Glass formulation and Testing for U.S. High-Level Tank Wastes: Project 17210, Year 1 Status

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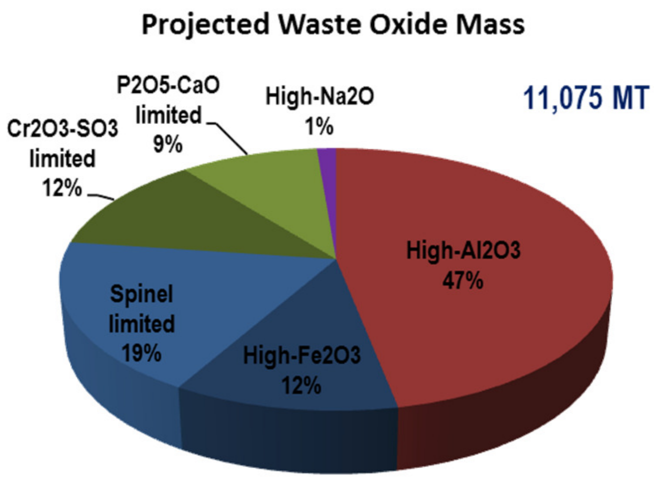
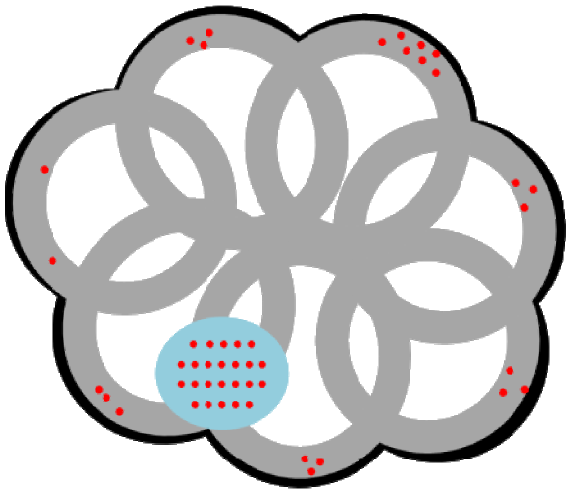
Presentation Outline

- Background and Objectives
- Research Approach
  - Definition of two tasks
- Task 1: Glass Property Data with Systematic Composition Variation
  - Results for year 1
  - Planned accomplishments for year 2
- Task 2: Nepheline Model Development
  - Results for year 1
  - Planned accomplishments for year 2
- Summary and Conclusions
- Acknowledgements

Background

- Hanford is currently storing over 200,000 m^3 of high-level tank waste
- The waste spans a broad range of composition but can be grouped into categories for purposes of glass formulation development:

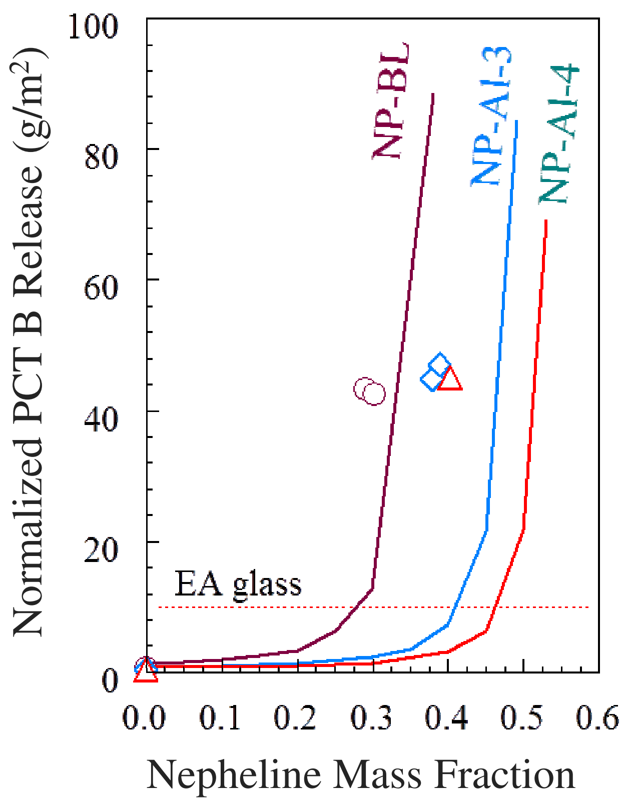


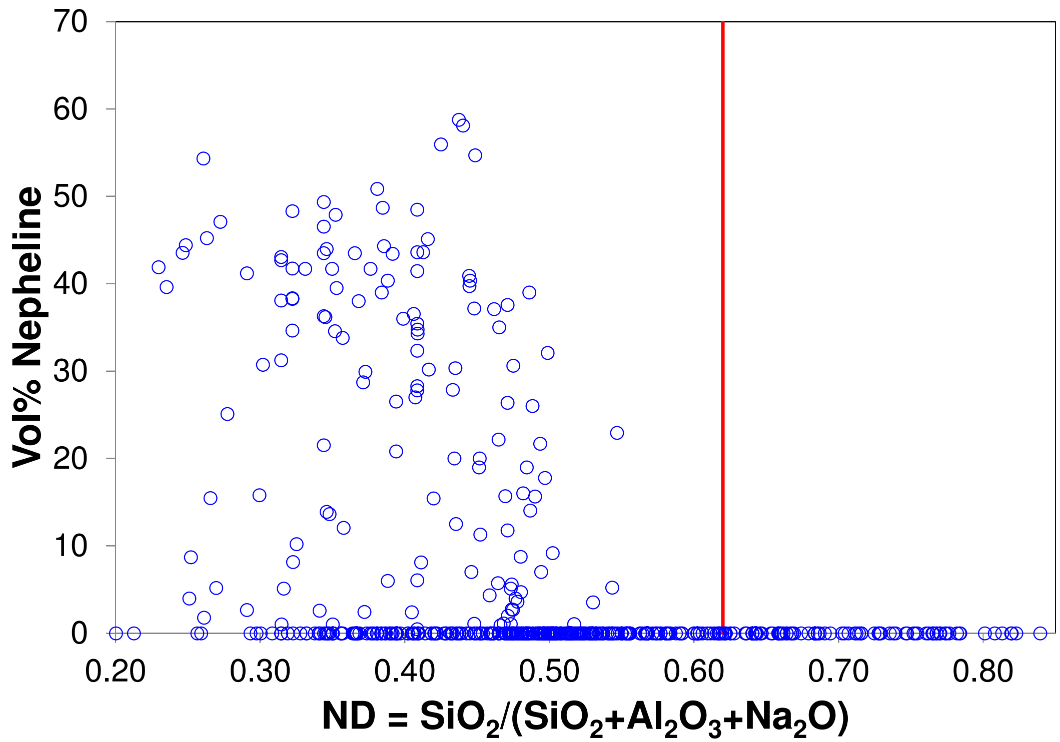


- Current glass property models were developed primarily for the high Fe wastes with moderate waste loadings
- A multi-lab effort is underway to expand the formulations and model to cover the full range of wastes at high waste loadings to reduce the cost and risk associated with tank waste cleanup (CUA, ORP, PNNL, SRNL)
- Development is focused on one group at-a-time with high-Al first

Nepheline in High-Al_2O_3 Hanford HLWs

- Prone to nepheline (ideally $NaAlSiO_4$) formation on slow cooling
  - Nepheline formation may significantly reduce durability of glass
  - Nepheline formation can be avoided, but current model is too conservative
- Al_2O_3 also increases liquidus temperature (T_L) and viscosity (η)





