Pacific Northwest
NATIONAL LABORATORY
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Low-Activity Waste Glass Formulation

PRESENTED BY JD VIENNA

PNNL-SA-132624

Expected Low Activity Waste Batch Compositions

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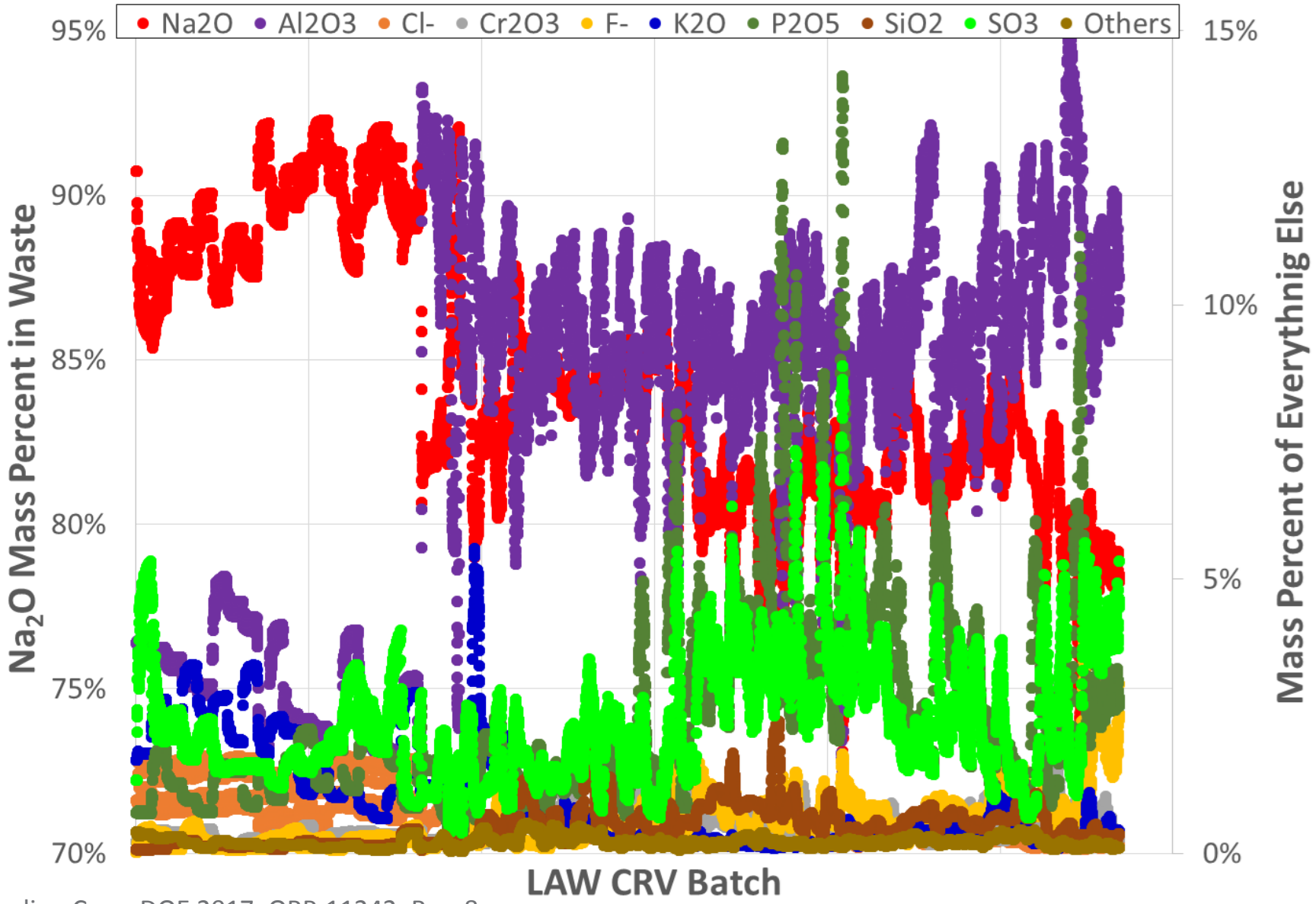
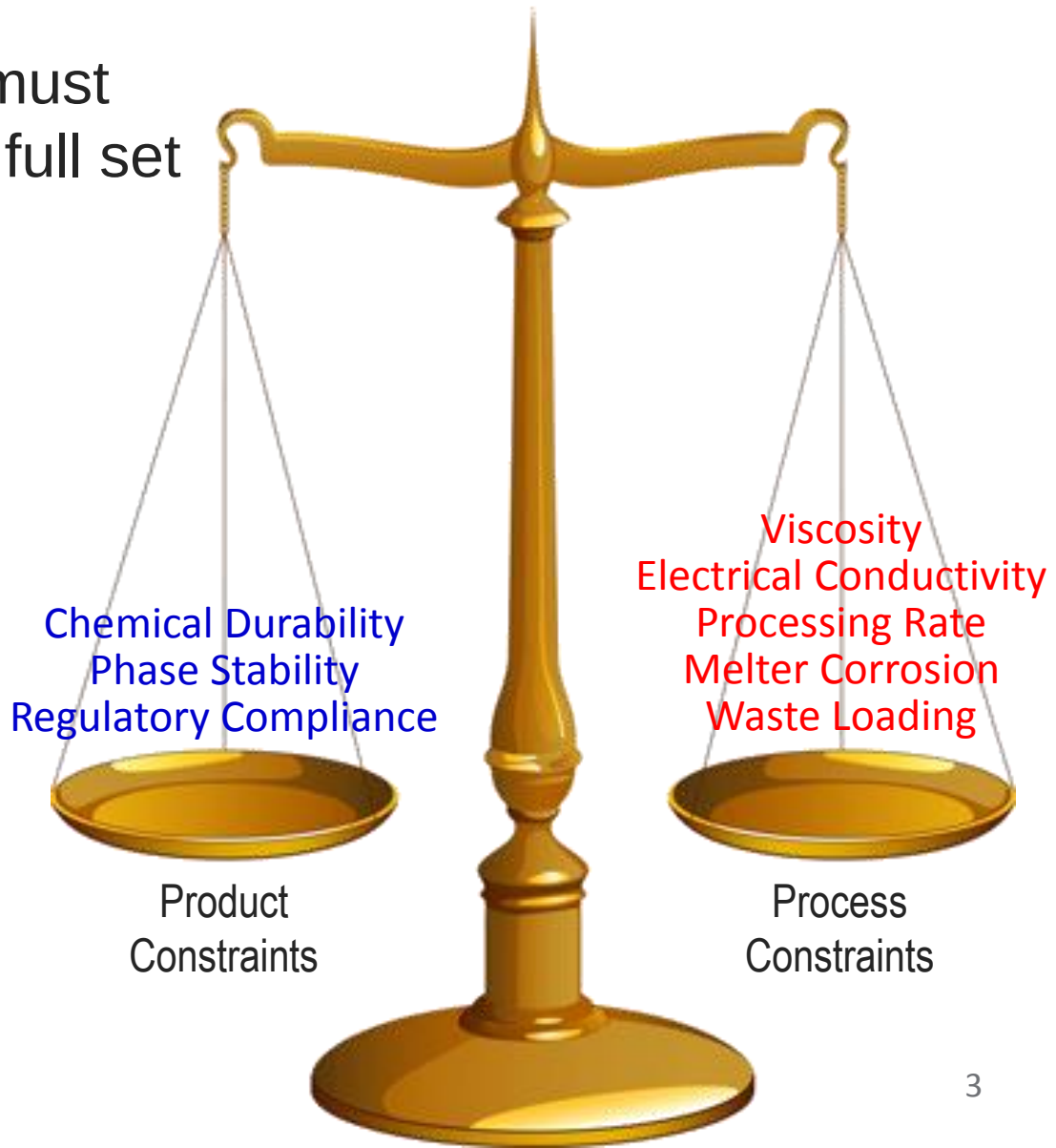


