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Recent Developments in the HLW Glass Formulation for the Hanford Tank Waste Treatment and Immobilization Plant and their Impacts on its Mission

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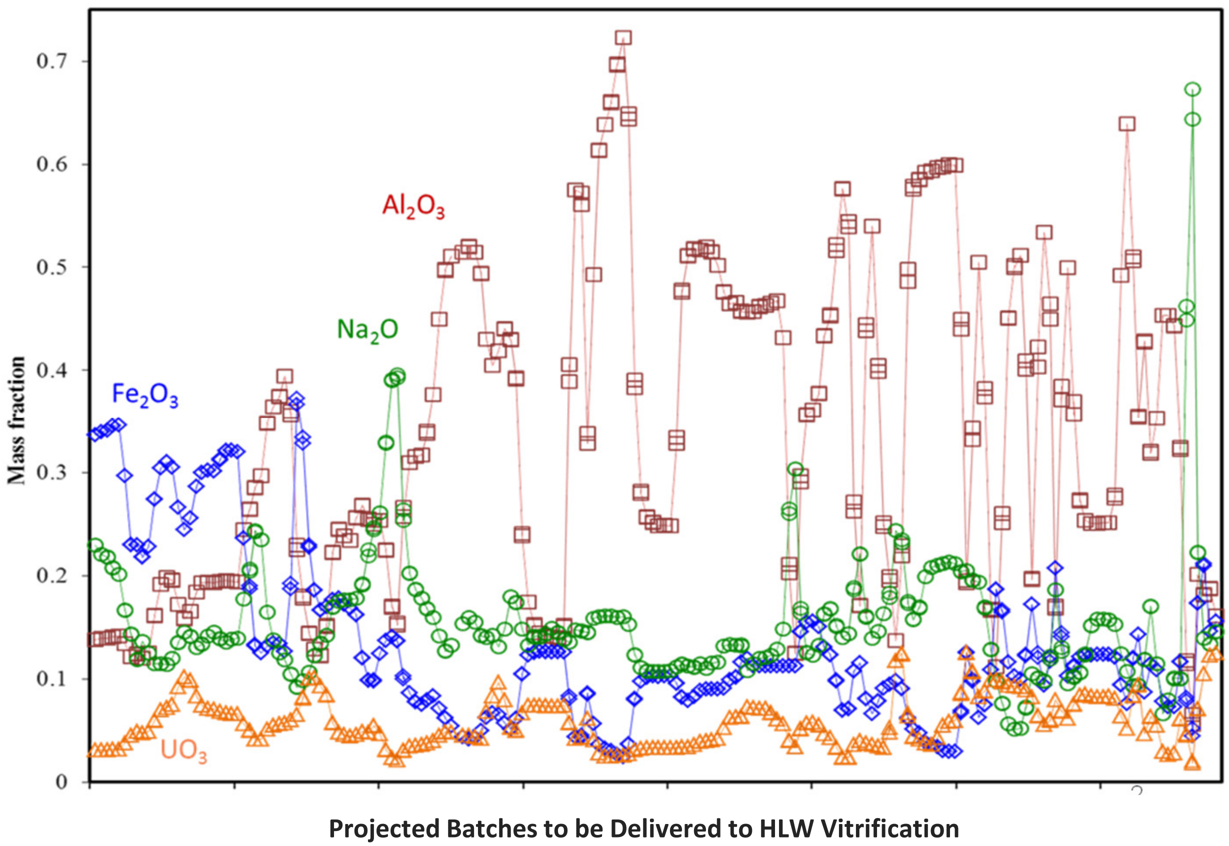
Hanford Tank Waste

- Hanford processed ~100,000 tU from 1943 to 1988 and generated 2,000,000 m^3 of liquid HLW
- Five major chemical processes were performed to generate and alter the HLW composition: bismuth phosphate, REDOX, U recovery, PUREX, and Cs/Sr recovery → resulting in a very diverse waste stream
- Roughly 200,000 m^3 of diverse neutralized HLW currently resides in 177 underground storage tanks
- The waste contains 64 chemical components that will vary from batch-to-batch to the HLW Vitrification Plant



Hanford Tank Waste Solution

- The DOE and their contractors are designing and building the Hanford Tank Waste Treatment and Immobilization Plant (WTP)
  - Receive tank waste, separate into high-volume low-activity and low-volume high-activity fractions, separately vitrify both fractions
  - Design and construction project 68% complete as of March 2014

Vitrification Technology Challenge

- Waste throughput will influence cleanup cost and schedule

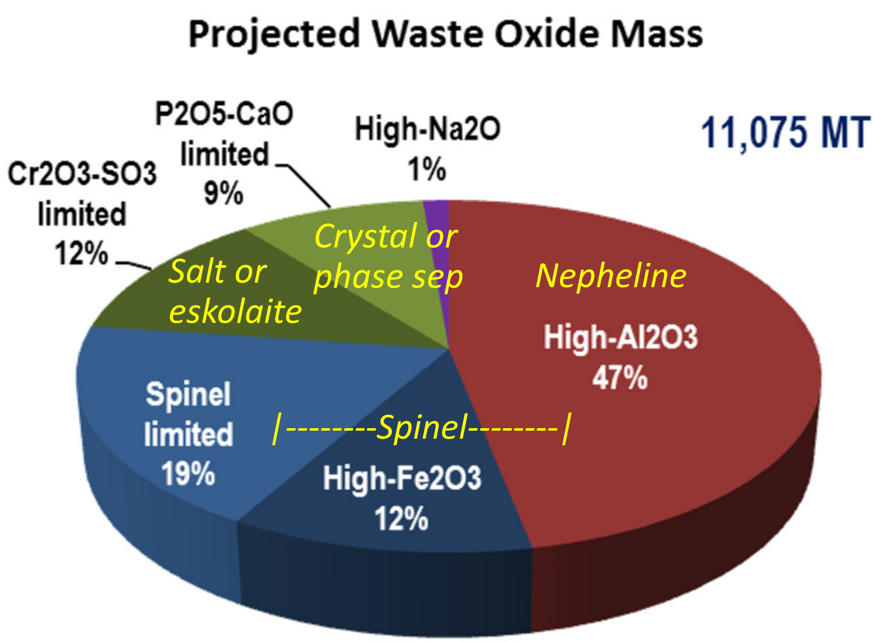
  Waste Throughput = Waste Loading × Processing Rate × Online Efficiency

