



U.S. DEPARTMENT OF
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DOE HLW Glass Degradation Model



**Material
Recovery &
Waste Form
Development**

**William Ebert
Argonne National Laboratory**

**NWTRB Briefing
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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?



Overview

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- ANL developed a bounding glass dissolution model to represent all US HLW glasses ca. 2002
- Used 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



- The saturation index defining the reaction affinity is the ratio of the activity of orthosilicic acid [$Q = a(\text{H}_4\text{SiO}_4)$] 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).



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 values for temperature dependence parameter E_a and pH dependence parameter η likely to be bounding for HLW glasses
 - Used data from short-term ASTM C1220 tests in which value of $(1-Q/K)$ remains near 1 and k_{long} is negligible, so that

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

- Extracted parameter values of η and E_a based on boron release of from series of ASTM C1220 tests conducted at constant pH and temperature
- Compared with dependencies extracted from data in literature

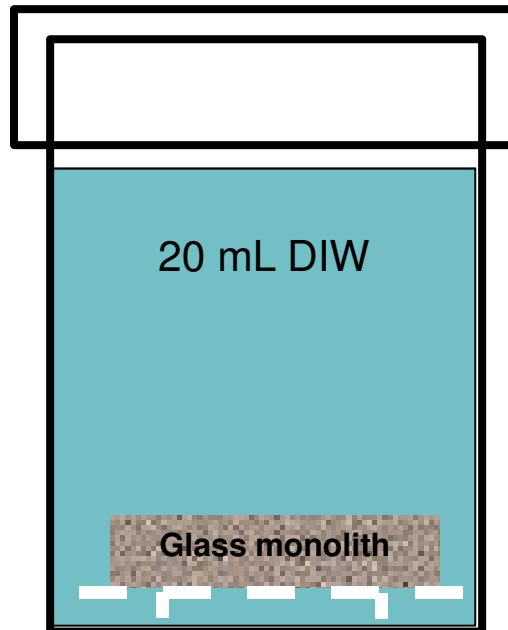


Monolith specimen: 10 cm³ leachant/cm² area ($S/V = 10 \text{ m}^{-1}$)

steel reaction vessel at 90 °C

Batch tests conducted for different durations in DIW buffered at different pH

Analyzed solution for dissolved glass constituents



Measured concentrations were normalized to S/V ratio and mass fraction of element in each glass:

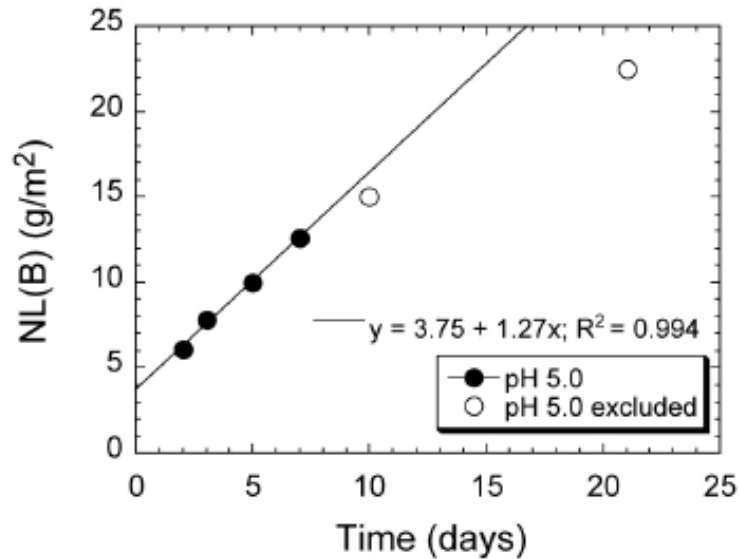
$$NL(i) = \frac{[i]}{(S/V) f(i)}$$

Normalized mass loss $NL(i)$ has units g glass m^{-2} .



