Strategy to Predict Radionuclide Release from Glass Waste forms

E.M. Pierce

July 13, 2009

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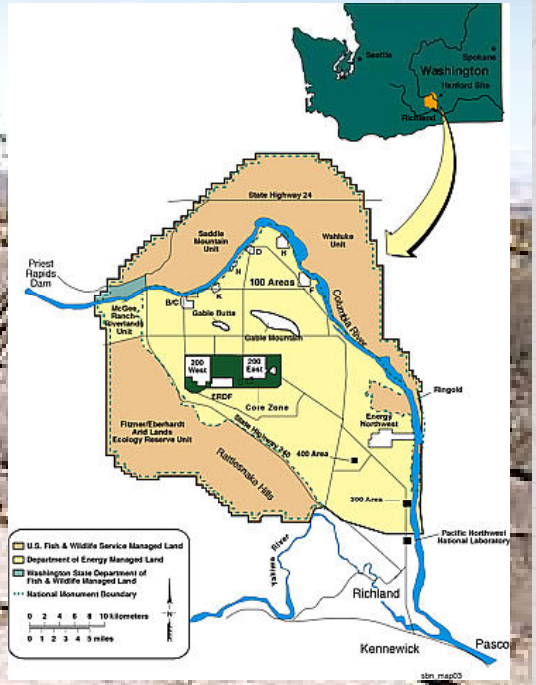
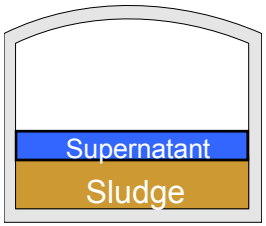
Background



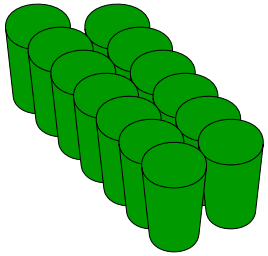
- 177 Buried Single- and Double-Shell Tanks
- Produce HLW and high Na bearing LAW glasses
- Bury LAW in a Shallow Subsurface Burial Facility (IDF)

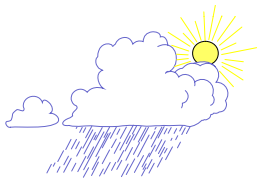
Background



HLW

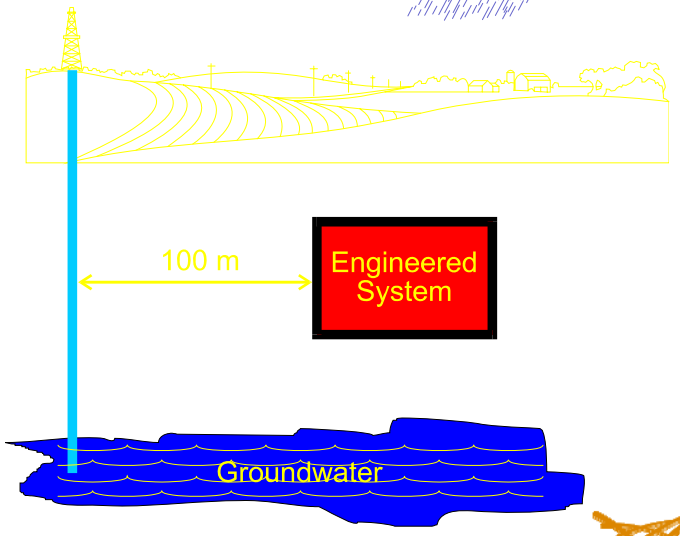
LAW





What are the risk to the public & natural environment?

Predict the long-term behavior of the source-term.



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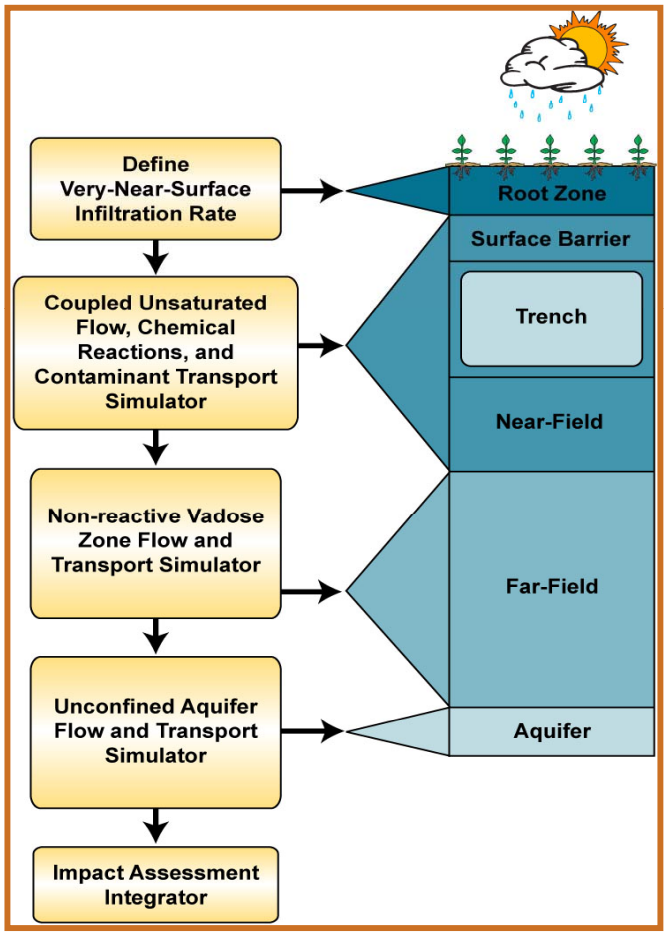
Overview of Integrated Strategy

- Subsurface water and gas flow
- Waste glass dissolution
- Transport of aqueous and gaseous chemical species
- Kinetic and equilibrium chemical reactions
- Secondary mineral dissolution and precipitation
- Coupling between hydraulic properties and mineral precipitation and dissolution