- Increasing the waste loading and processing rate without significant impacts on facility online efficiency is the focus of our research

- Increasing the loading of potentially troublesome components in HLW glass may also reduce waste pretreatment requirements thereby simplifying the overall WTP process

Approach

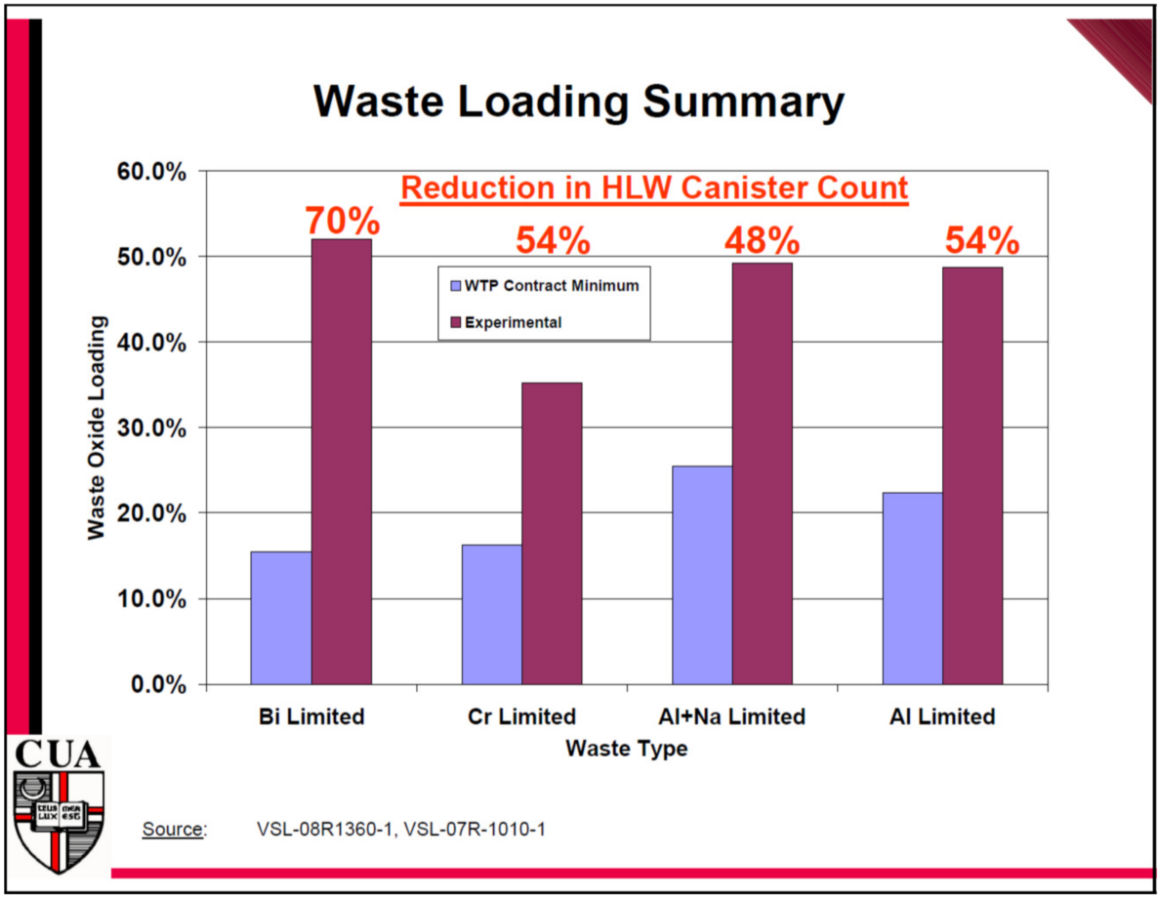
- Waste compositions grouped into categories based on the factors that limit loading in glass



- Develop advanced glasses for wastes in each category (with high waste loading and melter throughput) to define composition boundaries
- Develop glass property data and models within each composition boundary
- Use models to optimize glass, operate plant, qualify resulting glass

High-Level Waste Glass Formulation Results

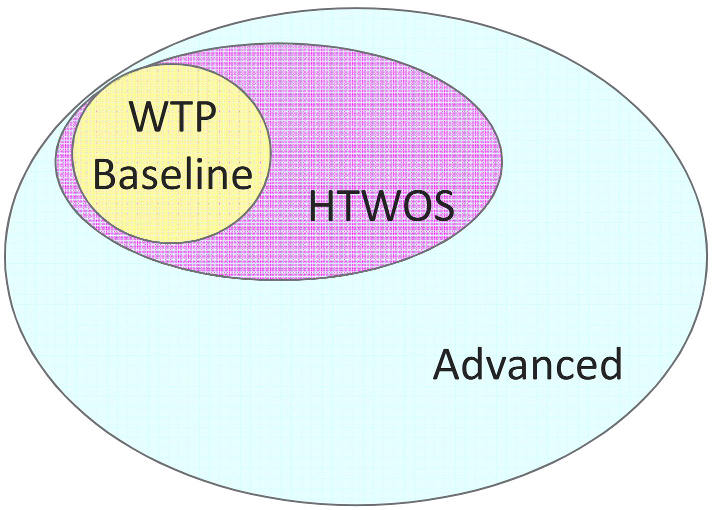
- Many recent reports and presentations have shown increased loading of individual HLW compositions in glass
  - To date, 226 simulated HLW glasses with high waste loading and 305 glasses within the current WTP Baseline (relatively low waste loading) have been fabricated and characterized
  - Many of which have been processed successfully in scaled melter tests



- Challenges are to: 1) use existing data to estimate the glass to be produced from all the wastes, and 2) to develop data with sufficient coverage of the expanded region to model properties.

