Stage 3 HLW Glass Degradation Model

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U.S. DEPARTMENT OF ENERGY

Nuclear Energy

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?

Development of DOE Glass Degradation Model

- Use well-established mechanistically-based rate expression for borosilicate glass dissolution to limit radionuclide release rates
  - Based on mineral dissolution kinetics (e.g., Lasaga 1983, Aagaard and Helgeson 1982)
  - Modified for application to borosilicate waste glasses (e.g., Grambow 1985)

- Extracted dependencies on glass composition, pH, and temperature from QA-compliant test data
  - Confirmed general application of dependencies by comparisons with literature data

- Represented dependencies on solution composition probabilistically by using bounding values
  - Confirmed applicability of model to wide range of waste glass compositions by comparisons with literature data

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} = minimum 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)

- The rate-limiting step for glass corrosion is reaction 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 defining 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 (Grambow 1985).
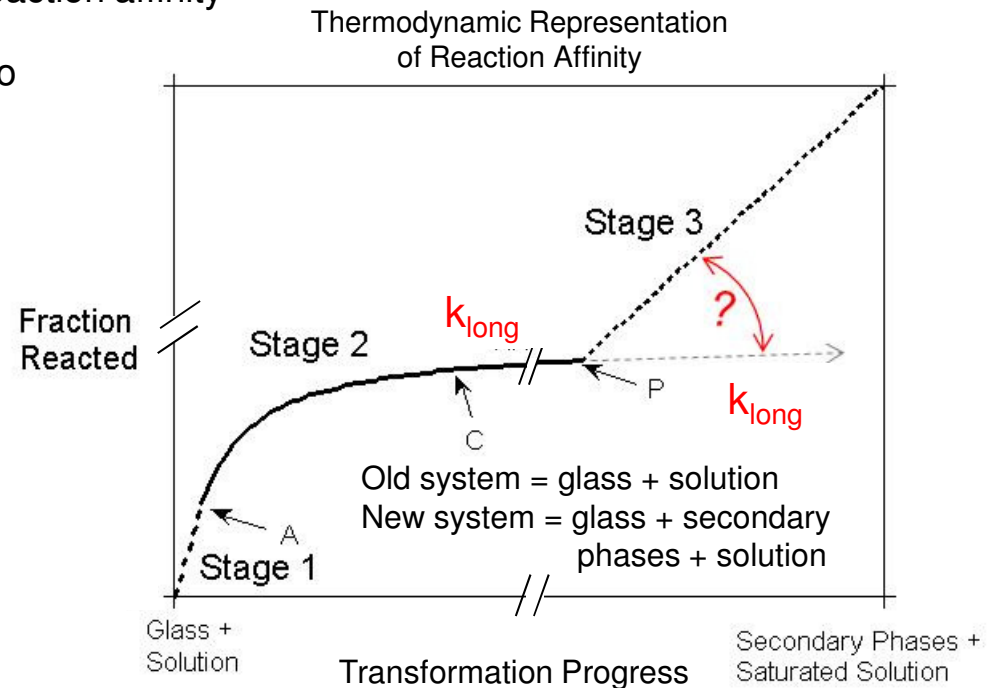
Conceptual Glass Degradation Model Based on Experimental Observations

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

rate coefficient   reaction affinity

- 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).

- Higher Stage 3 rate may be triggered (at P) if and when secondary phases form that establish new equilibrium state for system (reaction affinity for new system > reaction affinity for original system at residual rate).

- Stage 3 behavior has not been observed in tests with all waste glasses and conditions triggering Stage 3 remain to be quantified.

Thermodynamic Representation of Reaction Affinity

Fraction Reacted

Stage 3

k_{long}

Stage 2

?

P

C

k_{long}

Old system = glass + solution
New system = glass + secondary phases + solution

A

Stage 1

Glass + Solution

Transformation Progress

Secondary Phases + Saturated Solution

Different Test Methods Used to Highlight Different Stages

- Different test methods and conditions are being used to study glass dissolution under different degrees of saturation (different reaction affinity).

- Different test conditions generate fluids having different degrees of saturation that result in different extents of reaction progress within laboratory time-frame.

- Challenge for calculating long-term rate is determining **if** and **when** Stage 3 occurs.

Thermodynamic Representation of Reaction Affinity
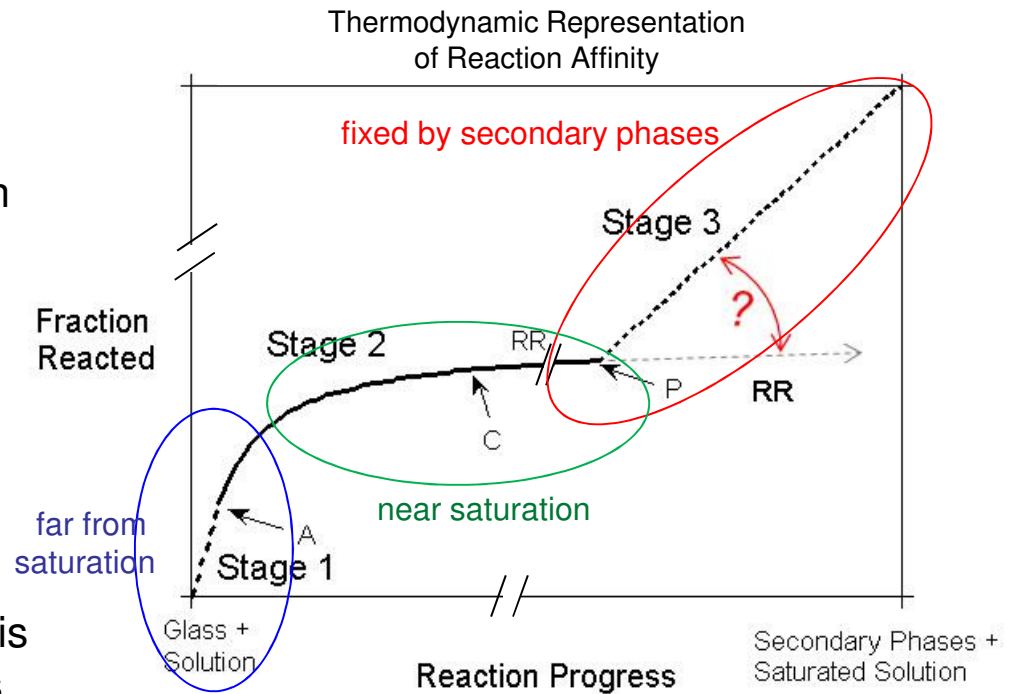
Solution-mediated transformation of glass to thermodynamically stable secondary phases
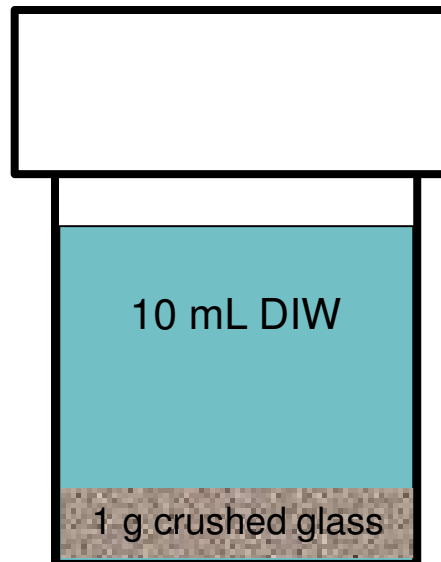
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ASTM C1285 Product Consistency Test
highlights Stage 2 and Stage 3 behavior

Method A under specified test conditions for direct comparisons.

Method B under various test conditions for measuring degradation behavior.

PCT A:

-100 +200 mesh glass
1 g glass/10 g water
(S/V typically 2000 m^{-1})
stainless steel vessel
90 °C
7 days
Onset of Stage 2

PCT B:

Various size fractions
Various mass ratios
Various leachants
(S/V ~1000 – 23,000 m^{-1})
static solution
stainless steel or Teflon vessel
40 -200 °C
1 day – several years
Onset of Stage 3

10 mL DIW

1 g crushed glass

PCT-B usually run as a series of batch tests. Test solutions analyzed at end of test.

Measured concentrations of glass constituents [i] normalized to their mass fractions in glass $f(i)$ and the geometric glass surface area-to-solution volume (S/V) ratio used in test:

$$NC(i) = \frac{[i]}{f(i)} \qquad NL(i) = \frac{[i]}{(S/V)f(i)}$$

i = B, alkali metals, Si for Method A
i = all constituents for Method B

$NC(i)$ normalized concentration
$NL(i)$ normalized mass loss

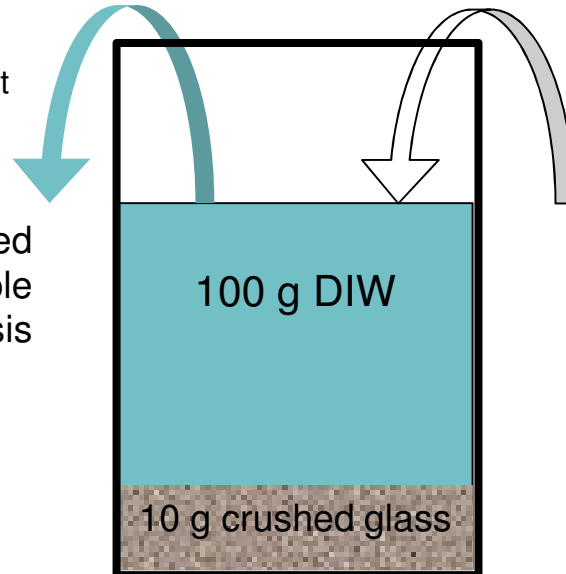Solids analyzed at end (optional).

