U.S. DEPARTMENT OF ENERGY | OFFICE OF ENVIRONMENTAL MANAGEMENT

Applications of the EPA Leaching Environmental Assessment Framework (LEAF) to Low Activity Waste Glass

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VANDERBILT® C R E S P The University Of Sheffield.

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Pacific Northwest NATIONAL LABORATORY

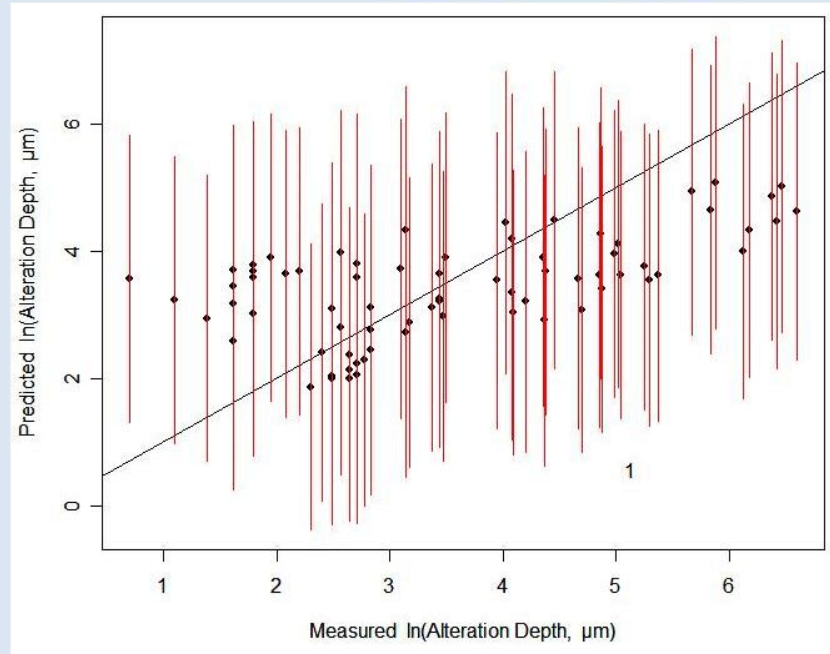
OFFICE OF RIVER PROTECTION United States Department of Energy

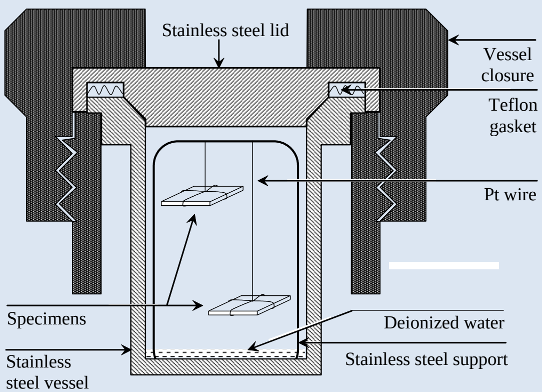
Programmatic Need

- DOE is committed to vitrification of low activity waste (LAW) at Hanford.
- Waste form performance is determined based on leaching test results which are extrapolated to disposal scenarios as part of performance assessments.
- Current leaching tests for LAW do not reflect anticipated disposal conditions and do not provide comparative information for other waste forms.
- Leaching tests that reflect disposal conditions may facilitate more flexible waste loading envelopes for LAW formulation.

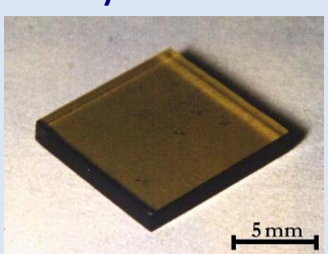
Current durability test to qualify wastes

2.2.2.17.3 "The glass corrosion rate shall be measured using at least a seven (7)-day vapor hydration test run at ***200°C****". "The measured glass alteration rate shall be less than 50 grams/(m^2 day)".*





0 days



15 days

The Vapor Hydration Test (VHT)

- ✘ High variability between labs
- ✘ High variability between operators
- ✘ Inconsistent with assessment of glass durability under the anticipated disposal conditions
- ✘ Large uncertainties in dissolution rate

L E A F

Leaching Environmental Assessment Framework

A Decision Support System for Beneficial Use and Disposal Decisions in the United States and Internationally…

- Four leaching test methods
- Data management tools
- Geochemical speciation and mass transfer modeling
- Quality assurance/quality control for materials production
- Integrated leaching assessment approaches

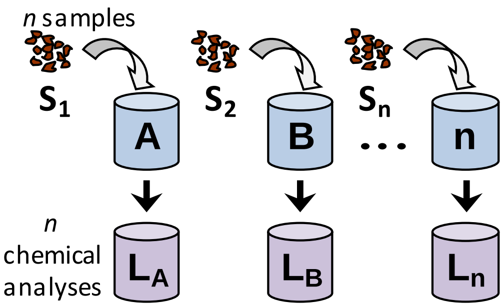
… designed to identify characteristic leaching behaviors for a wide range of materials and scenarios.

More information at http://www.vanderbilt.edu/leaching

Method 1313 Overview

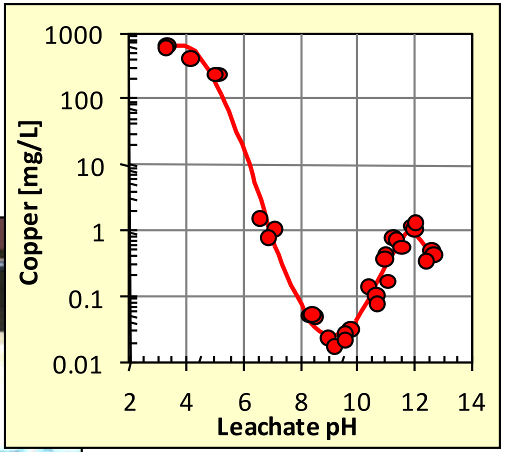
Parallel Batch as f(pH) Leaching Test

- Approximates equilibrium for many materials



Test Specifications

- 9 specified target pH values plus natural conditions
- Size-reduced material
- L/S = 10 mL/g-dry
- Dilute HNO_3 or KOH
- Contact time based on particle size
  - ❑ 18-72 hours
- Reported Data
  - ❑ Equivalents of acid/base added
  - ❑ Eluate pH and conductivity
  - ❑ Eluate constituent concentrations



