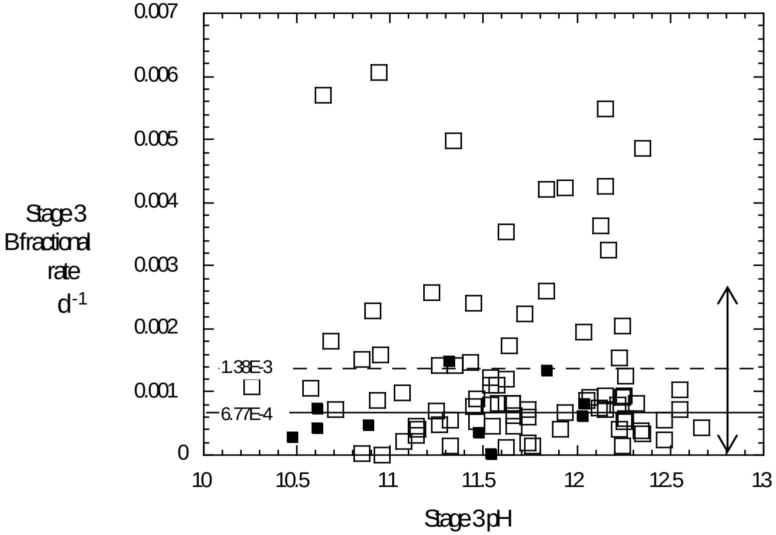
y-intercept of Stage 2 fit used to define mass glass dissolved prior to residual rate

Increases in B, Na, and Si releases beyond Time P are attributed to the generation of secondary phases at that increase affinity for glass dissolution.

Ebert and Jerden 2016

No Correlation Between Stage 1, 2, or 3 Rates and pH Values





Average Stage 2 fractional rate = 2.3 x 10^{-5} d^{-1}

Average Stage 3 fractional rate = 1.3 x 10^{-3} d^{-1}

127 LAW glasses open symbols, dashed
16 HLW glasses filled symbols, solid

arrows show 1 standard deviation for LAW.

- Laboratory tests show wide range of glass compositions reacted under the same conditions gives similar Stage 2 residual rates and similar Stage 3 rates.
- No correlation of Stage 3 trigger with glass composition or solution pH attained in test.
- Major effect of glass composition is if and when Stage 3 is triggered.

What Triggers Stage 3?

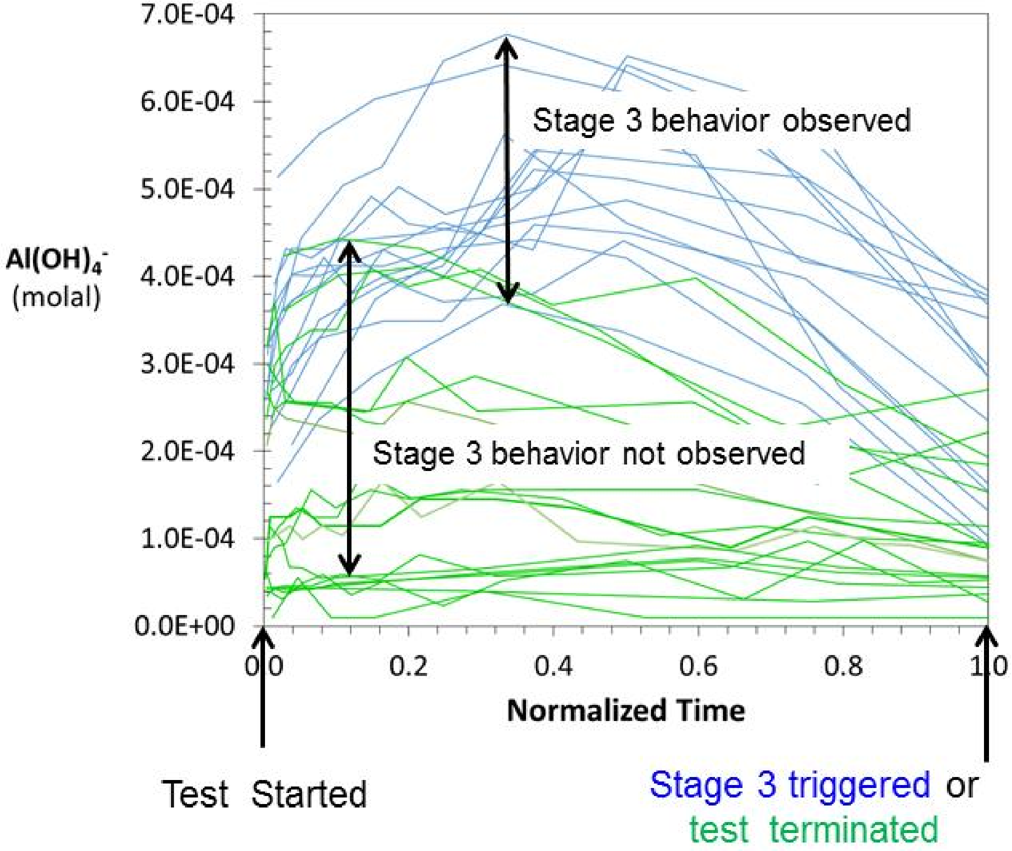
Stage 3 was triggered in tests with ~80% of the glasses, but no correlation of when it was triggered with glass composition was found.

