Glass Formulation and Durability Studies at the Vitreous State Laboratory

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UNITED STATES
NUCLEAR WASTE TECHNICAL REVIEW BOARD
Summer Board Meeting
Wednesday, June 21, 2017

Overview

- Glass formulation development and testing
- Glass corrosion tests at VSL
- Range of glass compositions
- Resumption and factors affecting time to resumption
- Ion exchange
- Affinity term
- Summary and conclusions

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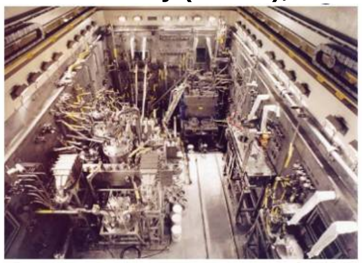
Glass Formulation and Process Development

West Valley (WVDP), NY



SRS – M Area

Sellafield, UK

Savannah River DWPF

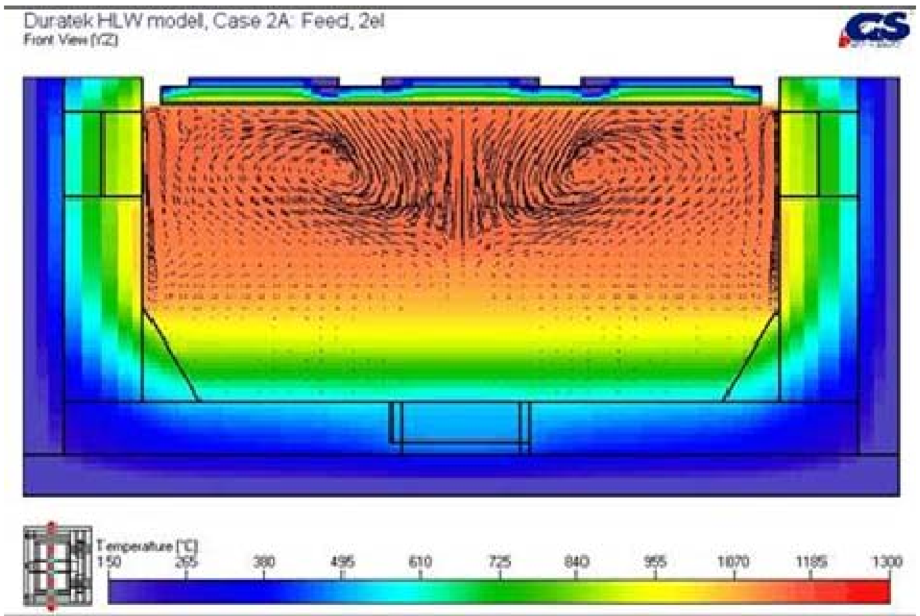
Rokkasho, Japan

- Developed the glass formulations used at WVDP and SRS M-Area
- Support to Hanford WTP since 1996
- Support to Rokkasho since 2005
- Support to DWPF since 2009
- VSL Joule Heated Ceramic Melter (JHCM) Systems:
  - *The largest array of JHCM test systems in the US*
  - *The largest JHCM test platform in the US*

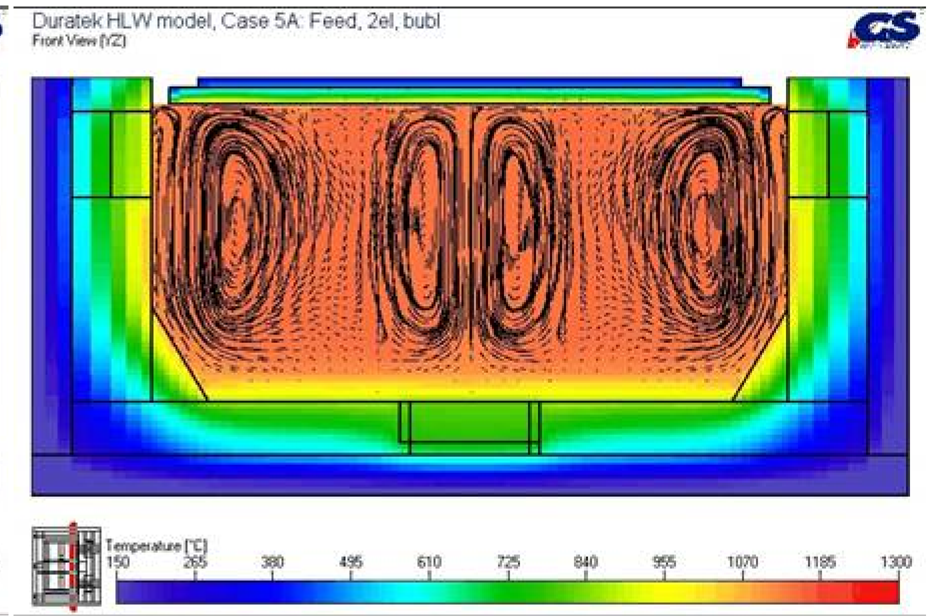
3 scales, 60X scale-up across VSL test melters

Melt Rate Enhancement: Bubblers

- Conventional JHCMs rely on natural convection in a viscous melt
- Melt rate is limited by heat and mass transport at the cold cap
- VSL invented active melt pool mixing using bubbler arrays
- Provides drastic increases in melt rates (up to 5X)
  - Used successfully at SRS M-Area
  - Incorporated into Hanford WTP LAW and HLW melters
  - Retro-fitted into Savannah River DWPF melter



Unagitated JHCM
(West Valley, DWPF pre-2010)



Agitated JHCM
(M-Area, WTP LAW, WTP HLW)

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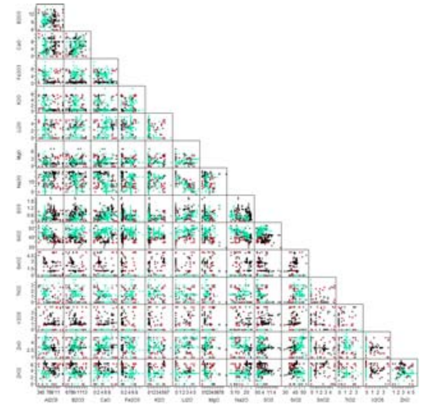
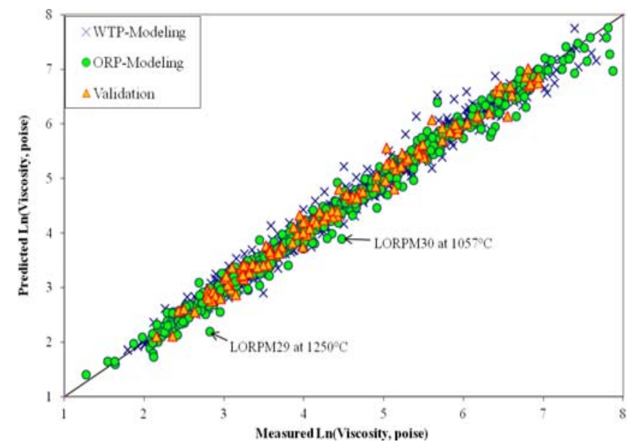
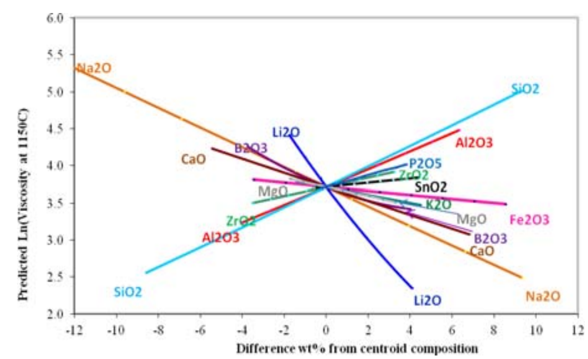
Formulation and Implementation

- West Valley
  - VSL glass formulation, 550,00 kg glass; no bubblers
- SRS M-Area
  - VSL glass formulations, 1,000,00 kg glass; 2X rate boost
- DWPF
  - VSL glass qualification for SB8 and SB9; ~2,400,000 kg glass; 2X rate boost
- WTP LAW Pilot (Atkins)
  - VSL glass formulations, 3,200,000 kg glass; up to 4X rate boost
- WTP HLW Pilot (VSL)
  - VSL glass formulations, 400,000 kg glass; up to 5X rate boost
- WTP HLW
  - VSL baseline and advanced glass formulations
- WTP LAW
  - VSL baseline and advanced glass formulations







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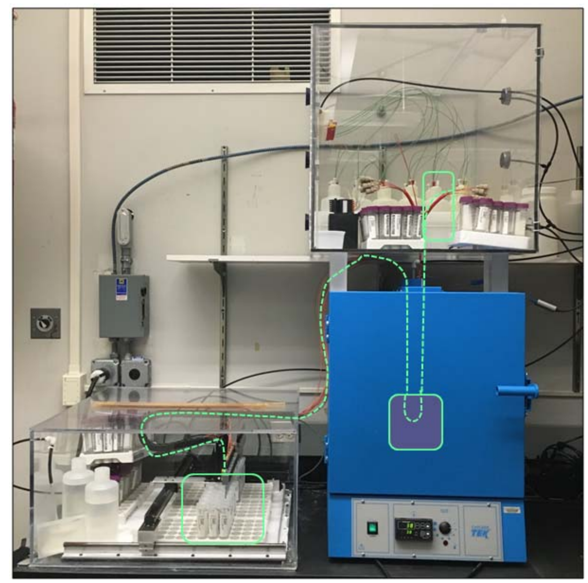
Glass Corrosion Tests Performed at VSL

- Longest running tests started in 1981: 36 years
- Many different test types over wide range of conditions on numerous samples:

  - PCT (ASTM C1285)
  - VHT (ASTM C1662)
  - Pulsed-flow
  - IAEA
  - TCLP (EPA Method 1311)
  - Soxhlet (ISO 16797)
  - SPFT
  - MCC 3
  - MCC 1
  - ANS/ANSI 16.1



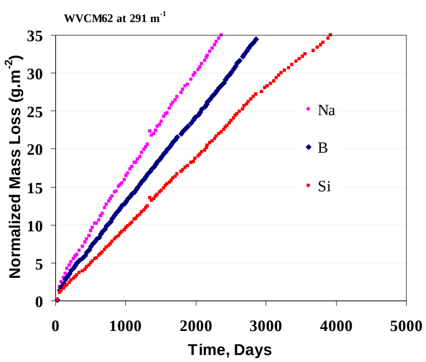
“Pulsed-Flow” Tests

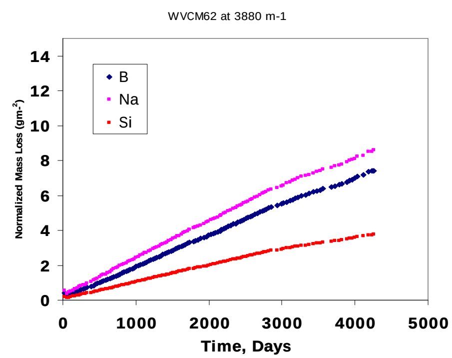
25% replacement pulsed flow tests

- Longest running test started in 1981 (36 yrs)
- 187 samples in triplicate or duplicate
- 40, 55, 70, and 90^{o}C
- 13 S/V ratios between 5 and 3880 m^{-1}
- Powders and monoliths
- DIW and ground waters, including EJ-13
- Replacement intervals of 1, 3, 6, and 12 months
- Teflon and steel vessels
- Includes natural analogs