Titration Curve and Liquid-solid Partitioning (LSP) Curve as Function of Eluate pH

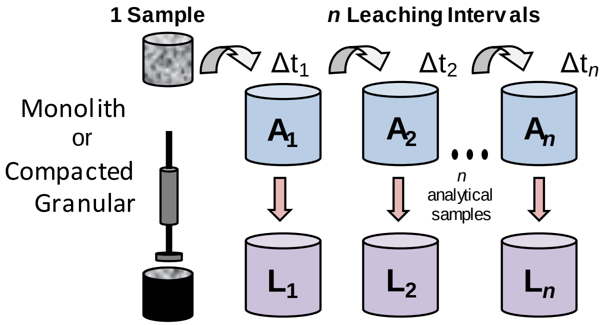
Method 1315 Overview

Mass-Transfer Test

- Semi-dynamic tank leach test

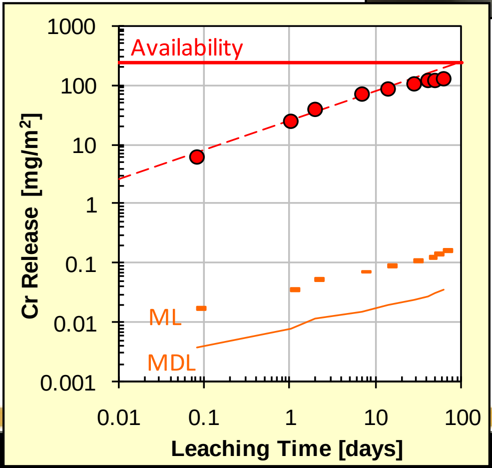
Test Specifications

- Material forms
  - ❑ monolithic (all faces exposed)
  - ❑ compacted granular (1 circular face exposed)
- DI water so that waste dictates pH
- Liquid-surface area ratio (L/A) of 9±1 mL/cm^2
- Refresh leaching solution at cumulative times
  - ❑ 2, 25, 48 hrs, 7, 14, 28, 42, 49, 63 days
- Reported Data
  - ❑ Refresh time
  - ❑ Eluate pH and conductivity
  - ❑ Eluate constituent concentrations



Monolithic

Granular



Flux and Cumulative Release as a Function of Leaching Time

Project Objectives

- Evaluate suitability of EPA LEAF Methods 1313 and 1315 for evaluation of LAW glass
  - Can the key constituents in eluates be measured?
  - Can different LAW glass compositions be distinguished?
  - Are modifications or additional specifications needed for testing LAW glass?
- Determine methods reproducibility of the methods when applied to LAW glass
- Determine if the methods can be used to provide mechanistic information with respect to LAW glass degradation
  - Can leaching kinetics and thermodynamics be measured?
  - How do results compare with information from other test methods?
  - How do results compare with long-term environmental degradation of similar glasses?

Study Design

Phase I – Screening studies

- Testing multiple glass formulations
- Testing at multiple temperatures
- Evaluating need for test method modifications or additional specifications – sample preparation, scalability

Phase II – Interlaboratory Validation

- Single glass (LAW-A44) tested at 3 laboratories, 6 replicates per laboratory

Phase III – Degradation Kinetics and Thermodynamics

- Multiple glass formulations (LAW-A44, ORP-LB2, ISG, UK-MW5)
- Temperatures: 22, 40, 60 C
- Method 1313 – 1d, 2d, 4d, 7d; 1 g; 5 replicates (single lab)
- Method 1315 – 5 replicates (single lab)

Phase IV – Comparisons with Field Aged Glasses

Glass Compositions

Reported compositions					Measured by Sheffield ICP-MS			
	LAW A44	ORP LB2	LAW A23			LAW A44	ORP LB2	LAW A23
Oxide	Wt %	Wt %	Wt %		Oxide	Wt %	Wt %	Wt %
Al_2O_3	6.20	10.00	9.86		Al_2O_3	6.39	9.76	10.02
B_2O_3	8.90	7.30	4.23		B_2O_3	9.56	7.95	4.66
CaO	1.99	1.10	4.38		CaO	2.21	1.19	4.50
CdO	-	-	-		CdO	0.004	0.007	0.004
CeO_2	-	-	-		CeO_2	0.00	0.016	0.00
Cl	0.65	0.11	0.36		Cl	-	-	-
Cr_2O_3	0.10	0.52	0.10		Cr_2O_3	0.11	0.57	0.11
Cs_2O	0.00	0.15	0.00		Cs_2O	0.00	0.14	0.00
Fe_2O_3	6.98	1.10	7.30		Fe_2O_3	7.44	1.24	7.91
F	0.01	0.49	0.12		F	-	-	-
K_2O	0.50	0.12	3.10		K_2O	0.58	0.19	3.38
Li_2O	0.00	0.00	2.04		Li_2O	0.00	0.00	2.06
MgO	1.99	1.10	2.04		MgO	1.82	0.98	2.00
MnO_2	0.00	0.06	0.00		MnO_2	0.00	0.067	0.00
MoO_3	0.01	0.00	0.00		MoO_3	0.013	0.00	0.00
Na_2O	20.00	25.00	20.00		Na_2O	21.32	26.04	20.76
NiO	0.00	0.04	0.00		NiO	0.00	0.051	0.00
P_2O_5	0.03	0.23	0.08		P_2O_5	-	-	-
Re_2O_7	0.10	0.10	010		Re_2O_7	0.069	0.057	0.036
SO_3	0.10	0.52	0.040		SO_3	0.11	0.53	0.063
SiO_2	44.55	39.88	40.15		SiO_2	41.19	37.07	37.15
SnO_2	0.00	1.08	0.00		SnO_2	0.00	0.00	0.00
TiO_2	1.99	0.00	0.00		TiO_2	2.103	0.130	0.01
V_2O_5	0.00	2.00	0.00		V_2O_5	0.00	2.24	0.00
ZnO	2.96	3.65	3.28		ZnO	3.28	4.07	3.66
ZrO_2	2.99	5.44	2.99		ZrO_2	3.00	5.47	3.02
Total					Total	99.20	97.76	99.35

Elements for the *Interlab* study:

LAW A44

1. Al
2. B
3. Ca
4. Cr
5. Fe
6. (K - KOH)
7. Mg
8. Na
9. Re
10. Si
11. Ti
12. Zn
13. Zr

For **ORP LB2**, *Kinetics* add Cs and V

Screening Results – Key Findings

Method 1313

- Use of 2 screens preferred (150 – 75 µm particle size)
- 48 h contact time
- 1 g sample size
- 22 ± 2 C