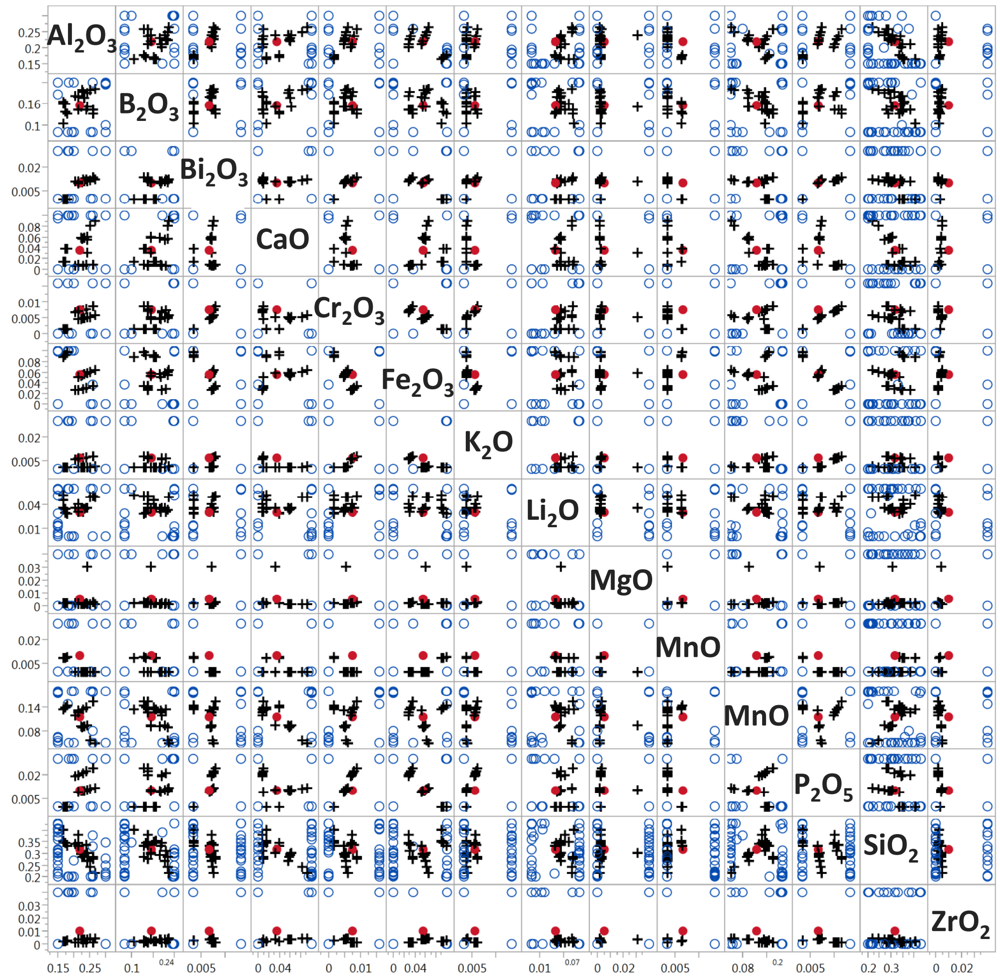
Two Related Tasks

- Task 1: Develop glass property-composition models covering the region of interest for Hanford high-Al HLW glasses
  - Define the composition region of interest
  - Design a matrix of glass composition with systematic composition variation across the region of interest
  - Fabricate and test properties for matrix glasses
  - Evaluate data and fit property-composition models
- Task 2: Develop an approach for predicting formation of nepheline in slow cooled glass melts that is less conservative than the current ND
  - Evaluate potential modeling approaches to represent complex compositional relationships
  - Fit preliminary models using initial dataset
  - Collect data focused at the composition region of highest uncertainty and most applicability to Hanford high-Al HLW glass compositions
  - Fit final model with combined dataset from tasks 1 and 2

Task 1: Matrix Design

- Defined the composition region of interest based on projected glasses with high-Al HLW and existing glass formulations with high WL
- Developed matrix using modern statistical design methods
  - 40,000 extreme vertices
  - 45 new compositions to backfill 22 existing glasses