100% replacement IAEA tests

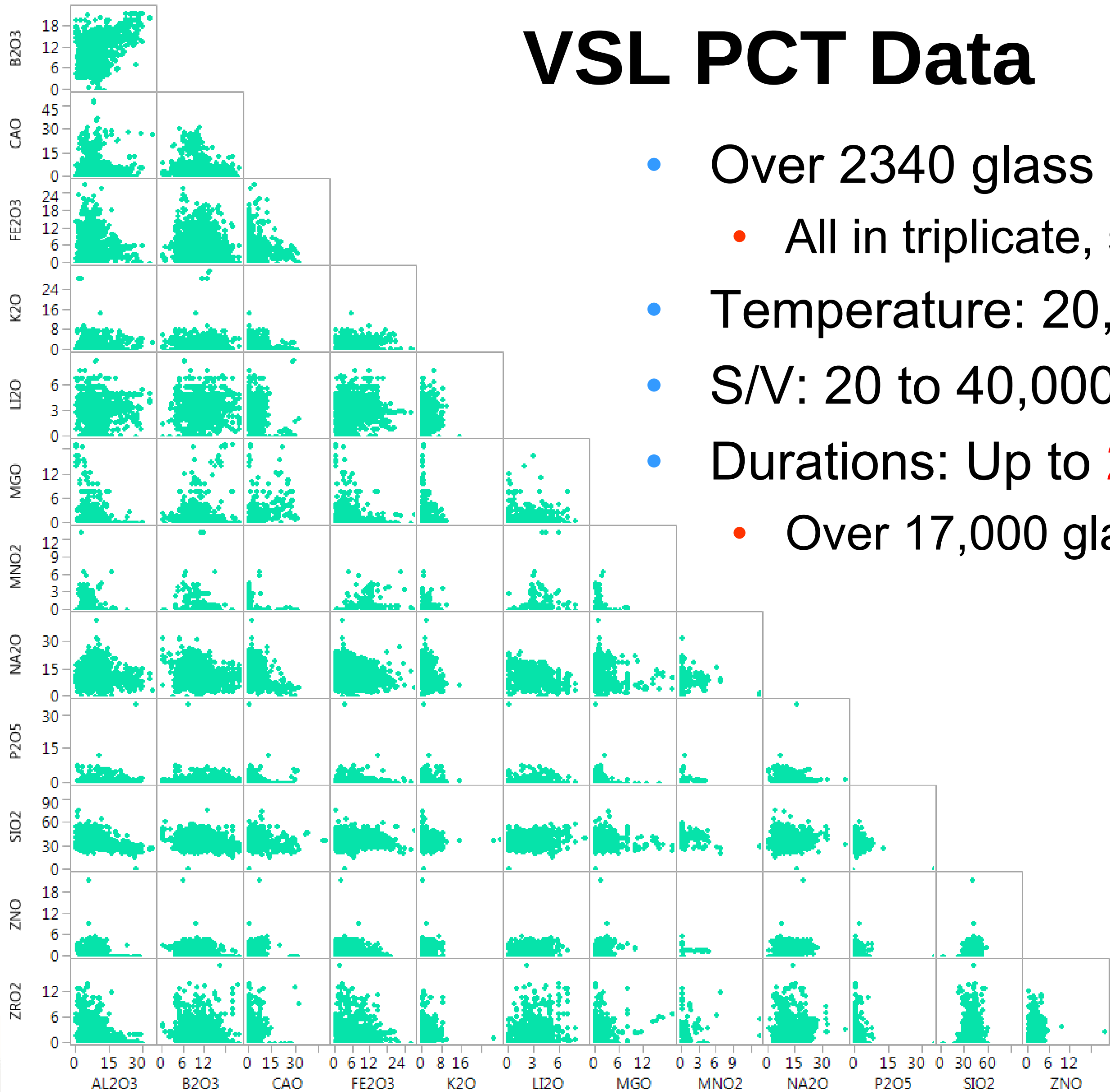
- Longest running test started in 1981 (36 yrs)
- 52 samples in triplicate or duplicate
- 23, 40, 55, 70, and 90^{o}C
- 6 S/V ratios between 6 and 580 m^{-1}
- Powders and monoliths
- DIW
- Replacement intervals of 1, 3, 6, and 12 months
- Teflon vessels





VSL PCT Data

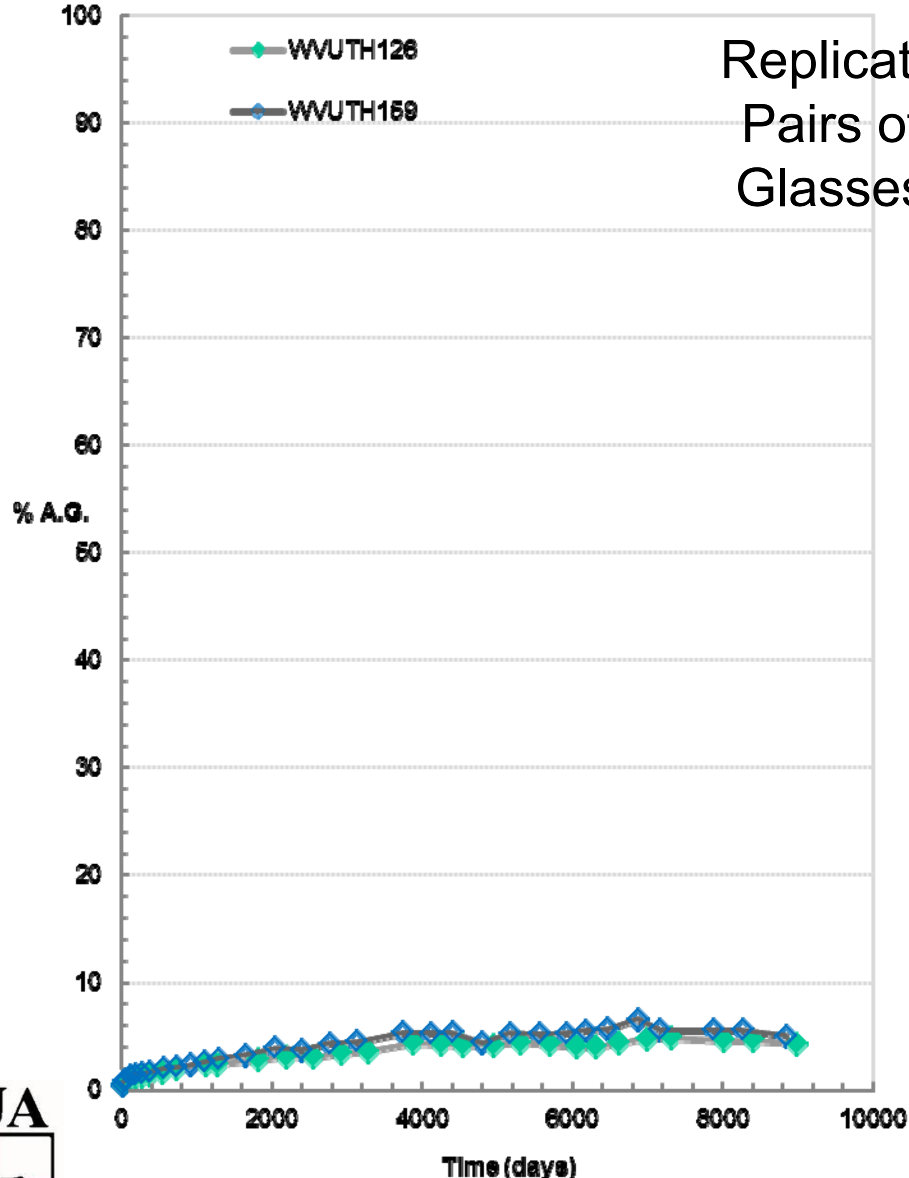
- Over 2340 glass compositions
  - All in triplicate, so over 7000 tests
- Temperature: 20, 40, 90, 120 °C
- S/V: 20 to 40,000 m^{-1}
- Durations: Up to 25 years, ongoing
  - Over 17,000 glass-time points

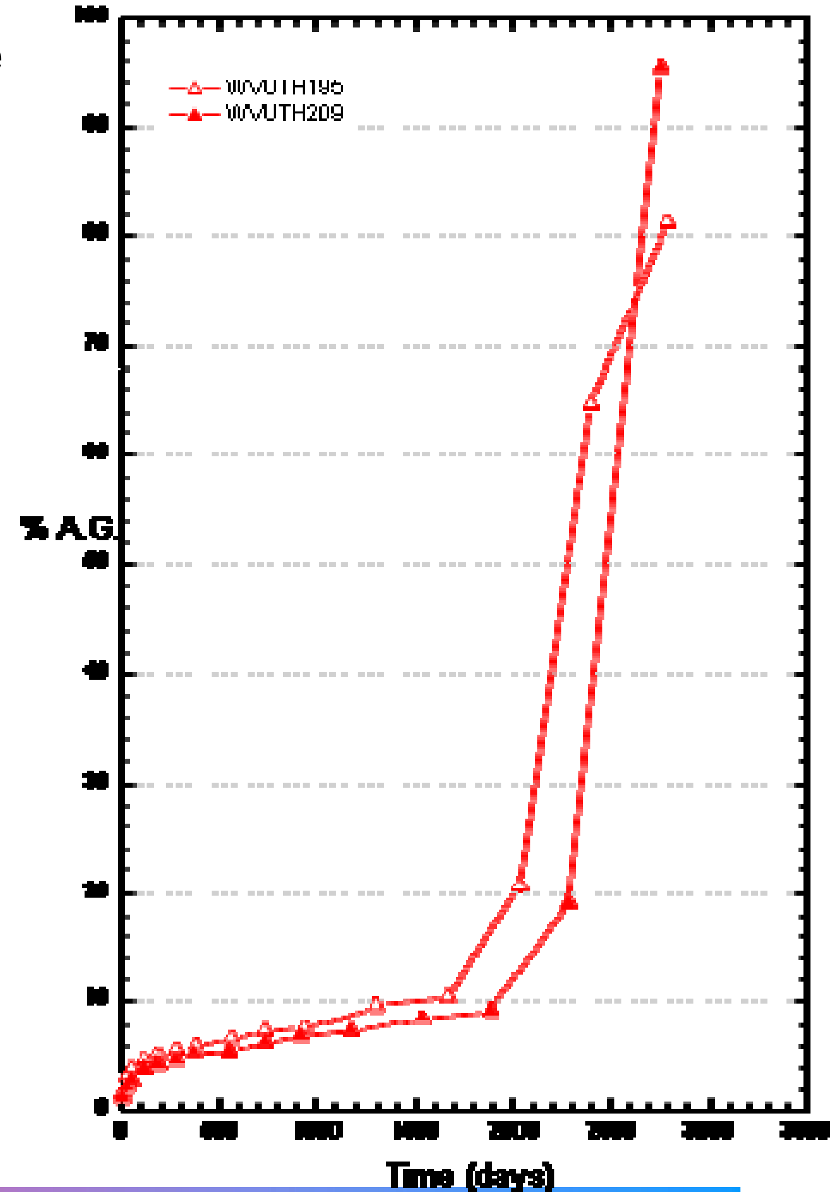


Scatter-plot matrix showing wt% of main glass components only

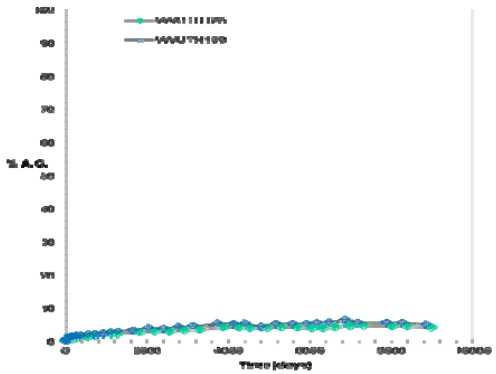
Percent Altered Glass Based on Normalized Boron Concentration