Geochemist's Workbench used to calculate pH and speciation of solution compositions for tests in ALTGLASS database in which Stage 3 was triggered and tests in which it was not.

This shows a decreasing Al concentration ***in solution*** preceded the Stage 3 trigger.

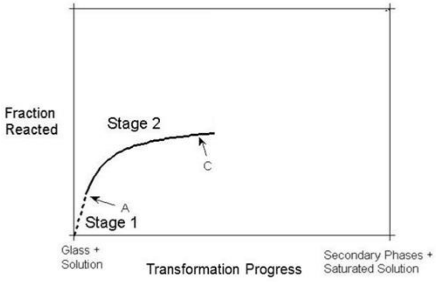
It appears that a threshold Al concentration must be attained *and then Al removed from solution* before Stage 3 is triggered.

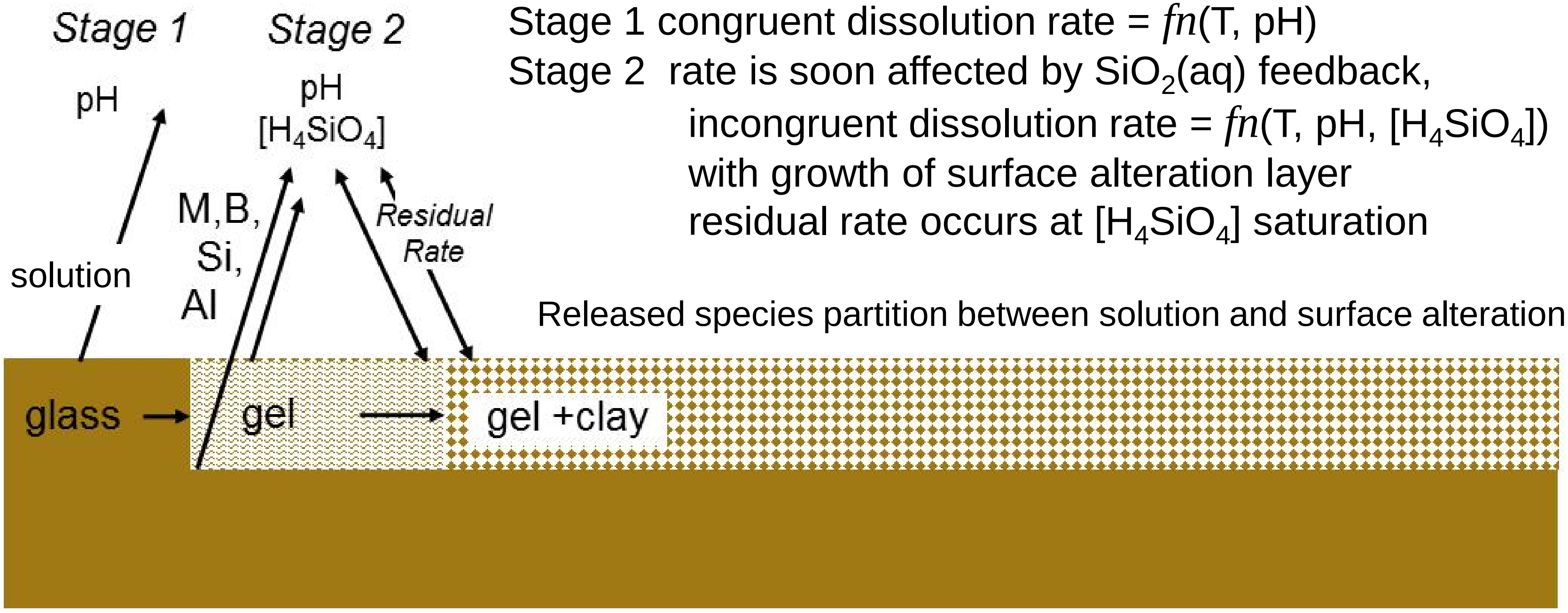
On-going tests are focused on roles of pH and Al and Si concentrations on triggering secondary phase precipitation and Stage 3.



Ebert and Jerden (2016)

Proposed Stage 3 Mechanism Being Evaluated (schematic)





Stage 1 congruent dissolution rate = *fn*(T, pH)
Stage 2 rate is soon affected by SiO_2(aq) feedback,
incongruent dissolution rate = *fn*(T, pH, $[H_4SiO_4]$)
with growth of surface alteration layer
residual rate occurs at $[H_4SiO_4]$ saturation

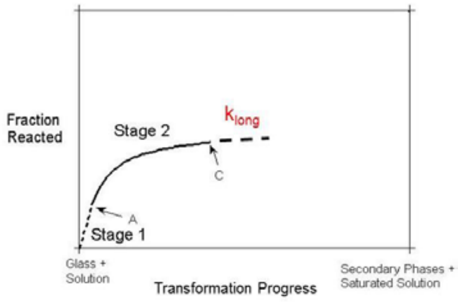
Released species partition between solution and surface alteration layer