Models Developed Based on Advanced Glass Formulations with High Waste Loading

- Advanced models aimed at giving a preliminary estimate of the maximum waste loading that can be obtained over broad waste composition region



WTP Baseline

- Narrowest range
- Sufficient uncertainty quantification for plant operation
- Full QA data and models
- Appropriate for plant operation

HTWOS Model

- Broader range
- No uncertainty quantification
- Not QA models (some QA data)
- Appropriate for conservative mission planning

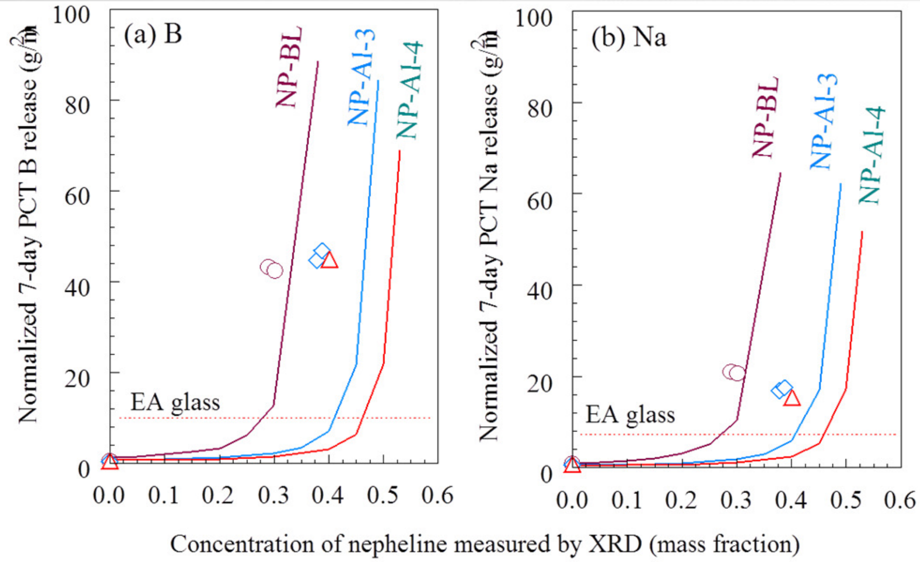
Advanced Models

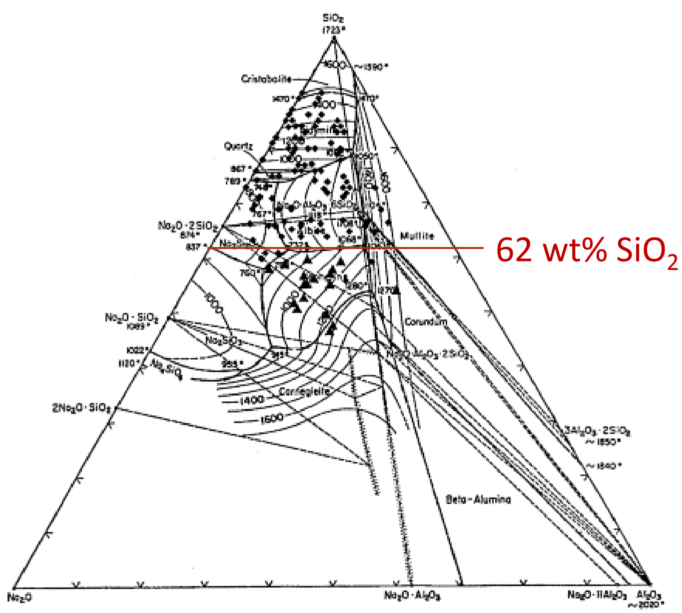
- Broader yet range
- Uncertainty quantification in process
- QA compliant data and models in process of validation
- Appropriate for mission planning and research

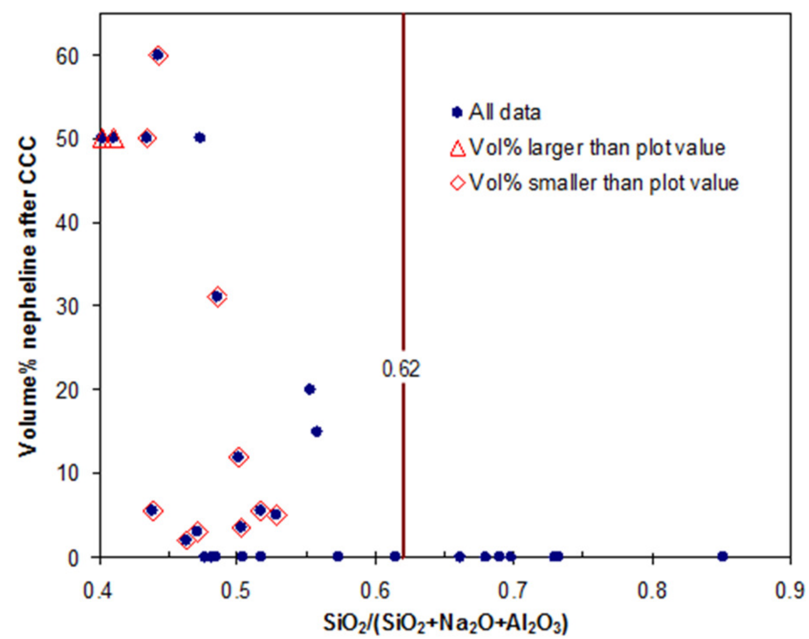
- Advanced models for key properties that limit waste loading most:
  - Nepheline formation on canister cooling
  - Spinel fraction as a function of temperature
  - Sulfate salt formation
  - among others