Modified PCT-B: Partial Replacement

Long-term tests were conducted at the Catholic University of America Vitreous State Laboratory 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).*
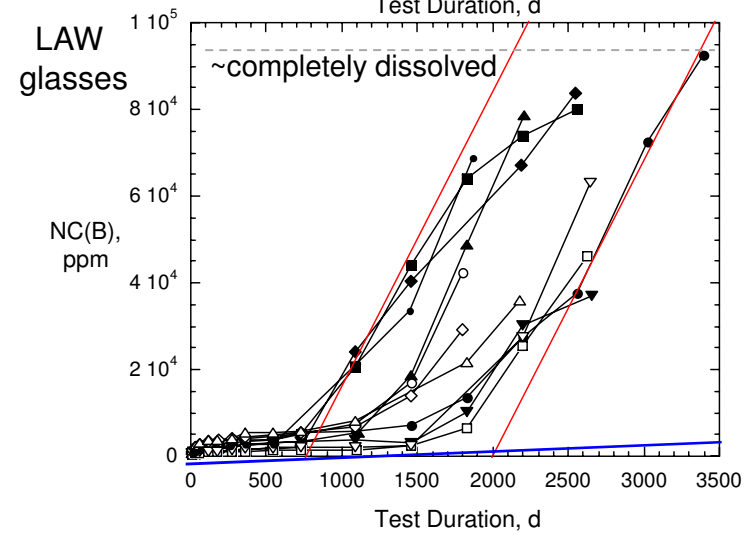DOE NE report FCRD-SWF-2013-000339

Removed
4 mL sample
for analysis

100 g DIW

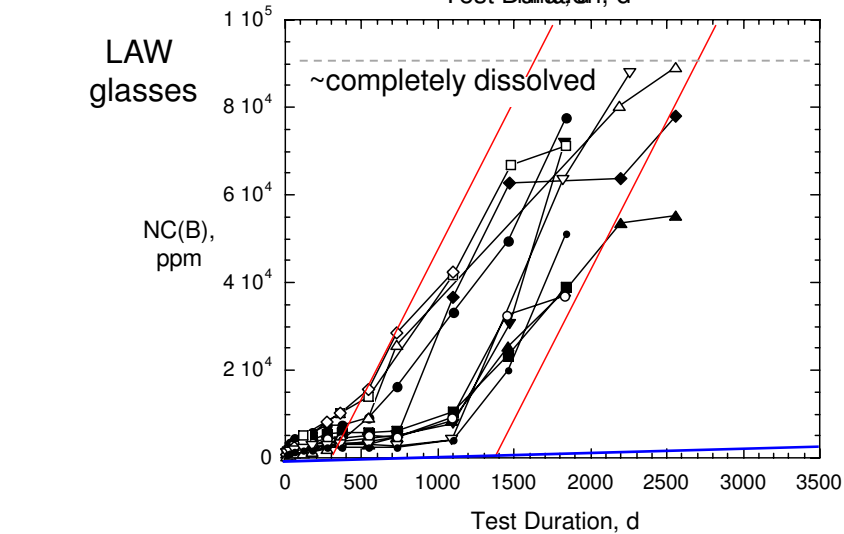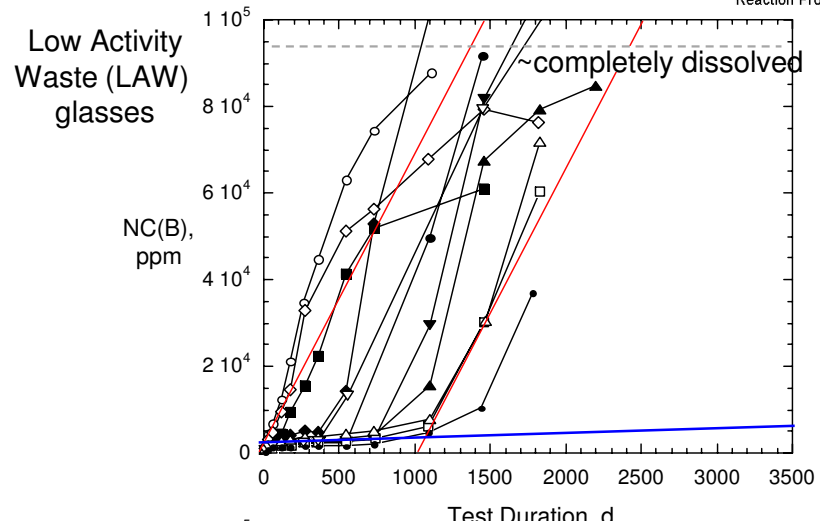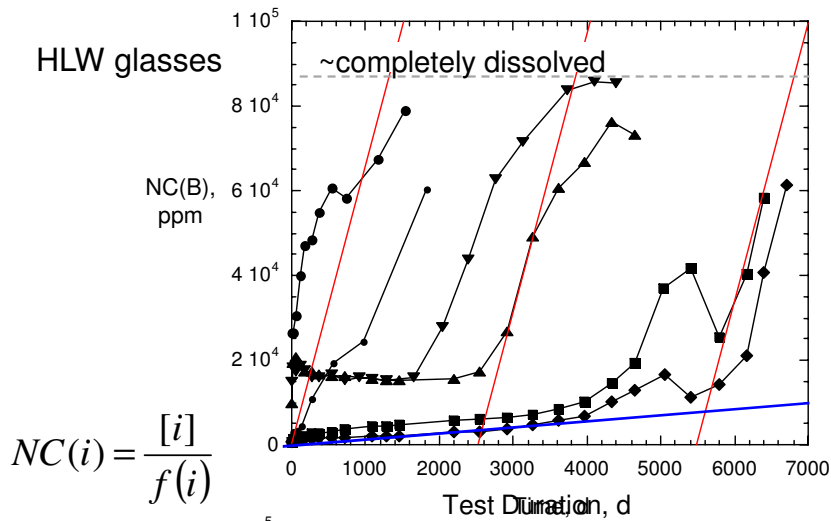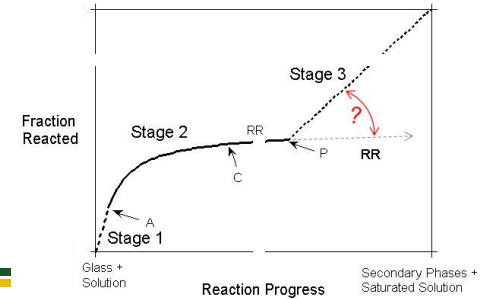Replaced with
4 mL DIW

10 g crushed glass

Advantage: Exchange method provides extremely valuable very long-term data.

Disadvantage: Addition of DIW perturbs solution compositions and contributes uncertainty to derived rates.

(Other tests conducted with smaller aliquants without replacement.)

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Long-term Modified PCT-B with Stage 3 Behavior

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

HLW glasses

Low Activity Waste (LAW) glasses

LAW glasses

LAW glasses

Blue lines show representative residual rate and red lines show representative Stage 3 rate.
Tests with different glasses have essentially the same Stage 2 and Stage 3 rates.

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No Direct Correlation Between Glass Composition and Stage 3 Trigger

LAW glasses (open symbols)

HLW glasses (filled symbols)