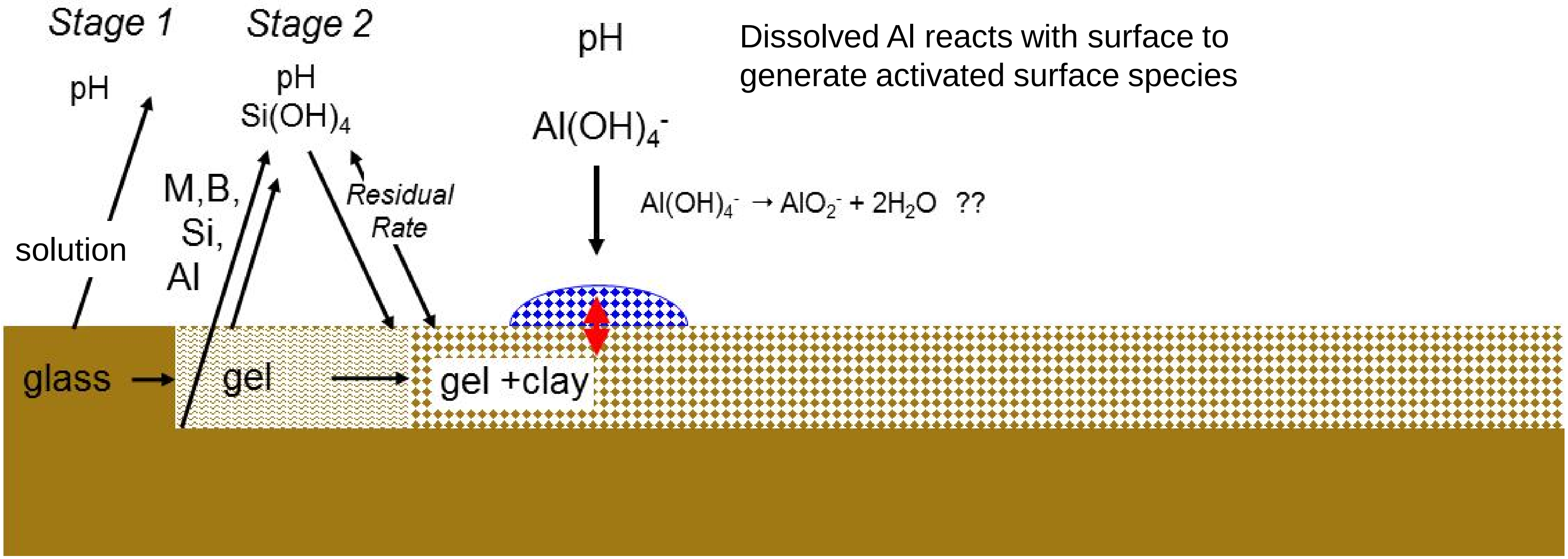
<u>glass/gel/clay</u>
glass and gel dissolution generates saturated solution to nucleate zeolite & precursors

time

M = alkali metal

Stage 3 Trigger Step 1





Dissolved Al reacts with surface to generate activated surface species

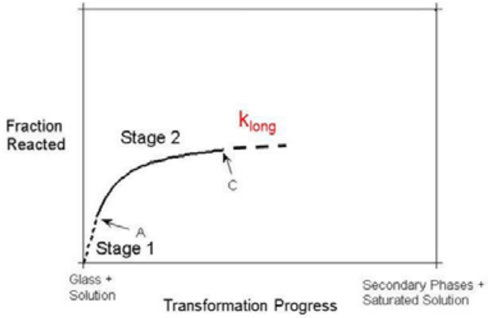
glass/gel/clay
glass & gel dissolution
generate saturated solution to
nucleate zeolite & precursors