Temperature and pH Coefficients Determined from ASTM C1220 Tests with SRL 202G Glass

e.g., 10 m^{-1} ; pH 5.0; $90 \text{ }^\circ\text{C}$

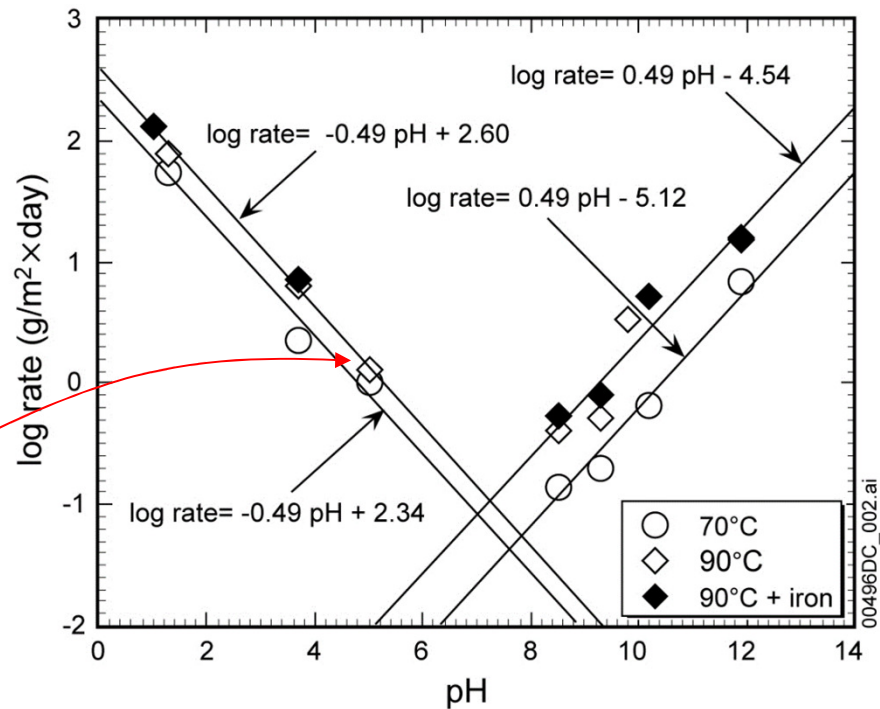


$\log \text{ rate} = \log (1.27) = 0.104$

Dissolution rates were determined graphically as $\Delta \text{NL(B)} / \Delta t$ in units $\text{g glass m}^{-2}\text{d}^{-1}$.

Roll over is due to decreasing affinity term and only solid points were used to determine rate.

pH values were measured at room temperature.



acid leg: $\eta = -0.49$

alkaline leg: $\eta = 0.49$

$E_a = 31 \text{ kJ/m}$

$E_a = 69 \text{ kJ/mol}$



Comparison with Values Derived from Literature Data

Glass	Temperature (°C)	η	E_a (kJ/mol)	Reference
Acidic Solutions				
CSG	25, 50, 70	-0.70	60	Knauss et al. 1990
MW	30, 50, 70, 90	-0.43	32	Abraitis et al. 2000
Binder Glass	40, 70, 90	-0.36	72	Fanning et al. 2003
DOE model		-0.49	31	
Alkaline Solutions				
CSG	40, 70, 90	0.49	85	Knauss et al. 1990 ^a
MW	30, 50, 70, 90	0.43	56	Abraitis et al. 2000
LD6-5412	20, 40, 70, 90	0.40	75	McGrail, et al. 1997
R7T7	90	—	59	Delage and Dussossoy 1991
R7T7	90	0.39	--	Gin et al. 1994
Binder Glass	40, 70, 90	0.64	83	Fanning et al. 2003
DOE model		0.49	69	



Quantify Effect of Glass Composition

- Determined parameter value k_0 for glass composition dependence that is likely to be bounding for all HLW glasses
 - Used data from 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 ASTM C1220 (MCC-1) tests with nine reference glasses to measure glass composition dependence in alkaline solutions
- Deconvolved pH and temperature terms from measured rate to calculate k_0
- Determined how much k_0 varied with glass composition



Glass Composition Dependence k_0 Determined from ASTM C1220 Tests at 90 °C with Several Glasses

Glass	Elemental Mass %					rate NR(B) , g/(m ² ·d)	pH	log ₁₀ (k ₀) [g/(m ² ·d)]
	Al	B	Fe	Na	Si			
LD6-5412	6.82	1.66	0.09	15.0	27.5	0.47	9.3	5.04
Hanford-L	6.33	2.75	4.03	14.8	17.9	0.97	9.5	5.26
Hanford-D	5.36	2.17	16.1	11.7	14.1	1.8	10.5	5.04
WV ref 6'	3.17	4.00	8.41	5.93	19.2	0.69	9.5	5.11
SRL 51S	2.79	2.30	8.53	7.11	26.3	0.66	9.9	4.90
SRL 165U	2.16	2.10	8.21	8.04	24.7	1.0	9.6	5.23
SRL 202U'	2.03	2.48	7.97	6.61	22.9	0.69	9.8	4.97
SRL 131U	1.73	3.00	8.85	8.95	20.4	1.2	9.8	5.21
PNL 76-68	0	2.79	6.41	10.5	19.8	1.1	9.2	5.46

HLW

$$rate_G = k_0 \cdot 10^{\eta pH} \cdot \exp(-E_a/RT)$$

for all 9 glasses: $\log(k_0) = 5.14 \pm 0.17$ (1 σ) relative standard deviation = 3.3%
 for HLW glasses: $\log(k_0) = 5.07 \pm 0.13$ (1 σ) relative standard deviation = 2.6%

Effect of glass composition is taken into account adequately by pH and T terms.