Oxide	Min	Max	Centroid
SiO_2	**20**	**43**	**31.5**
Al_2O_3	**15**	**30**	**22**
B_2O_3	8	22	15.5
Na_2O	5	18	11.5
Fe_2O_3	0	10	5.5
CaO	0	10	3.5
Li_2O	0	6	3
P_2O_5	0	3	1
ZrO_2	0	4	1
Bi_2O_3	0	3	1
MnO	0	3	1
Cr_2O_3	**0**	**1.6**	**0.75**
K_2O	0	3	0.7
MgO	0	4	0.5
Others	1.55	1.55	1.55



Task 1: Glass Fabrication

- Batched oxide and carbonate material and homogenized using agate mill
- Melted 1 hour in Pt/Rh crucibles with tight lids and quenched on SS
- Glass ground to powder in WC mill and re-melted 1 hour
- Of the 45 experimental compositions
  - 33 produced homogeneous glasses
  - Nepheline crystallized in 3 glasses
  - Salt segregation in 2 glasses
  - High crystallinity (mostly spinel) formed in 7 glasses
- Some fraction of failed compositions was expected due to the extreme composition envelope and design method
- Iteratively adjusted failed compositions until successful glasses were obtained
  - 94 total compositions melted to obtain 45 experimental glasses

Task 1: “Failed Compositions”

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- 94 unique melt compositions fabricated
  - 4-6 containing nepheline
  - 12 with segregated salt
  - 45 with high crystallinity

= “failed comps”

= Acceptable comps

Nepheline Containing Glasses

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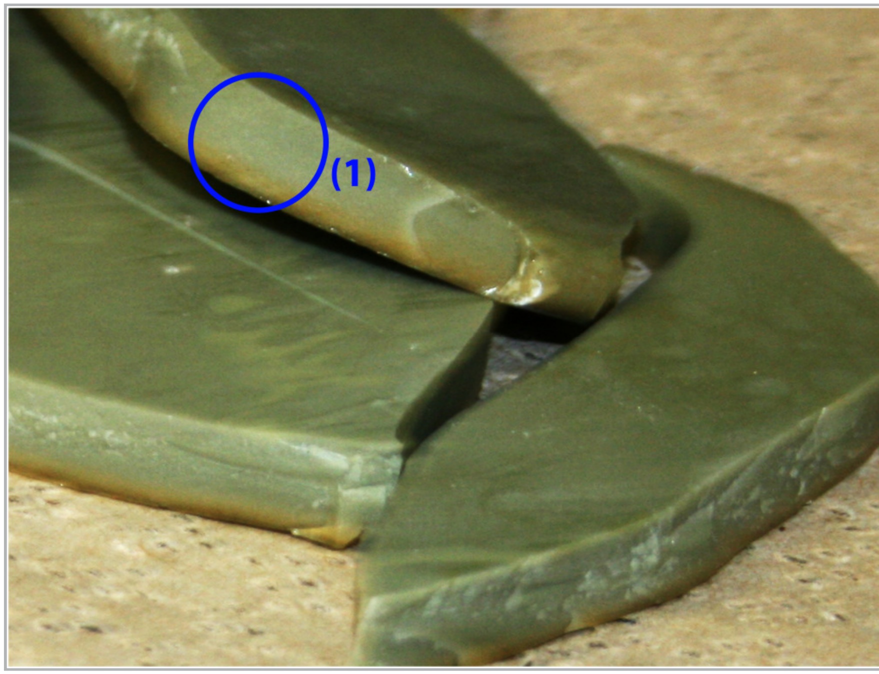
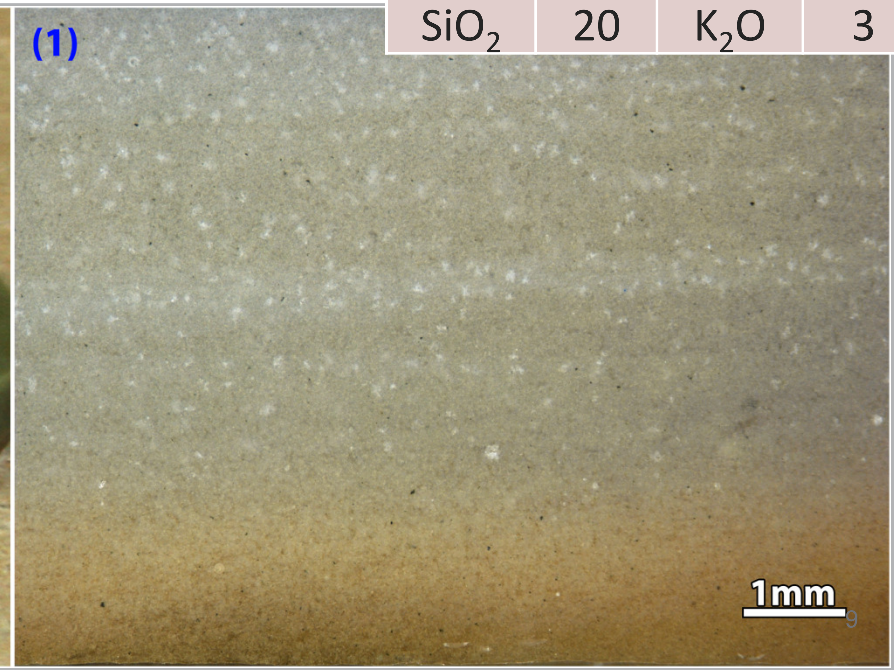
- Between 4 and 6 compositions formed nepheline on quenching
- A preliminary model for nepheline precipitation during CCC (described in Task 2) successfully separated nepheline forming glasses from the other compositions