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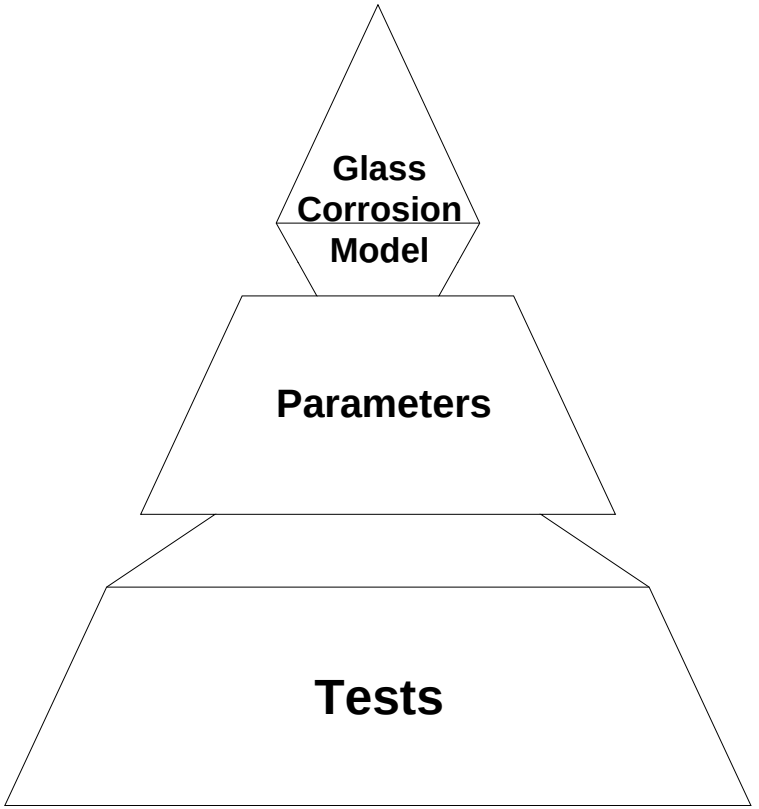
Integrated Strategy cont.

- Glasses tested span the expected WTP processing
- Laboratory Tests Methods:
  - VHT, PCT, MCC-1, SPFT, & PUF
- Quantify parameters from test data
- Parameterize Glass Corrosion Model (rate law)
- Validate Rate Law through lab and field-scale experiments
  - PUF experiments (column test)
  - Lysimeter experiments



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Glass Test Methods

- PCT (B) – Long-term behavior under saturated conditions
- SPFT – Determine parameters for fixed set of environmental conditions (e.g. pH, T, silicic acid) for input to reactive transport codes
- PUF – Determine long-term behavior under disposal facility-relevant conditions
- VHT – Determine secondary phases produced once glass degrades; quick surrogate for PUF

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Rate Law Model For Glass Corrosion

$$r = \vec{k}_o a_{H^+}^{\pm \breve{\eta}} \exp\left(-\frac{E_a}{RT}\right)\left(1-\frac{Q}{K(T)}\right)^{\sigma}$$

Rate constant

pH coef.

Activation Energy

Equilibrium Constant

Temkin Coefficient

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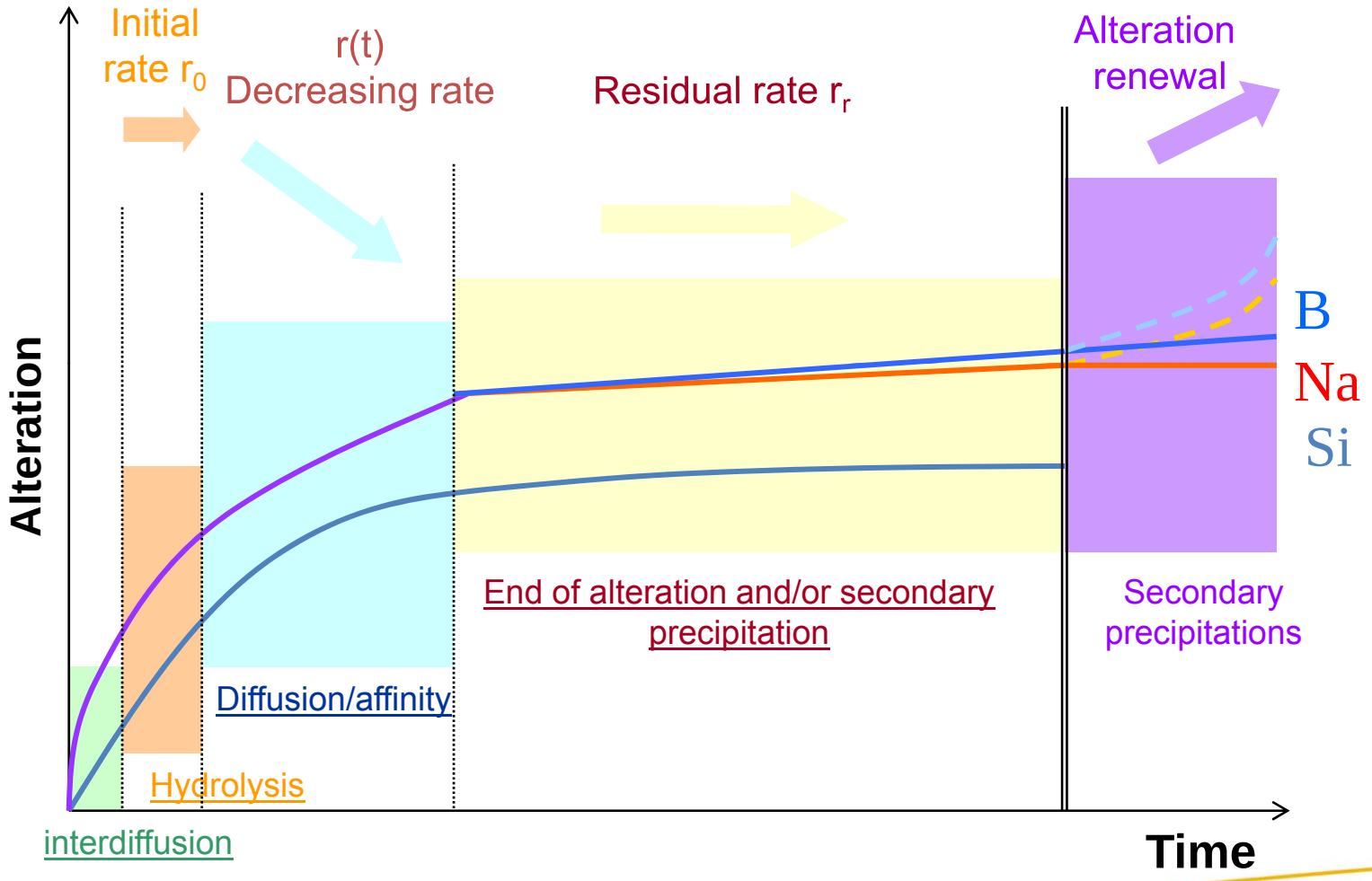
Dissolution mechanisms of glass – general scheme