Trigger Time, d

Note semilog plots

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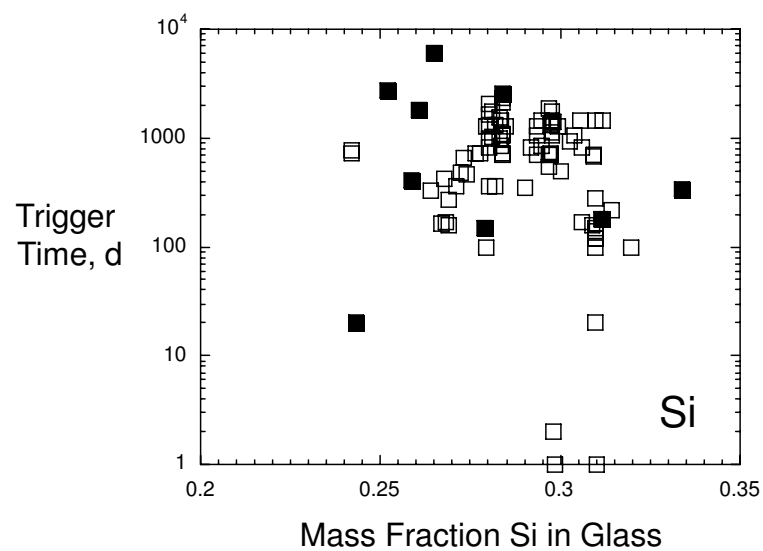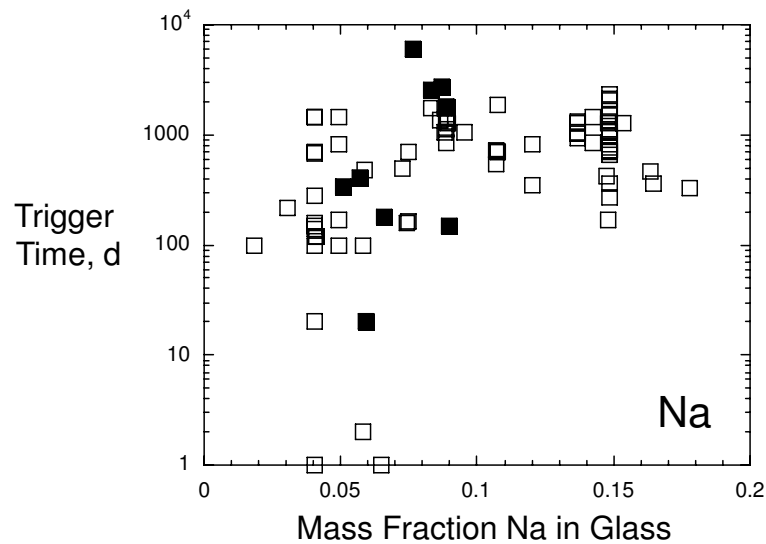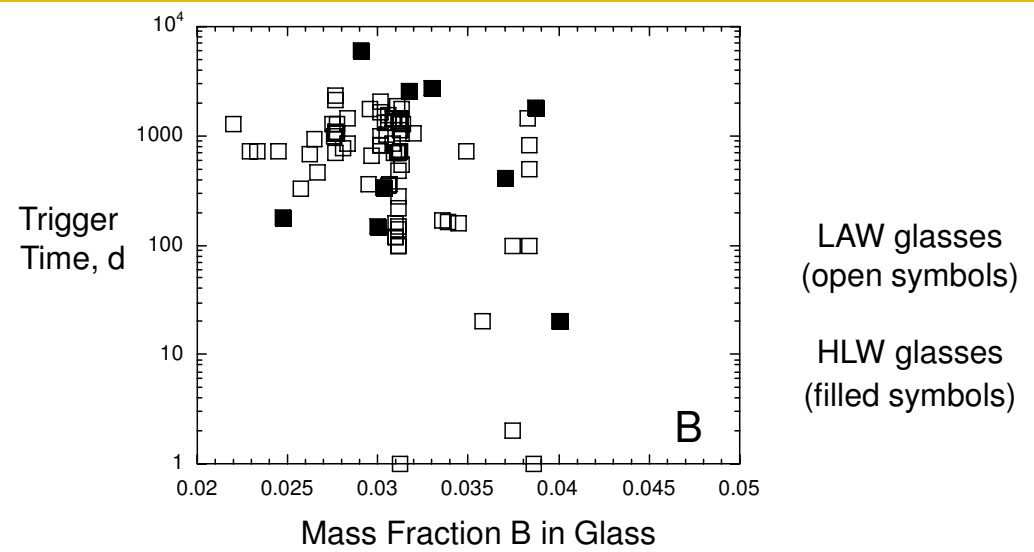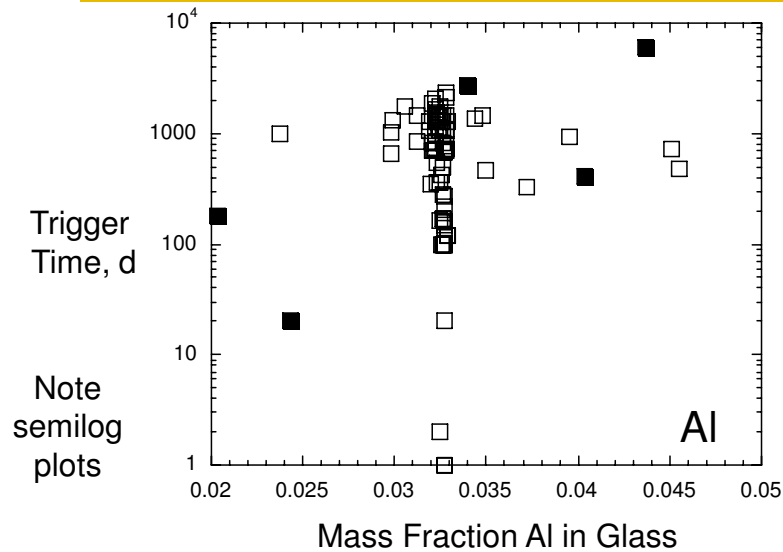
Modified PCT with SON68

SON68 is reference glass previously thought not to trigger Stage 3

NL(B), g m^{-2}

0.13 g m^{-1} d^{-1}

pH 11.5

pH 11.0

0.012 g m^{-1} d^{-1}

pH 10.5

Time, d

$$NL(i) = \frac{C(i)}{S/V \, f(i)}$$
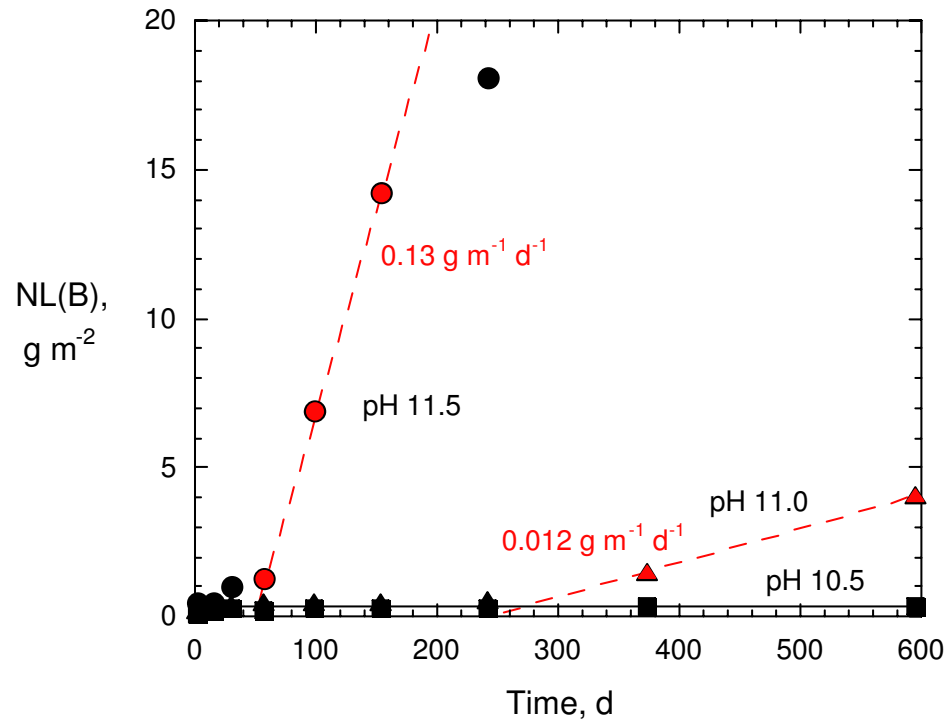
5000 m^{-1} at 90 °C in leachants with imposed pH values.

Even with high pH values imposed and maintained, the Stage 3 trigger does not occur until the solution becomes adequately enriched in species needed to grow stable secondary phases (probably Al and Si).

Dissolved concentrations and pH are both important for triggering Stage 3.

Appears that

1- a threshold **solution** composition (and pH) must be attained to trigger Stage 3.

2- nucleation kinetics delay the Stage 3 trigger.

Gin and Mestre (2001).

[Al] Behavior in ALTGLASS Database

Geochemist's Workbench was used to calculate pH and speciation of solution compositions for several tests in which Stage 3 was triggered and tests in which it was not.
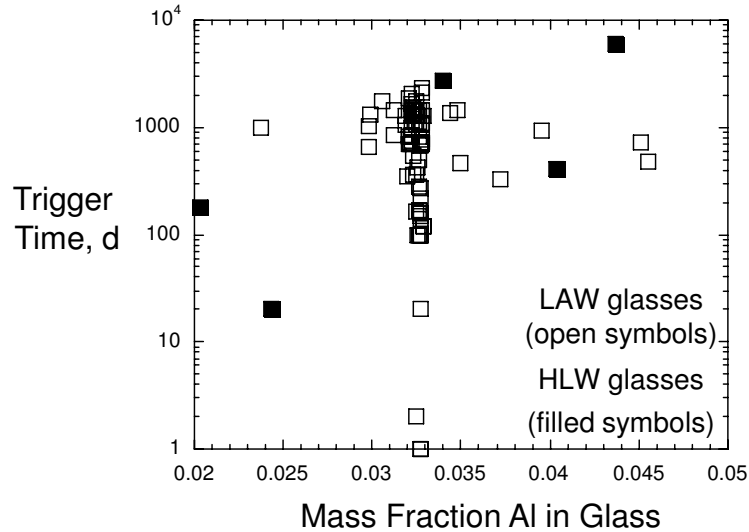(Stage 3 triggered in tests with ~80% of the glasses)

LAW glasses (open symbols)

HLW glasses (filled symbols)

Trigger Time, d

Mass Fraction Al in Glass

Stage 3 trigger not correlated with Al content **of glass**.

However, tests show decreasing Al concentration **in solution** precedes Stage 3 trigger.

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

On-going tests are focused on roles of Al and secondary phase precipitation.