SP8 Baseline Case, DOE 2017, ORP-11242, Rev. 8

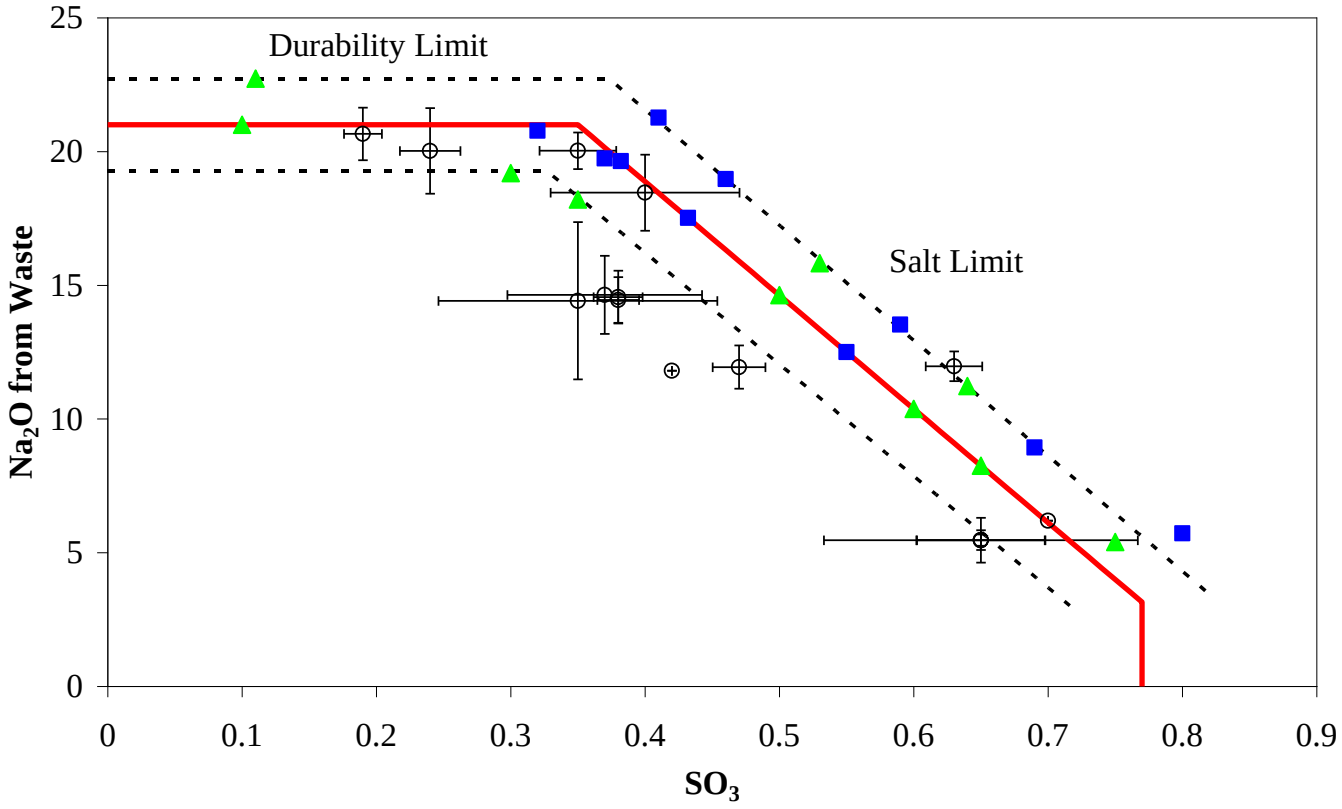
Glass Property Composition Constraints

- Each glass formulation must simultaneously satisfy a full set of requirements
  - Product quality
  - Processability
  - Regulatory/contractual
  - Economic



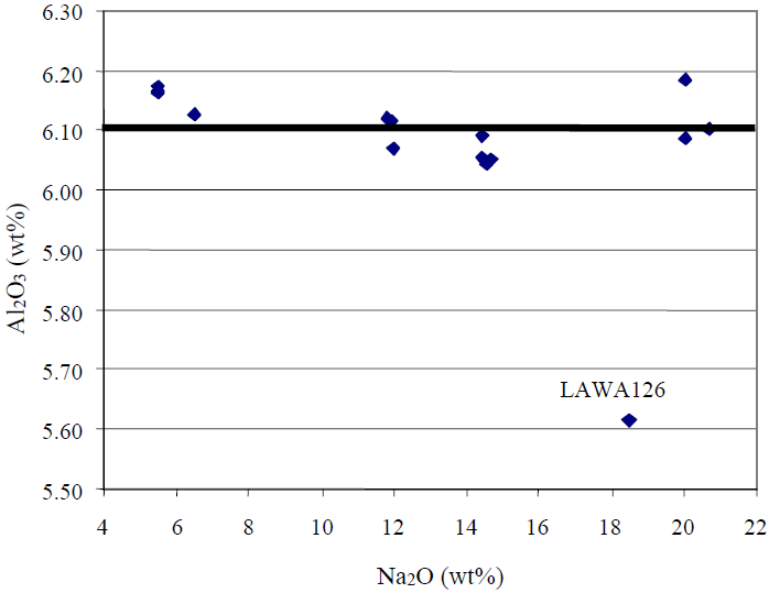
Continuum of Glass Composition Based on Na_2O:SO_3 Ratio