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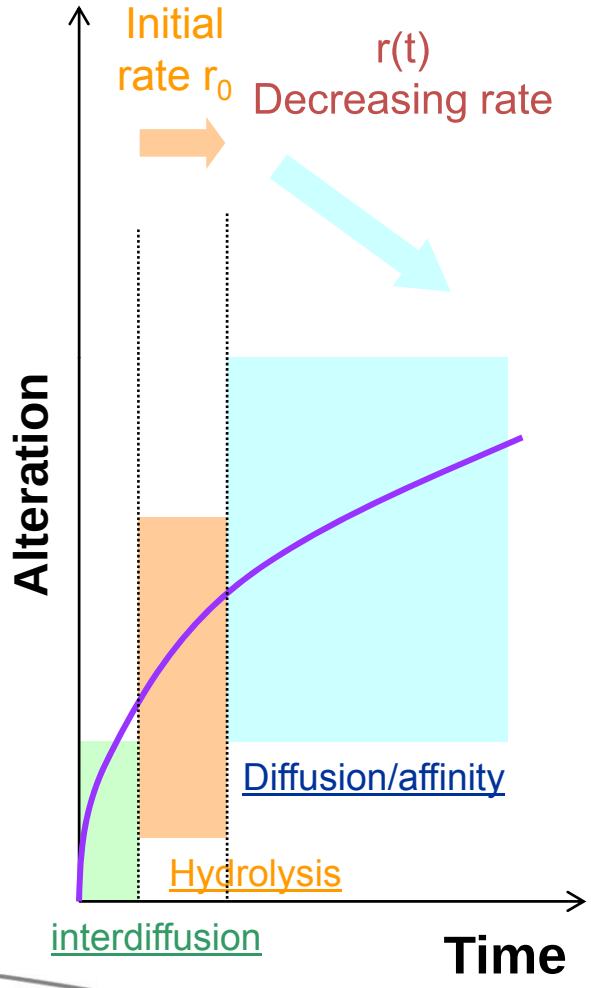
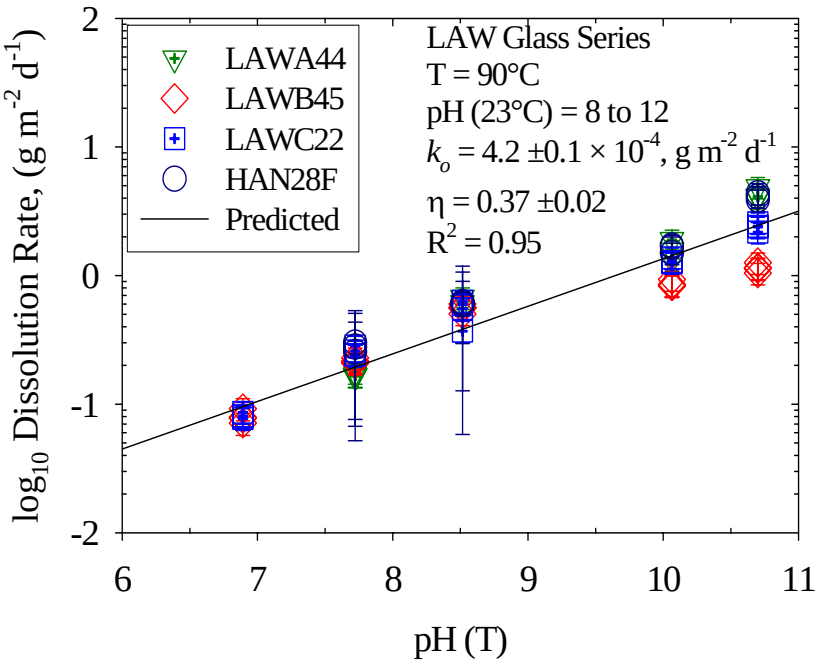
Dissolution mechanisms of glass –
interdiffusion, hydrolysis, and affinity



Pierce et al. (2008). App. Geochem. Vol. 23, No. 9, pp. 2559



Test Methods:
SPFT experiments (preferred)
Short-term PCT/MCC-1
Parameters Determined: *r*, η, E_a, and *K*(T)