Method 1315

- VHT coupon size (1 cm x 1 cm x 0.2 cm thick)
- 600 grit polished, annealed
- 22 ± 2 C

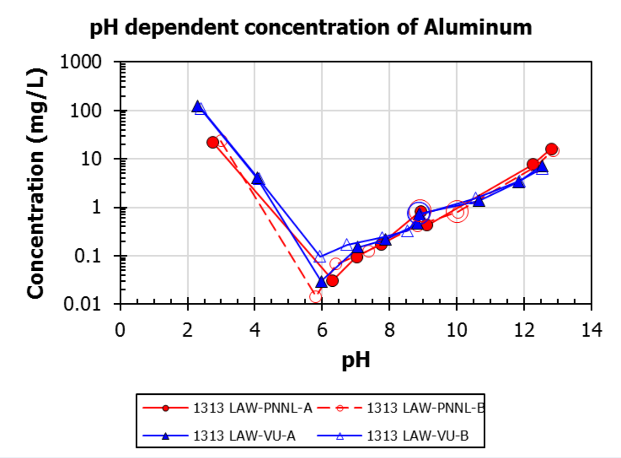
LAW-A44 (glass grains)

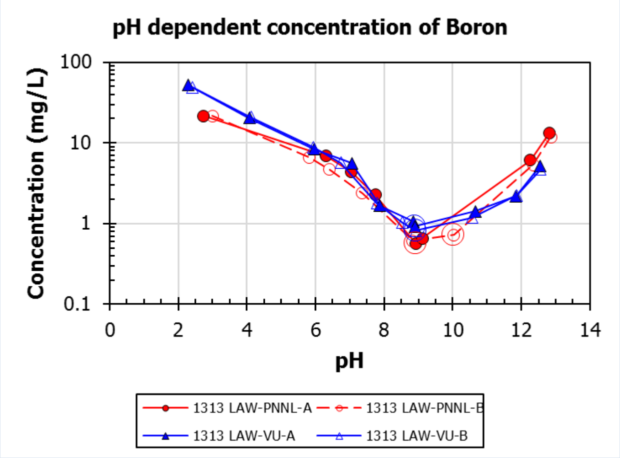
Tube rotator (L/S=10 mL/g, 1 g sample)