- Baseline glasses formulated and successfully tested up to pilot scale followed distinct composition trends
- Modest waste loadings appropriate for plant commissioning with minimal risk
- Generally durability limited at high soda extreme, salt limited at high sulfate extreme

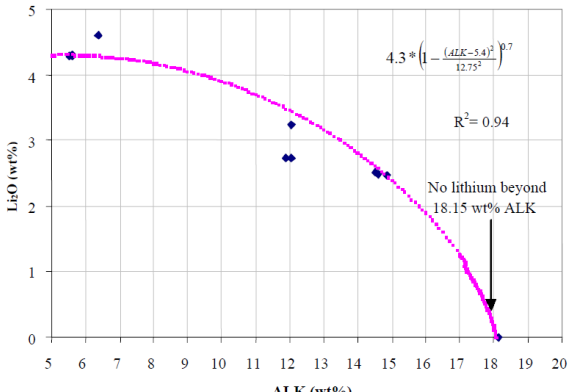


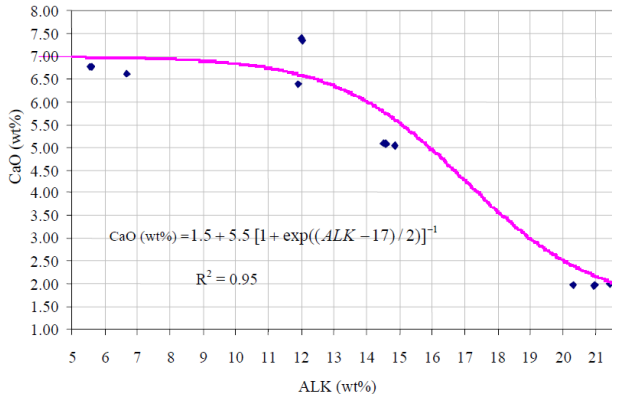
Continuum of Glass Compositions

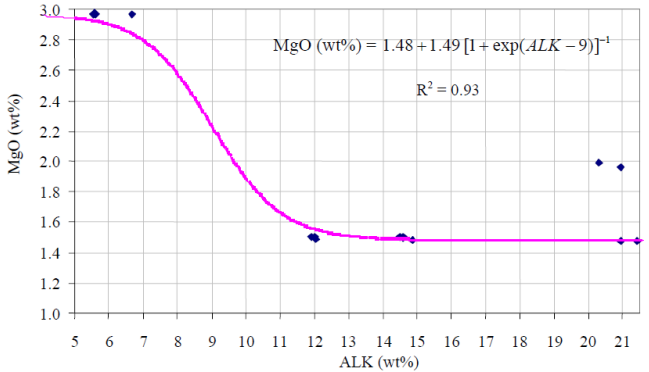
- Constant concentrations of:
  - Al_2O_3 (6.1)
  - B_2O_3 (10)
  - Fe_2O_3 (5.5)
  - TiO_2 (1.4)
  - ZnO (3.5)
  - ZrO_2 (3)
- Concentrations of CaO, Li_2O, and MgO based on alkali concentration
- SiO_2 is 1-sum of everything else