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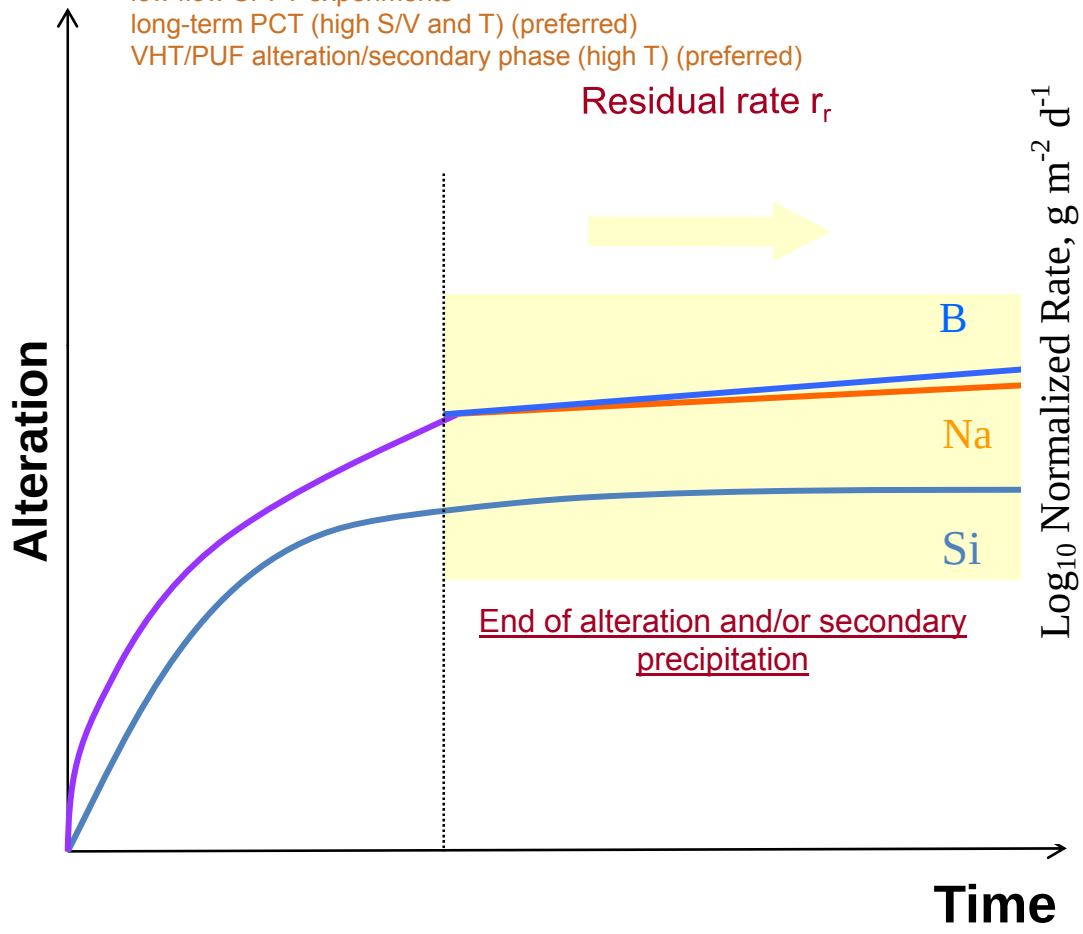
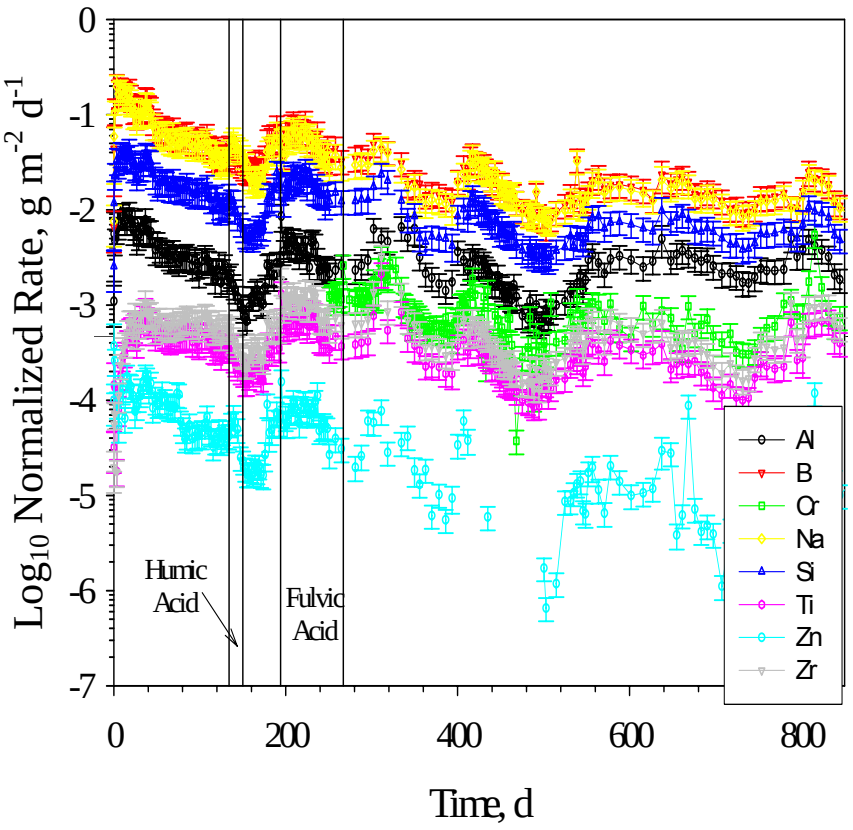
Dissolution mechanisms of glass –
Residual Rate

Test Methods:
low flow SPFT experiments
long-term PCT (high S/V and T) (preferred)
VHT/PUF alteration/secondary phase (high T) (preferred)