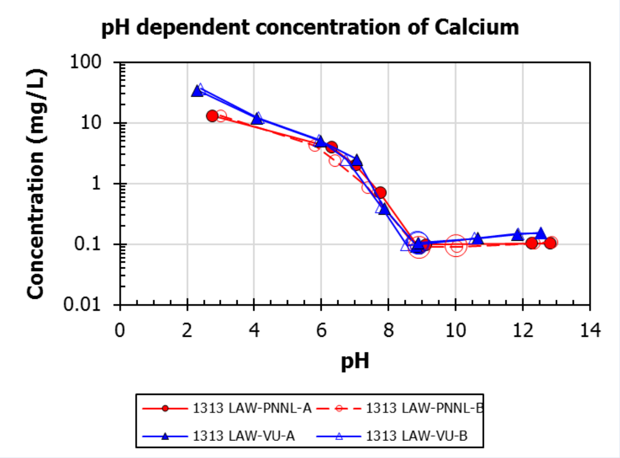
LAW-A44 Coupon in holder

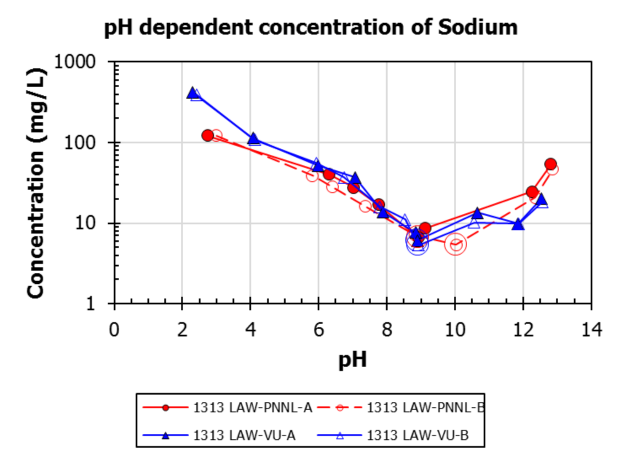
Extraction vessel with sample

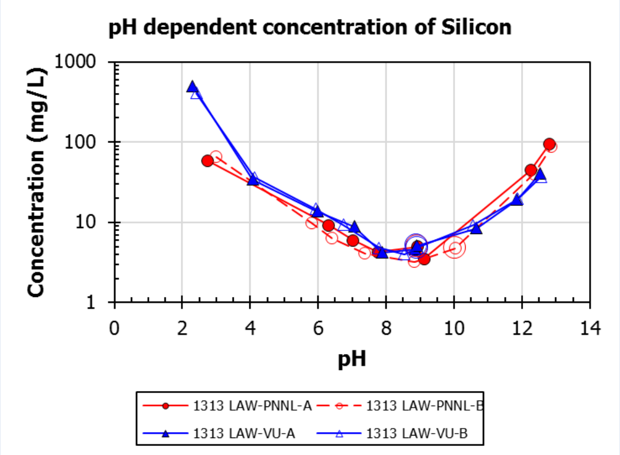
Reproducibility – Method 1313

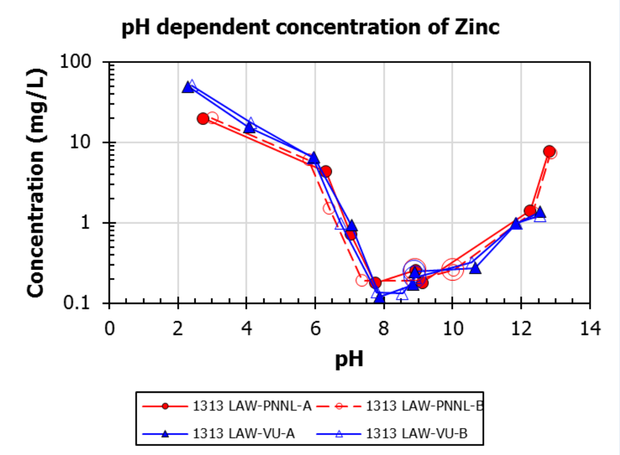




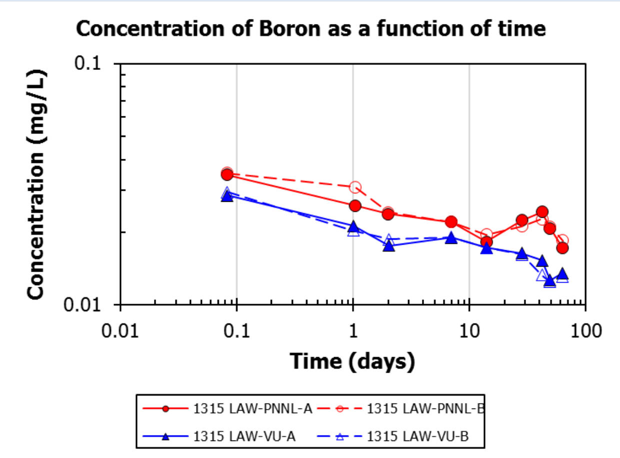


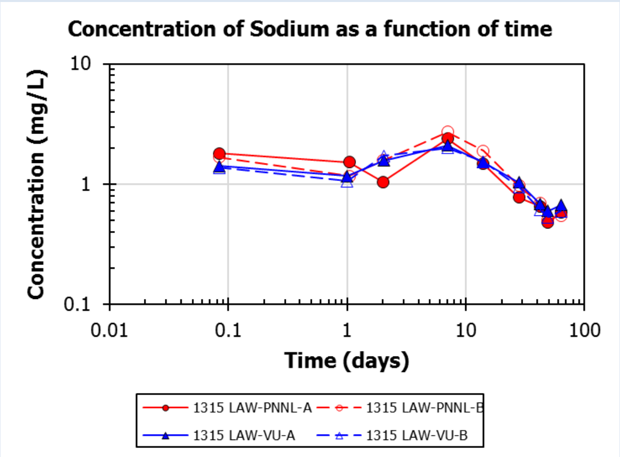