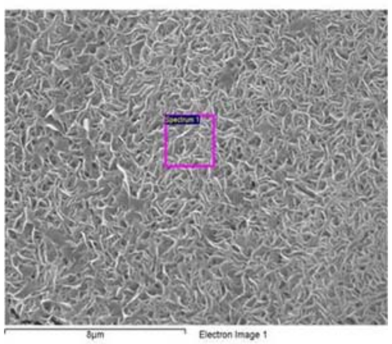
Replicate Pairs of Glasses



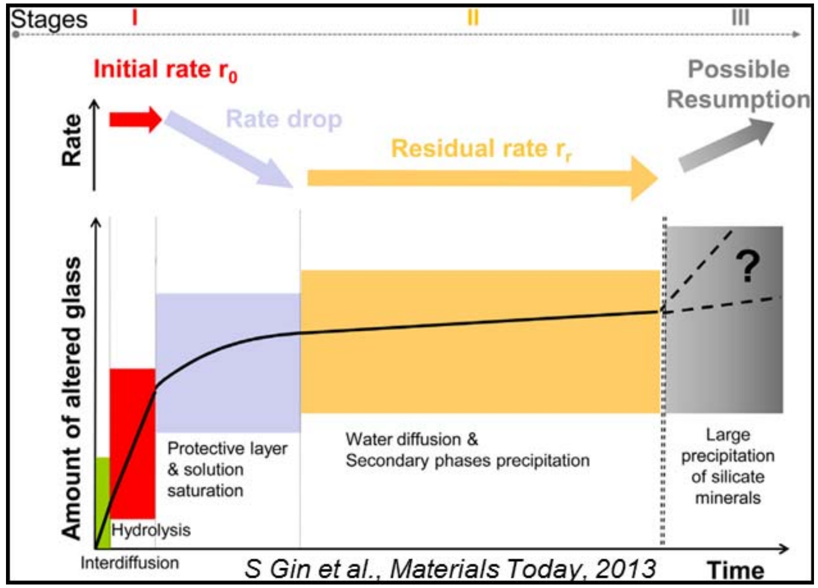


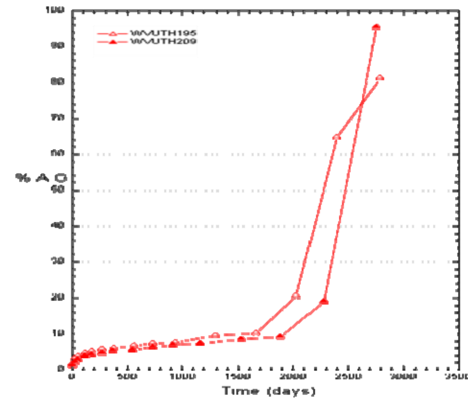
Resumption





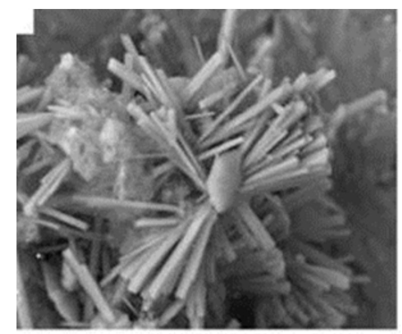
Slow growth of smectite phyllosilicates





For 98 West Valley glasses tested at VSL:

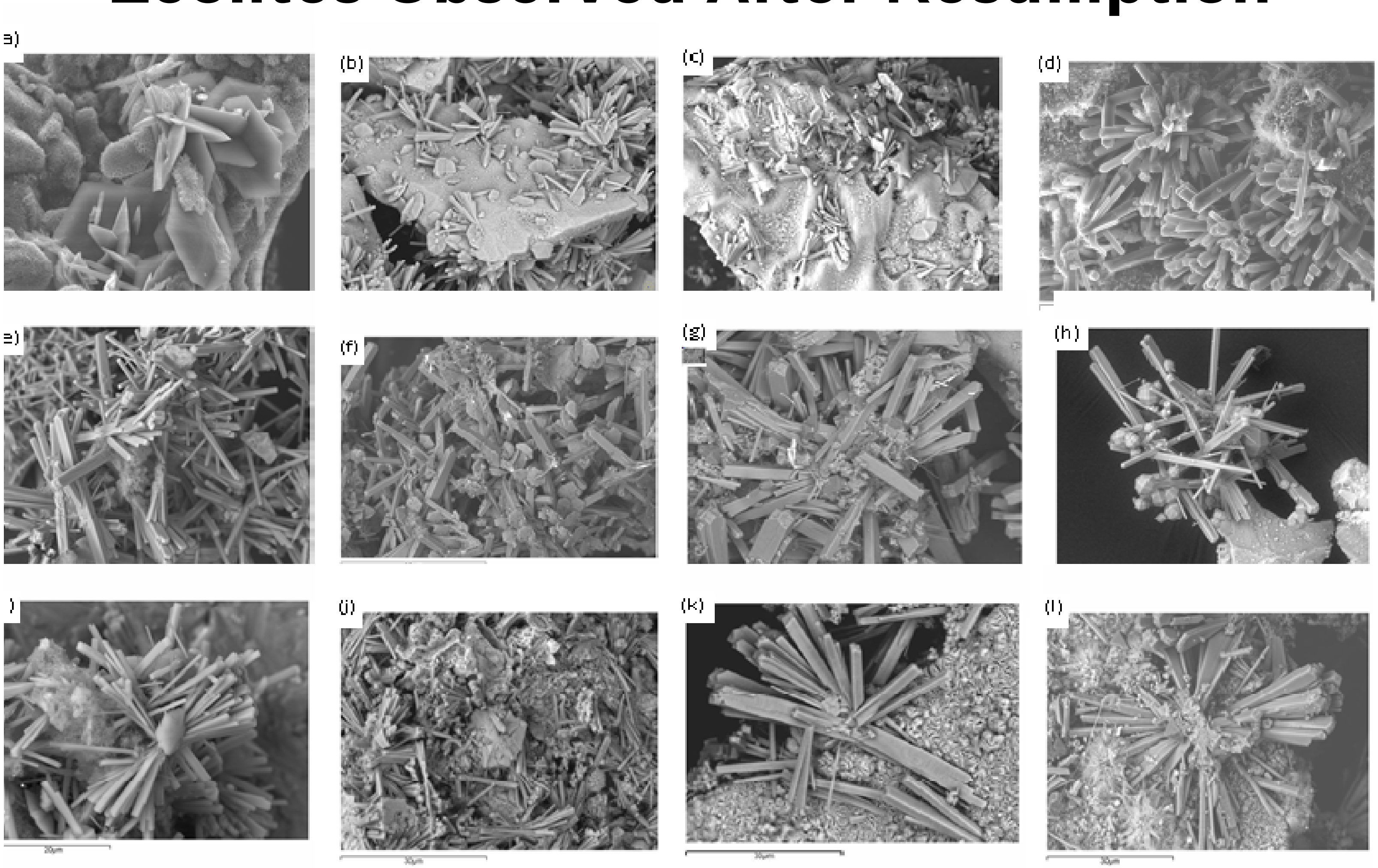
- No resumption was observed below **pH 10.7**
- Almost all of the glasses with a pH above 11 were subject to a resumption of alteration



Zeolites

Ribet, Muller, Pegg, Gin, Frugier, MRS Symp (2004)
Muller, Ribet, Pegg, Gin, Frugier, Ceram Trans (2005)

Zeolites Observed After Resumption

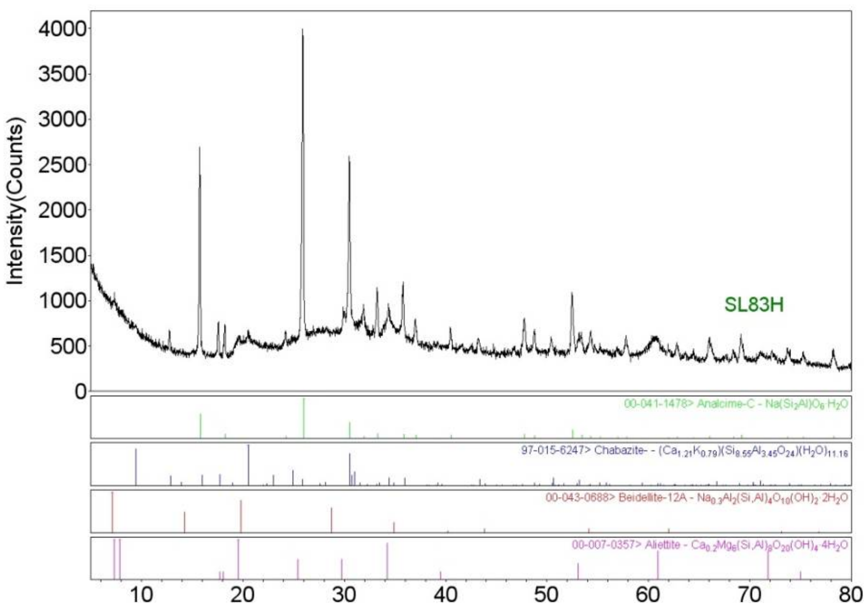


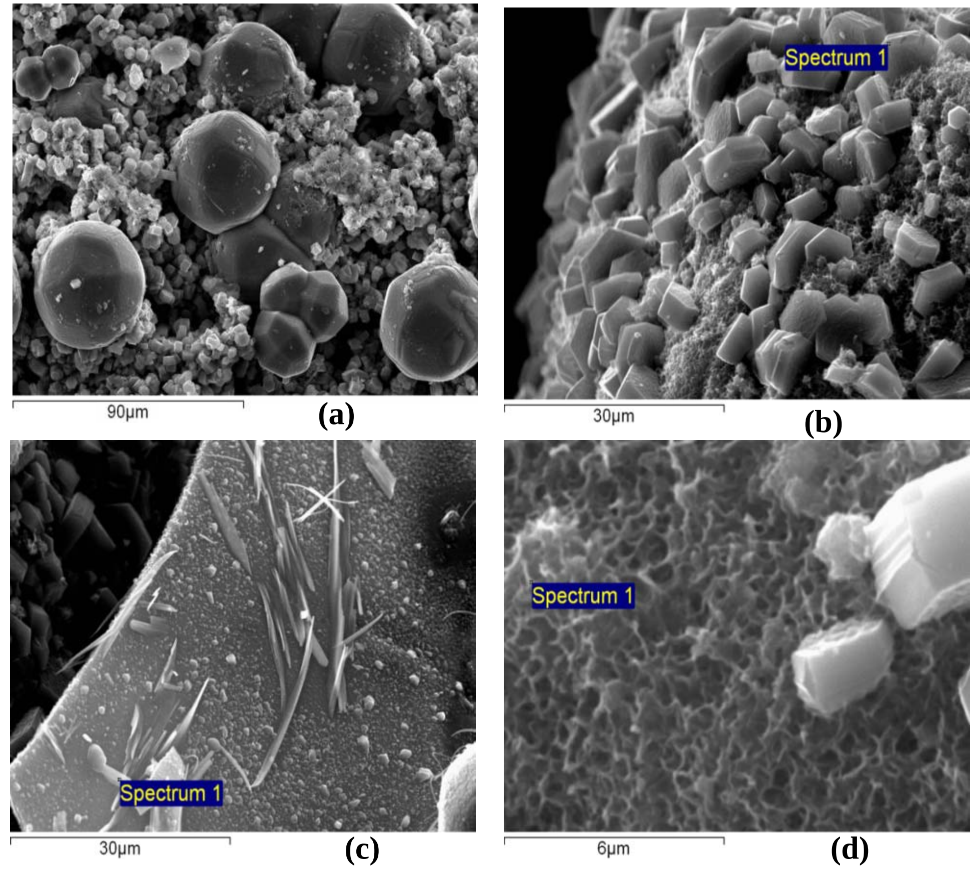
(a) WVUTh198 (b) WVCM59 (c) WVUTh195 (d) WVUTh199 (e) WVUth202 (f) WVUTh191 (g) WVUTh189 (h) WVUTh203 (i) WVUTh194 (j) WVUTh123 (k) WVUTh157 (l) WVUTh208

Muller, Ribet, Pegg, Gin, Frugier, Ceram Trans (2005)

Smectities and Zeolites

Glass LAWA83 at 5915 days after resumption; PCT, 90°C, 2000 m^{-1}





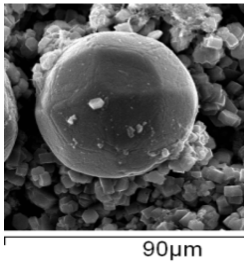
Large *dodecahedral* structures (~ 40 µm) characteristic of analcime (a), a smaller hexagonal layered structure, probably gmelinite, (a, b and d), and acicular (c), and underneath, a phyllosilicate showing a more fibrous morphology (d).