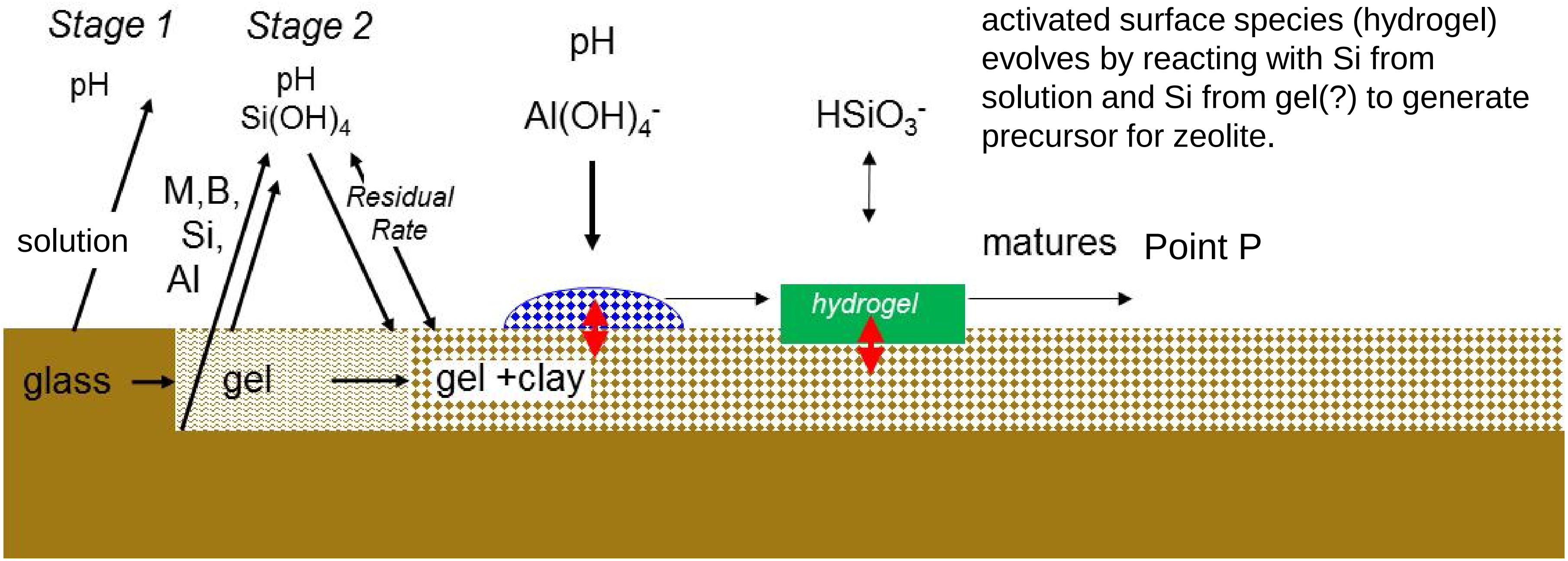
Al-based embryo
AlO_2^- is the origin of the zeolite
framework charge.
OH^- is catalyst/mineralizer

Jantzen et al. (2017)

time

Stage 3 Trigger Step 2





activated surface species (hydrogel) evolves by reacting with Si from solution and Si from gel(?) to generate precursor for zeolite.

glass/gel/clay

Al-based embryo

AlO_2^- is the origin of the zeolite framework charge

OH^- is catalyst/mineralizer

Al+Si-based precursor

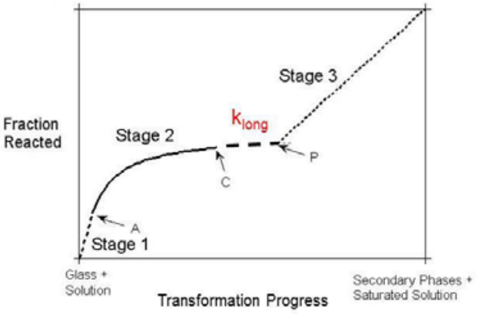
SiO_2 is the primary building unit forming the zeolite framework

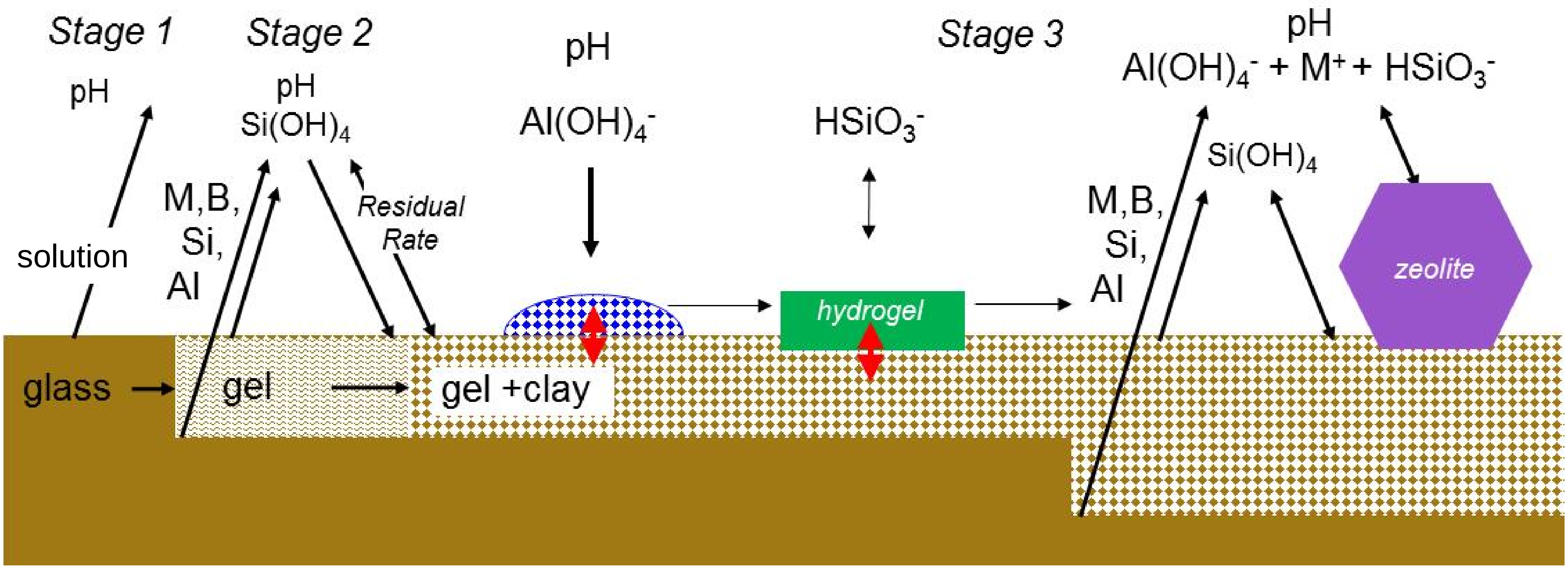
Jantzen et al. (2017)

time

Evolution of glass surface to support formation of either clays or zeolites as simulated using strong base-weak acid model.