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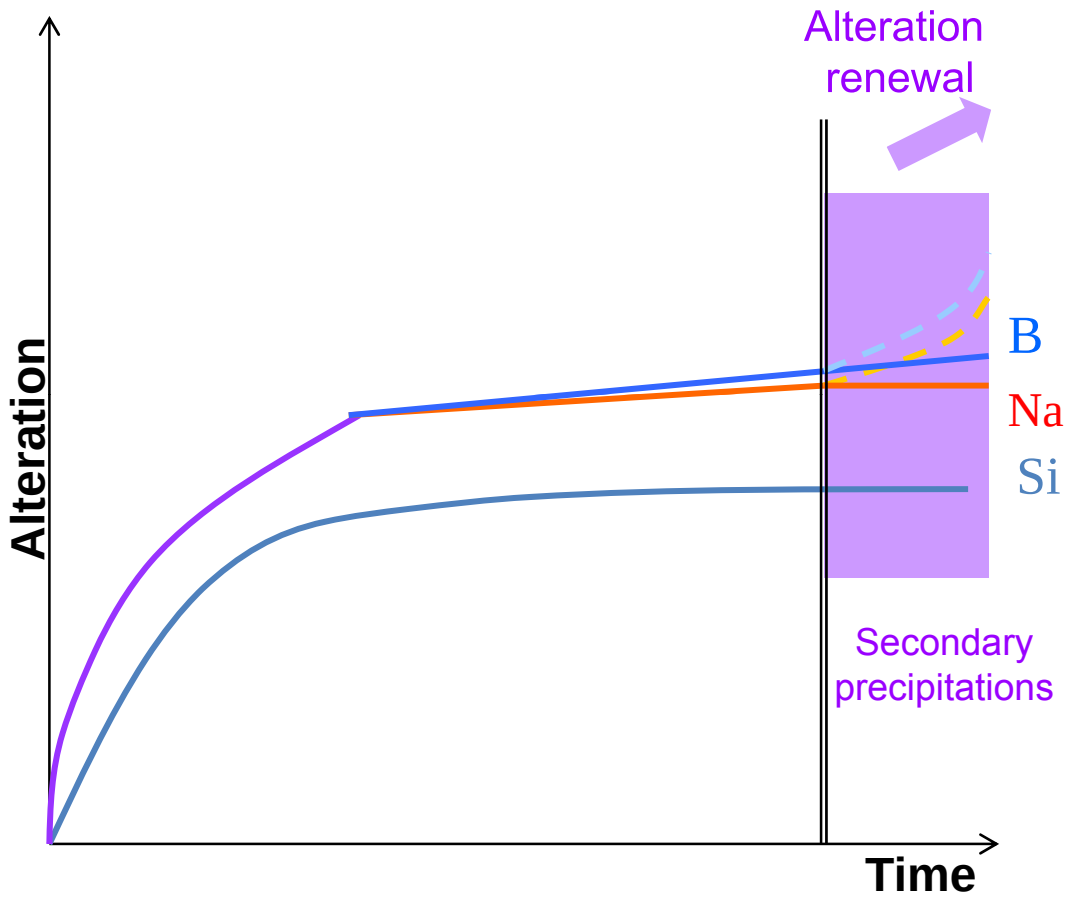
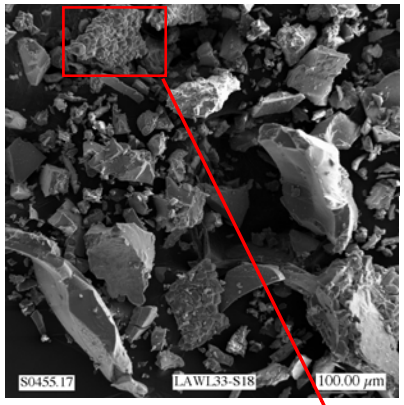
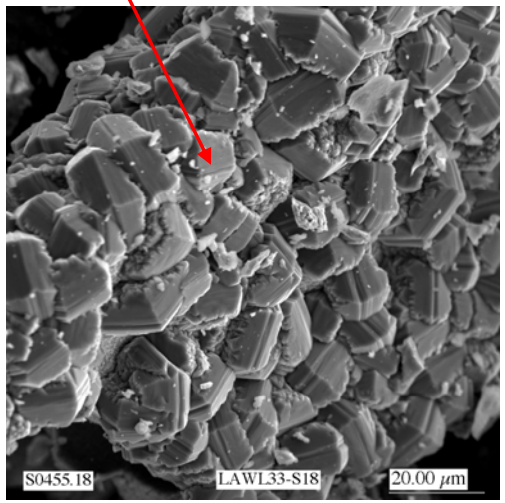
Dissolution mechanisms of glass –
Alteration Renewal







Secondary phase precipitation reaction consumes aqueous components causing more glass to dissolve.

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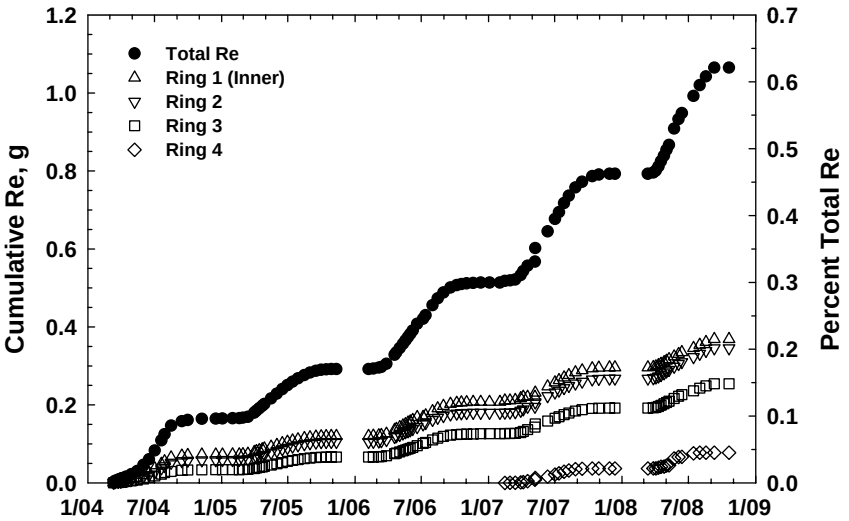
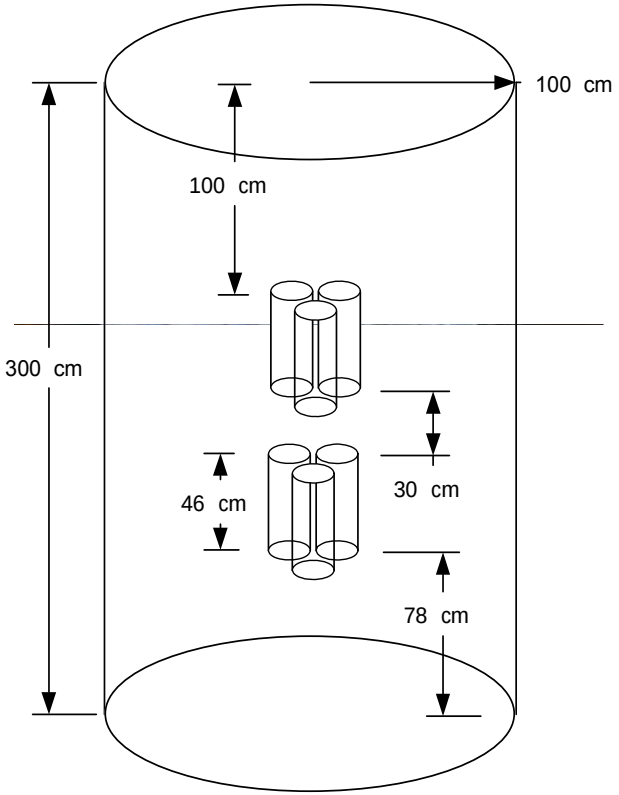
Integrated Strategy – Model Validation