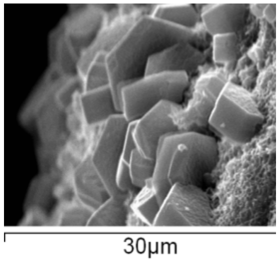
Zeolites and Smectites

Resumption

	Na	Mg	Al	Si	P	K	Ca	Ti	Fe	Zn	Zr	O
LAWA83 im4	1.03	0.01	1.01	2.90	–	0.01	0.01	0.02	0.06	0.03	–	8.0
LAWA83 im5	0.95	–	0.99	2.88	0.04	0.02	0.07	0.01	0.04	0.02	–	8.0
LAWA83 im7	0.87	–	0.91	3.01	–	–	–	0.02	0.10	0.05	–	8.0
LAWA84 im5	0.90	–	0.95	3.00	0.01	0.03	–	0.02	0.04	–	–	8.0
LAWA84 im6	0.92	0.05	0.92	3.00	0.03	0.02	0.02	0.02	0.04	0.02	–	8.0
LAWA127R2 SL33-3 – im7	0.80	0.04	1.04	2.93	–	0.20	–	–	0.05	–	–	8.0
LAWA134 SL33-9 – im6	0.79	0.10	0.79	2.91	–	0.19	0.06	0.03	0.12	0.07	0.04	8.0
	0.82	0.10	0.89	2.90	–	0.19	0.03	0.05	0.09	0.05	–	8.0
LAWA136 SL33-15 – im6	0.76	0.12	0.87	2.95	–	0.19	0.03	–	0.11	0.05	–	8.0
	0.80	0.10	0.96	2.91	–	0.19	–	–	0.10	0.04	–	8.0

Empirical formula similar to $Na(Al,Si)Si_2O_8$ including traces of Ti, Fe and Zn,
Compatible with any zeolite formula such as $(Na_{(1-x\ y-z)}Fe_xZn_yTi_z)_4[Al_4Si_8O_{24}].n(H_2O)$



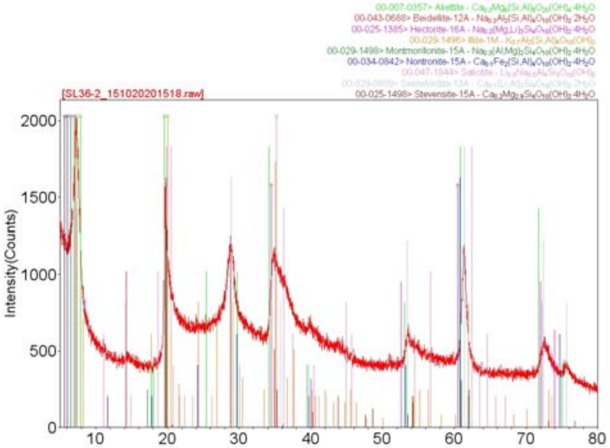


Si/Al ~ 3

No Resumption

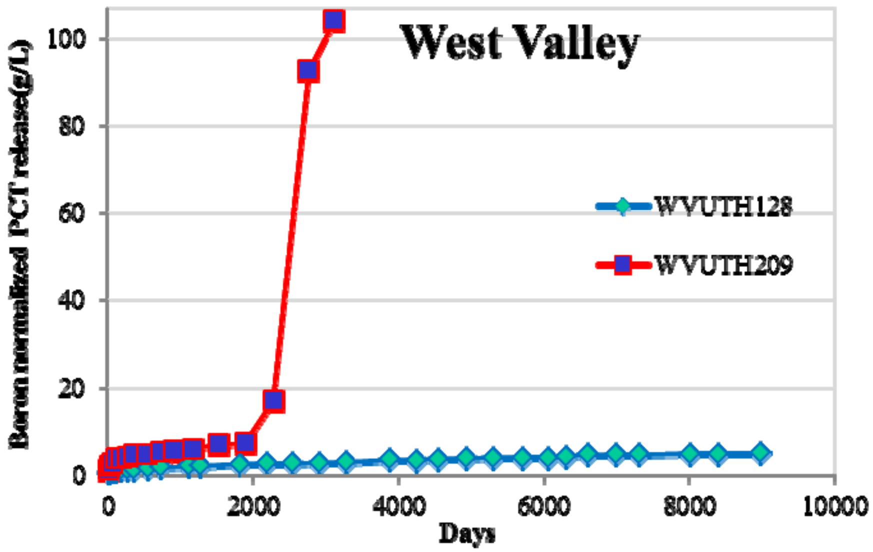
	Na	Mg	Al	Si	K	Ca	Ti	Fe	Zn	O
A100CC-im2 Empirical formula on avg.	0.55	0.23	0.40	3.91	–	0.03	0.06	0.51	0.36	10.0
$Na_{0.5}Mg_{0.2}Fe_{0.5}Zn_{0.4}Al_{0.4}Si_4O_{10}$ (as well as $K_{0.04}$ not shown)										
	Na	Mg	Al	Si	K	Ca	Ti	Fe	Zn	O
LAWB94 im6	–	0.49	0.65	3.96	–	0.05	0.04	0.25	0.26	10.0
LAWB94 im2	–	0.41	0.66	3.94	–	0.05	0.04	0.26	0.30	10.0
$(Mg_{0.5}Fe_{0.3}\ Zn_{0.3})Al_{0.7}Si_4O_{10}$ (trace Ca and Ti) could also contain lithium that is not detectable by EDS										
	Na	Mg	Al	Si	K	Ca	Ti	Fe	Zn	O
LAWA127R2 SL333-6 im6	–	0.89	0.28	3.54	0.39	0.08	0.09	0.74	0.46	10.0
$K_{0.4}Mg_{0.9}Fe_{0.7}Zn_{0.5}Al_{0.3}Si_4O_{10}$										
	Na	Mg	Al	Si	K	Ca	Ti	Fe	Zn	O
LAWA135 SL33-12 – im3	–	0.76	0.38	3.55	0.29	0.06	0.11	0.60	0.44	10.0
$K_{0.3}Mg_{0.8}Fe_{0.6}Zn_{0.4})Al_{0.4}Si_{3.6}O_{10}$ (trace Ca and Ti) + Zr (0.06 to 0.1 at%)										
	Na	Mg	Al	Si	K	Ca	Ti	Fe	Zn	O
LAWA136 SL33-15 – im6	0.75	0.66	0.40	3.44	0.26	0.08	0.13	0.55	0.39	10.0
$(Na_{0.8}K_{0.3}Mg_{0.6}Fe_{0.5}Zn_{0.3})Al_{0.4}Si_{3.5}O_{10}$ (trace Ca and Ti) + Zr (0.05 to 0.1 at%)										