Muller et al. 2004; VSL-04L4460-1, Rev. 2





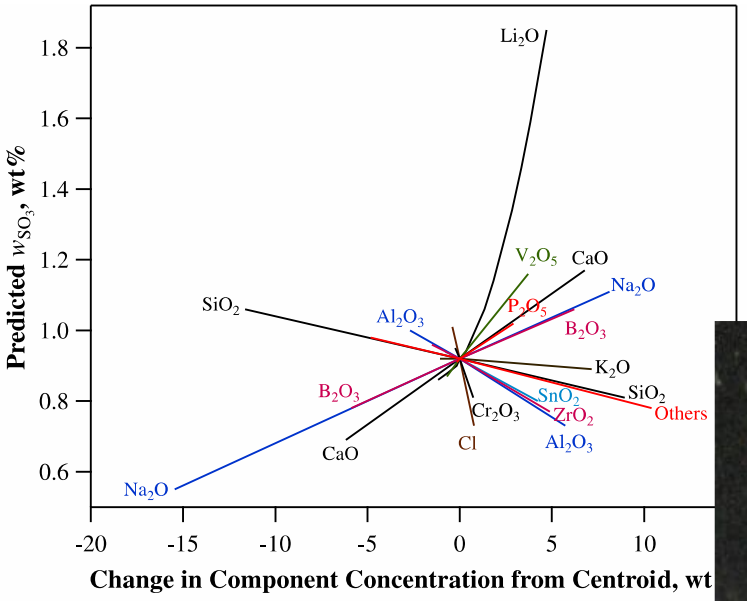


Advanced Glass Development

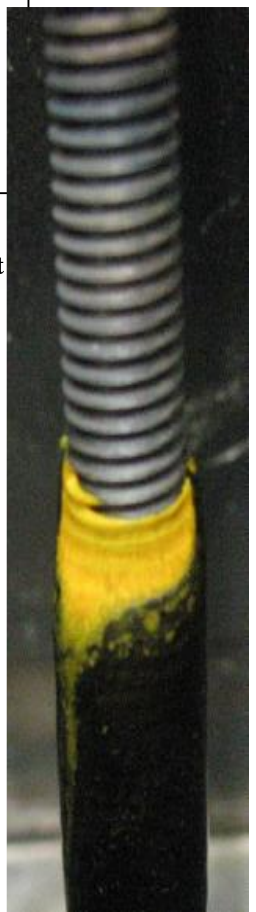
- Previous “baseline” glass development was aimed at commissioning of the plant with a limited range of waste compositions (specified in contract) and modest waste loadings
- Current research to reduce operations risks (in startup and operations) and improve efficiency
  - Primarily aimed at maximizing waste loading and operational flexibility while not significantly impacting design or on-line availability/processing rate
  - ORP led; PNNL and VSL primary; SRNL, WSU, Rutgers, INL, SwRI, Sheffield U, SHU, Vanderbilt U, ICT, USC support
- Modeling and testing at bench and melter scale is underway to enable application of these advances in startup and operation

Primary Challenges to Increased Waste Loading

- Sulfate-based salt segregation
  - Corrosive to melter materials, increase volatility, may impact waste form
  - Increased most by Cl^-, SO_4^{2-}, CrO_4^{2-} which are rich in some wastes and concentrated in off-gas recycle
  - Decreased most by Li_2O, V_2O_5, and CaO used as additives to improve solubility
- V_2O_5 impact?
  - "There is no experimental evidence from XANES, EXAFS, or Raman spectroscopy of vanadium providing additional sulfur bonding sites in borosilicate glass by the presence of vanadium–sulfur bonds or of vanadium bonding to sulfate tetrahedra"



Composition effects on sulfate solubility; from Vienna et al. 2014. J. *Am. Ceram. Soc.*, **97**(10):3135–3142.

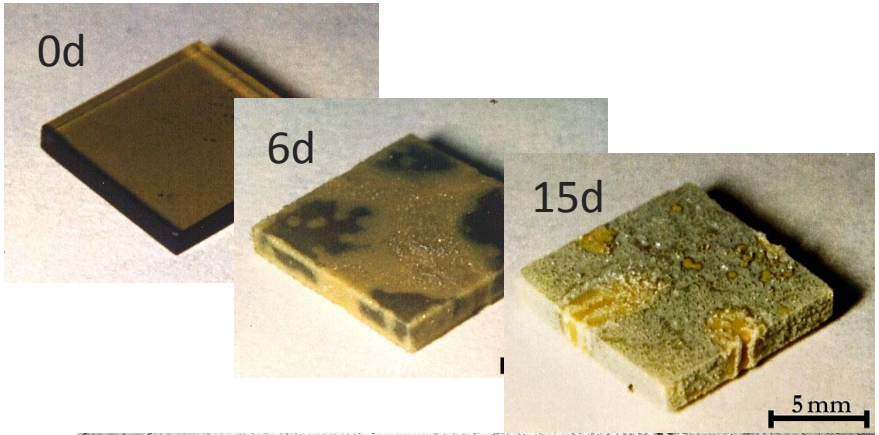


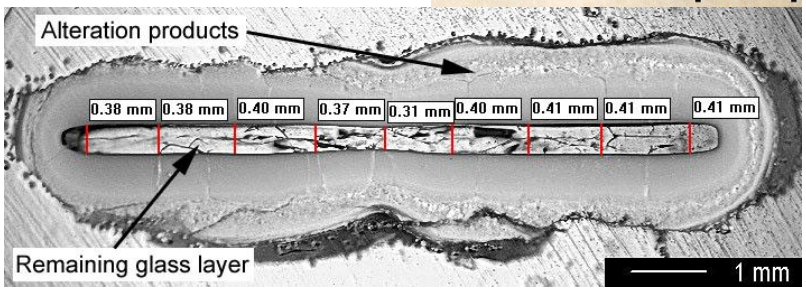
All-thread rod indicating salt accumulation; from Matlack et al. 2009. VSL-09R1510-2, CUA, Washington, DC.