$Al(OH)_4^-$ (molal)

Stage 3 behavior observed

Stage 3 behavior not observed

Normalized Time

Test Started

Stage 3 triggered or test terminated

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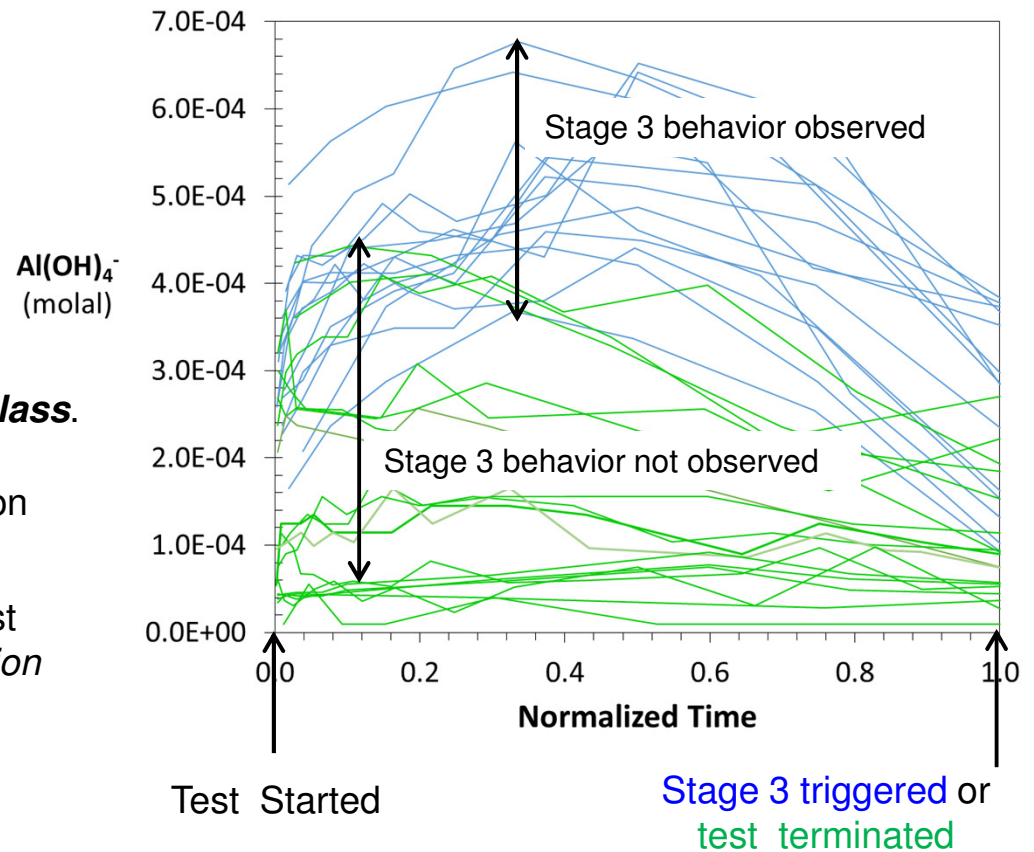
Perturbed PCT with AFCI Glass to Relate Solution Composition to Stage 3

PCT-B with AFCI glass demineralized water
2000 m^{-1}
90 °C

EXAMPLE: AFCI glass is a generic reference glass made during Advanced Fuel Cycle Initiative program known to trigger Stage 3

Interrupt test after 98 days to perturb pH, [Si], both, or neither

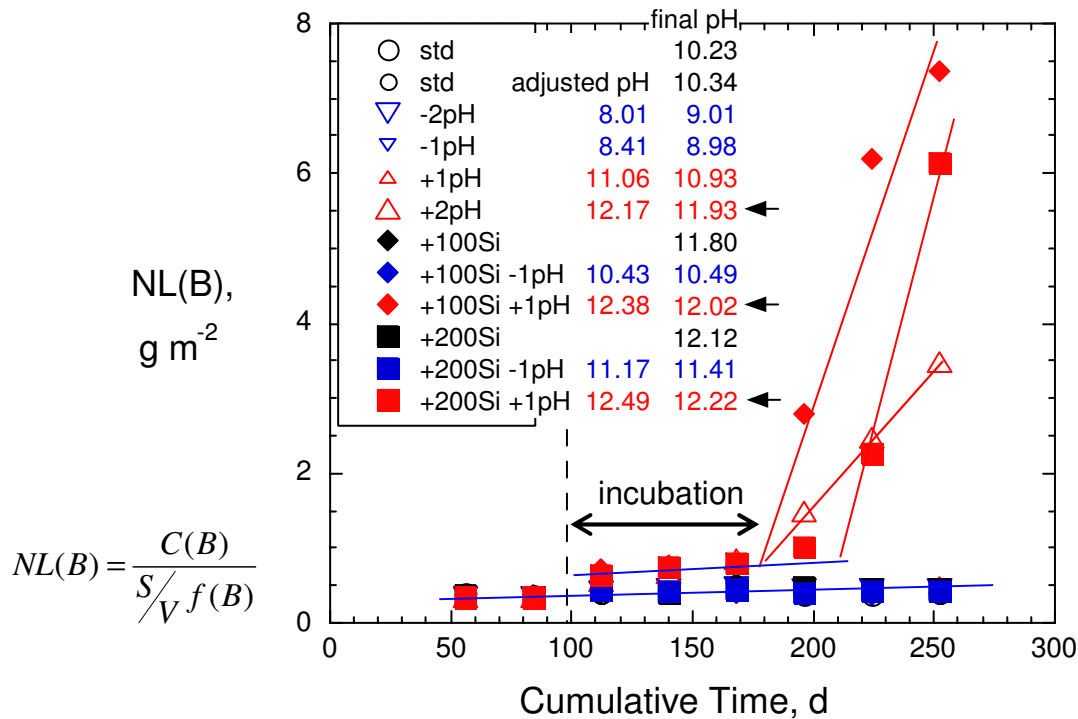|			final pH
○	std		10.23
○	std	adjusted pH	10.34
▽	-2pH	8.01	9.01
▽	-1pH	8.41	8.98
△	+1pH	11.06	10.93
△	+2pH	12.17	11.93 ←
◆	+100Si		11.80
◆	+100Si -1pH	10.43	10.49
◆	+100Si +1pH	12.38	12.02 ←
■	+200Si		12.12
■	+200Si -1pH	11.17	11.41
■	+200Si +1pH	12.49	12.22 ←

NL(B), g m^{-2}

$$NL(B) = \frac{C(B)}{\frac{S}{V} f(B)}$$

incubation

Cumulative Time, d

Take 1-mL aliquots without replacing.

Use NL(B) to measure residual rate and indicate Stage 3 trigger.

Negligible impact of perturbations on residual rates, but Stage 3 is triggered in some tests…after ~100-day incubation period.

Incubation period and Stage 3 rates similar after perturbations to pH and to both the pH and [Si].

Stage 3 was not triggered by perturbing [Si] alone.

Three perturbations trigger Stage 3, other perturbations have no effect.

Al and Si Solution Behavior
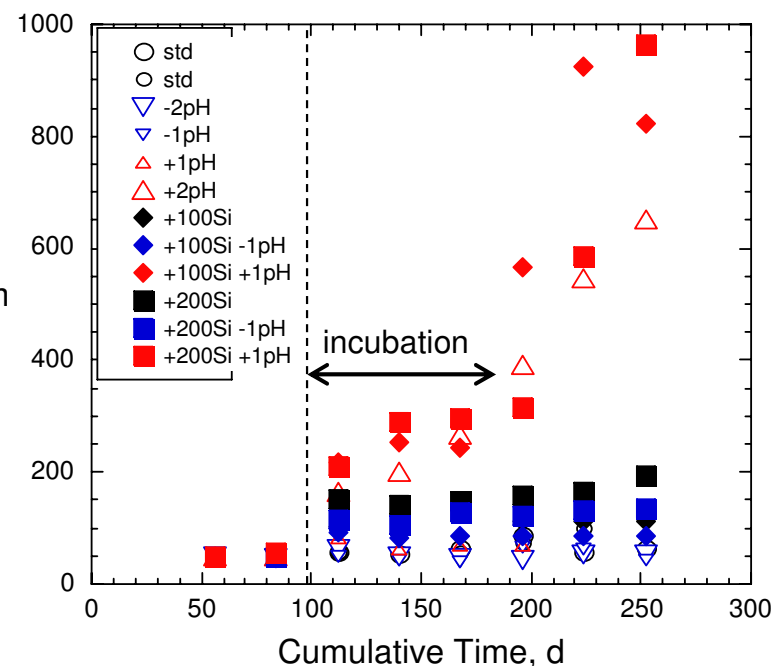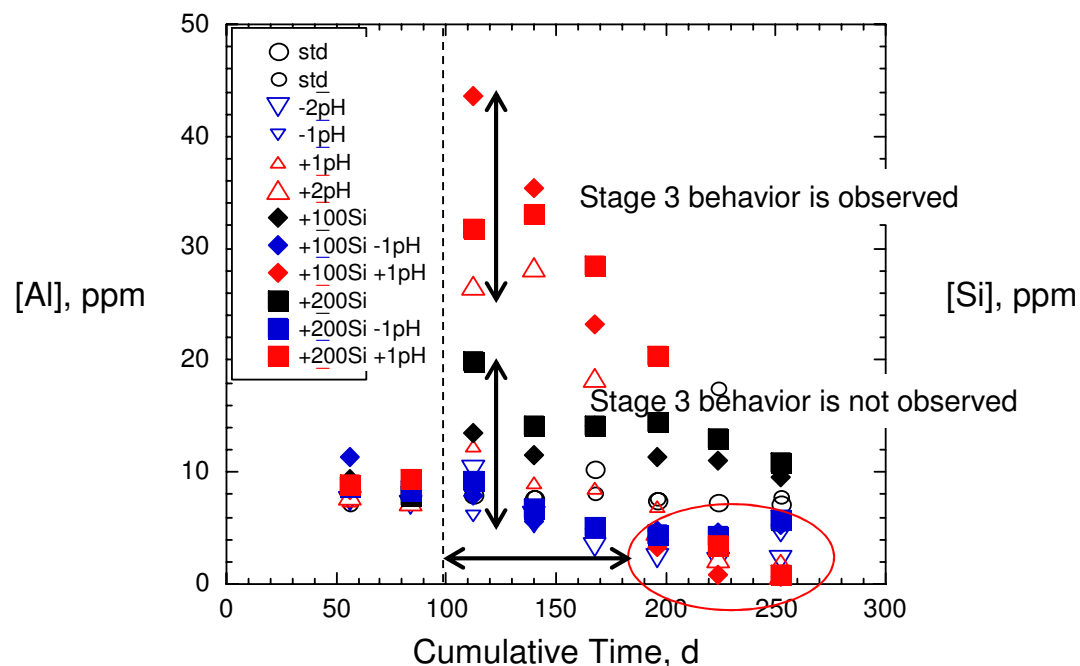
1. Al concentrations increase immediately in perturbed tests that later show Stage 3 behavior.
2. Al concentrations decrease prior to Stage 3 trigger and remain very low during Stage 3.
3. Si concentrations increase in Stage 3, but stay constant in tests that don't trigger Stage 3.
4. Results are consistent with role of Al precipitation seen in ALTGLASS data prior to Stage 3 trigger.