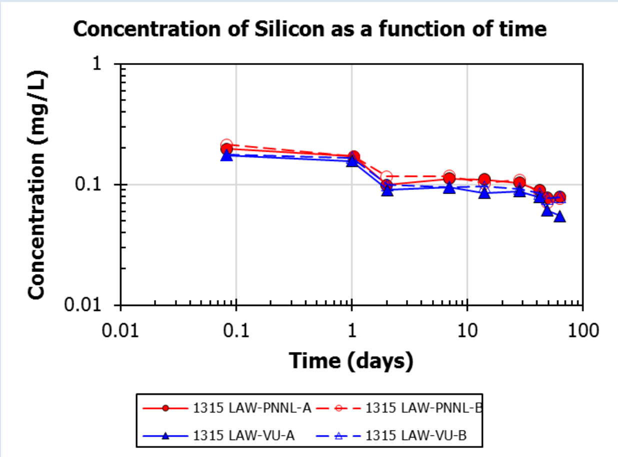


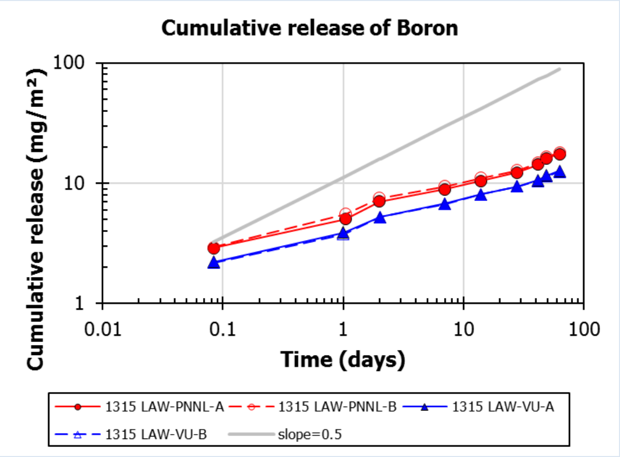


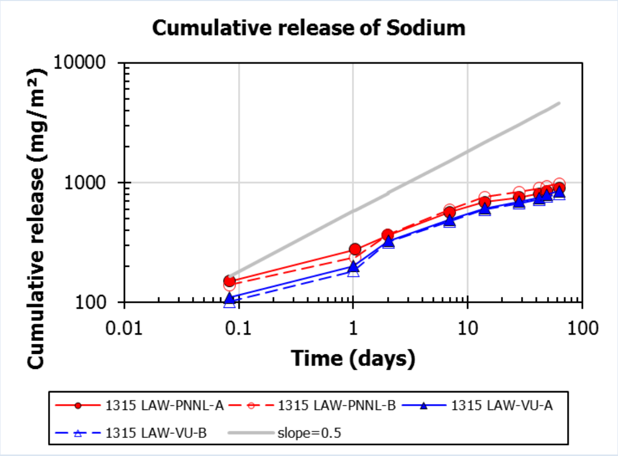
Reproducibility – Method 1315

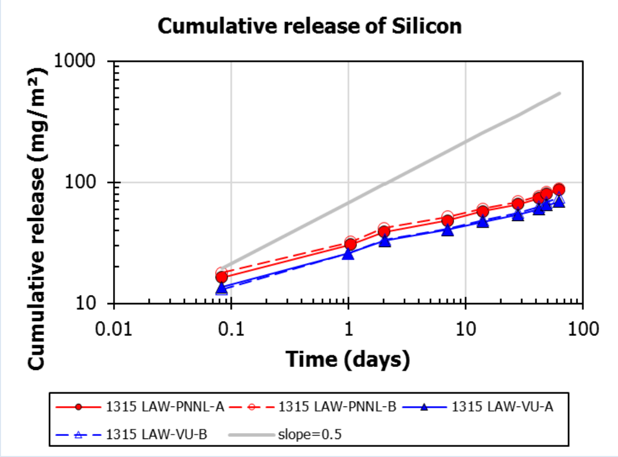






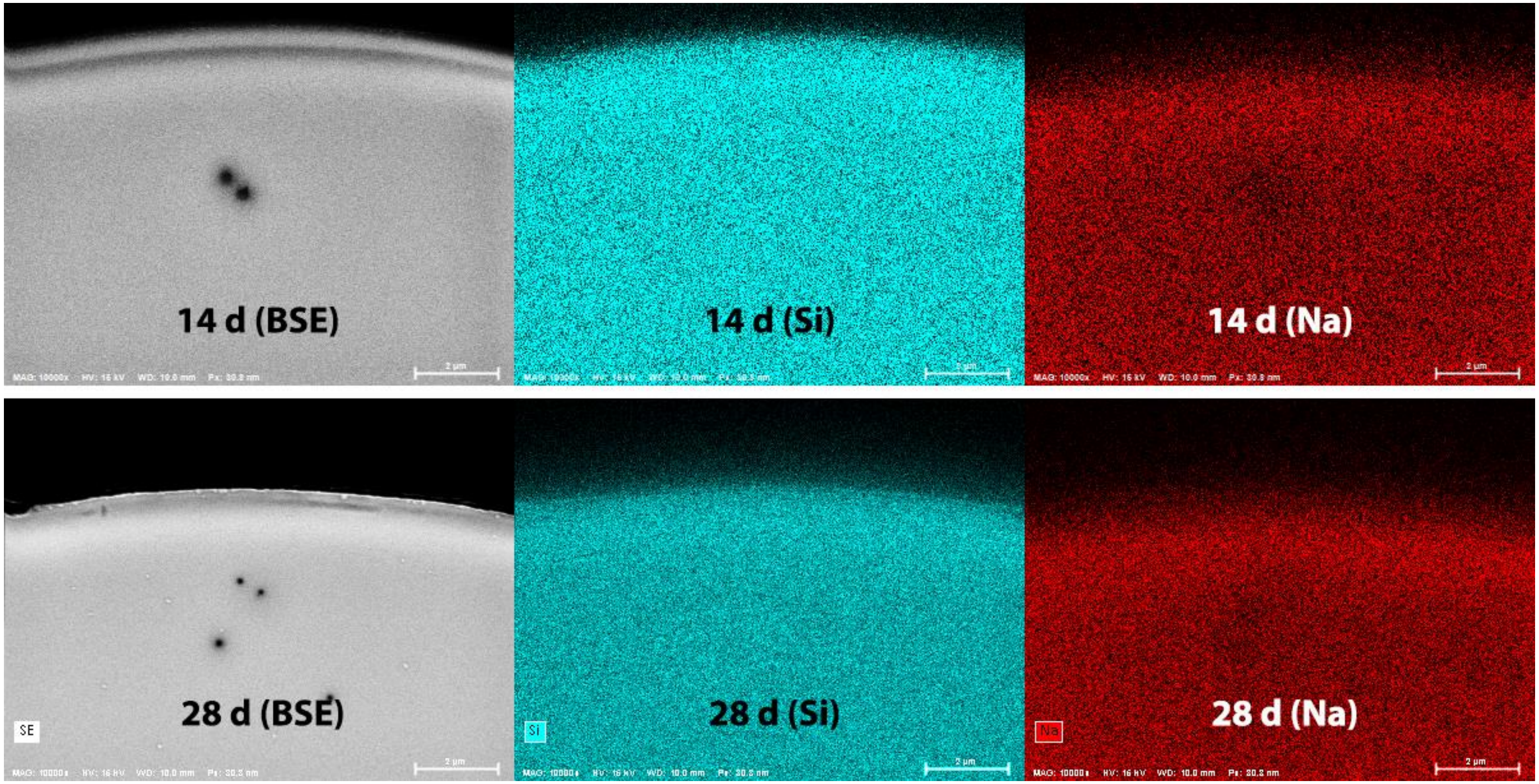






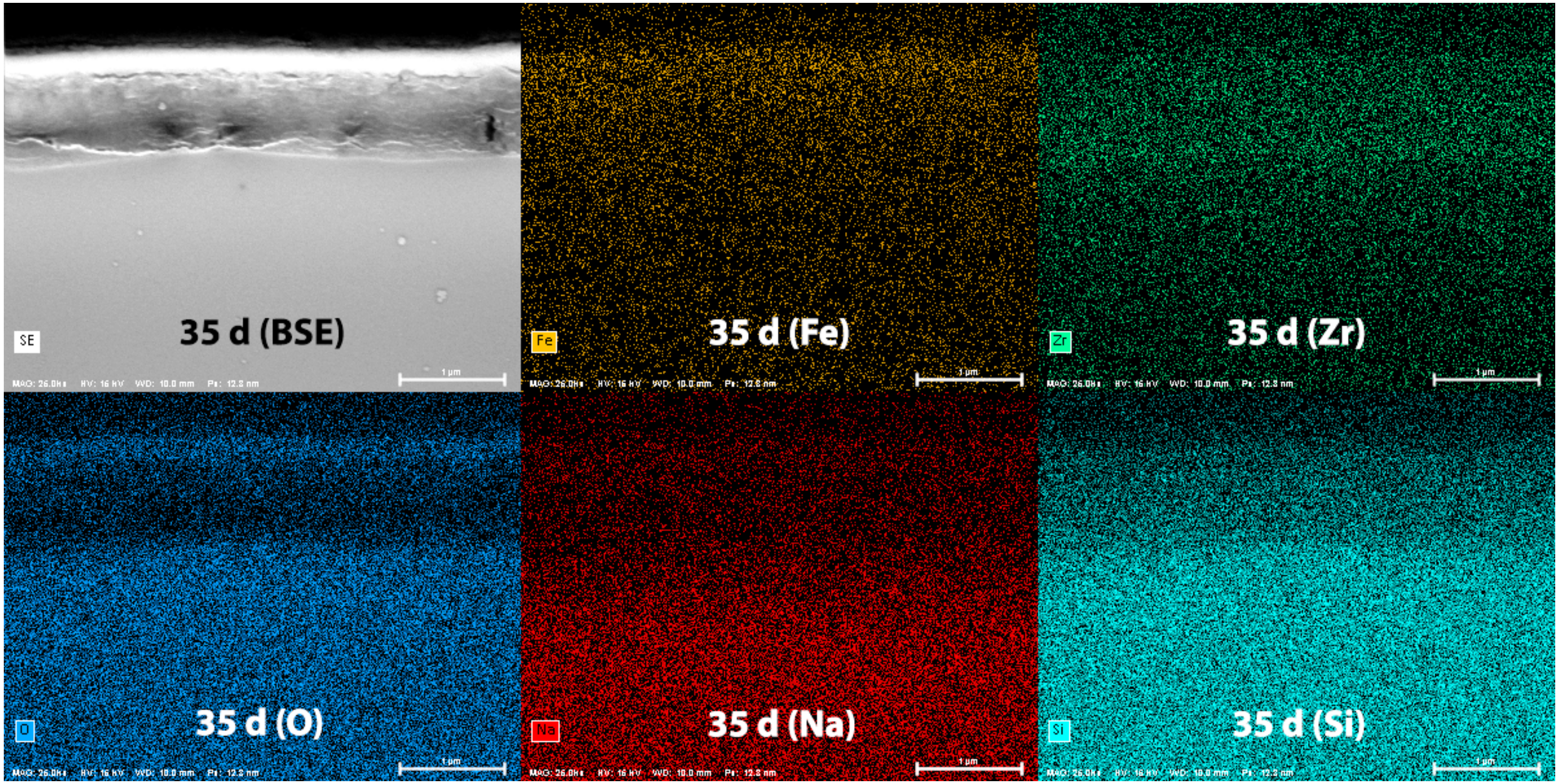
14-d vs 28-d @ 10kx magnification – EDS mapping