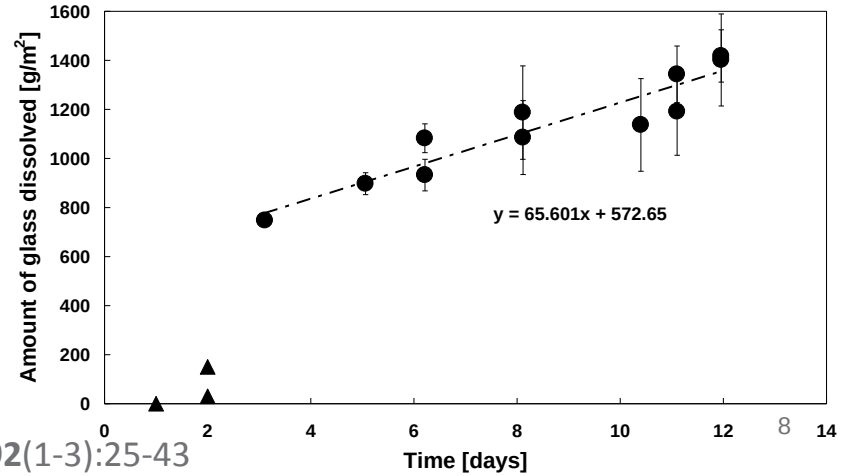
McKeown et al. 2002. J. Non-Crys. Sol. **298**:160–175

Primary Challenges to Increased Waste Loading

- Vapor hydration test (VHT)
  - Hydrothermal test (DIW, 200°C, monolith)
  - Contract requirement (Spec 2.2.2.17) (along with Product Consistency Test)
- VHT may indicate of propensity for corrosion acceleration
- Key assumptions
  - Processes occurring at 200°C are compatible with those at 15°C
  - Acceleration can occur in an open flowing system at 15°C
  - VHT can be consistently measured
  - VHT can be reliably predicted as a function of feed composition