Quantify Effect of Solution Composition

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

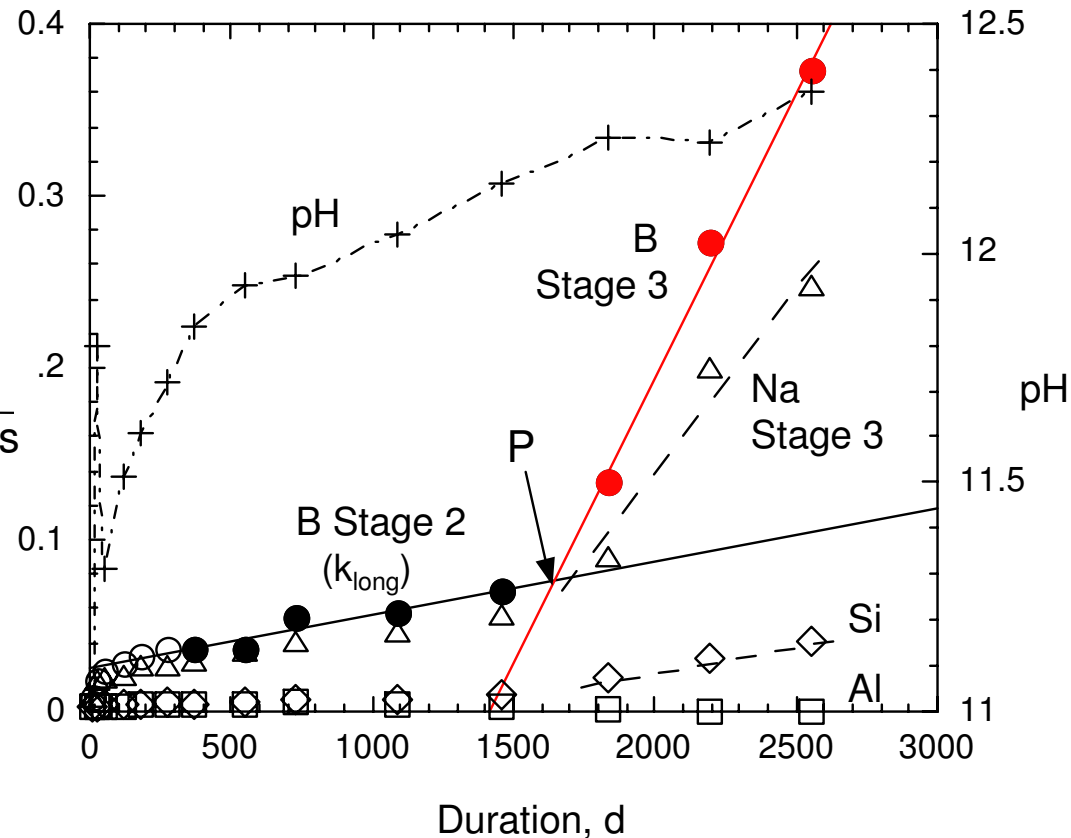
- Value of Q (which is $[H_4SiO_4]$) changes over time as glass, EBS materials, etc. dissolve, alteration phase precipitate, and ground water flows.
- Value of $(1-Q/K)$ and glass dissolution rate change as value of Q changes:
 - For borosilicate waste glasses: $Q = a(H_4SiO_4)$ $K_{glass} = \text{constant}$
 - Glass dissolution rate slows as solution approaches saturation
- Secondary phase formation affects glass dissolution rate



Experimental Observation of Stage 3

Modified PCT
LAW glass LAWA88
demineralized water
 $\sim 2000 \text{ m}^{-1}$
90 °C