Nepheline - $NaAlSiO_4$

- Nepheline formation can significantly reduce the chemical durability of glass
- Constraints can be easily employed to reduce the risk of nepheline formation
- These constraints are conservative and limit the achievable waste loading for high Al wastes

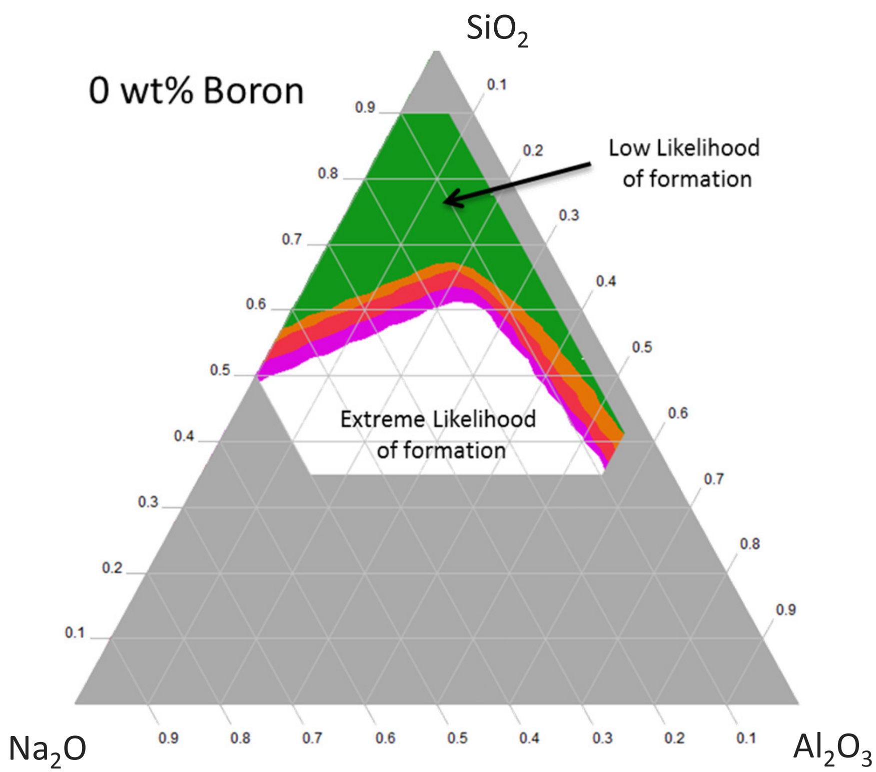


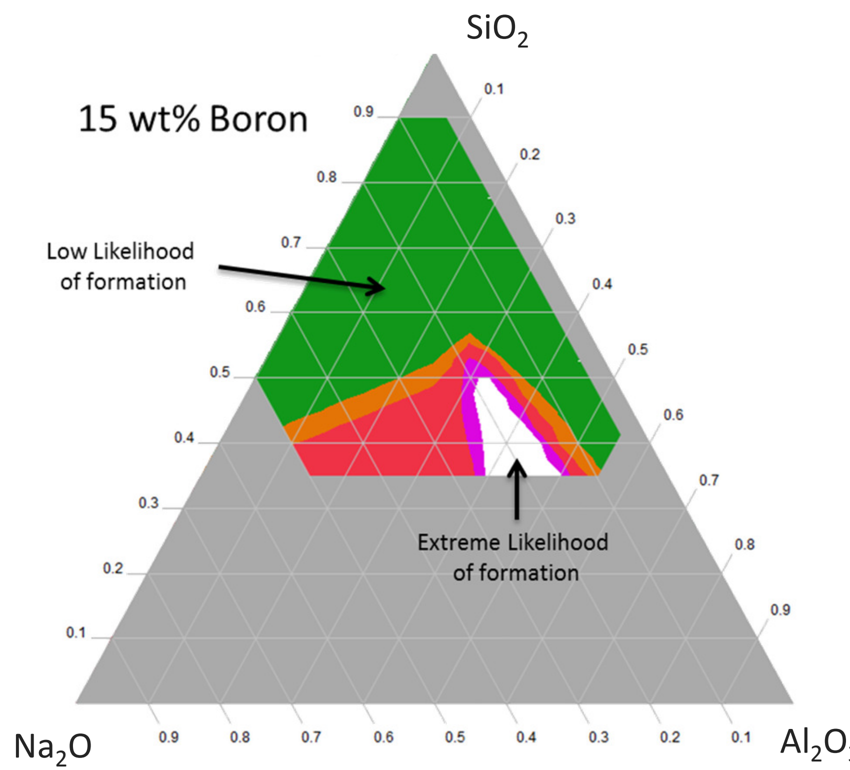




Nepheline Model

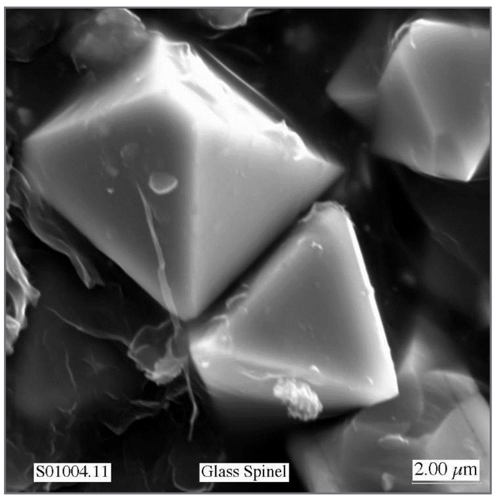
- More complicated model form is required to reduce conservatism
- One approach is neural network model which is used in the preliminary models, other options are being pursued