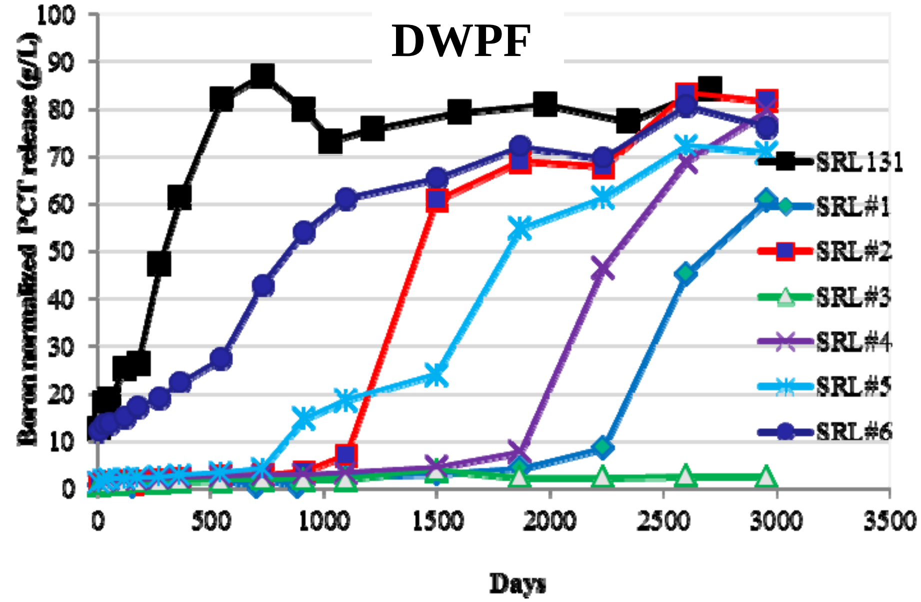
Si/Al ~ 8 - 12

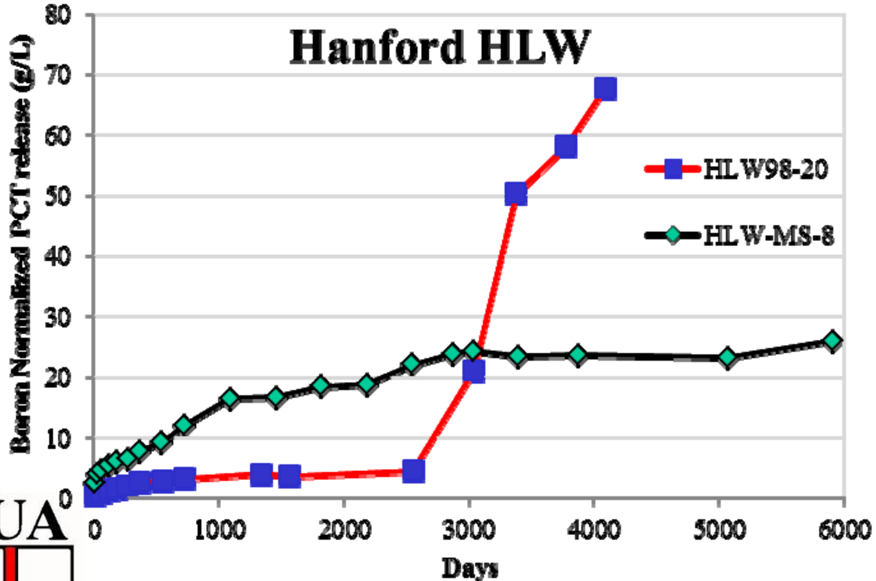


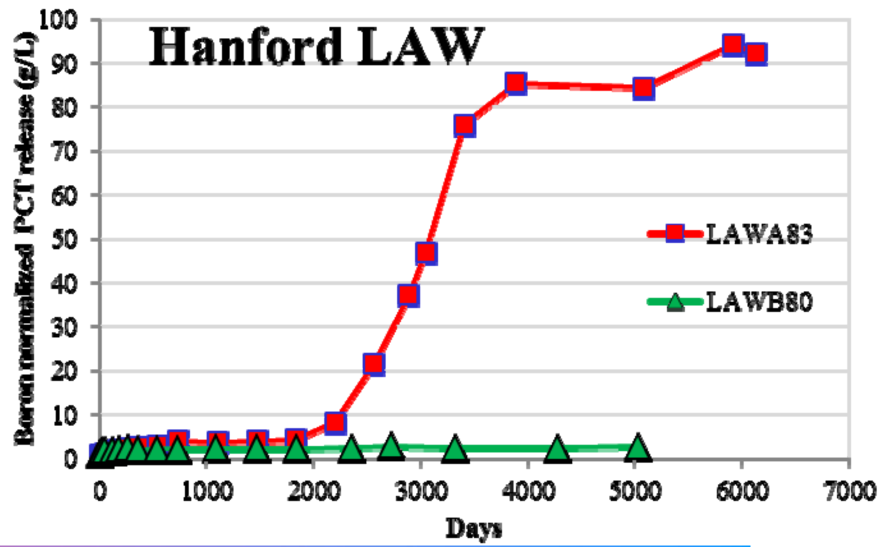
VSL-17R4090-1, 2017

Resumption Occurs in Many Types of Waste Glasses









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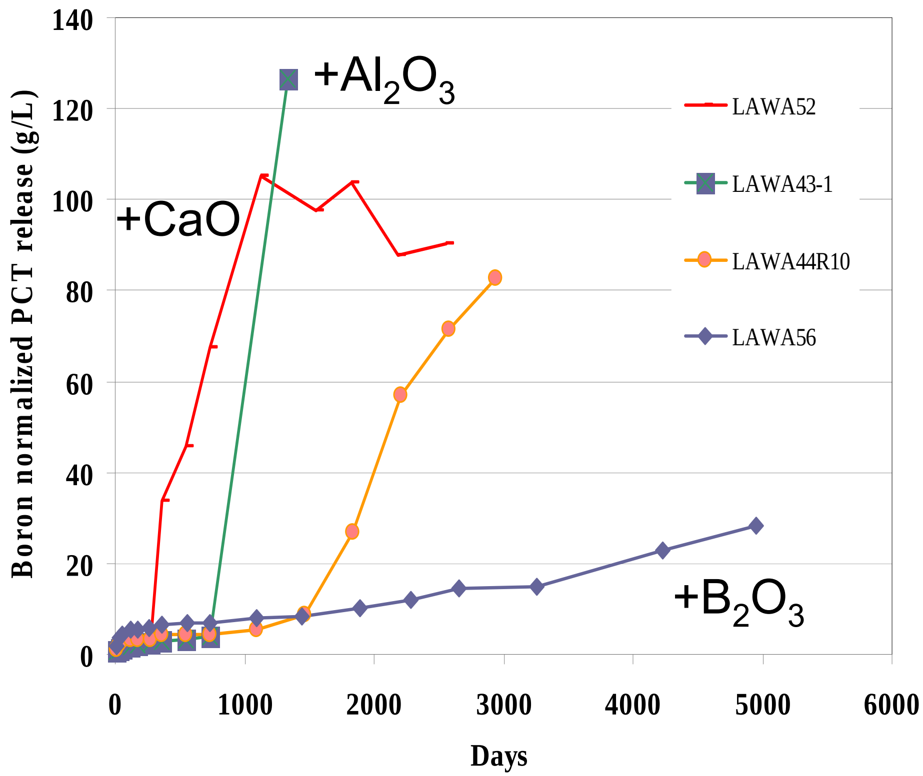
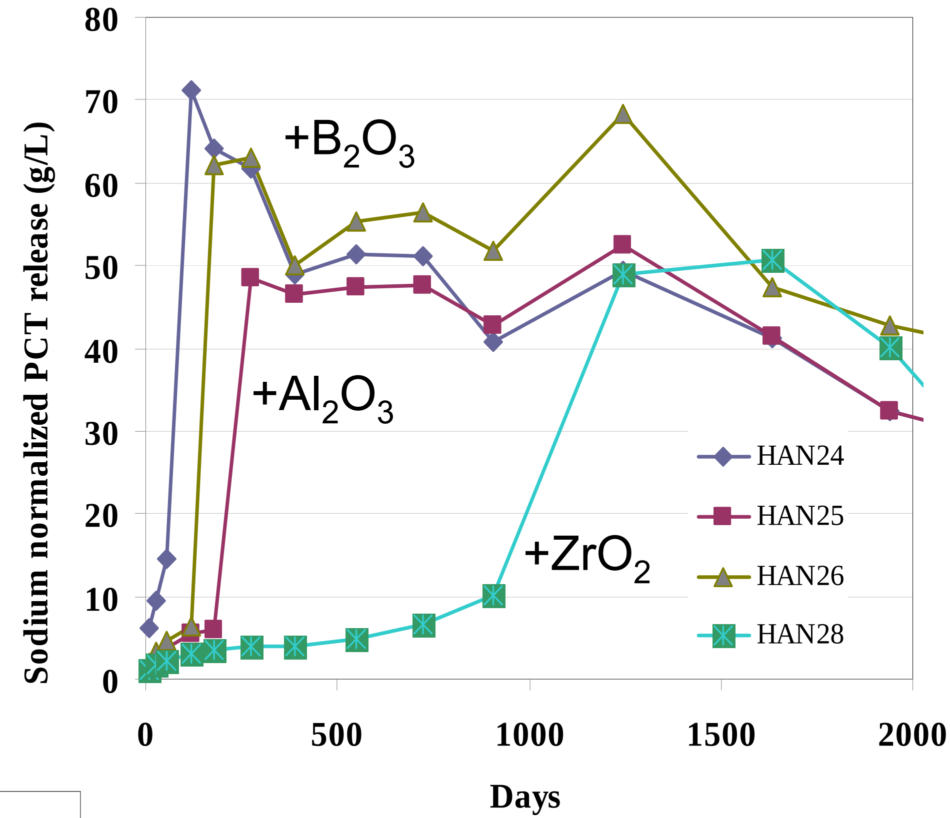
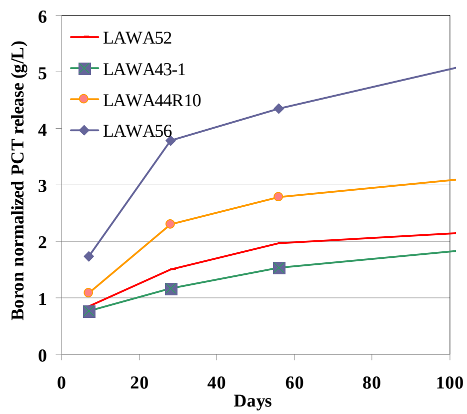
Factors Affecting Resumption: Glass Composition





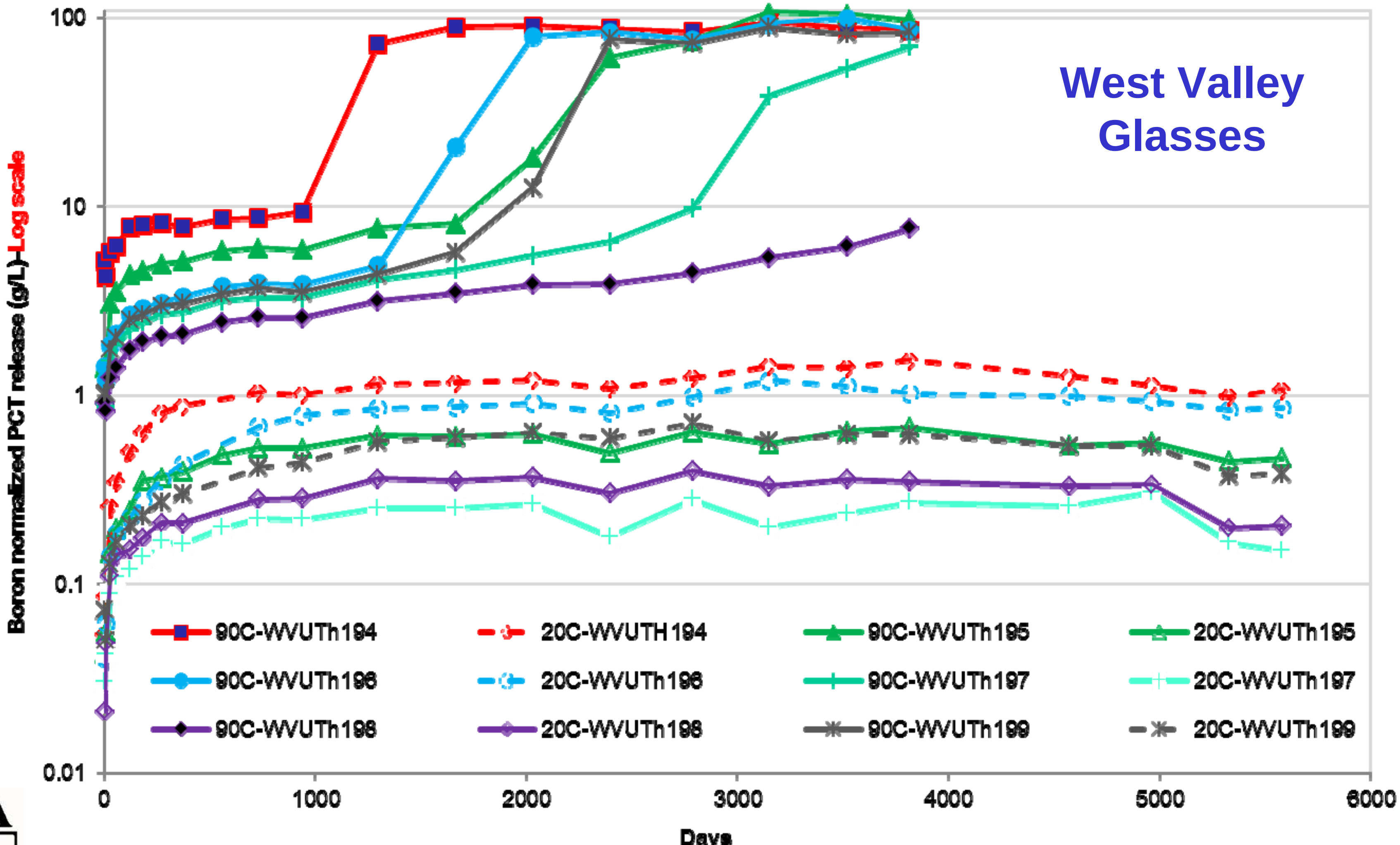
VSL-11R2270-1, 2011



Mazur, Muller, Gan, Buechele, Lai, Pegg, DOE/CH-9601, (1996)
Buechele, Lai, Pegg, Ceram Trans (2000)