- Si present all the way to the edge of the fibers
- Na was depleted from the outer surfaces of both sets of fibers



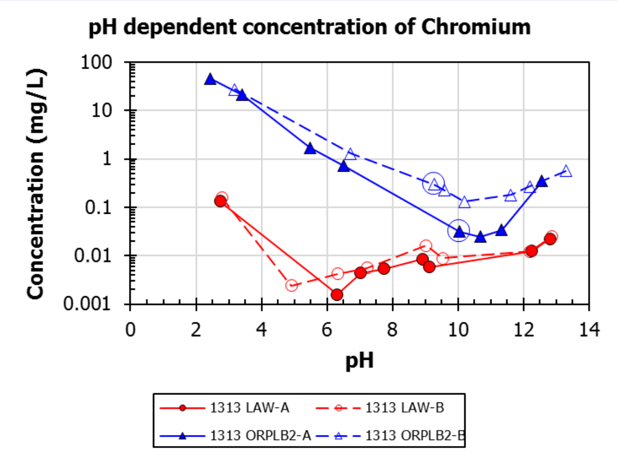
35-d @ 25kx magnification – EDS mapping

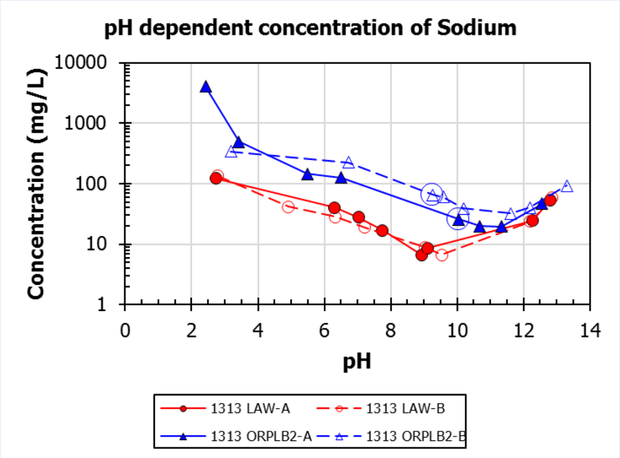
- Outer surface was concentrated in Fe and Zr
- Outer surface was depleted in Na and Si