Oxide	wt%	Oxide	wt%
Al_2O_3	25.5	Na_2O	18
B_2O_3	8	Li_2O	6
SiO_2	20	K_2O	3

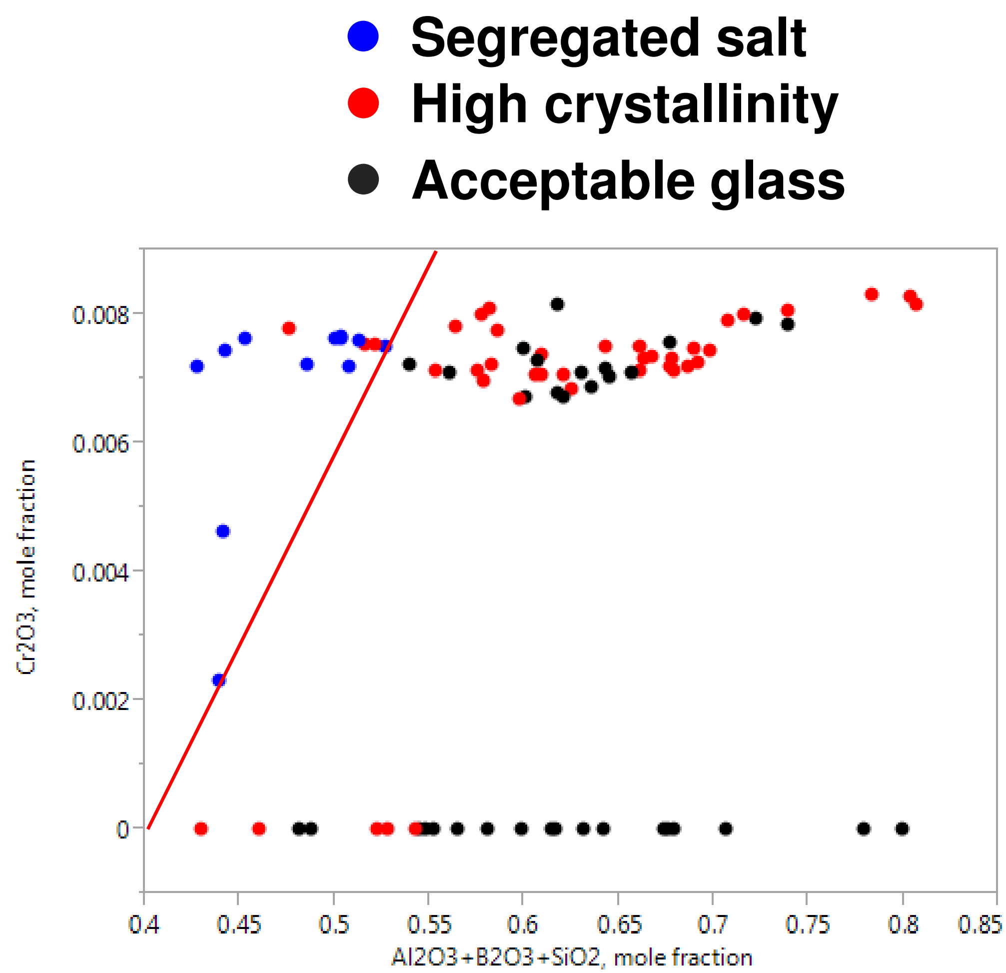




Salt Containing Glasses

- 12 compositions formed a segregated salt phase on quenching
- Only glasses high in Cr_2O_3 and low in combined Al_2O_3+B_2O_3+SiO_2