Factors Affecting Resumption: Temperature

Resumption observed at 90ºC but not yet at 20ºC



Factors Affecting Resumption: Temperature

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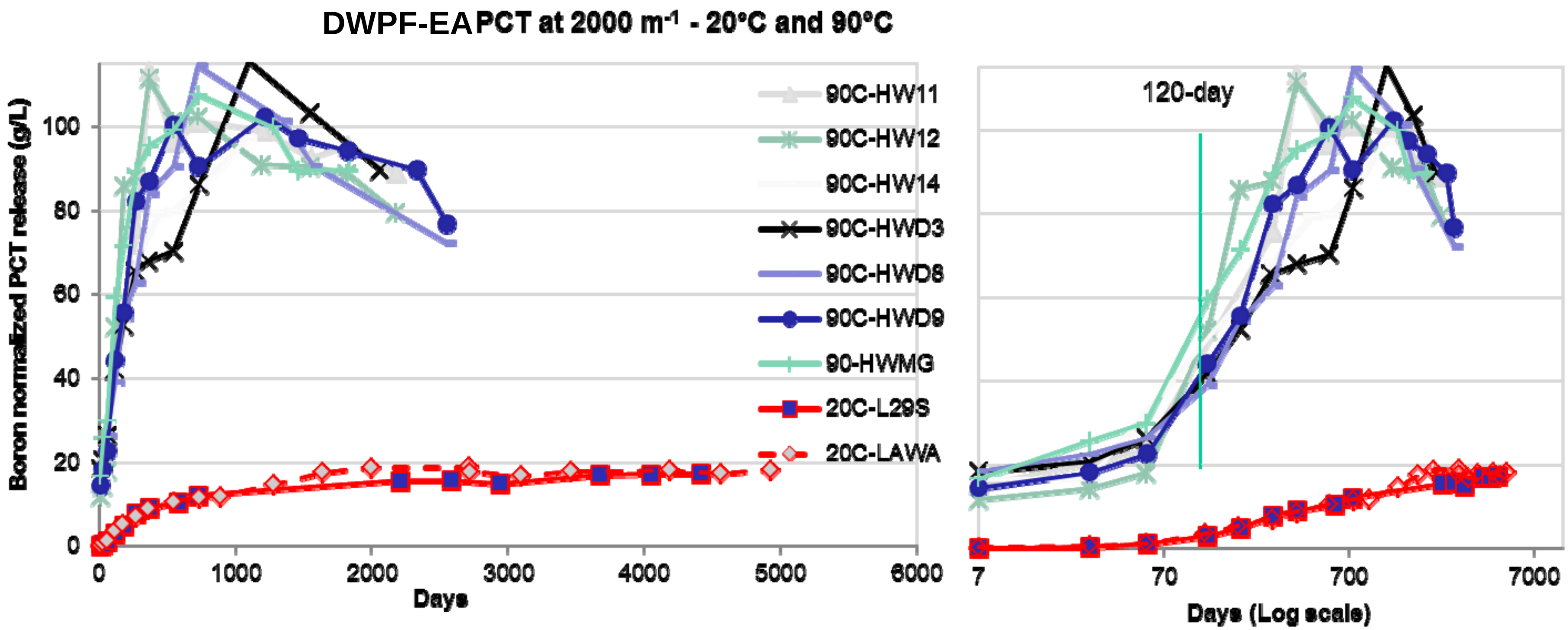
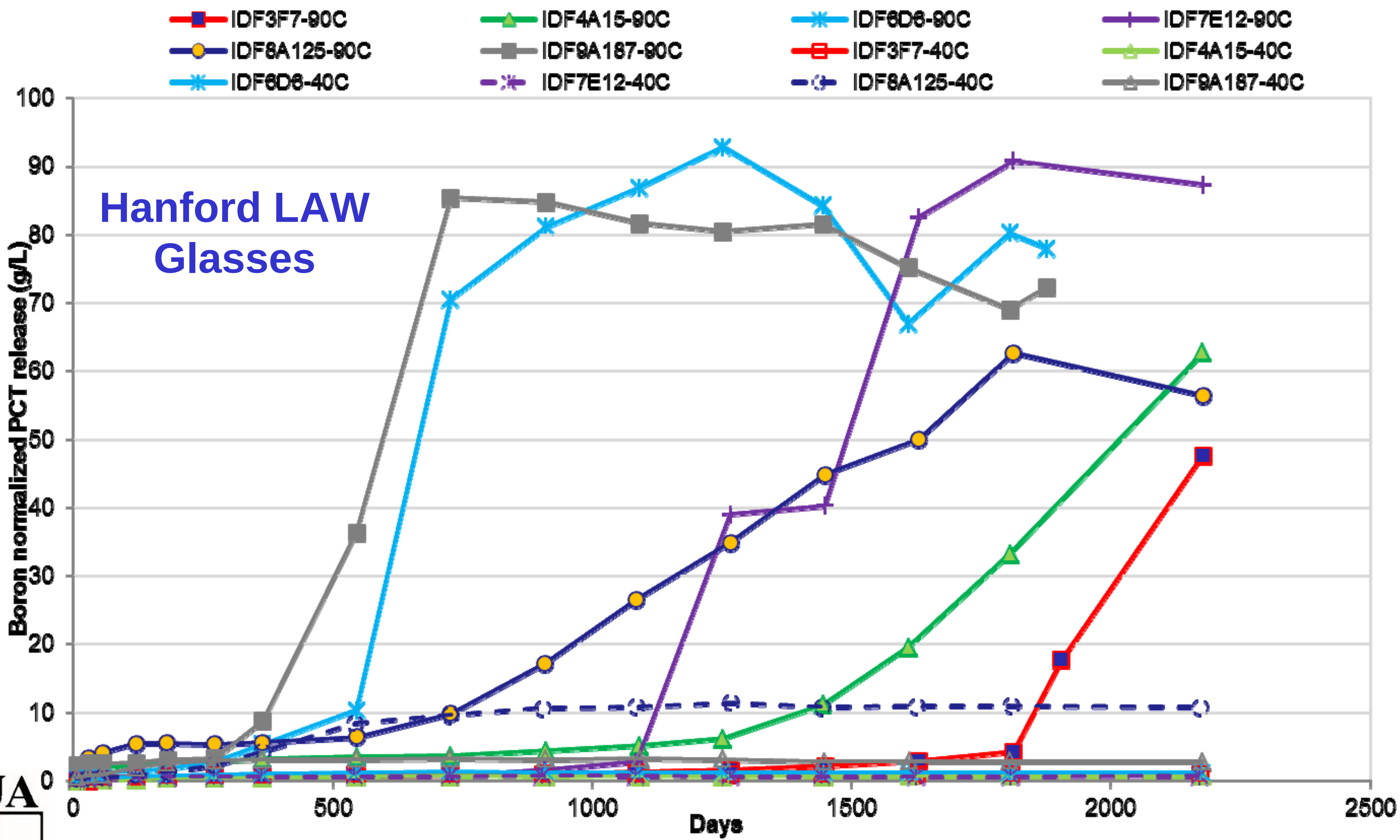


DWPF Glasses

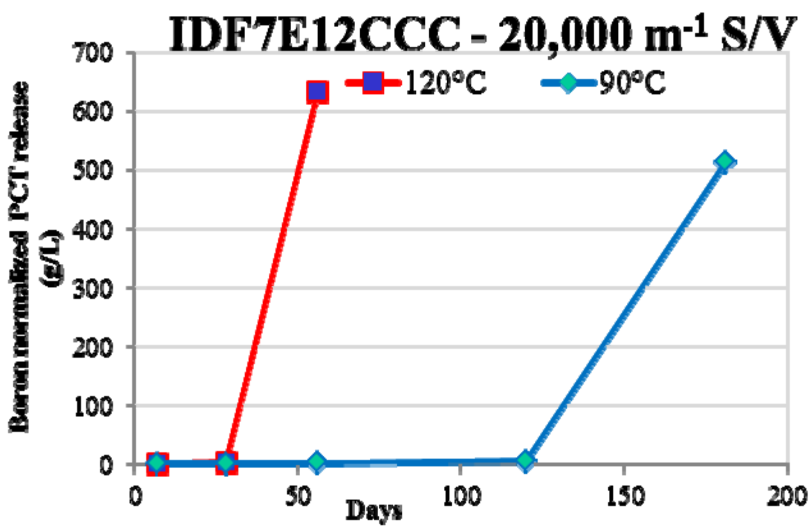
Factors Affecting Resumption: Temperature

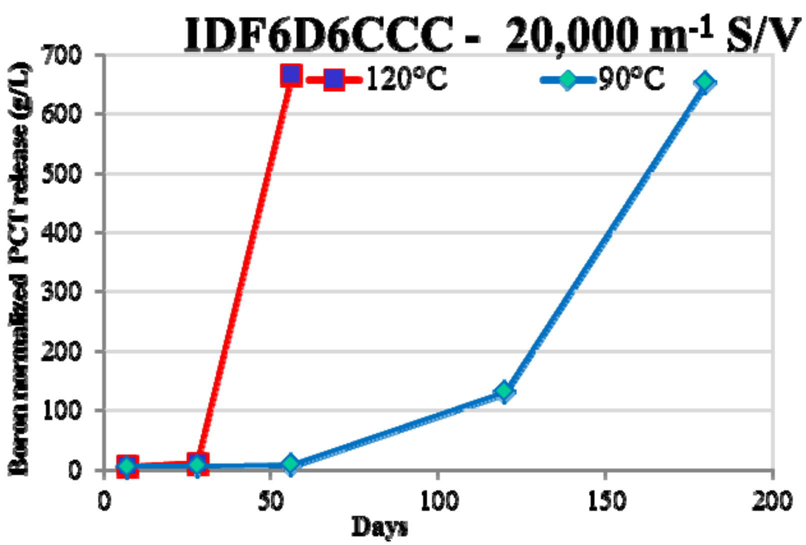
Resumption observed at 90°C but not yet at 40°C



Factors Affecting Resumption: Temperature

Resumption observed at 120^{o}C and at 90^{o}C



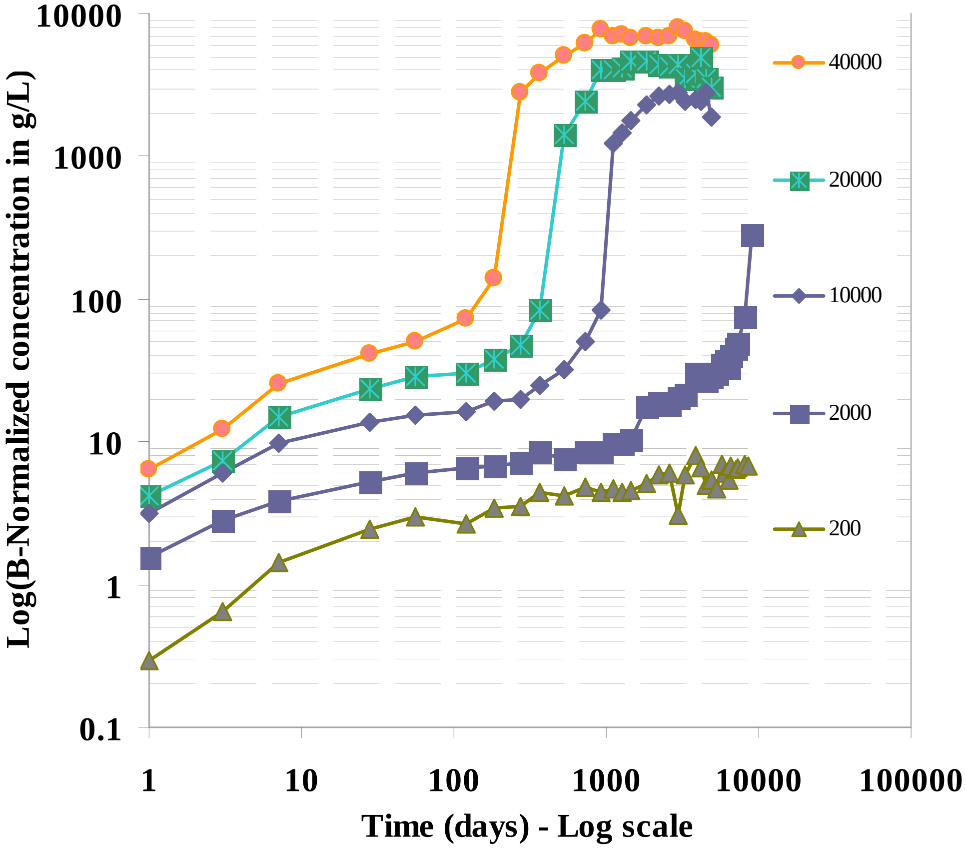


Temperature Dependence of Resumption

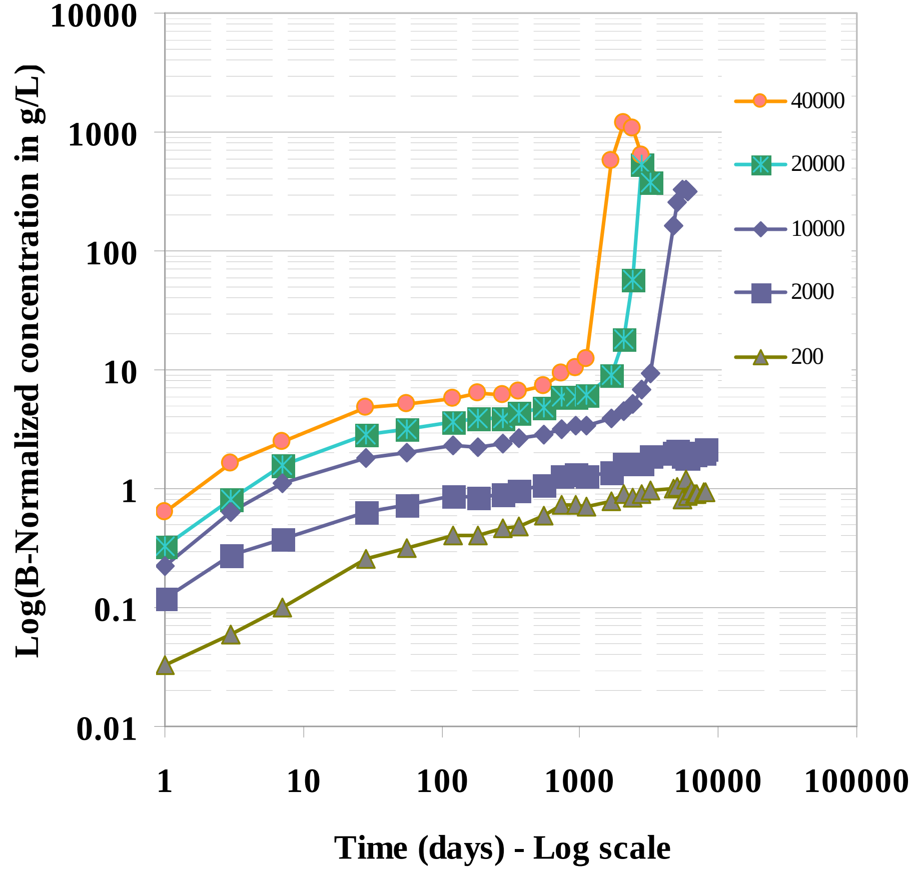
- Important factor for projections to repository scenarios
- With caveats, an effective "Activation Energy" for resumption can be estimated from each of the above data data sets:
  - WV, 90 & 20^{o}C > (8 – 22) kJ/mol
  - DWPF, 90 & 20^{o}C > 57 kJ/mol
  - LAW, 90 & 40^{o}C > (11 – 38) kJ/mol
  - LAW, 120 & 90^{o}C 60 kJ/mol