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Increased pH 2 units by adding NaOH

Δ AFCI_6 +2 pH

Increased [Si] by adding K_4SiO_4 glass
Increased pH 1 units by adding NaOH

◆ AFCI_9 +100 Si +1 pH
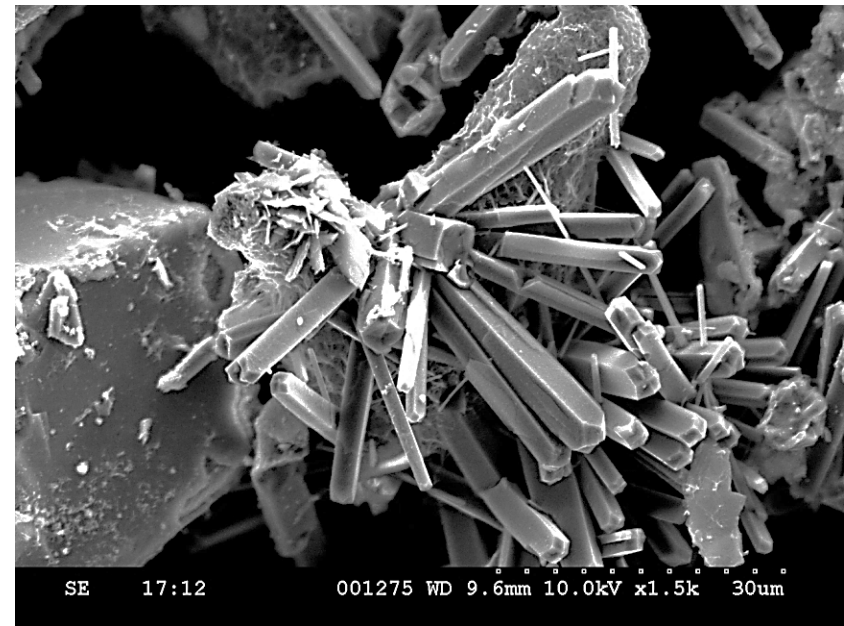
Adding Seed Crystals Shortens Delay in Stage 3 Trigger due to Nucleation Step

S_{seed} and S_{glass} are surface areas of glass and seeds in test

$\dfrac{S_{seed}}{S_{glass}}$	
▷	1.1
+	0.28
○	0.16
□	0.07
◇	no seeds

Re-equilibration of solution after all glass converted to alteration phases.
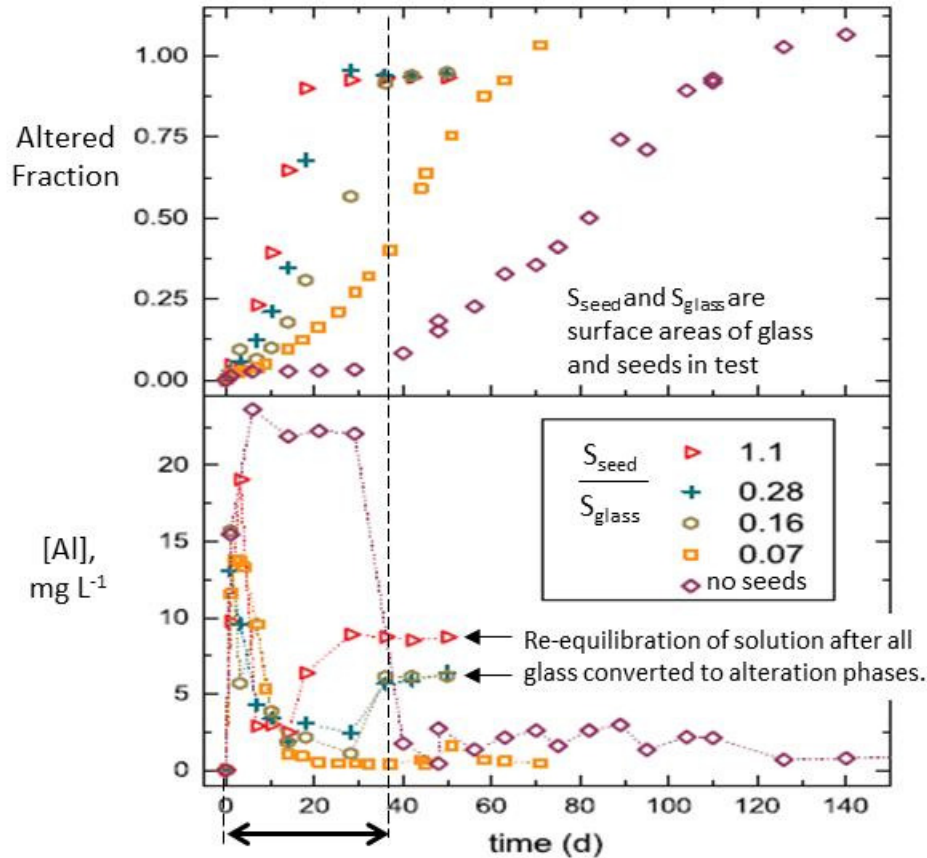
Same Al increase/decrease seen in seeded and unseeded tests.

based on Fournier et al. (2017). Contribution of zeolite-seeded experiments to the understanding of resumption of glass alteration. *npj Materials Degradation* (in press)

International Simple Glass after corrosion

Na chabazite formed in test

synthetic zeolite Na P2 seed crystals

10 µm
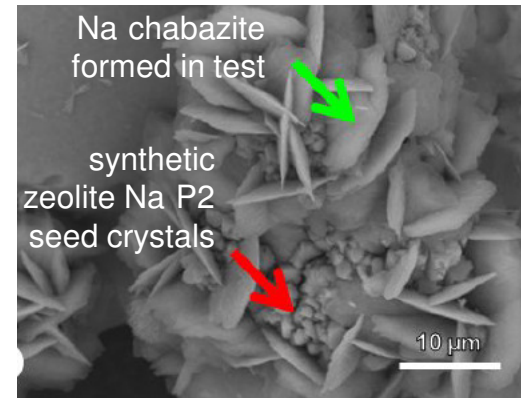
ISG glass
PCT-B
demineralized water
1770 m^{-1}
90 °C

Seeding tests demonstrate important role of secondary phase nucleation that must be taken into account in glass degradation model.

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Proposed Stage 3 Mechanism Being Evaluated (schematic)

Stage 1   *Stage 2*

pH   pH
        [H$_4$SiO$_4$]

M,B,
Si,   *Residual Rate*
Al

glass → gel → gel +clay

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$_4$SiO$_4$])
    with growth of surface alteration layer
    residual rate attained at [H$_4$SiO$_4$] saturation