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

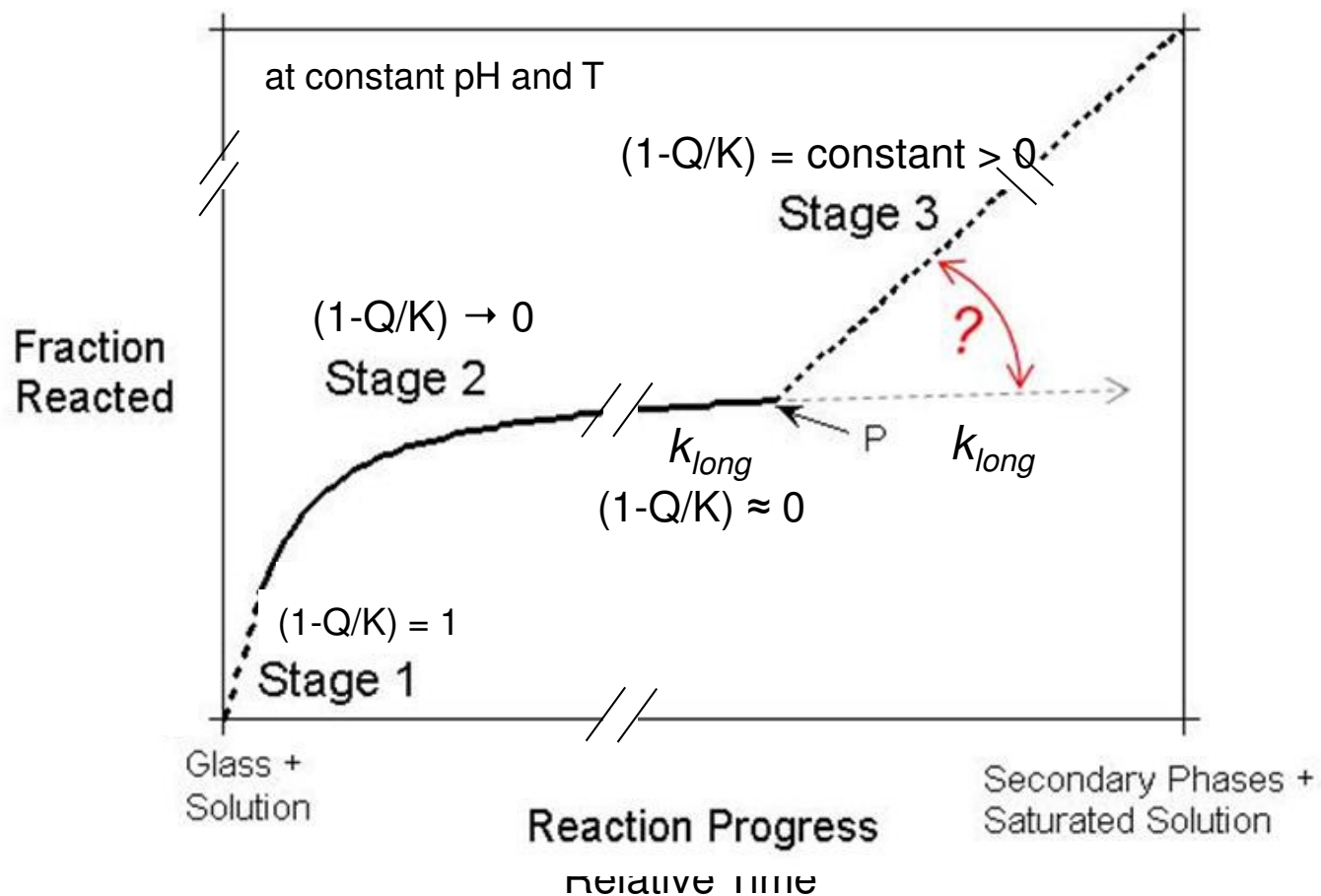


Increases in B, Na, and Si releases are attributed to the generation of secondary phases such as analcime at Point P that affect reaction affinity for glass dissolution.



Reaction Progress Plot

Thermodynamic Representation
of Reaction Affinity



Mass transport limitations are not represented explicitly



- Conditions triggering/controlling Stage 3 rate not fully understood
- Analytical form of affinity term for Stage 3 not known
- Bounding model approach used at that time
- Used lumped term to bound effects of glass composition and reaction affinity
- Potential changes in glass dissolution rate due for Stage 3 processes are bounded in the model by using a probability distribution for rate in alkaline solutions that provides
 - upper rate that bounds possible Stage 3 rates
 - lower rate that bounds residual rates
- Advances in understanding and modeling Stage 3 behavior will be discussed in later talks