If Stage 3 Mechanism Dominates





Al-based embryo | Al+Si-based precursor | $MAlSiO_4$ Secondary Phase

Stage 3 trigger Step 1 | Stage 3 trigger Step 2 | Stage 3 growth and ripening

time

Transfer of Al from glass to secondary phases through solution is probably rate-limiting process. This maintains $Al(OH)_4^-$ at a low steady-state concentration fixed by the glass dissolution rate and secondary phase precipitation rate, but [Si] and [M] continue to increase. This is consistent with experimental observations.

Reaction Affinity Term Representing Effect of Secondary Phase Precipitation

Affinity term for Stage 3 represents coupled kinetics of glass dissolution and secondary phase precipitation in a common solution

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

(for small deviations from equilibrium)

$k^{dis}_{forward}$ = kinetic rate coefficient for glass dissolution *fn* (k_0, pH, T)

$k^{pptn}_{forward}$ = kinetic rate coefficient for secondary phase precipitation *fn* (pH, T, [?])

$\Delta G_{r\,dis}$ = free energy change for glass dissolution reaction

$\Delta G_{r\,pptn}$ = free energy change for secondary phase precipitation reaction

R = gas constant

T = temperature

Ebert, W.L. (2015). Stage 3 Model for Coupled Glass Dissolution and Secondary Phase Precipitation Reactions. DOE NE report FCRD-MRWFD-2015-000763.

Based on:
Nagy, K.L., Blum, A.E., and Lasaga, A.C. (1991). “Dissolution and precipitation kinetics of kaolinite at 90 ºC and pH 3: The dependence on solution saturation state.” *American Journal of Science, 291,* 649-686.
Alekseyev, V.A., Medvedeva, Prisyagina, N.I., Meshalkin, S.S., and Balabin, A.I. (1997). “Change in the dissolution rates of alkali feldspars as a result of secondary mineral precipitation and approach to equilibrium,” Geochimica et Cosmochimica Acta, 61, 1125-1142.

Limiting Cases for Coupled Dissolution and Precipitation Rates

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

(for small deviations from equilibrium)

Helgeson partial equilibrium model: secondary phases precipitate instantaneously and remain in equilibrium with solution (positive feedback):

$$k_{forward}^{pptn} >> k_{forward}^{dis} \qquad \Delta G_{r\ pptn} = 0 \qquad rate_{coupled}^{ss} = k_{forward}^{dis}\left(1 - \exp\left(\frac{\Delta G_{r\ dis}}{RT}\right)\right)$$

Zhu-Blum-Veblen (ZBV) model: secondary phases precipitate slowly and regulate the primary phase (glass) dissolution rate close to equilibrium (negative feedback):