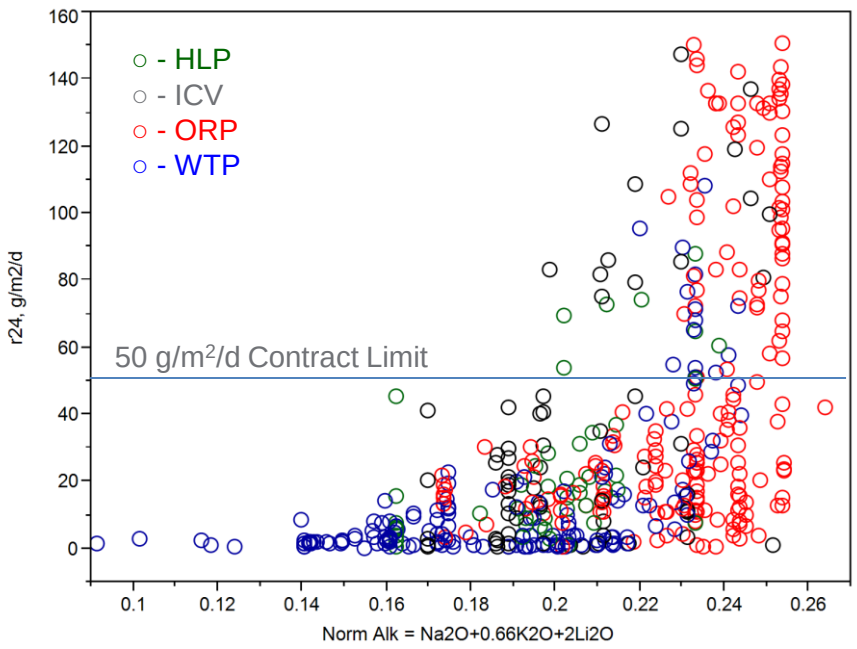


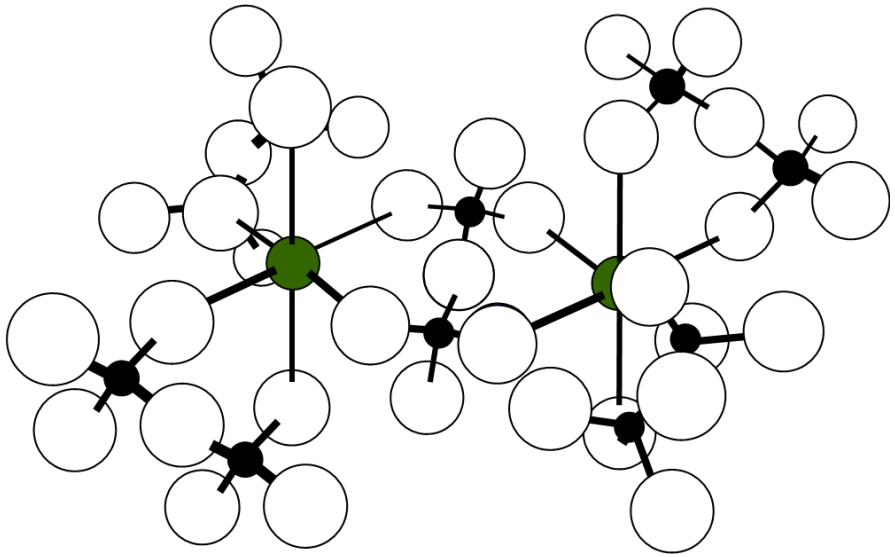


Jiricka et al. 2001, J. Non-Cryst. Sol., **292**(1-3):25-43

Primary Challenges to Increased Waste Loading

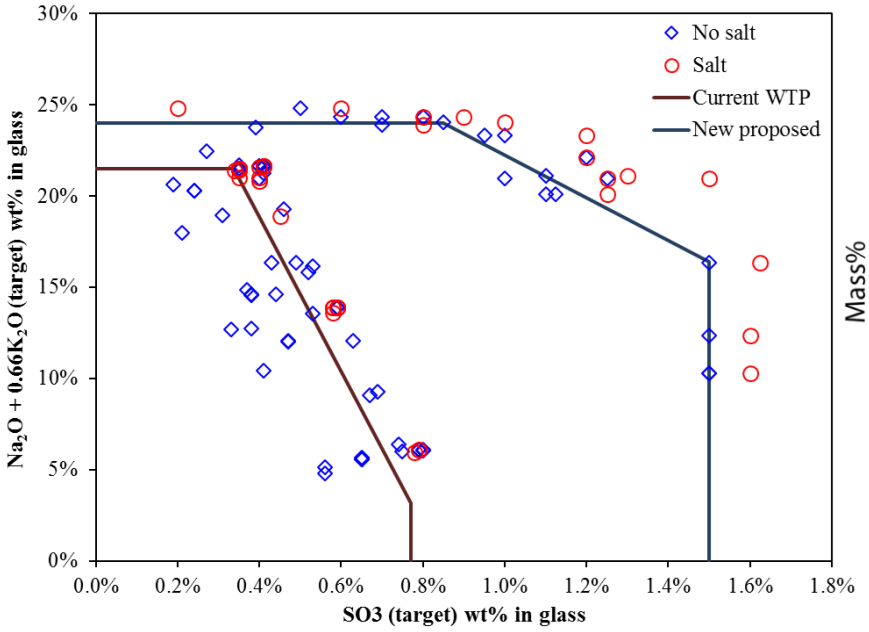
- VHT rate increased most by alkali, decreased most by high valence oxides (ZrO_2, SnO_2, etc)
- Very non-linear composition effects (subject to high uncertainty)
- Blend of ZrO_2 and SnO_2 added to higher alkali glasses to reduce VHT rate