Factors Affecting Resumption: S/V

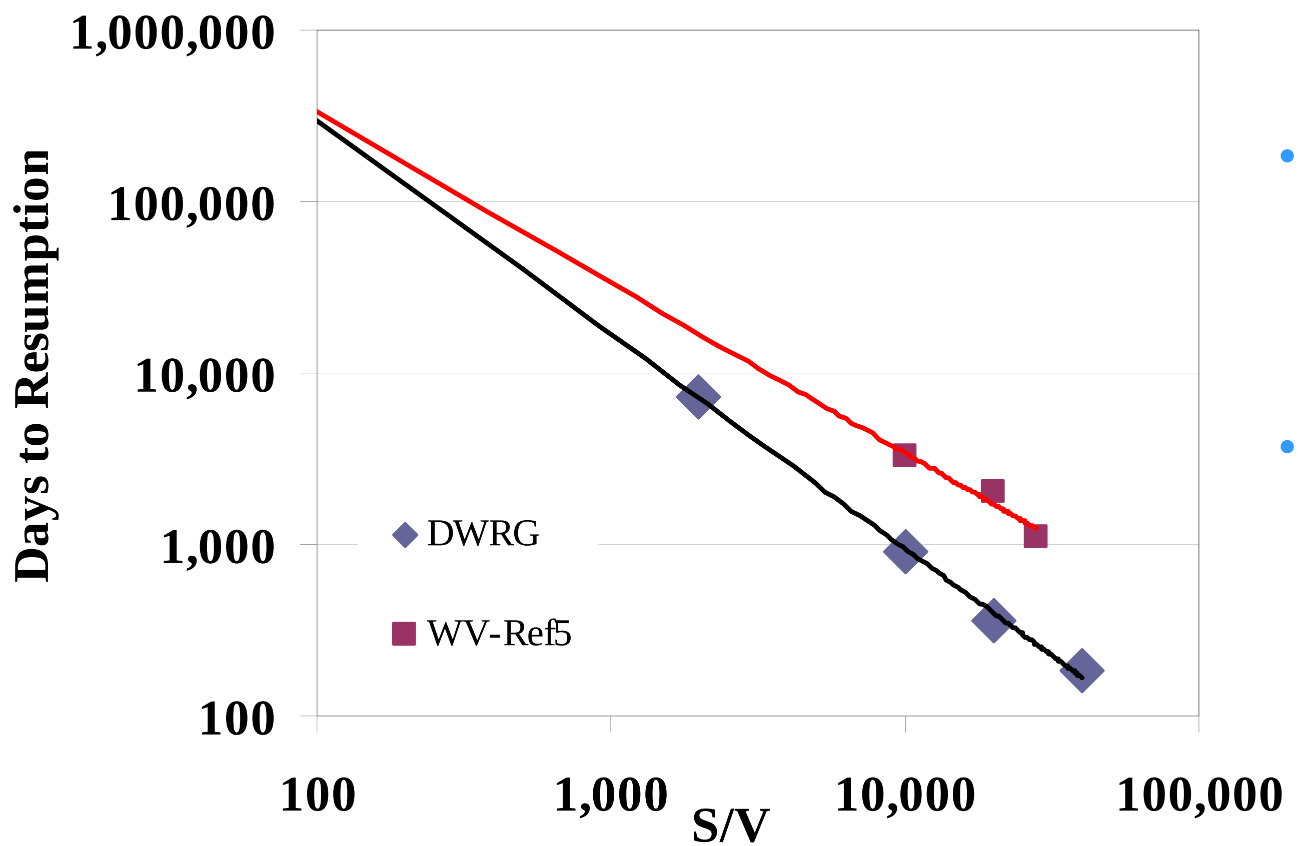
DWPF DWRG at various S/V (m^{-1})



WV Ref 5 at various S/V (m^{-1})

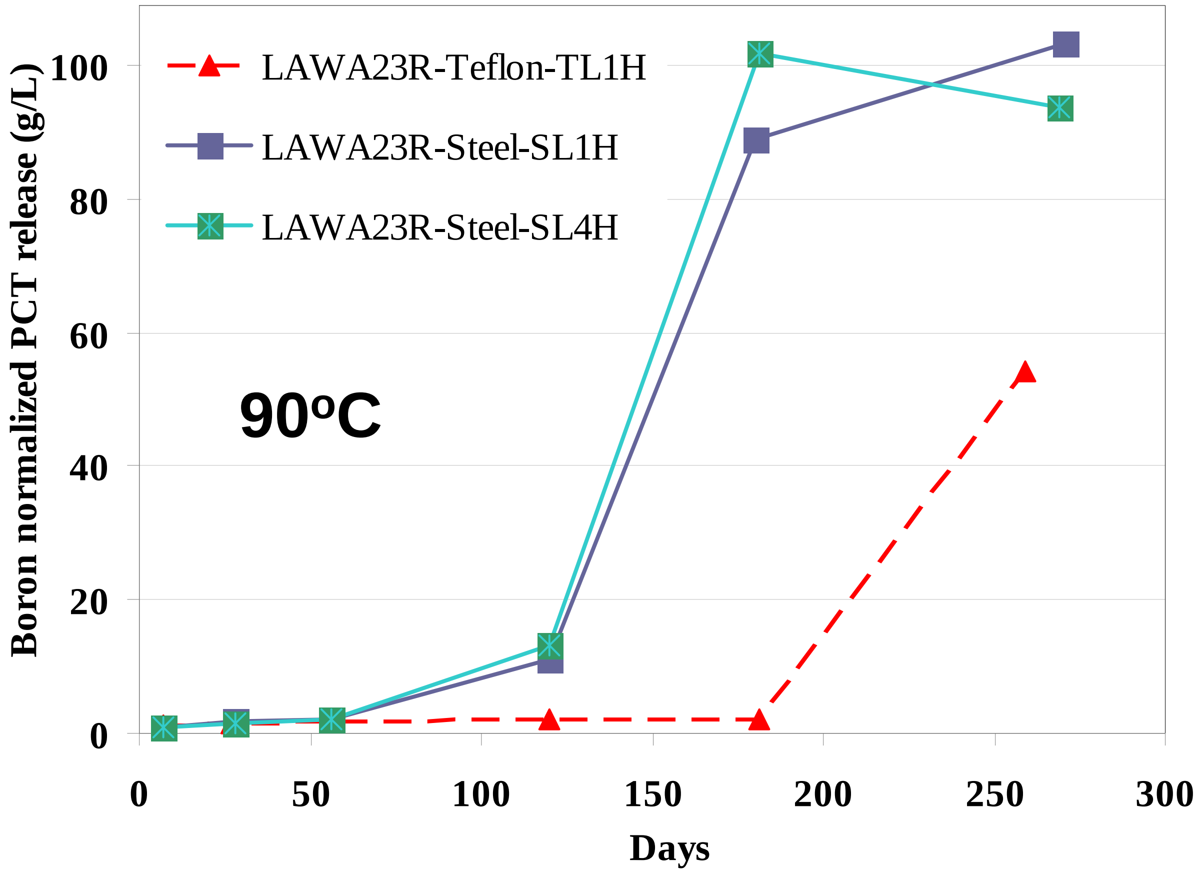


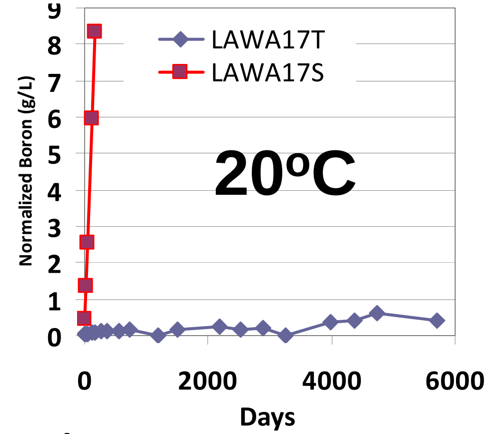
Factors Affecting Resumption: S/V

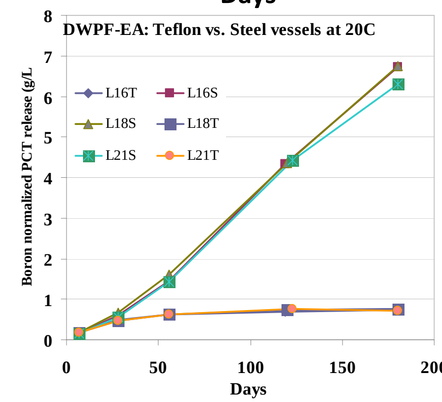


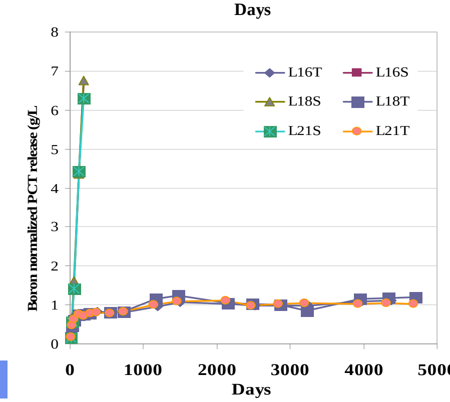
- Power law dependence of time to resumption on S/V
- Exponent is about 0.99 (WV) to 1.25 (DWRG)

Factors Affecting Resumption: Buffering









Teflon vessels are permeable to CO_2, which buffers the solution and delays resumption

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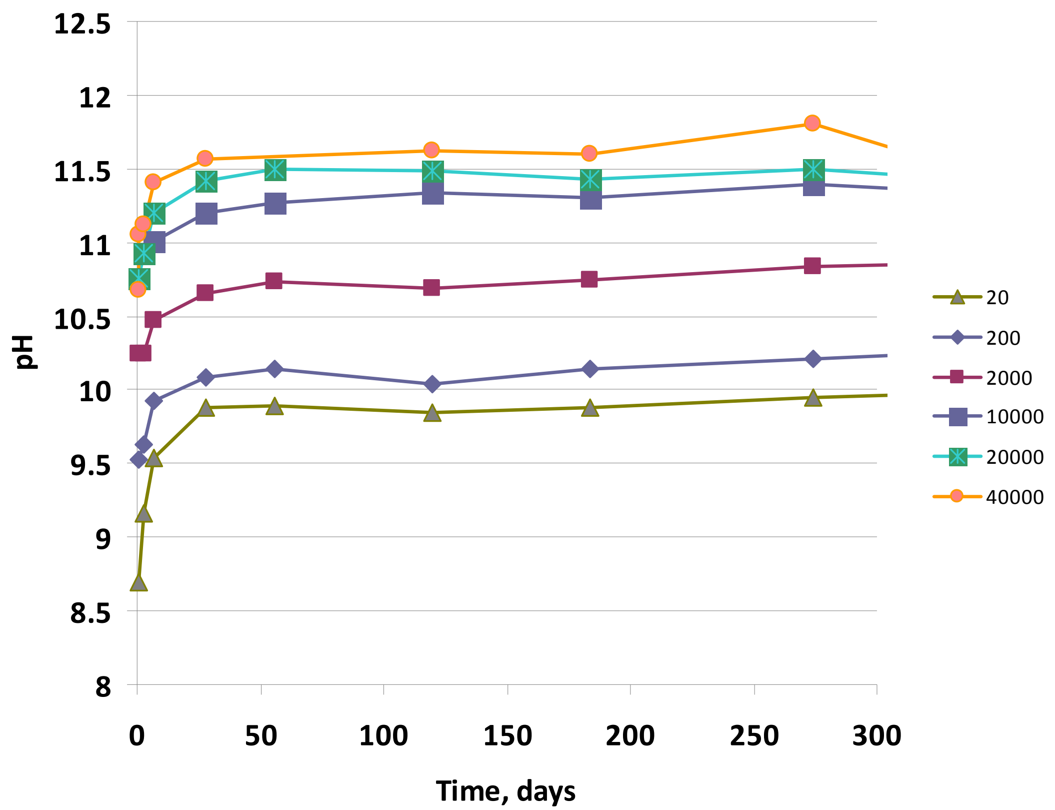
Effect of S/V on Leachate pH