- 3 glass containing lysimeters were buried on site
  - 2 durable glasses (actual WTP glass)
  - 1 less durable glass (HAN28F)
- Six 40-kg glass cylinders buried in 2002 per lysimeter
- 3-times the natural infiltration rate via irrigation





Re (chemical analogue for Tc-99) release from HAN28F glass (poorly durable glass).

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Next Step

- Son of GLAMOR
  - DOE-NE funded
  - Participants: US Nat. lab/University and International research
- Develop consensus rate law for glass corrosion in range of disposal environments
- Focus on improving the understanding of residual rate, r_∞
- Facilitate model development
  - Near-field model → modeling and simulation activity
  - Capture process level detail across-scales

P. van Iseghem, S. Gin, B. Grambow, B. P. McGrail, D.M. Strachan, and G. Wick (2003). *A critical evaluation of the dissolution mechanism of HLW glasses in conditions of relevance for geologic disposal*. R-3702, European Commission.

Summary

- Strategy for predicting glass corrosion must be an integrated approach
- Important to conduct model validation experiments under conditions that mimic the open flow and transport conditions
  - PUF method
  - Field Experiment Lysimeter
- Additional equations maybe needed to model the residual rate
  - IEX and Hydrated layer effect
- Techniques to predict long-term glass behavior based on glass composition/structure

Questions?????

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Backups

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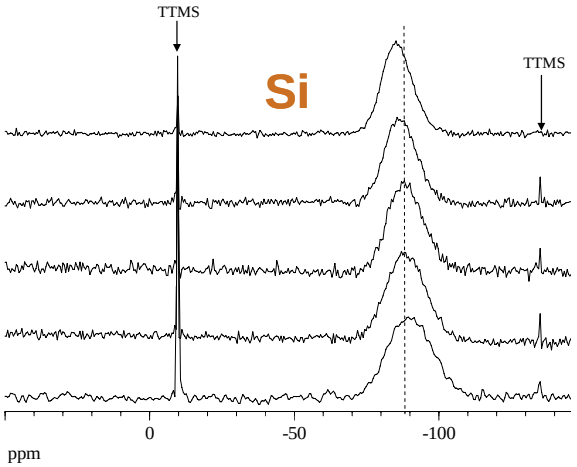
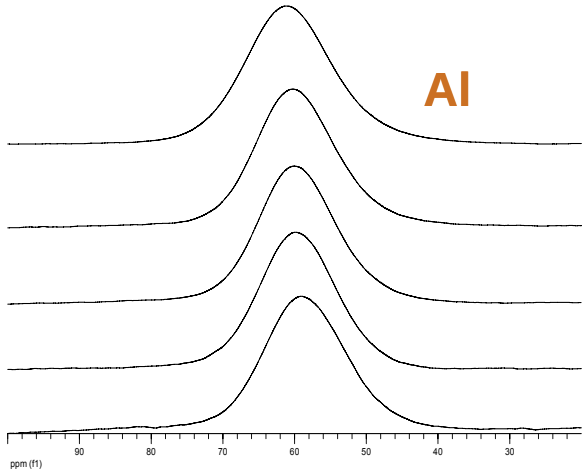
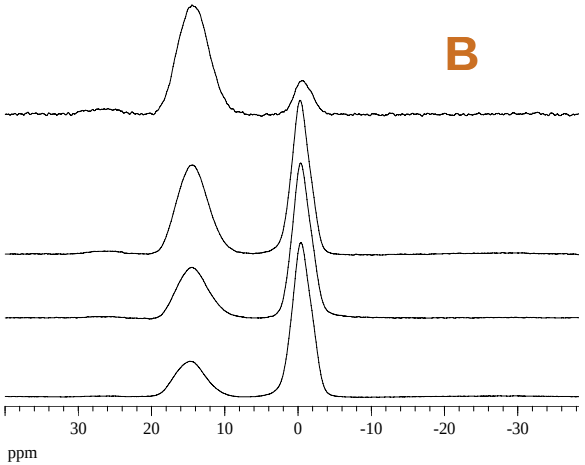
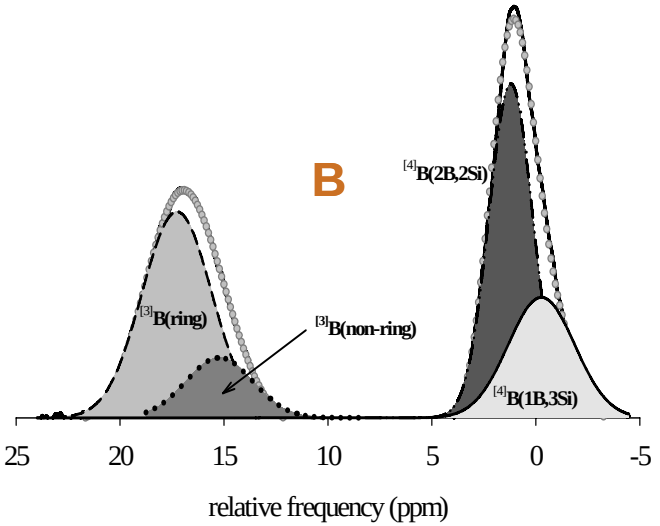
Glass Structure and Forward Rate Relationship