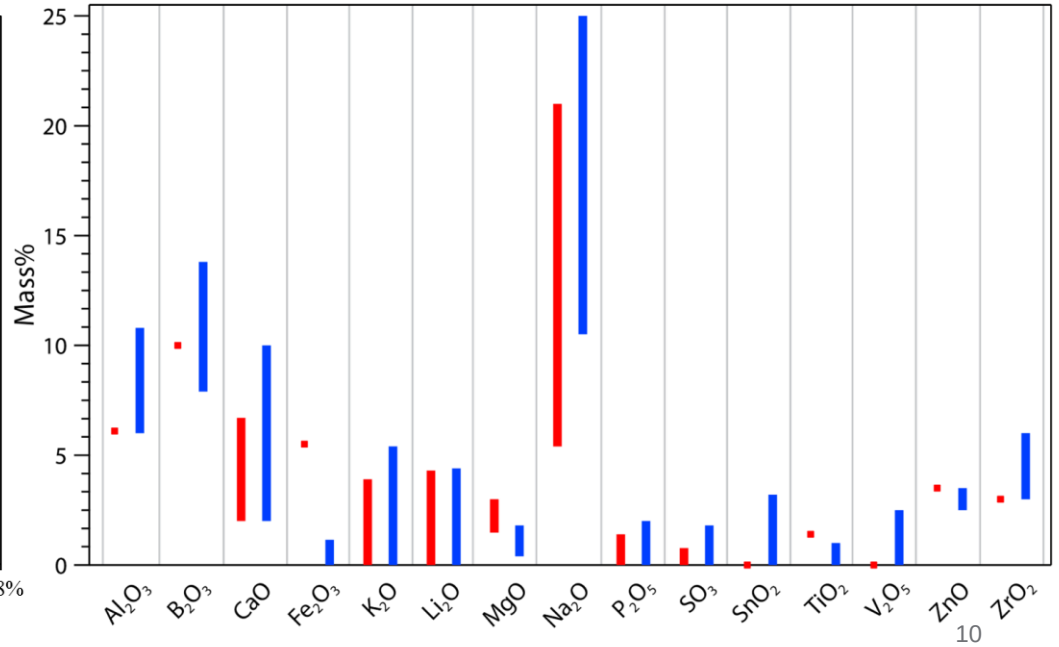




LAW Advanced Glass Formulations

- Model each key property as function of composition
- Numerically optimize glass while accounting for process and prediction uncertainties
- Advanced glasses significantly more tolerant to S, Cl, etc. (less sensitive to recycle stream)

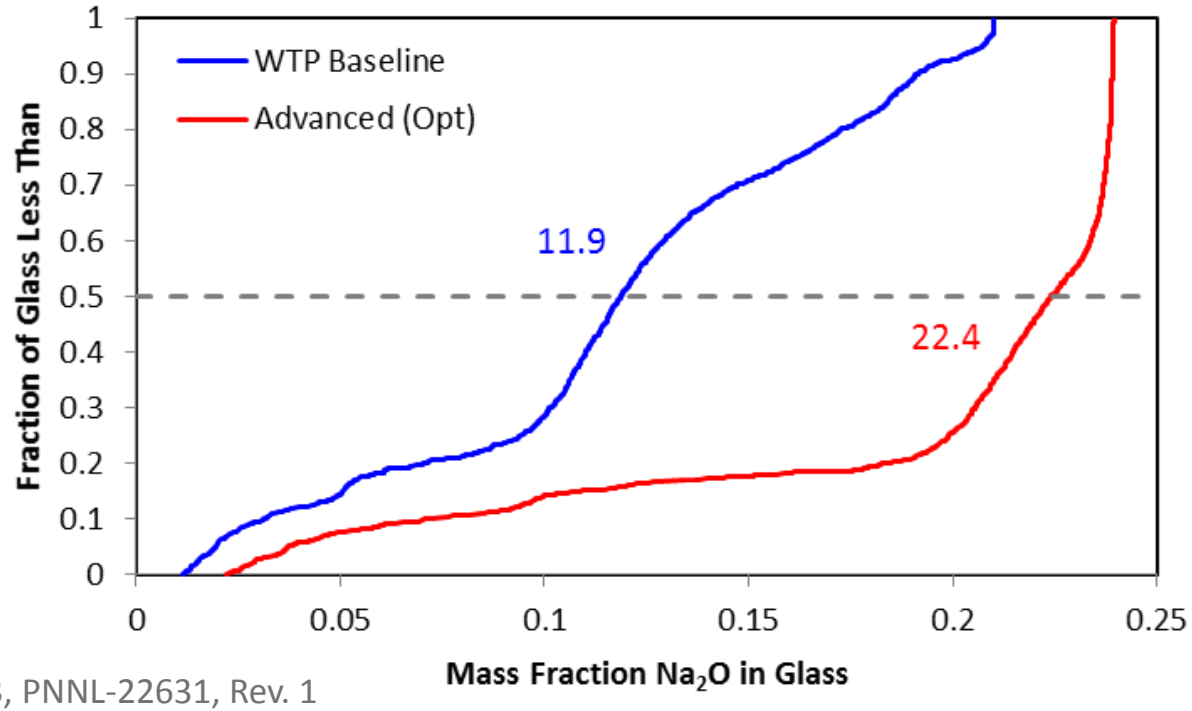




Vienna et al. 2016, PNNL-25835

Significant Increase in Waste Loading

- Loading of LAW in glass is roughly double in advanced glasses (weighted average 22.4 wt% Na_2O)
  - Roughly 5.5% higher waste loading (less glass) would be produced if VHT constraint were relaxed
  - Additional conservatisms have been identified and are being addressed to add processing flexibility/robustness



Vienna et al. 2013, PNNL-22631, Rev. 1

Thanks for your attention!