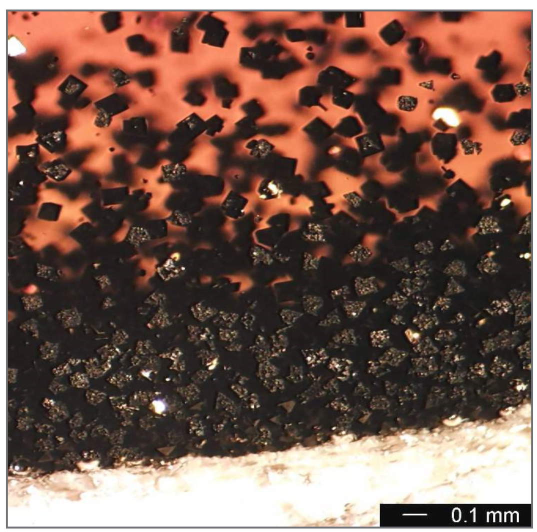


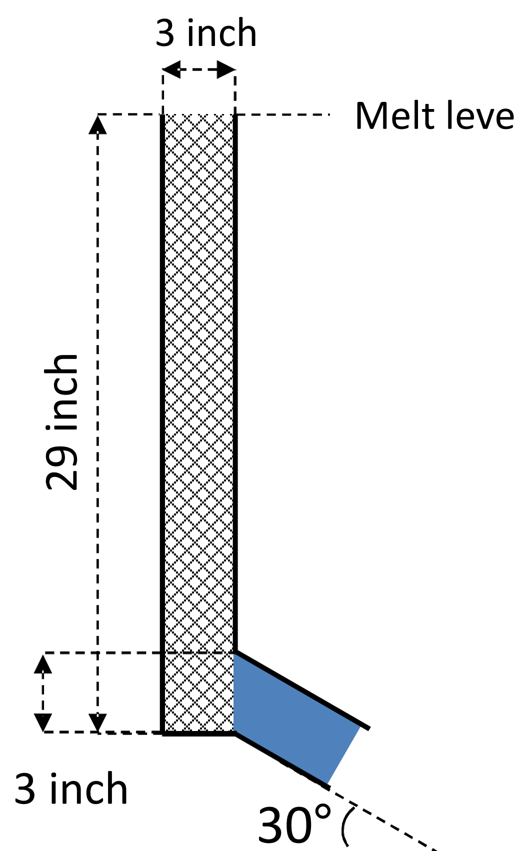


Spinel – $(Fe,Mn,Zn,Ni)(Fe,Cr)_2O_4$

- Can form in the melter during normal operation and idling
- Mostly passes through to the canister – very little impact on glass
- May accumulate in the melter – primarily concerned with pour-spout riser
- Limits the loading for waste with high Fe, Cr, Mn, Ni, and Al
- WTP Baseline and HTWOS limit $T_{1\%}$ < 950°C



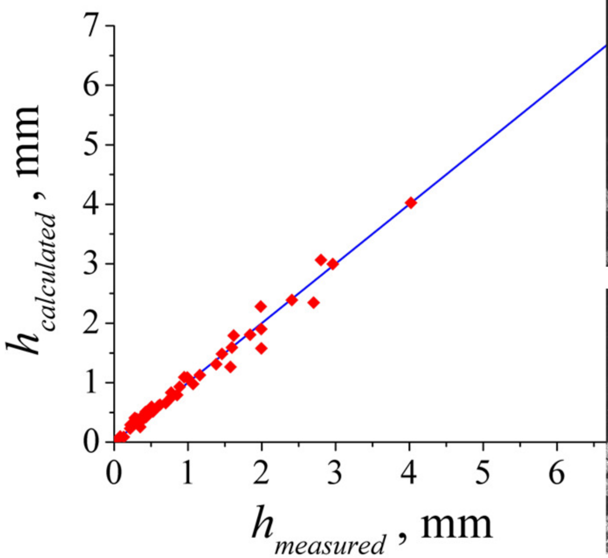


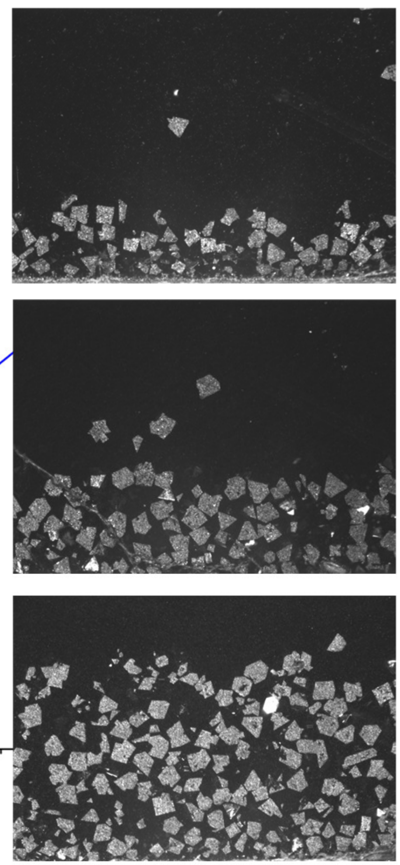


Spinel Model

- Two approaches pursued to avoid potential problem with spinel:
  1. Predict accumulation rate of spinel in pour-spout riser
  2. Predict equilibrium concentration of spinel in melt