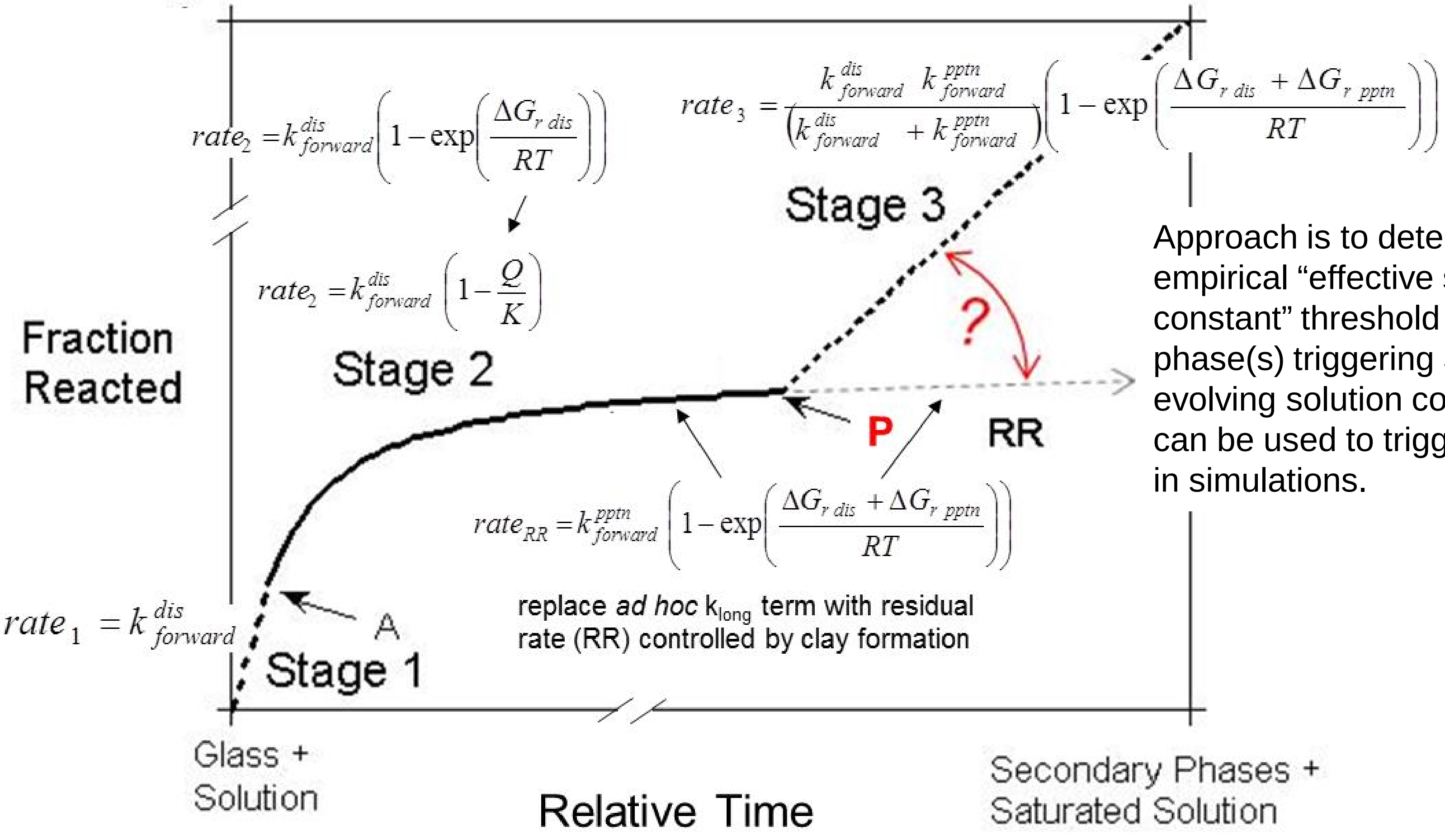
$$k_{forward}^{pptn} << k_{forward}^{dis} \qquad rate_{coupled}^{ss} = k_{forward}^{pptn}\left(1 - \exp\left(\frac{\Delta G_{r\ dis} + \Delta G_{r\ pptn}}{RT}\right)\right)$$

Coupling of free energy terms “arrests” the reaction affinity for the system to maintain a constant rate, which is observed experimentally for residual and Stage 3 rates.

Helgeson, H.C. (1968). “Evaluation of irreversible reactions in geochemical processes involving minerals and aqueous solution—I. Thermodynamic relations.” Geochimica et Cosmochimica Acta 32, 853-877.

Zhu, C., Blum, A.E. and Veblen, D.R.D. (2004) A new hypothesis for the slow feldspar dissolution in groundwater aquifers. Geochimica et Cosmochimica Acta 68, (abstract 2.2.32) A148.

Four Rate Laws Represent Observed Changes in Degradation Behavior



$$rate_1 = k^{dis}_{forward}$$

$$rate_2 = k^{dis}_{forward}\left(1-\exp\left(\frac{\Delta G_{r\ dis}}{RT}\right)\right)$$

$$rate_2 = k^{dis}_{forward}\left(1-\frac{Q}{K}\right)$$

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

$$rate_{RR} = k^{pptn}_{forward}\left(1-\exp\left(\frac{\Delta G_{r\ dis} + \Delta G_{r\ pptn}}{RT}\right)\right)$$

replace *ad hoc* k_{long} term with residual rate (RR) controlled by clay formation

Approach is to determine an empirical “effective solubility constant” threshold to represent phase(s) triggering Stage 3 so evolving solution composition can be used to trigger Stage 3 in simulations.

Parameterizing Stage 3 and Residual Rates

Based on test results in ALTGLASS database, constant Stage 3 rate persists until glass is completely dissolved and changing surface areas of corroding glass and precipitating phases didn’t affect Stage 3 rates.

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

(for small deviations from equilibrium)

Measured Stage 3 rates are essentially constant and reaction affinity for coupled reactions is constant (ZBV model), so value of coupled kinetic term must remain constant while glass remains.

Treat lumped kinetic terms as single term to simplify rate equations and measure empirical dependence of coupled rates on pH, T, and possibly [Al]:

Stage 3 $rate_3 = fn\ (k_0,$ pH, T, [?])

Residual $rate_{RR} = fn\ (k_0,$ pH, T, [?])

NWTRB questions addressed

i. What are the recent improvements in DOE models for HLW glass corrosion? How are these improvements helpful to the DOE HLW geologic disposal program?

ii. How do the models take account of the important glass corrosion mechanisms and the range of environmental conditions expected for different repository host-rock types and near-field environments? How are environmental conditions such as dissolved organic matter and the presence of microbial life being investigated?