"simple four component alumino-borosilicate glasses"









- Si-O Tetrahedra (Backbone)
- $[AlO_4]$-Na Similar to Si-O
- $[BO_4]$-Na Similar to Si-O
- NBO Sites in high Na-bearing glasses
  Na >> ($^{[4]}$Al+$^{[4]}$B+$^{[4]}$Fe)

Icenhower, McGrail, Shaw, Pierce et al. (2008). Geo. Et. Cos. Chim. Vol. 72, No. 12, pg. 2767

Pierce et al. (accepted with revision). Geo. Et. Cos. Chim.

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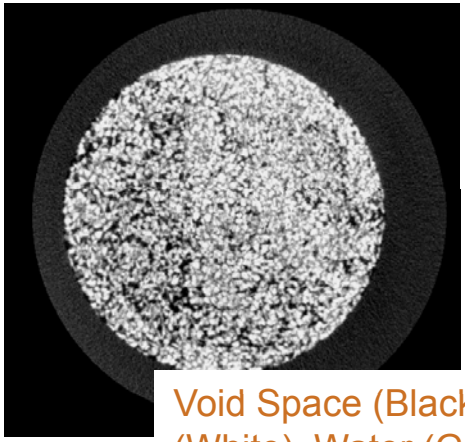
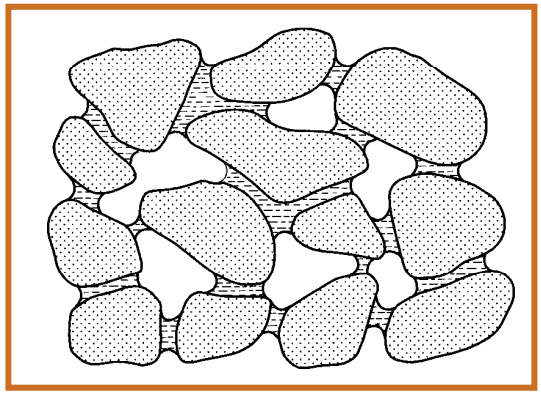
Pressurized Unsaturated Flow Apparatus



XMT-CT Scan

Void Space (Black), Particles (White), Water (Grey)

- Accelerate “aging” of Waste Forms
  - Hydraulically Unsaturated
  - Steady Volumetric Flow Rate
  - Elevated Temperature
- Real-time monitoring
  - Bulk Water Content
  - Effluent Chemistry
  - Real-time pH & EC
- Transport properties
  - Reactive and Non-reactive Tracers
- Spatial Imaging via X-ray Micro-tomography
- Computed Tomography
  - Changes in Pore Structure
  - Moisture Distribution



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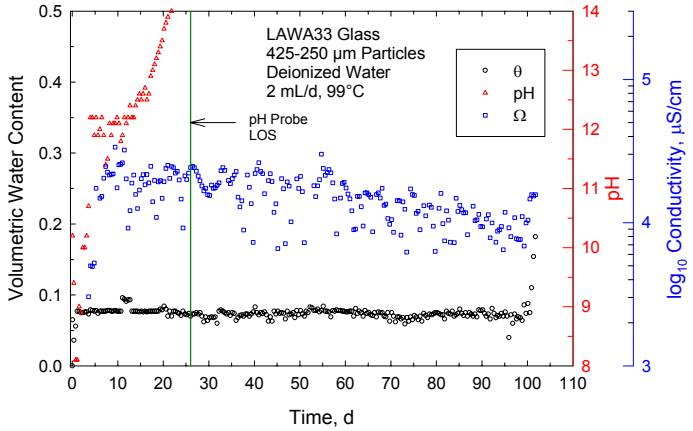
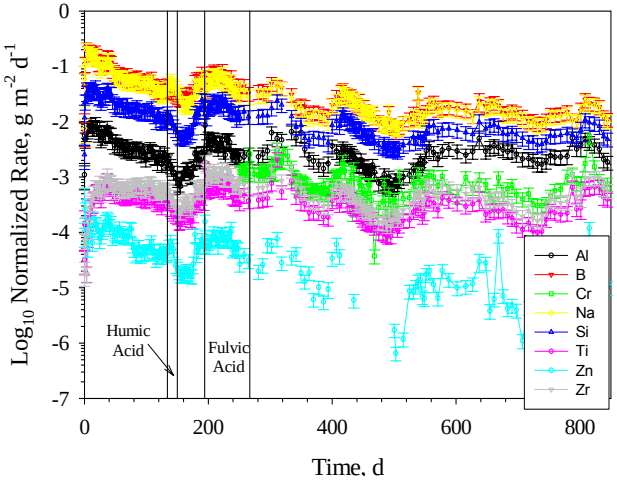
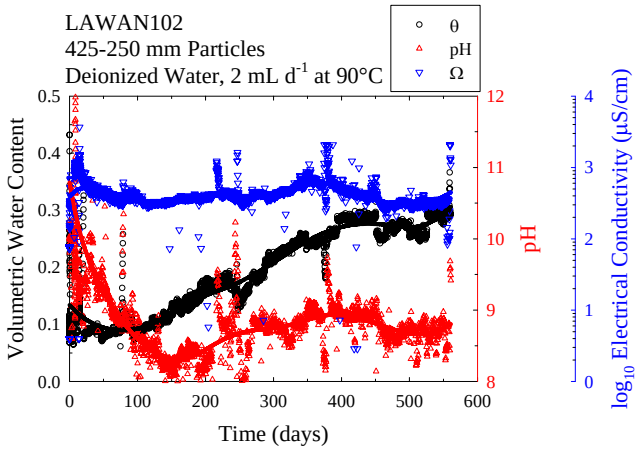
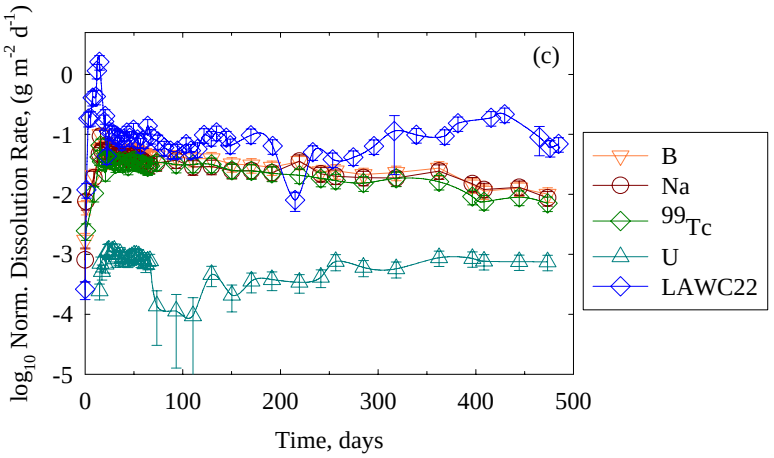
PUF Results: Test Metrics and Rates