Modeling Effects of Solution Composition

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

- Combine dependency on solution composition with glass composition term in one lumped term $k_E = k_0 \cdot (1-Q/K)$

$$acidic\ rate = k_{E, acid} \cdot 10^{-0.49pH} \cdot \exp(-31/RT)$$

$$alkaline\ rate = k_{E, alkaline} \cdot 10^{0.49pH} \cdot \exp(-69/RT)$$

- Maximum and minimum values of k_E were used to bound dissolution rates measured for representative HLW glasses under different test conditions
 - Maximum model rates provide upper bound to measured Stage 3 rates
 - Minimum model rates represent or provide lower bound for k_{long}



- Minimum k_E in **acidic** solutions = $8.41 \times 10^3 \text{ g m}^{-2} \text{ d}^{-1}$
 - based on rates measured in ANL drip tests with a representative DWPF glass made with SRL 165 frit. (Fortner and Bates 1996)
 - Expected to be most probable for acidic solutions.
- Minimum k_E in **alkaline** solutions = $2.82 \times 10^1 \text{ g m}^{-2} \text{ d}^{-1}$
 - derived from rates in vapor hydration tests with representative DWPF and WVDP glasses. (Ebert 2003b)
 - Expected to be most probable for alkaline solutions.
- Maximum k_E in **acidic** solutions = $1.15 \times 10^7 \text{ g m}^{-2} \text{ d}^{-1}$
 - derived from rates in C1220 tests with a representative DWPF glass SRL 202G. (Ebert 2003a)
- Maximum k_E in **alkaline** solutions = $3.47 \times 10^4 \text{ g m}^{-2} \text{ d}^{-1}$
 - based on rates from 7-day PCT results for set of representative DWPF, WVDP, and Hanford glasses. (Ebert 2003a)



Example: Values of $\log k_E$ Derived from Results of 7-d PCT at 90 °C

Glass	NL(B), g/m ²	NR(B), g/(m ² ·d)	pH(room temp)	$\log k_E$, g/(m ² ·d)
SRL 51S a	0.267	0.0381	10.66	3.29
SRL 51S b	0.247	0.0353	10.33	3.42
SRL 165U	0.308	0.0440	10.31	3.52
SRL 202U	0.298	0.0426	10.42	3.45
SRL 131U	4.81	0.687	11.63	4.07
SRL202G	0.608	0.0869	11.11	3.42
WV ref 6	0.270	0.0386	9.98	3.63
Hanford-D	0.361	0.0516	10.67	3.41
PNL 76-68	1.23	0.171	9.43	4.54
Hanford-L	0.475	0.0679	10.96	3.39
LD6-5412	0.082	0.0117	11.20	2.51
EA	8.21	1.17	11.87	4.18

3.36

3.57 ± 0.97 (2σ)

mean + 2σ

$\log_{10} k_E = 4.54$

$k_E = 3.47 \times 10^4 \text{ g m}^{-2} \text{ d}^{-1}$

$$\log_{10} k_E = \log_{10} \text{NR(B)} - 0.49 \times \text{pH} - \log_{10} \left[\exp\left(\frac{-69 \text{ kJ/mol}}{RT}\right) \right]$$



Example: Stage 3 Rates Measured at 90 °C and Derived log k_E Values

Glass	NR(B), g/(m ² ·d)	pH	log k_E , g/(m ² ·d)	Reference	DOE model
					Max. rate g/(m ² ·d)
EA	0.070	12.3	2.75	Ebert et al. 1998	4.35
SRL 131A	0.037	12.1	2.57	Ebert and Bates 1993	3.47
SRL 202A	0.032	12.0	2.55	Ebert and Bates 1993	3.10
SRL 200S	0.87	12.2	3.89	Feng et al. 1993	3.88
SAN60	0.074	9.8	4.00	Patyn et al. 1990	0.09
LD6-5412	0.40	12.0	3.65	Ebert, Bakel, and Brown 1996	1.04

Stage 3 rates are bounded by using the maximum rates calculated with $\log_{10} k_E = 4.54$