Species partition between solution and surface alteration layer
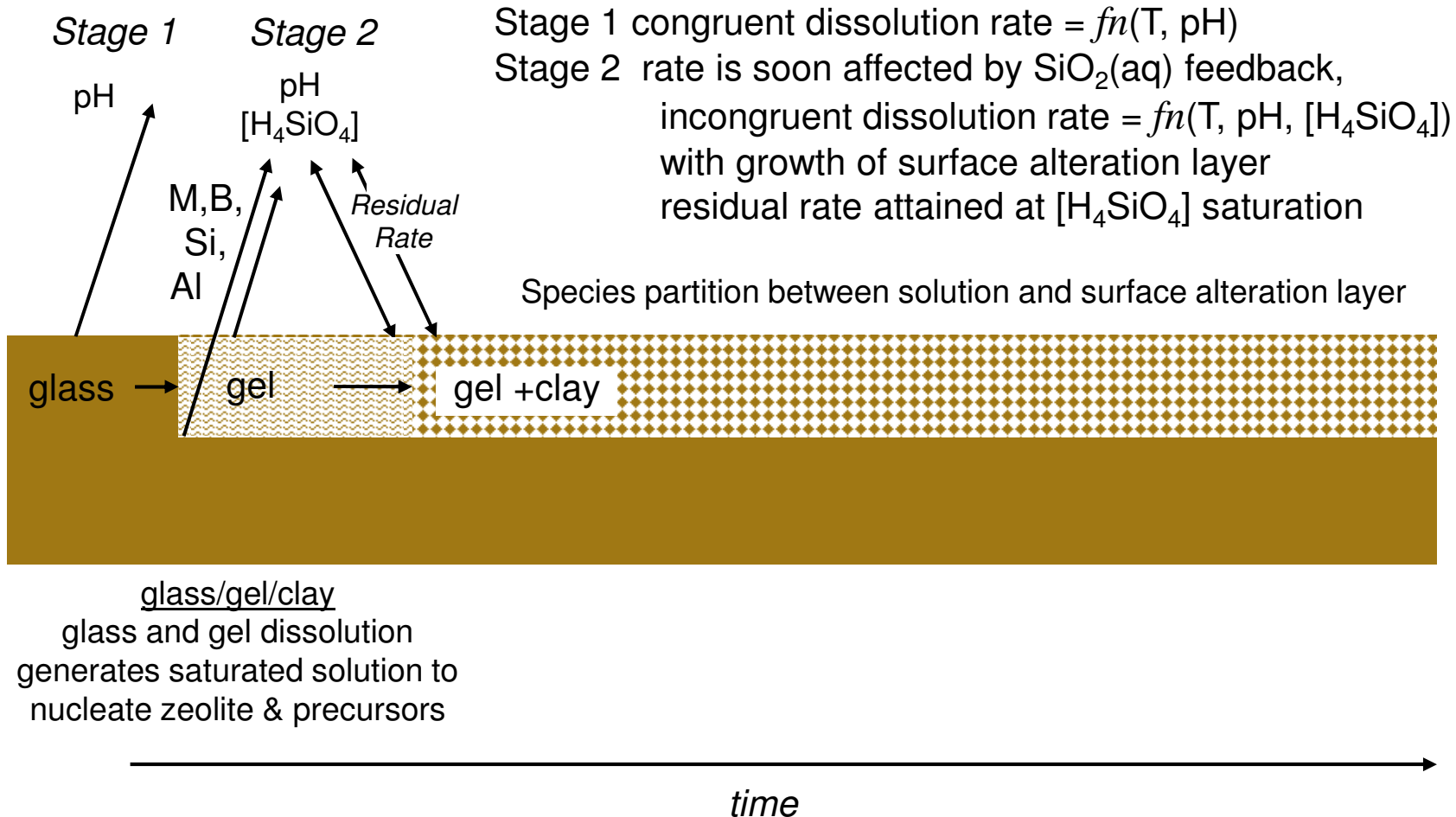
glass/gel/clay
glass and gel dissolution
generates saturated solution to
nucleate zeolite & precursors

time

M = alkali metal

Stage 3 Trigger Step 1

Stage 1   *Stage 2*   pH   Dissolved Al reacts with surface to
                                                        generate (poorly defined) activated
pH   pH   surface species (discussed later)
                 Si(OH)$_4$
                                             Al(OH)$_4^-$

M,B,   *Residual*
Si,   *Rate*   Al(OH)$_4^- \rightarrow$ AlO$_2^-$ + 2H$_2$O   ??
Al

glass → gel → gel +clay

glass/gel/clay   Al-based embryo
glass & gel dissolution   AlO$_2^-$ is the origin of the zeolite
generate saturated solution to   framework charge.
nucleate zeolite & precursors   OH$^-$ is catalyst/mineralizer

time

Stage 3 Trigger Step 2

Stage 1

pH

Stage 2

pH
$Si(OH)_4$

M,B,
Si,
Al

*Residual
Rate*

pH

$Al(OH)_4^-$

$HSiO_3^-$

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

matures

hydrogel

glass → gel → 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

time

Stage 3 Mechanism Dominates

Stage 1

pH

Stage 2

pH
$Si(OH)_4$

M,B,
Si,
Al

*Residual
Rate*

pH

$Al(OH)_4^-$

$HSiO_3^-$

Stage 3

pH
$Al(OH)_4^- + M^+ + HSiO_3^-$

$Si(OH)_4$

M,B,
Si,
Al

hydrogel

zeolite

glass → gel → gel +clay

Al-based embryo

Stage 3 trigger Step 1

Al+Si-based precursor

Stage 3 trigger Step 2

$MAlSiO_4$ Secondary Phase

Stage 3 growth and ripening

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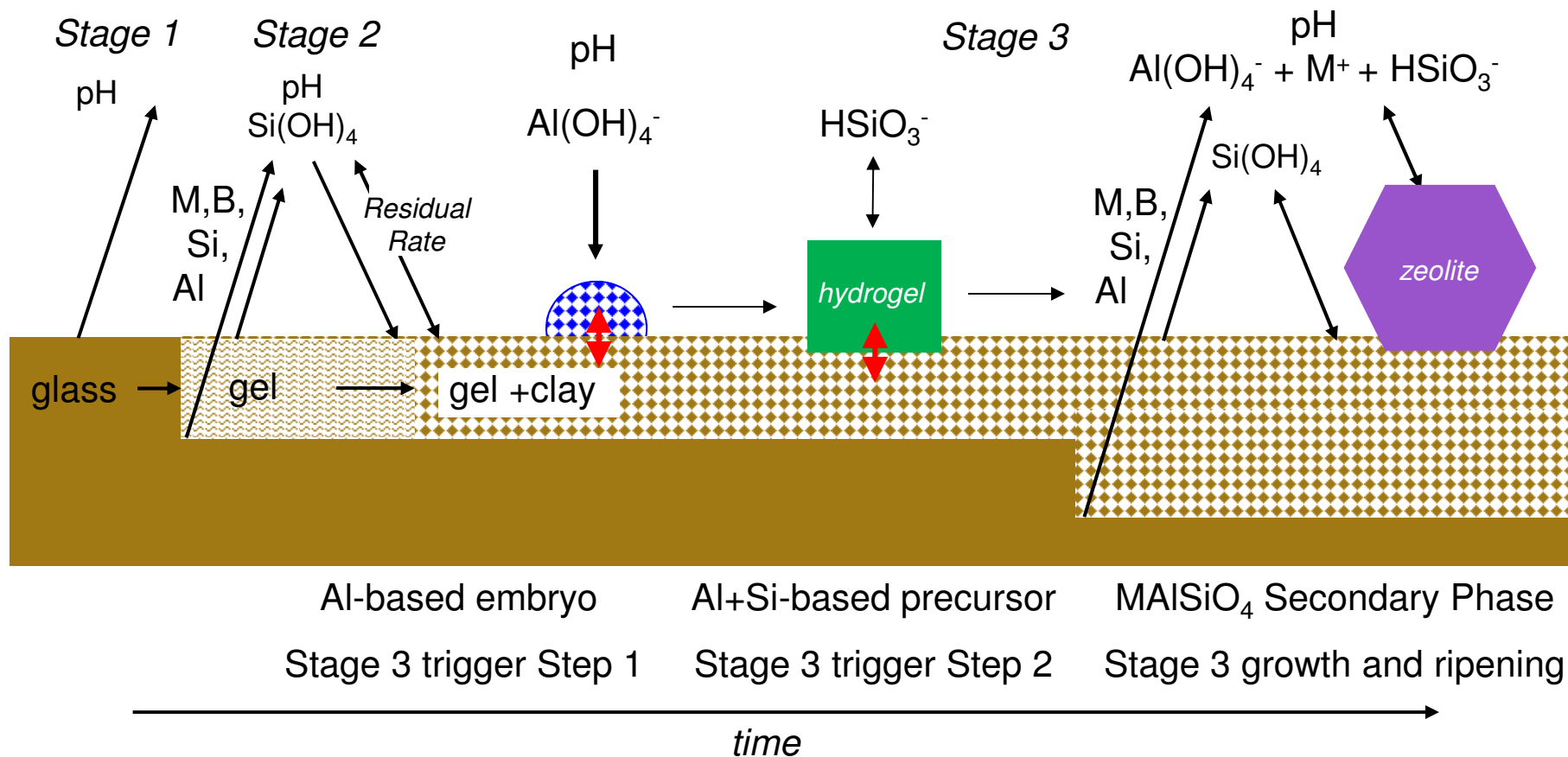
Transfer of Al from glass to secondary phases through solution is probably rate-limiting process.
This maintains $Al(OH)_4^-$ at a low steady-state concentration fixed by the glass dissolution rate and
secondary phase precipitation rate, but [Si] and [M] continue to increase.
This is consistent with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

Conceptual Model for Effect of Secondary Phase Precipitation on Reaction Affinity

Affinity term for Stage 3 represents coupled kinetics of glass dissolution and secondary phase precipitation

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

(for small deviations from equilibrium)

$k_{forward}^{dis}$ = rate coefficient for glass dissolution

$k_{forward}^{pptn}$ = rate coefficient for secondary phase precipitation

$\Delta G_{r\,dis}$ = 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.