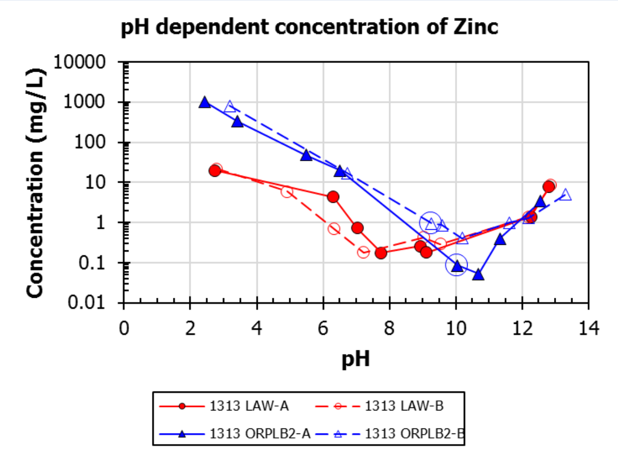


LAW-A44 vs. ORP-LB2

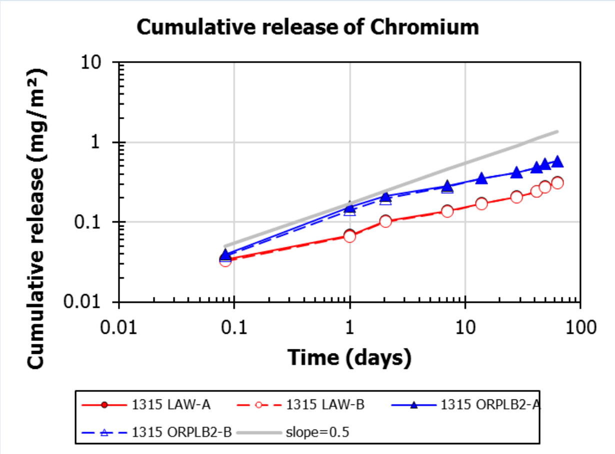
Method 1313

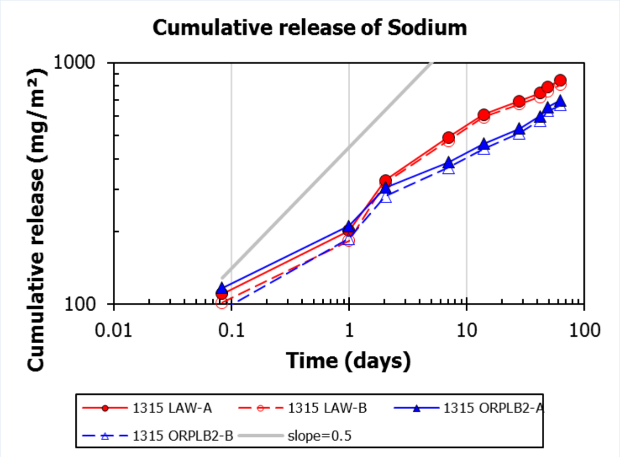


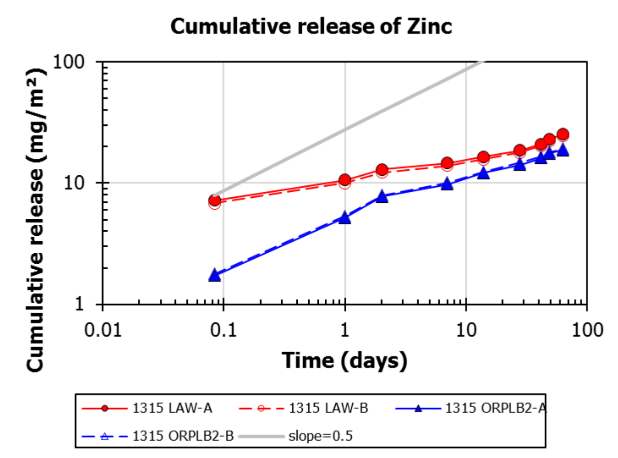




Method 1315

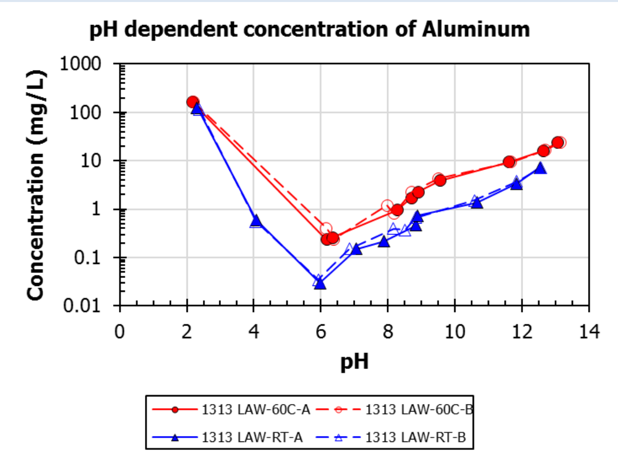


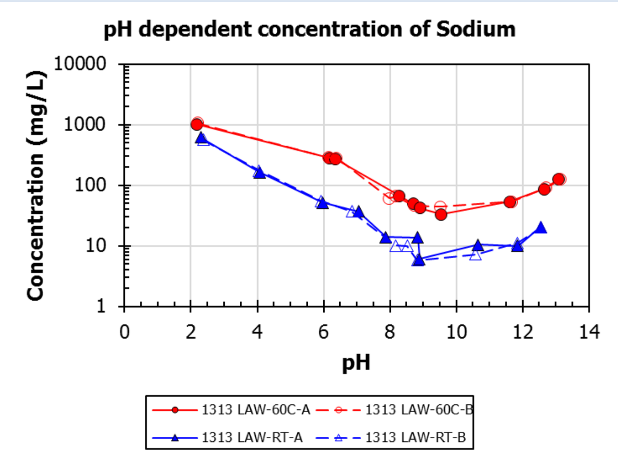


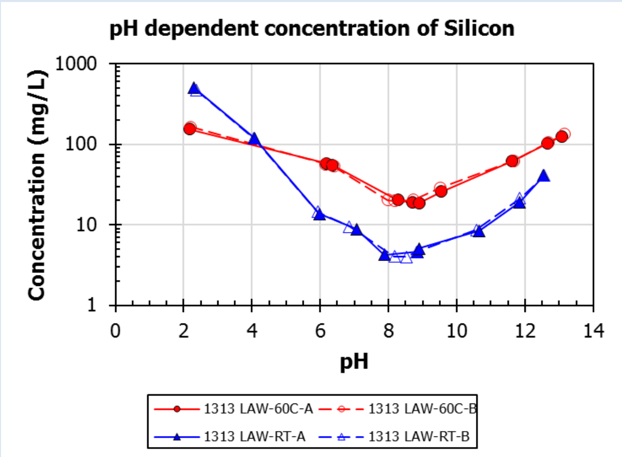


Temperature Effects

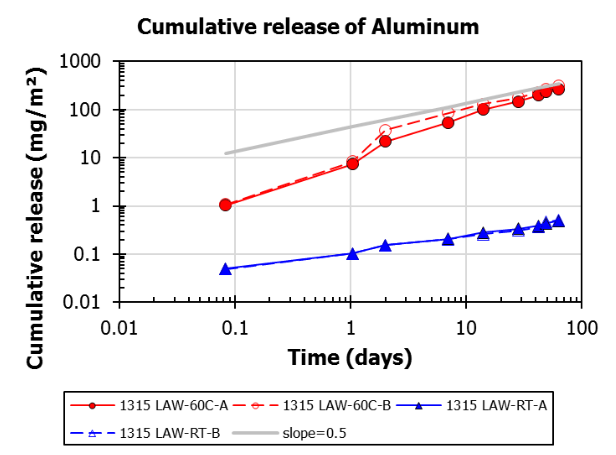
Method 1313

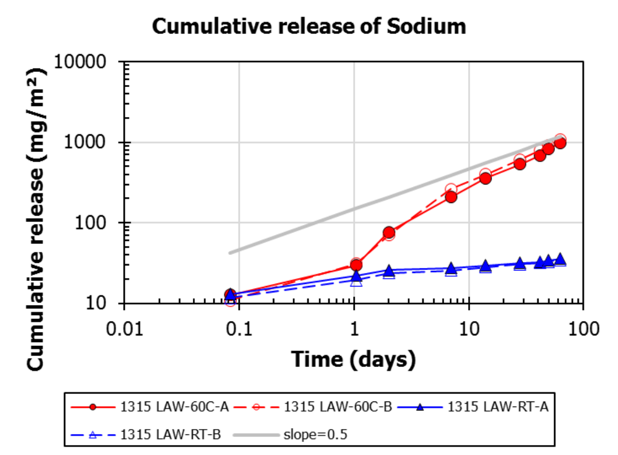


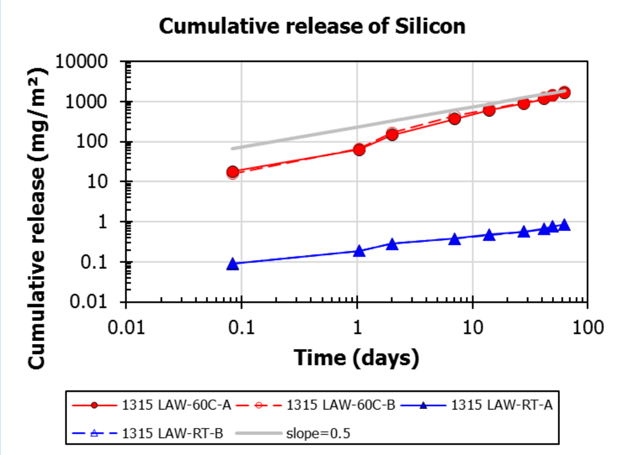




Method 1315







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Performance Assessment?