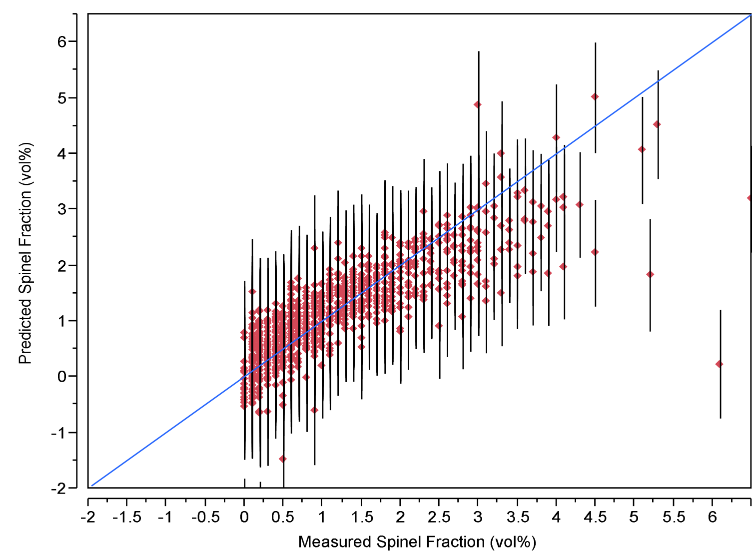
$$h = \sum_{i=1}^{7} h_i x_i + t \sum_{i=1}^{7} s_i x_i$$





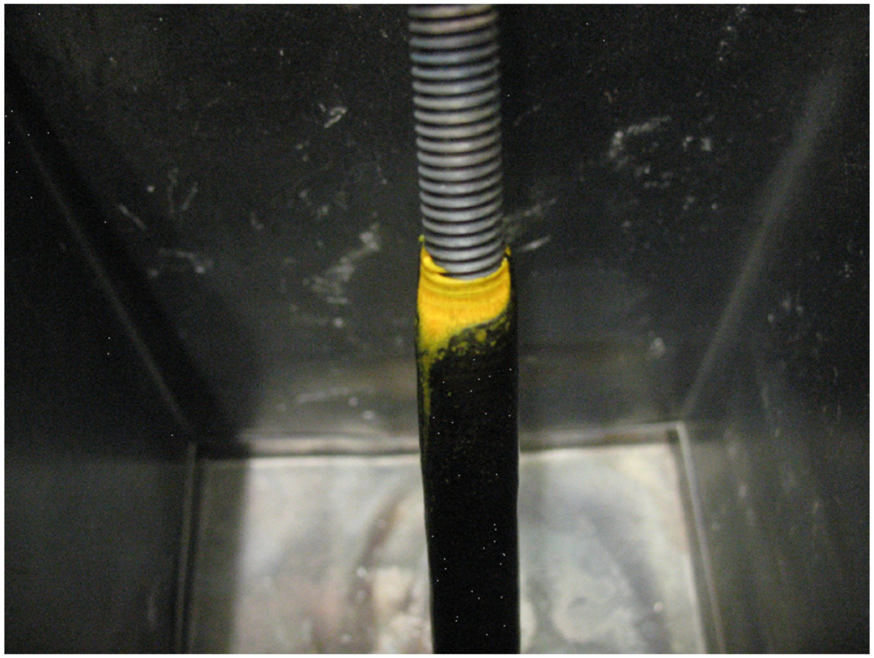
$$c_{Sp} = c_{sp,0} \left\{ 1 - \exp\left[-B_L \left(\frac{1}{T} - \frac{1}{T_L} \right) \right] \right\}$$

$$c_{Sp} \cong a + bT \;\Rightarrow\; c_{Sp} \cong \sum_{i=1}^{p} (a_i + b_i T)\, g_i$$



Salt Accumulation in Melter

- May reduce increase corrosion rate of melter and off-gas components
- Typically a problem with wastes relatively high in sulfate, chromate, and halides
- A traditional challenge has been how to correlate lab-scale measurements of sulfur solubility with salt formation in the dynamic melter process



Example salt probe showing sulfate salt from the top of a melter test. Courtesy of the Catholic University of America.