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

(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 close-to-equilibrium primary phase dissolution rate (negative feedback):

$$k_{forward}^{pptn} << k_{forward}^{dis} \qquad rate_{coupled}^{ss} = k_{forward}^{pptn}\left(1 - \exp\left(\frac{\Delta G_{r\,dis} + \Delta G_{r\,pptn}}{RT}\right)\right)$$
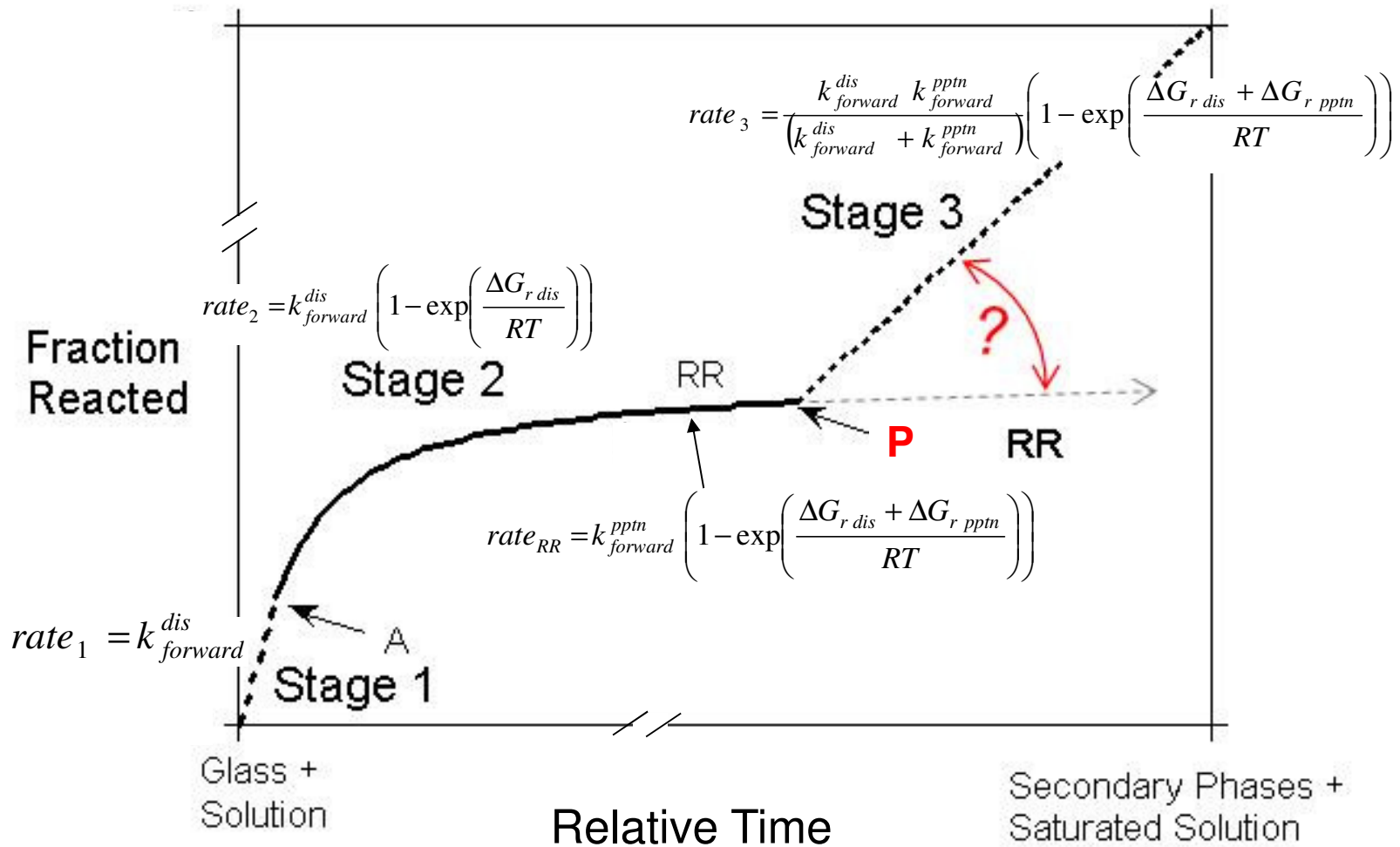
Otherwise, kinetics of both reactions contribute. Coupling of free energy terms "arrests" the reaction affinity for the system to <u>maintain a constant rate</u>, which is observed experimentally.

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.

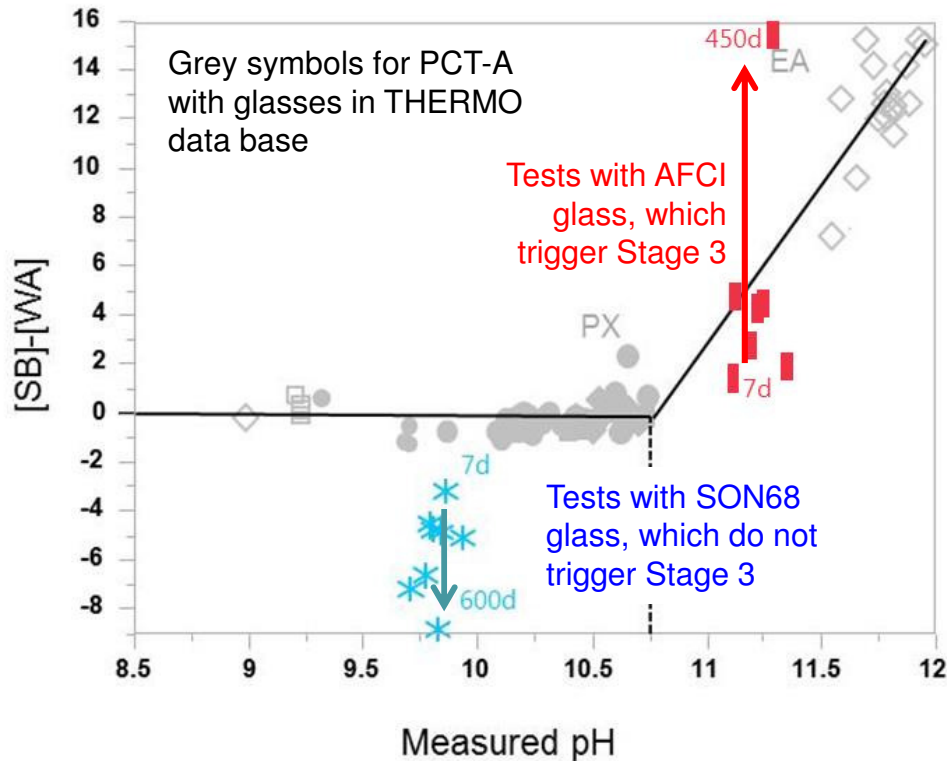# Four Rate Laws Represent Observed Changes in Degradation Behavior

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

Stage 3

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

Fraction Reacted

Stage 2

RR

?

P   **RR**

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

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

A

Stage 1

Glass + Solution

Relative Time

Secondary Phases + Saturated Solution

Status and Path Forward

- Tests with large numbers of LAW and HLW glasses have shown wide ranges of glass compositions have similar Stage 2 residual rates and similar Stage 3 rates, but test durations required to trigger Stage 3 vary significantly even for replicate tests.

- The conceptual Stage 3 model was developed by applying mineral transformation theory to observed glass dissolution behavior. The coupled kinetics model is consistent with measured solution evolution behavior, effects of nucleation kinetics, and aspects of industrial methods used to generate zeolites.

- On-going work to develop approaches for predicting the Stage 3 trigger and rate for use in waste glass simulations includes Informatics analysis of ALTGLASS data base, addition of new data, laboratory tests, application of geochemical-based methods and models, and application of models developed for process control.

- **Examples:**
  - SRNL strong base-weak acid model for solutions
  - Evolution of predicted surface complex composition and relationship to Stage 3 trigger

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Grey symbols for PCT-A
with glasses in THERMO
data base

Tests with AFCI
glass, which
trigger Stage 3

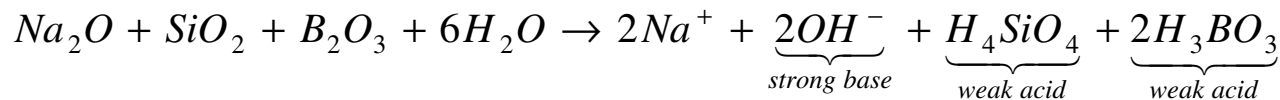Tests with SON68
glass, which do not
trigger Stage 3

The weak acid-strong base model represents effects of solution chemistry on glass dissolution behavior better than pH alone.

Resumption glass:
leachates become enriched in strong base.

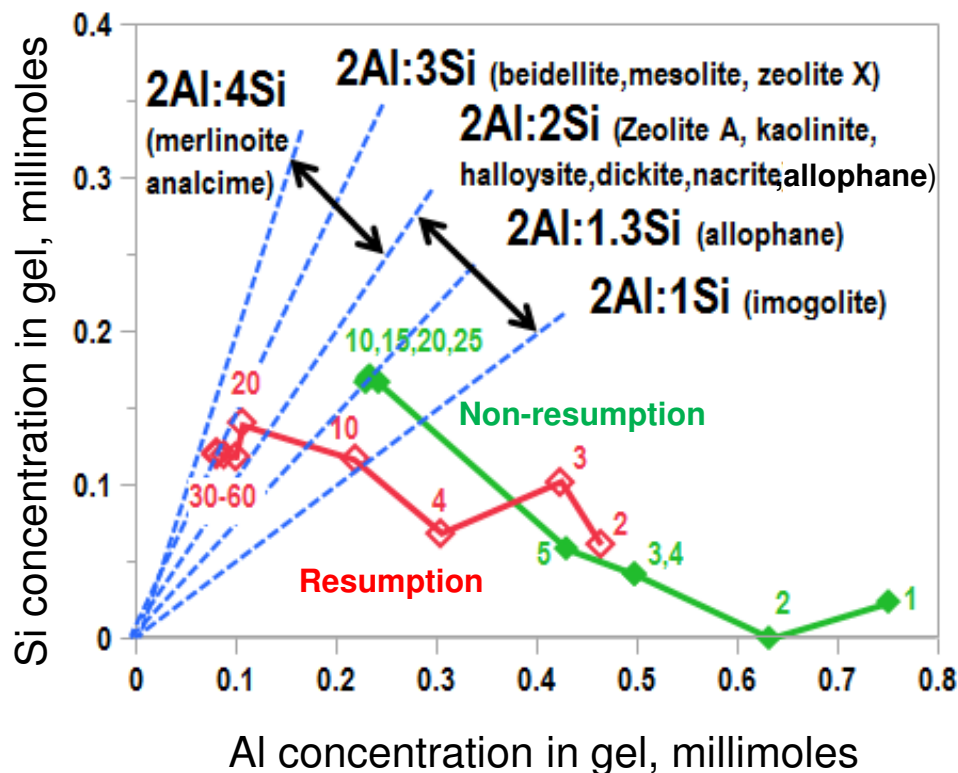Non-resumption glasses:
leachates become enriched in weak acids.