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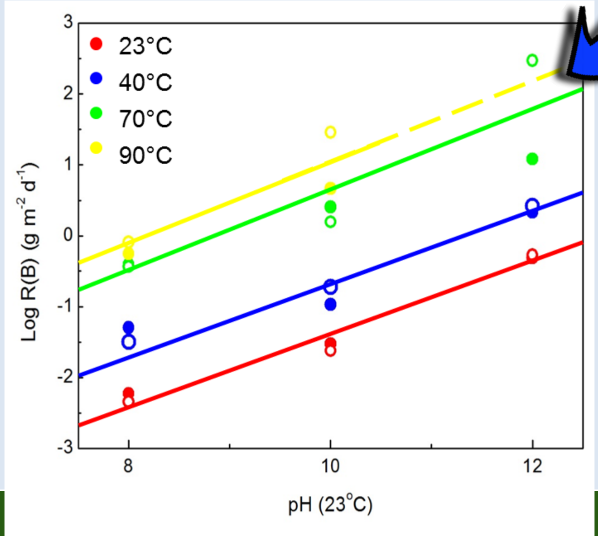
Transition State Theory

Rate constant — Activation Energy — "affinity term"

$$R_i = k_0 v_i e^{-E_a/RT} a_{H^+}^n \left[1 - \left(\frac{Q}{K}\right)^\sigma\right]$$

Dissolution rate — Stoichiometric function — Proton activity

If we are in the "forward rate" the affinity term becomes zero and we can determine the dependence of dissolution rate on temperature and pH for performance assessment.



- Results typically obtained by Single Pass Flow Through (SPFT) experiments
- Complex measurements
- Expensive to perform!

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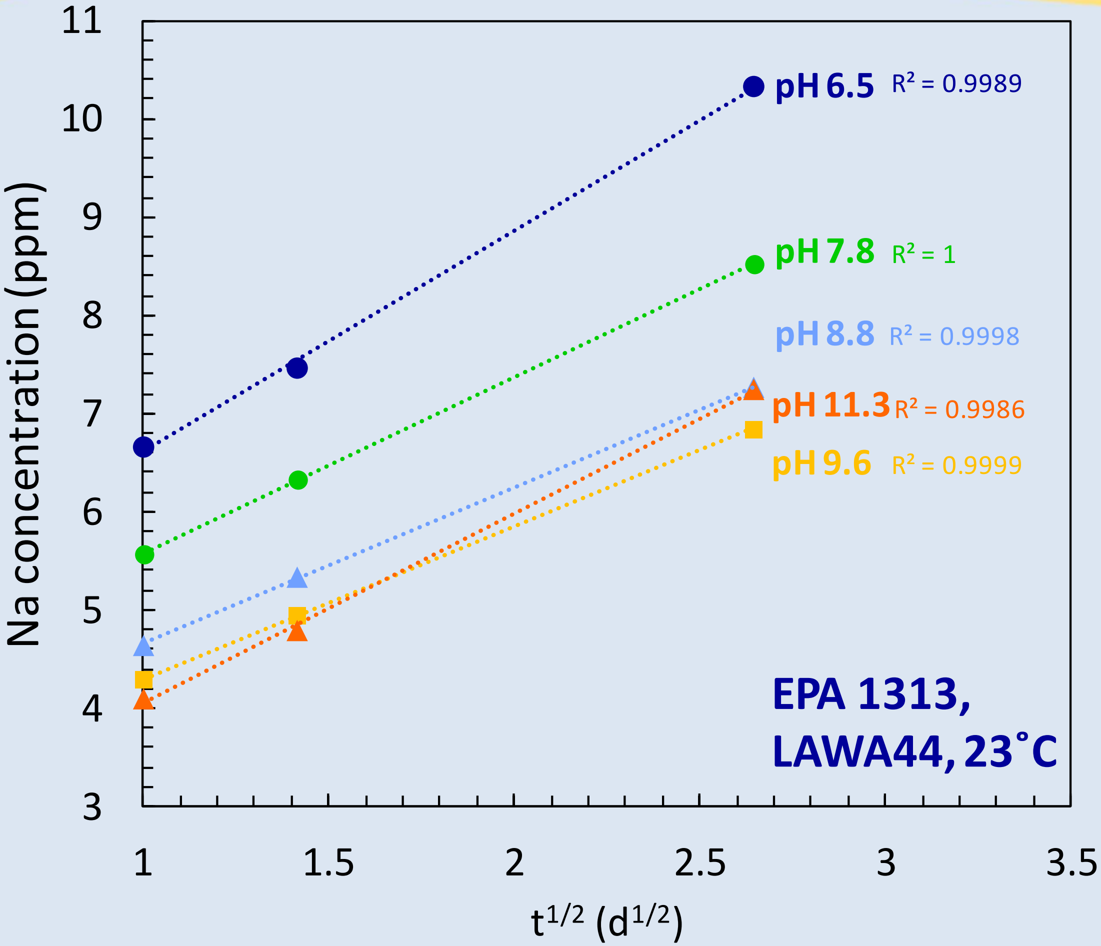
What *are* we measuring in EPA 1313?



- Agitation of the test should hinder surface layer formation and localised supersaturation
- Confirmed by geochemical modelling (PHREEQC, LLNL db) that shows under-saturation with regard to Si above pH 4

In theory, we *should* be able to use this test for performance assessment.

We're measuring a diffusion process! So likely in the forward rate.

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Next Steps

Phase I – Screening studies

- Completed

Phase II – Interlaboratory Validation

- Testing to be completed by December 2018
- Draft publication – Spring 2019

Phase III – Degradation Kinetics and Thermodynamics

- Testing to be completed by December 2018
- Draft publication – Spring 2019

Phase IV – Comparisons with Field Aged Glasses

- Field samples (Hillfort glass, ca. 300 y) being characterized
- Analogous glass compositions being formulated for Method 1313 and 1315 testing