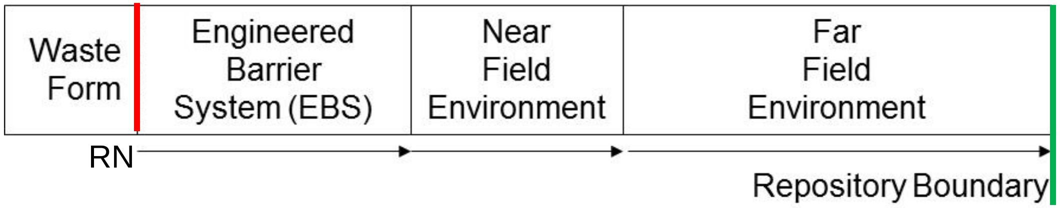
iii. How do the models take account of the wide range in DOE HLW glass compositions to be produced at the Waste Treatment and Immobilization Plant and the Defense Waste Processing Facility?

iv. How are the models and model parameters supported by experimental data, including the large database of glass dissolution experiments managed by DOE personnel?

v. What is DOE's technical basis for using the results of short-term, small-scale tests on glass corrosion to support assessments of long-term glass performance in a repository?

vi. How are the process-level models of glass corrosion and radionuclide release integrated into repository performance assessments? How important is glass performance to the overall safety case for different repository designs?

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



(not to scale)

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

Aqueous glass degradation is treated as a source term reaction. Biodegradation is a separate source term.

Separate terms used for sorption and other sinks, including radiocolloids, precipitation, radioactive decay, size exclusion, etc.

Glass degradation model provides the mass of each radionuclide that becomes available for transport in the GDSA system model and changes in the seepage water composition.

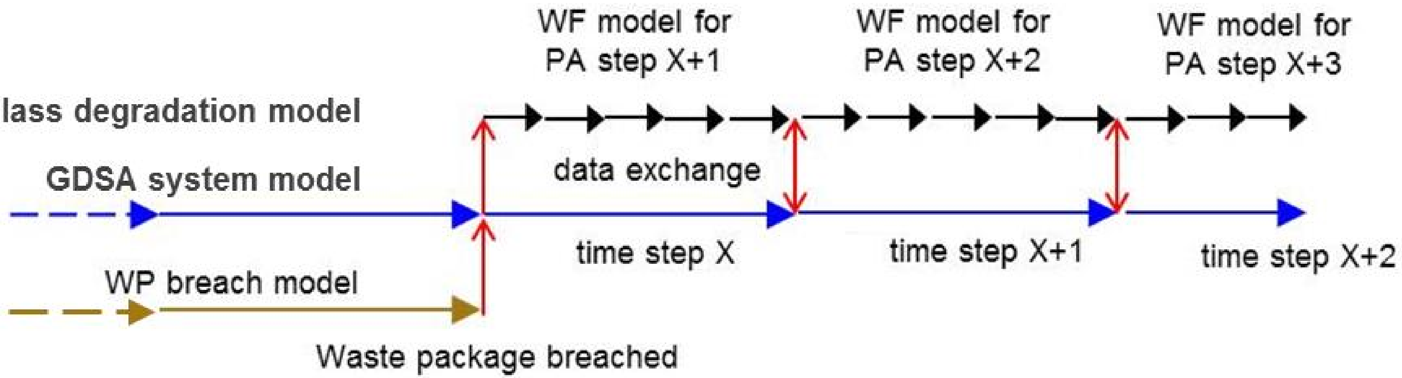
Interface Between Glass Model and Generic Disposal System Analysis (GDSA)

GDSA system model provides boundary conditions (e.g., liquid flux and volume) used to calculate the fractions of glass that corrode during the suite of waste form (WF) degradation time steps.

Shorter time steps (daughter steps) can be used in WF degradation models to provide fidelity with the degradation processes.

GDSA system model tracks and updates RN source masses and the pore water volume and composition in a breached waste package (WP).

Conceptual coupling of glass degradation and GDSA system models (schematic)



Benefits of Recent Improvements in DOE Glass Degradation Model to GDSA

- Approach being used in GDSA system model allows for implementing waste form degradation models that track solution composition.
- The proposed mechanistic model represents the effects of secondary phase formation explicitly with terms representing the Stage 3 trigger and Stage 3 rate.
- The new model links rate to key solution properties pH, [Al], [Si] that can be tracked in GDSA system model, including the impacts of other EBS materials and different near-field environments.
- Strategies to implement glass model in GDSA are being developed: data exchange with modules in GDSA, data storage, coding of rate equations, matching time steps, etc.
- The new model represents our improved understanding of the conditions required to trigger Stage 3 and provides confidence in using a non-conservative residual rate if those conditions are not predicted to occur.
- A reliable non-conservative glass corrosion model will reduce the dependence on other barriers to meet performance requirements and lower overall costs.