Measured pH values do not reflect either enrichment trend.

$$Na_2O + SiO_2 + B_2O_3 + 6H_2O \rightarrow 2Na^+ + \underbrace{2OH^-}_{strong\ base} + \underbrace{H_4SiO_4}_{weak\ acid} + \underbrace{2H_3BO_3}_{weak\ acid}$$

$$\underbrace{[SB] - [WA]}_{leachate} \equiv \underbrace{[Na + Li + K + Cs]_{millimoles}}_{leachate} - \underbrace{[B + Si]_{millimoles}}_{leachate}$$

Jantzen et al. (1995).

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Calculated Evolution of Gel Composition

Likelihood of Stage 3 behavior not correlated with the Al/Si ratio in glass, but appears to be correlated with Al/Si ratio attained in surface layer (gel).
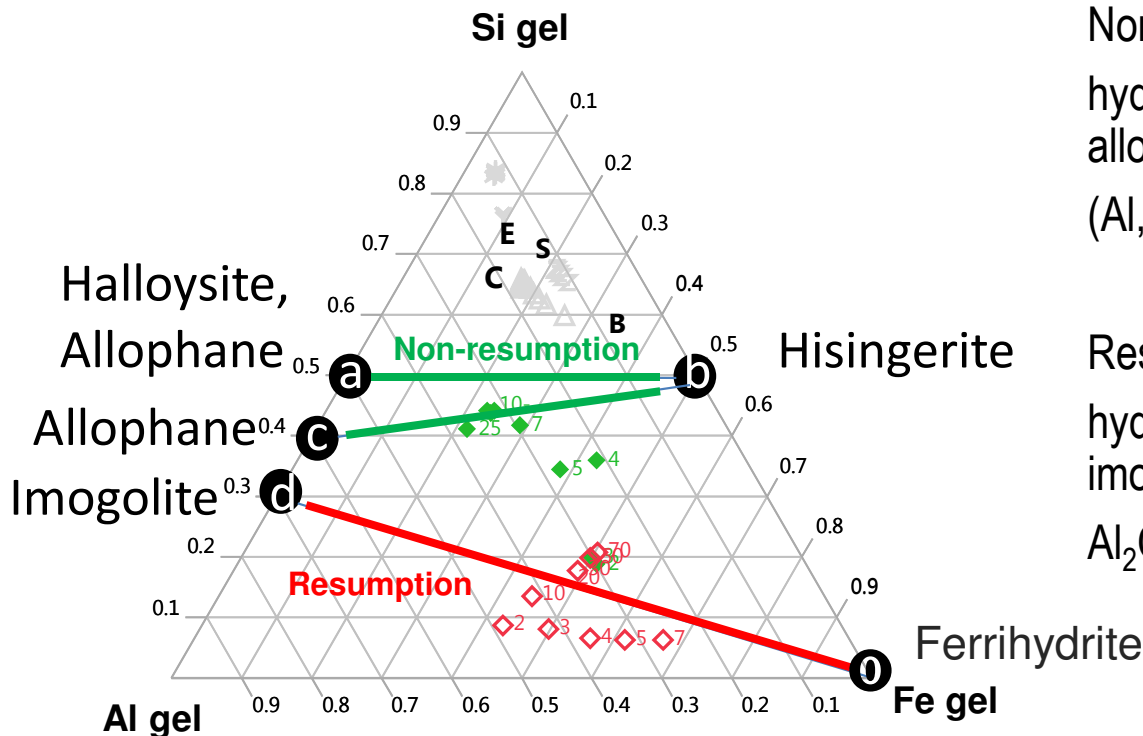
Resumption glasses:
form zeolite X (2 Al : 3 Si) and analcime (2 Al : 4 Si)

Non-resumption glasses:
form allophane (2 Al : 1.3 Si) and hisingerite (2 Fe : 2 Si)

Hydrogel compositions were calculated from differences between measured solution concentrations and those predicted for dissolution congruent with boron.

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Jantzen et al. (2017).

Non-resumption glasses:

hydrogels evolve along the allophane-hisingerite join
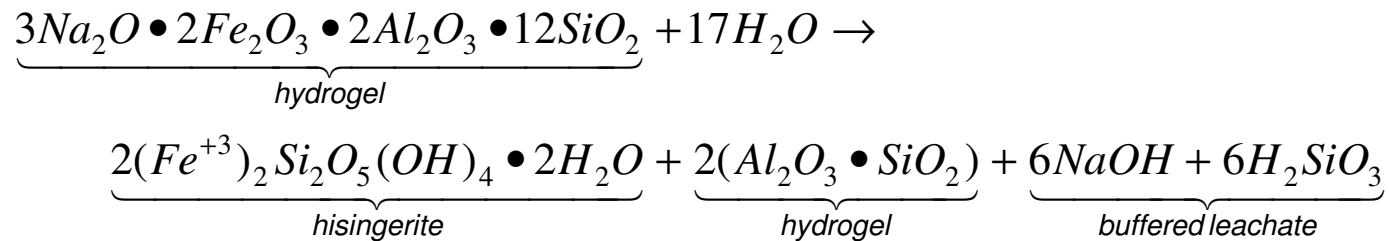
$(Al,Fe)_2O_3 \cdot 1.33 - Fe_2O_3 \cdot 2Si(OH)_4$

Resumption glasses:

hydrogels evolve along the imogolite-ferrihydrite join
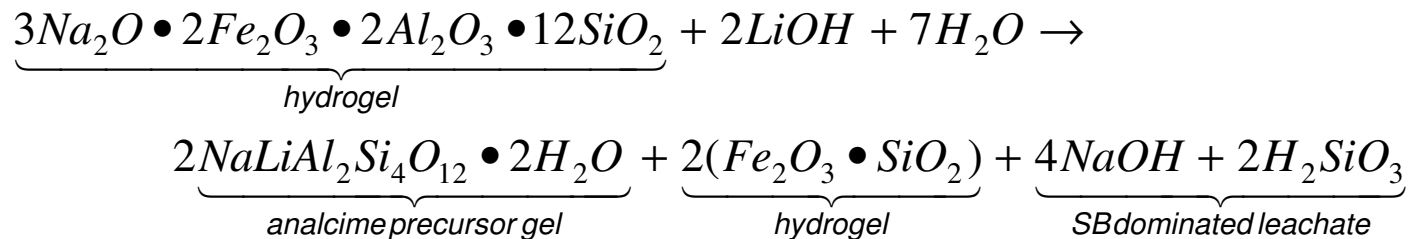
$Al_2O_3 \cdot Si(OH)_4 - Fe_2O_3 \cdot 0.5H_2O$

◇ Evolution of surface complex composition for glasses that **do** trigger Stage 3

◆ Evolution of surface complex composition for glasses that **do not** trigger Stage 3

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Jantzen et al. (2017).

Solution-Mediated Hydrogel Reactions Determine Resumption or Non-Resumption

Jantzen et al. (2017).

If leachate is not enriched in strong base:

$$\underbrace{3Na_2O \bullet 2Fe_2O_3 \bullet 2Al_2O_3 \bullet 12SiO_2}_{hydrogel} + 17H_2O \rightarrow$$

$$\underbrace{2(Fe^{+3})_2Si_2O_5(OH)_4 \bullet 2H_2O}_{hisingerite} + \underbrace{2(Al_2O_3 \bullet SiO_2)}_{hydrogel} + \underbrace{6NaOH + 6H_2SiO_3}_{buffered\,leachate}$$

If leachate is enriched in strong base:

$$\underbrace{3Na_2O \bullet 2Fe_2O_3 \bullet 2Al_2O_3 \bullet 12SiO_2}_{hydrogel} + 2LiOH + 7H_2O \rightarrow$$

$$\underbrace{2NaLiAl_2Si_4O_{12} \bullet 2H_2O}_{analcime\,precursor\,gel} + \underbrace{2(Fe_2O_3 \bullet SiO_2)}_{hydrogel} + \underbrace{4NaOH + 2H_2SiO_3}_{SB\,dominated\,leachate}$$

The incorporation of these process dependencies and strong base-weak acid model into Stage 3 model as triggering mechanism is being evaluated.

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- 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?

Most important uncertainties are (1) if and when Stage 3 is triggered under disposal conditions and (2) temperature and pH dependencies of residual and Stage 3 rates.

Technical uncertainties are being addressed by applying insights from geochemistry and industrial processing (including DWPF) to relate solution and solid properties to model Stage 3 trigger and by conducting focused laboratory tests to measure kinetic parameters.

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