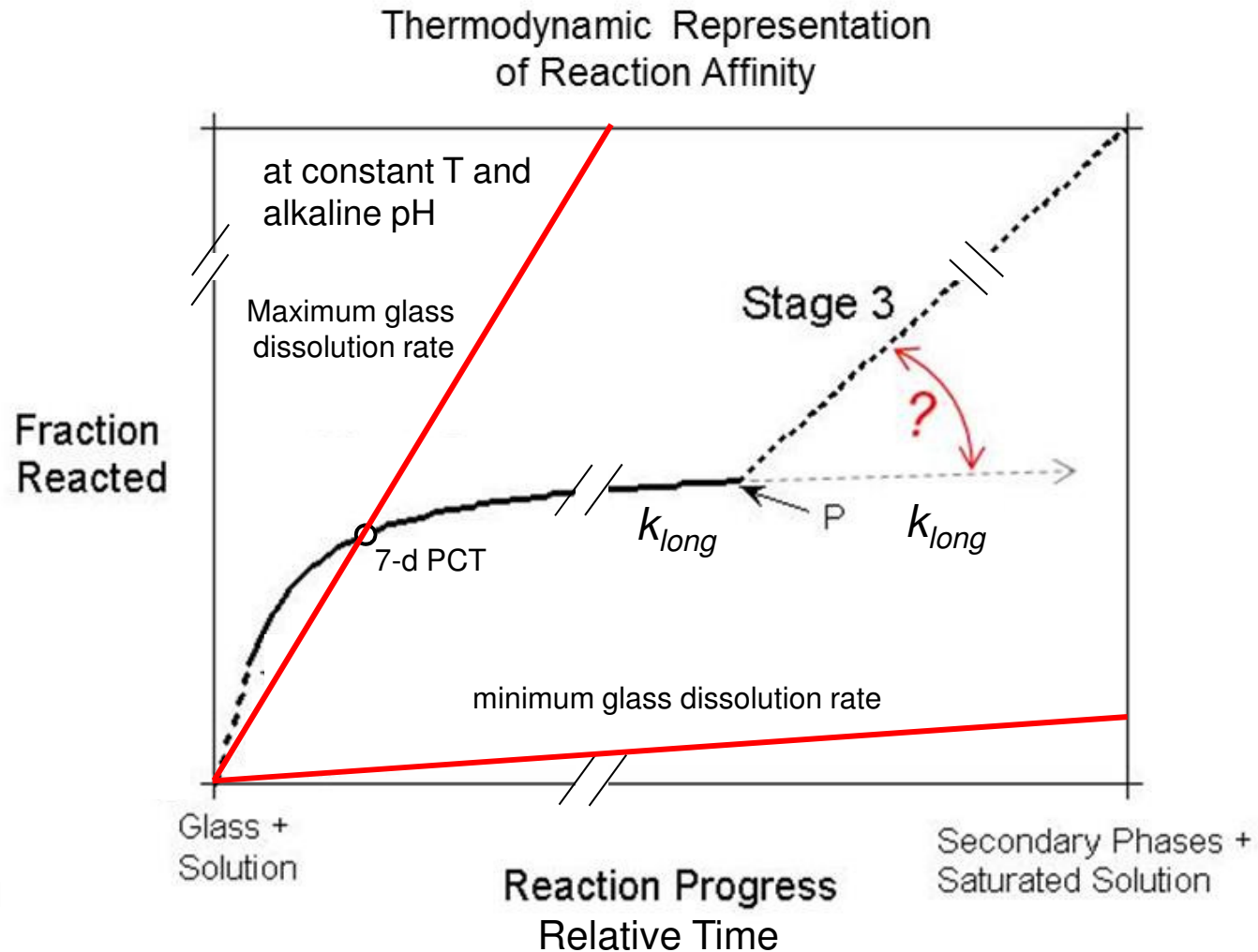
DOE glass model ca. 2004

$$rate_G = k_E \cdot 10^{\eta \text{pH}} \cdot \exp(-E_a/RT)$$

Glass model parameters: k_E, η, E_a
Environmental parameters: pH, T



Maximum and Minimum Model Glass Dissolution Rates in Alkaline Solutions (Illustrative)



Mass transport
limitations are
not represented
explicitly



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- How is the variability in DOE HLW glass composition taken account of in DOE's glass corrosion models?

The effect of glass composition on the corrosion rate is taken into account using an intrinsic rate coefficient, which was determined to be only weakly affected by glass composition. In the bounding model, the glass composition term is lumped with the reaction affinity term and the range of values used for the lumped parameter selected to bound measured dissolution rates.

- How well are the glass corrosion model parameters supported by experimental data?

The glass corrosion model parameter values were derived from appropriate experimental data and shown to be consistent with results available in the literature.

- 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?

The results of short-term, small-scale tests are not extrapolated to represent long-term performance in DOE models. Rather, models are based on technically defensible rate equations and laboratory tests are used to determine model parameter values that bound long-term performance in disposal facilities.



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