Sulfur Model

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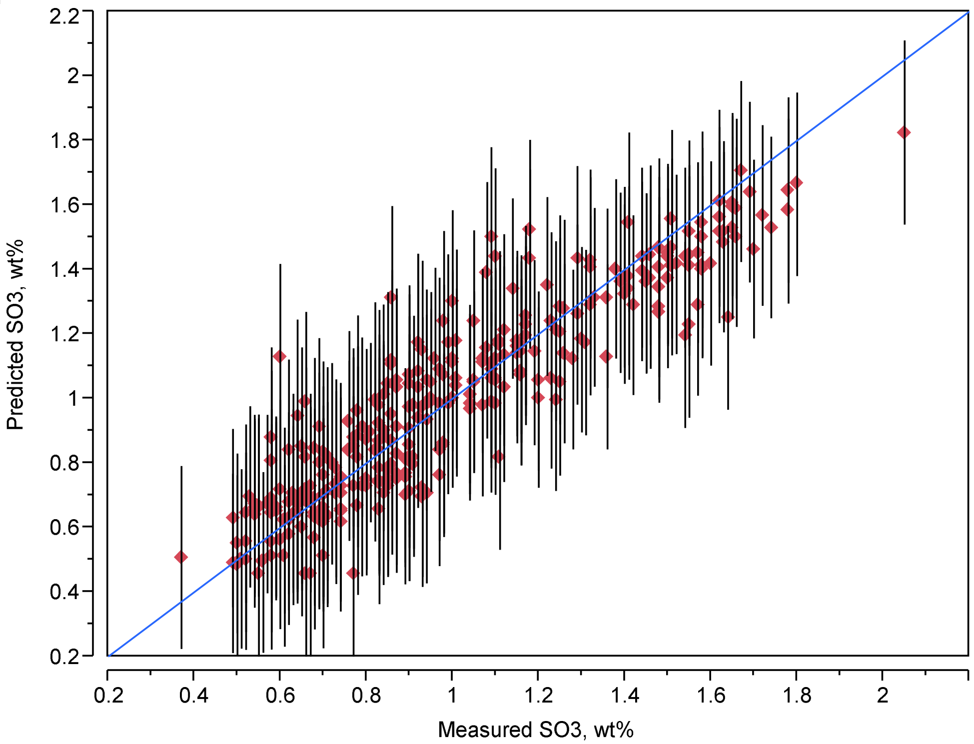
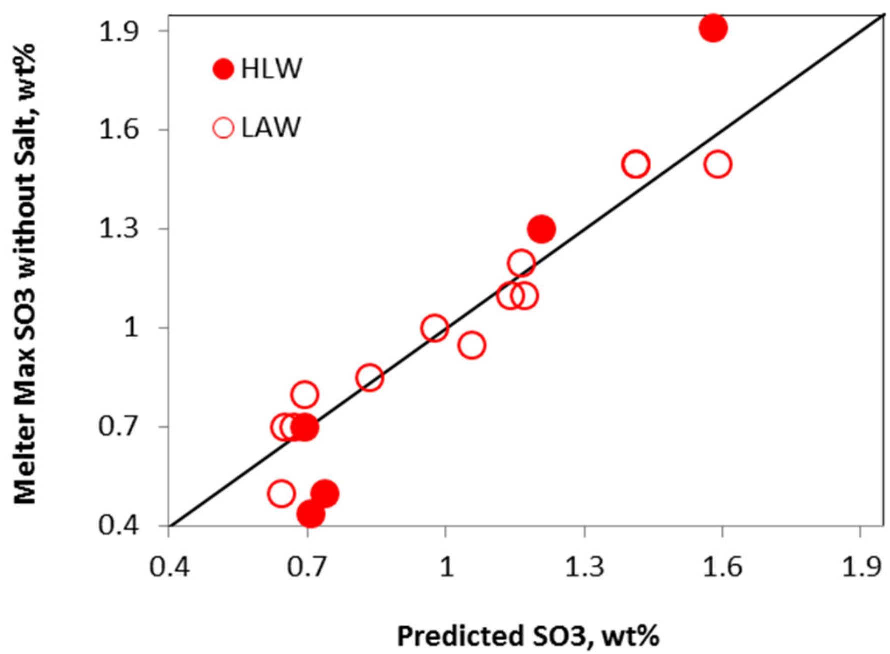
- A model was fit to crucible-scale sulfur solubility of 312 combined HLW and LAW glasses

$$w_{SO_3}^{Limit} = \sum_{i=1}^{p} s_i n_i + s_{Li_2O^2} n_{Li_2O}^2$$

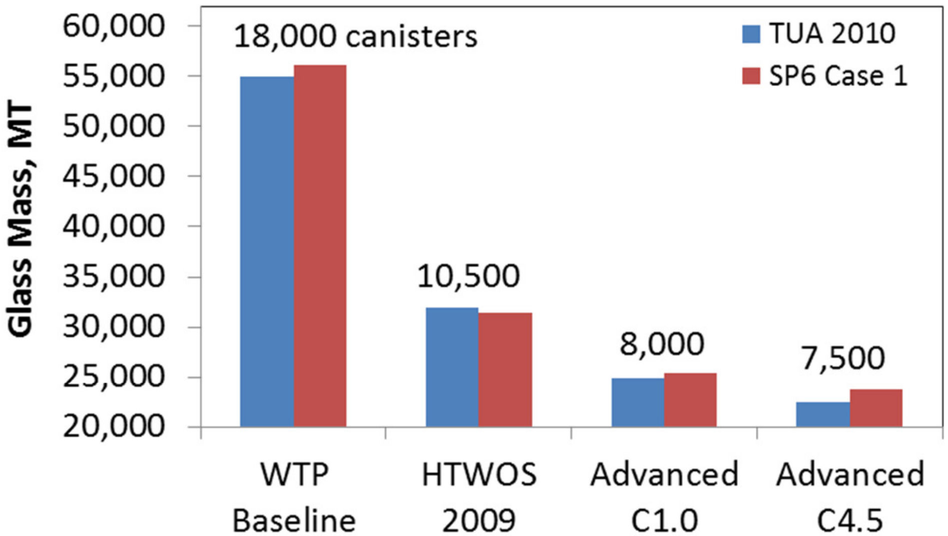
- The model was shown to predict the maximum concentration in melter feed without salt accumulation reasonably well