NWTRB Questions and Summary Responses

i. What are the recent improvements in DOE models for HLW glass corrosion? Mechanistic representation of Stage 3 behavior. How are these improvements helpful to the DOE HLW geologic disposal program? Decrease conservatism to more realistically represent barrier effect provided by glass waste forms.

ii. How do the models take account of the important glass corrosion mechanisms and the range of environmental conditions expected for different repository host-rock types and near-field environments? New model will represent chemical effects of environment. How are environmental conditions such as dissolved organic matter and the presence of microbial life being investigated? Represented as separate source and sink terms in transport model.

iii. How do the models take account of the wide range in DOE HLW glass compositions to be produced at the Waste Treatment and Immobilization Plant and the Defense Waste Processing Facility? Tests indicate primary impact of glass composition is on pH and solution chemistry controlling reaction affinity, which will be represented in new model.

iv. How are the models and model parameters supported by experimental data, including the large database of glass dissolution experiments managed by DOE personnel? Functional dependencies and parameter values are determined using data from long-term and short-term tests.

v. What is DOE’s technical basis for using the results of short-term, small-scale tests on glass corrosion to support assessments of long-term glass performance in a repository? Test methods and test conditions are selected to provide conditions highlighting particular aspects of degradation behavior.

vi. How are the process-level models of glass corrosion and radionuclide release integrated into repository performance assessments? Process-based glass model provides RN source terms due to aqueous corrosion, and is being encoded as module interfaced with GSDA system model. How important is glass performance to the overall safety case for different repository designs? To be determined, but new model is sensitive to different repository environments.

References

- Aagaard, P. and Helgeson, H.C. 1982. “Thermodynamic and Kinetic Constraints on Reaction Rates Among Minerals and Aqueous Solutions. I. Theoretical Considerations.” *American Journal of Science*, *282*, (3), 237-285. New Haven, Connecticut: Yale University.
- Alekseyev, V.A., Medvedeva, Prisyagina, N.I., Meshalkin, S.S., and Balabin, A.I. (1997). “Change in the dissolution rates of alkali feldspars as a result of secondary mineral precipitation and approach to equilibrium,” *Geochimica et Cosmochimica Acta, 61,* 1125-1142.
- 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.
- Ebert, W.L. (2015). Stage 3 Model for Coupled Glass Dissolution and Secondary Phase Precipitation Reactions. DOE NE report FCRD-MRWFD-2015-000763.
- Grambow, B. 1985. “A General Rate Equation for Nuclear Waste Glass Corrosion.” *Scientific Basis for Nuclear Waste Management VIII, Symposium held November 26-29, 1984, Boston, Massachusetts*. Jantzen, C.M.; Stone, J.A.; and Ewing, R.C., eds. 44, 15-27. Pittsburgh, Pennsylvania: Materials Research Society.
- Helgeson, H.C. (1968). “Evaluation of irreversible reactions in geochemical processes involving minerals and aqueous solution—I. Thermodynamic relations.” Geochimica et Cosmochimica Acta 32, 853-877.
- Jantzen, C.M. et al. (2013). SRNL Modeling Accelerated Leach Testing of Glass (ALTGLASS). DOE NE report FCRD-SWF-2013-000339.
- Jantzen, C.M., Trivelpiece, C.L., Crawford, C.L, Pareizs, J.M, and Pickett, J.B., “Accelerated Leach Testing of GLASS: I. Waste Glass Hydrogel Compositions and the Resumption of Accelerated Dissolution, and): II. Mineralization of Hydrogels by Leachate Strong Bases.” *International Journal of Applied Glass Science, 8[1]* 69-83 and 84-96 (2017).
- Lasaga, A.C. 1983. “Rate Laws of Chemical Reactions.” Chapter 1 of *Kinetics of Geochemical Processes*. Lasaga, A.C. and Kirkpatrick, R.J., eds. Reviews in Mineralogy Volume 8. Washington, D.C.: Mineralogical Society of America.
- Nagy, K.L., Blum, A.E., and Lasaga, A.C. (1991). “Dissolution and precipitation kinetics of kaolinite at 90 ºC and pH 3: The dependence on solution saturation state.” American Journal of Science, 291, 649-686.
- Neeway, J.J., Rieke, P.C., Parruzot, B.P., Ryan, J.V., and Asmussen, R.M. (2017) “The Dissolution Behavior of Borosilicate Glasses in Far-From Equilibrium Conditions.” *Geochimica et Cosmochimica Acta (in submission).*
- Papathanassiu et al. (2011). ILAW Glass Testing for Disposal at IDF: Phase 1 Testing. VSL-11R2270-1, Rev. A.
- Zhu, C., Blum, A.E. and Veblen, D.R.D. (2004) A new hypothesis for the slow feldspar dissolution in groundwater aquifers. Geochimica et Cosmochimica Acta 68, (abstract 2.2.32) A148.

Acknowledgements

This work is supported by the U.S. Department of Energy, Office of Nuclear Energy, Materials Recovery and Waste Form Development Campaign work package FT-17-AN030105.

Government License Notice: this presentation was created by UChicago Argonne, LLC, Operator of Argonne National Laboratory ("Argonne"). Argonne, a U.S. Department of Energy Office of Science laboratory, is operated under Contract No. DE-AC02-06CH11357. The U.S. Government retains for itself, and others acting on its behalf, a paid-up nonexclusive, irrevocable worldwide license in said presentation to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government.