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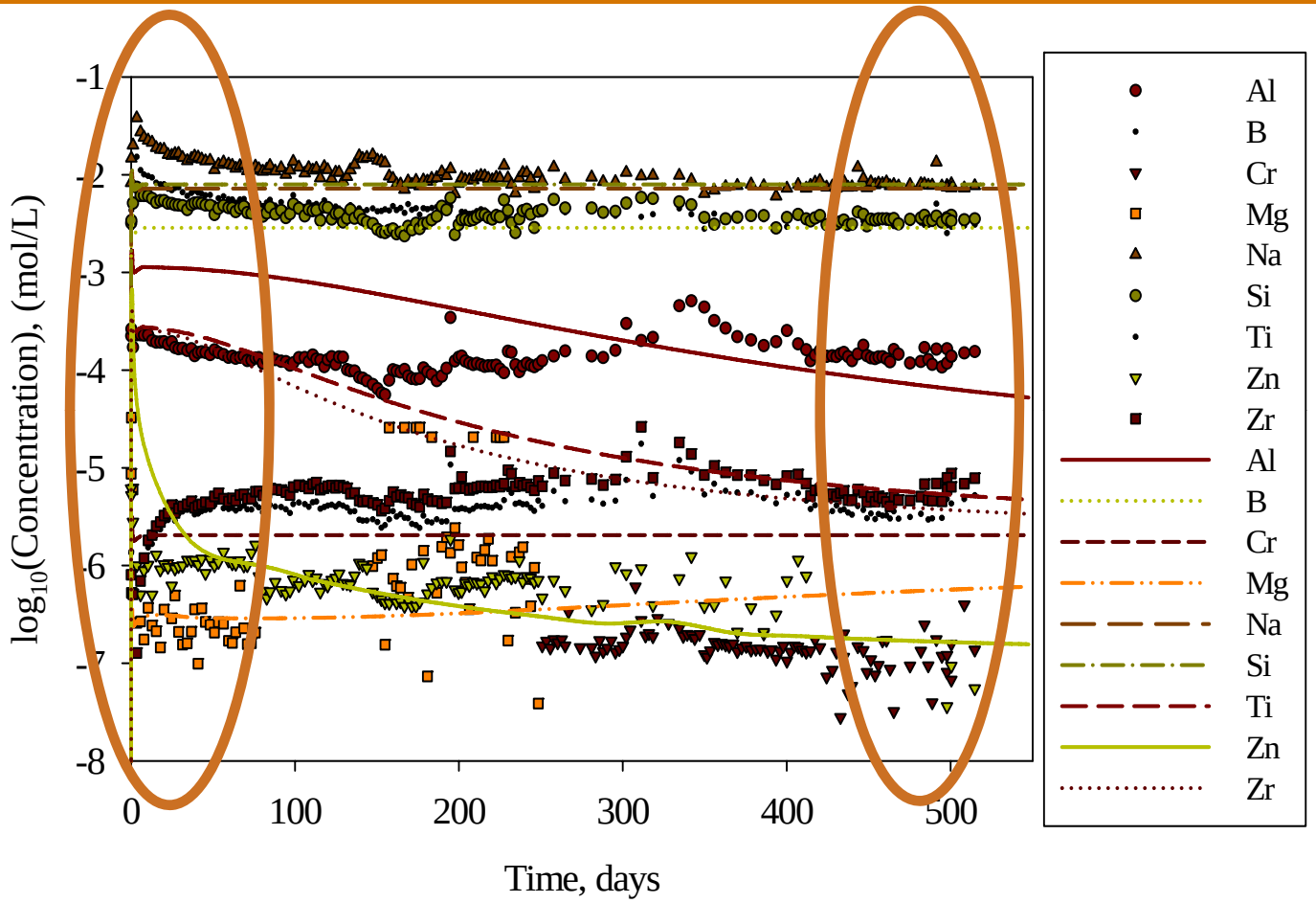
Predictive Modeling with 1-D STORM Reactive Transport Code for PUF test with LAWA44 at 99°C



Pierce et al. (submitted). Ceramic Transactions

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SON of Glamor, cont.

- Residual glass corrosion model
  - generate glass with well developed alteration
    - generate glass or saturated solution with tracers (isotopes)
    - react glass in closed system (high S/V, high temp, …)
    - include monolith in test (for surface analysis and further testing)
    - analyze composition of solution in contact with glass at r_∞
  - test glass with saturated solutions
    - low flow-rate SPFT or slow pulse flow*
    - measure reactions with tracers
    - analyze monolith profile for tracer components
  - all experiments to be modeled before determining parameters