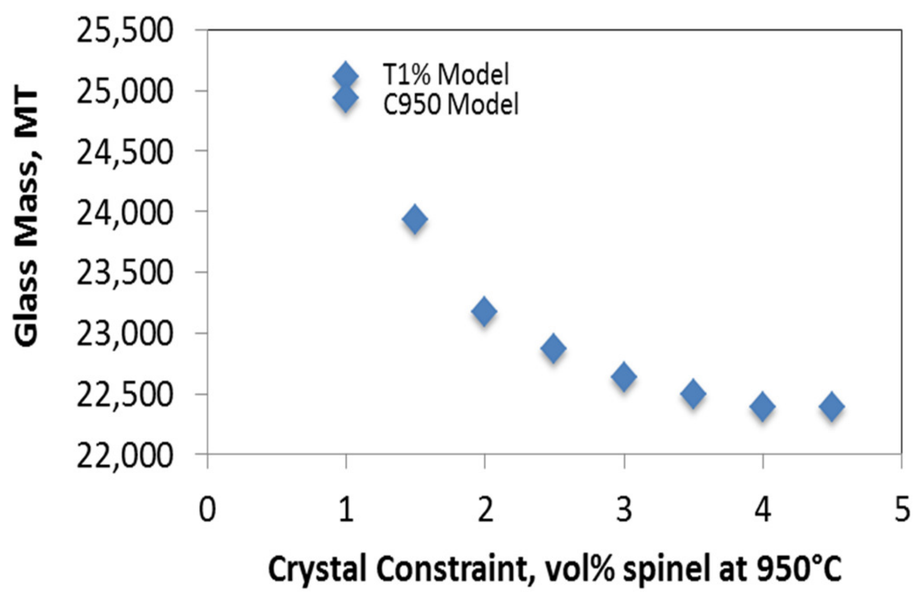




Impacts of Advanced Models on Glass Mass

- WTP Baseline yields highest glass mass
- HTWOS models give 40% reduction in glass
- Advanced model give further 20 to 30% reduction in glass (depending on spinel volume constraint)

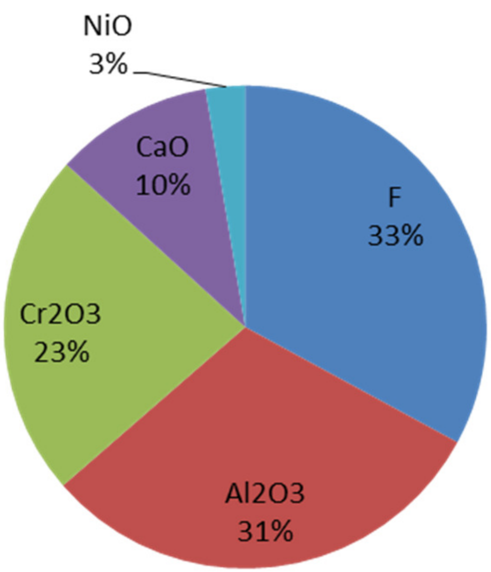




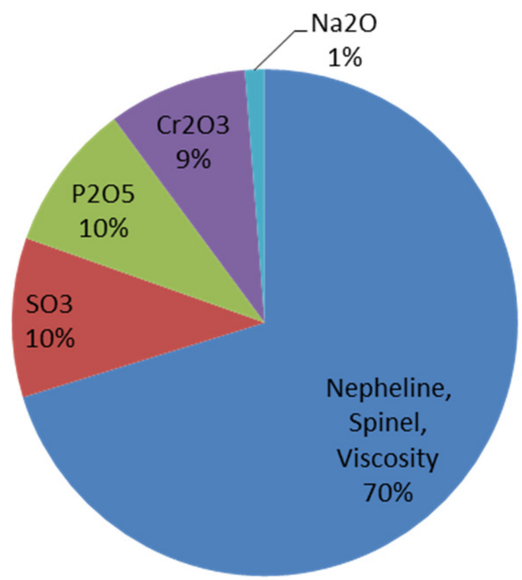
Impacts of Advanced Models on Glass Mass

- WTP Baseline glass limited by model validity constraints (MV -- range of data used to fit models)
- 70% of HTWOS glass limited by properties and 30% by MV constraints
- Advanced glass limited primarily by property limits with ~7% MV

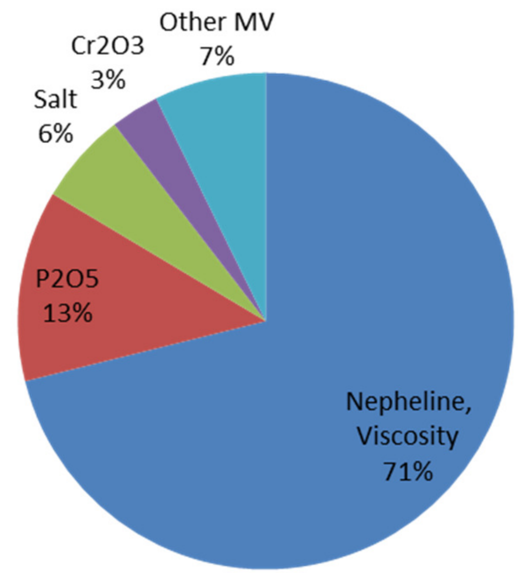
WTP Baseline



HTWOS 2009



Advanced (C4.5)



Summary and Conclusions

- Hanford HLW vitrification must handle a diverse range of waste compositions
- Loading of HLW in glass will influence the cost and schedule of cleanup
- High loaded glasses have previously been reported for individual waste composition estimates but extrapolation to the full range of wastes has not previously been possible
- Preliminary models have been developed for the properties found to be most influential on glass volume: nepheline formation, spinel concentration, and sulfur tolerance
- Applying these models has already shown the potential for significant increases in waste loading across the entire range of Hanford HLW

- Ongoing efforts
  - Complete data collection and advances in modeling approaches focusing primarily on nepheline, spinel, and salt formation
  - Complete qualification of existing or unqualified data activities and deliver glass models for use in plant operations

Acknowledgements

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- Thank you for your attention! Any questions?

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