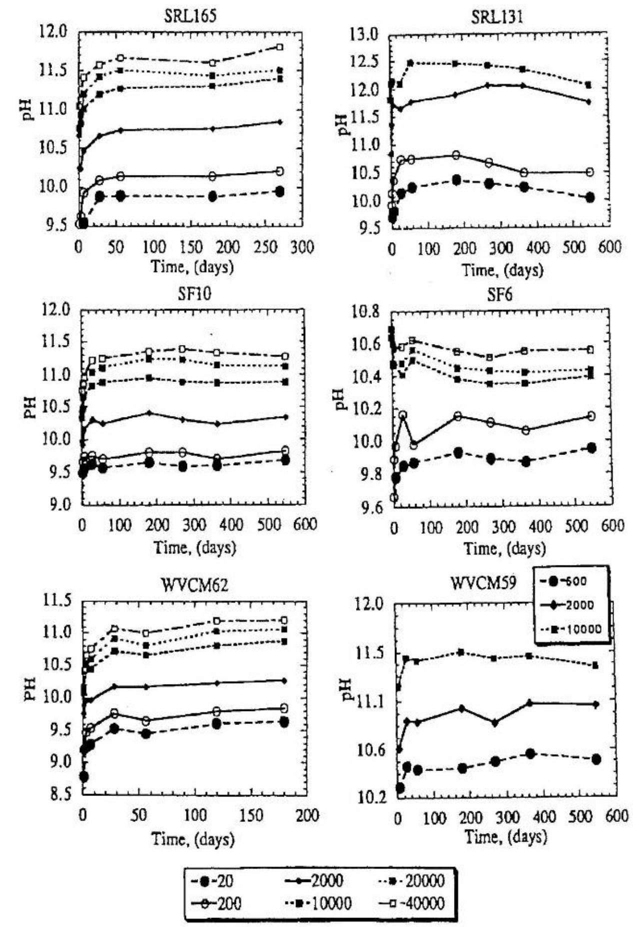


Fig. 1. Leachate pH data versus time showing the effects of S/V. The experimental uncertainty in the measured pH values is about 0.06 units.

Feng and Pegg, JNCS (1994)

Model for Effect of S/V on Leachate pH

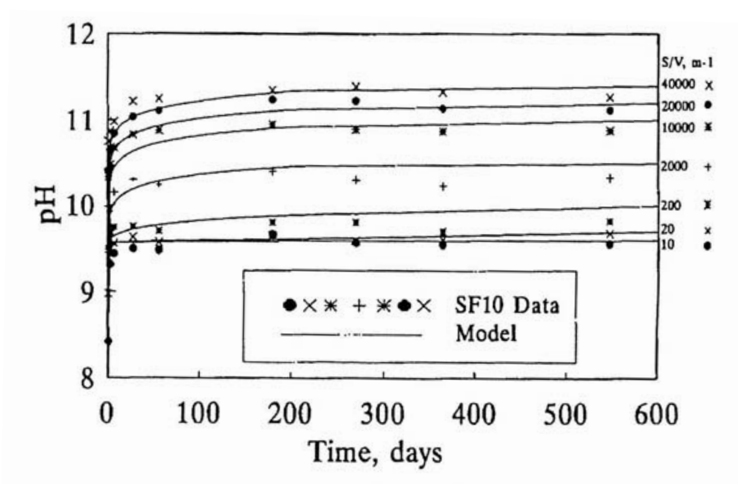
- Model combines affinity rate law with ion exchange

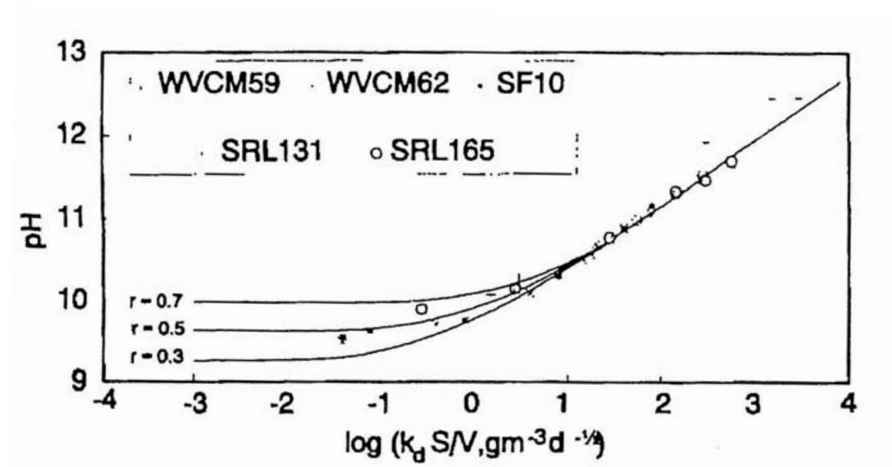
$$\frac{d[Si]}{dt} = k_f \frac{S}{V} \left(\frac{[H^+]_0}{[H^+]} \right)^{\beta} \left(1 - \frac{[H_4SiO_4]}{[H_4SiO_4]_{sat}} \right) \qquad \frac{d[R^+]}{dt} = \frac{1}{2} k_d \frac{S}{V} \left(\frac{[H^+]}{[H^+]_0} \right)^{\alpha} t^{-1/2}$$

- Processes are coupled through solution speciation and moving boundaries
- Limiting behavior gives

$$pH \sim \left(\frac{\mathrm{S}}{\mathrm{V}} \right)^{\gamma}, \text{where } \gamma = \frac{1}{1+\alpha} \qquad \text{Experimentally, } \gamma \approx \frac{2}{3}, \text{ giving } \alpha = \frac{1}{2}$$

- K_d, not k_0, determines the long-term behavior
- Reaction is driven by ion exchange – one potential contribution to residual rate





Feng and Pegg, JNCS (1994)

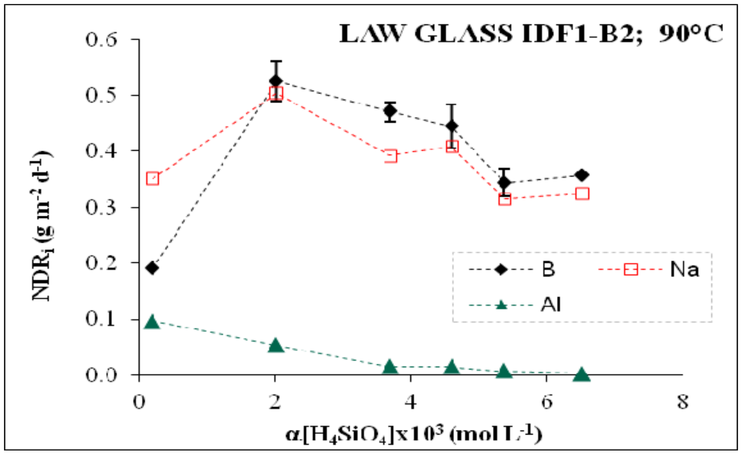
SPFT Testing to Determine Rate Law Parameters

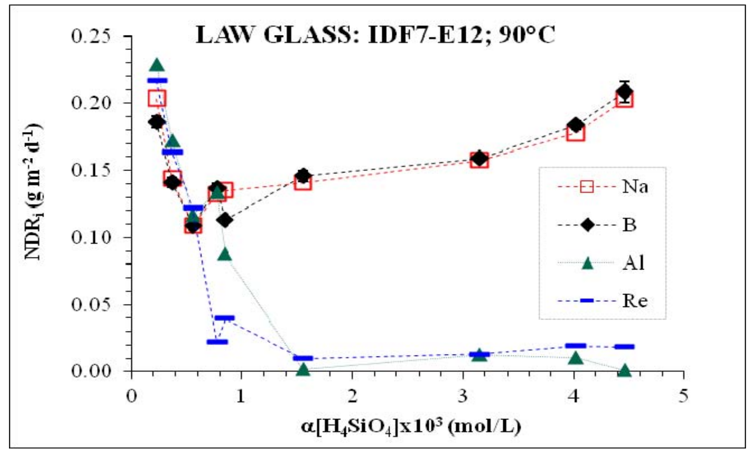
Hanford ILAW PA employs:

$$r = k_0 10^{\eta \cdot pH} \exp(-E_a / RT)[1-(Q/K_g)] + r_{IEX}$$ (McGrail (2001))

with Q=$a[H_4SiO_4]$. But deviations from this affinity term have been observed:

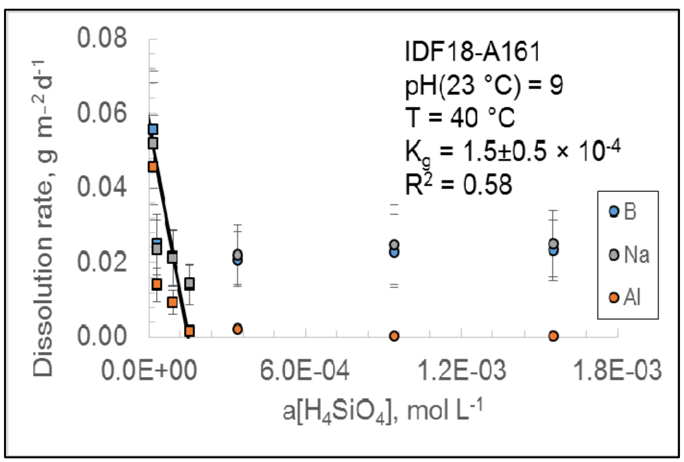
VSL-11R2270-1, 2011

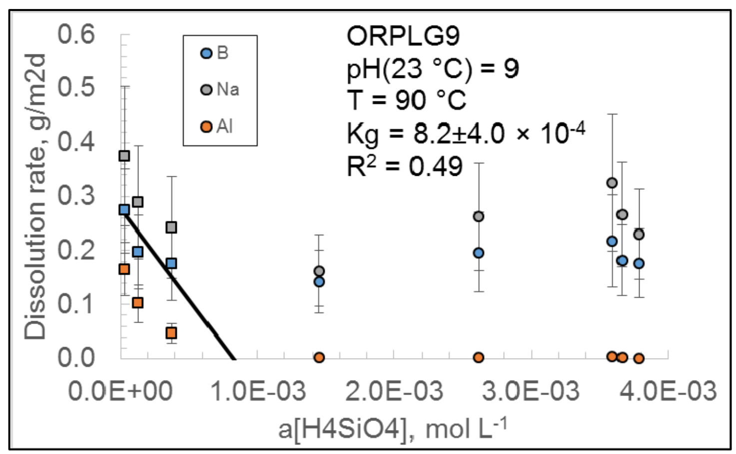




VSL-17R3860-1, 2017

PNNL-26169, 2017





PNNL-26169, 2017

Summary and Conclusions

- VSL has collected a set of data on glass corrosion that is uniquely extensive in terms of test duration, glass compositional range, and test conditions
- Resumption is observed for many glasses over a range of test conditions
- The time to resumption is increased at lower temperature, pH, S/V
- Understanding and quantifying these effects is important for projecting the implications of resumption in repository scenarios
- Ion exchange processes may be important in long-term, near-saturation conditions
- Deviations from the simple affinity term have been observed and need to be understood

Acknowledgements

- Isabelle Muller, Adonia Papathanassiu, Konstantin Gilbo, Miguel Penafiel, Chu-Fen Feng, Andrew Buechele, David McKeown, Miguel Hung, Charles Viragh, Xiangdong Feng, Shiben Xing, Shantao Lai, Wing Kot, Hao Gan, Ronnie Barkatt, Pete Macedo

- All of the staff of VSL and Atkins

- Internal VSL funding for the long-term data

- DOE-EM, DOE-ORP, WRPS, BNI, SRR, WVDP, many others