Oxide	wt%	Oxide	wt%
Al_2O_3	18.2	Li_2O	6
B_2O_3	8	K_2O	3
SiO_2	20	Cr_2O_3	1.6
Na_2O	14.7		



High Crystallinity Glass

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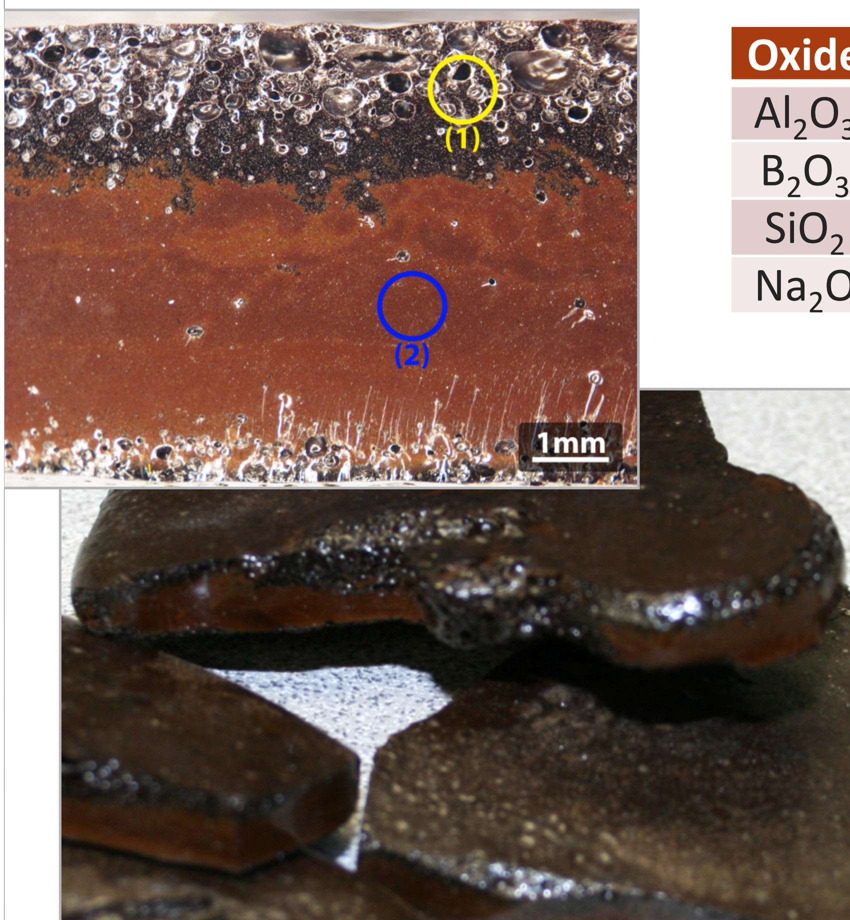
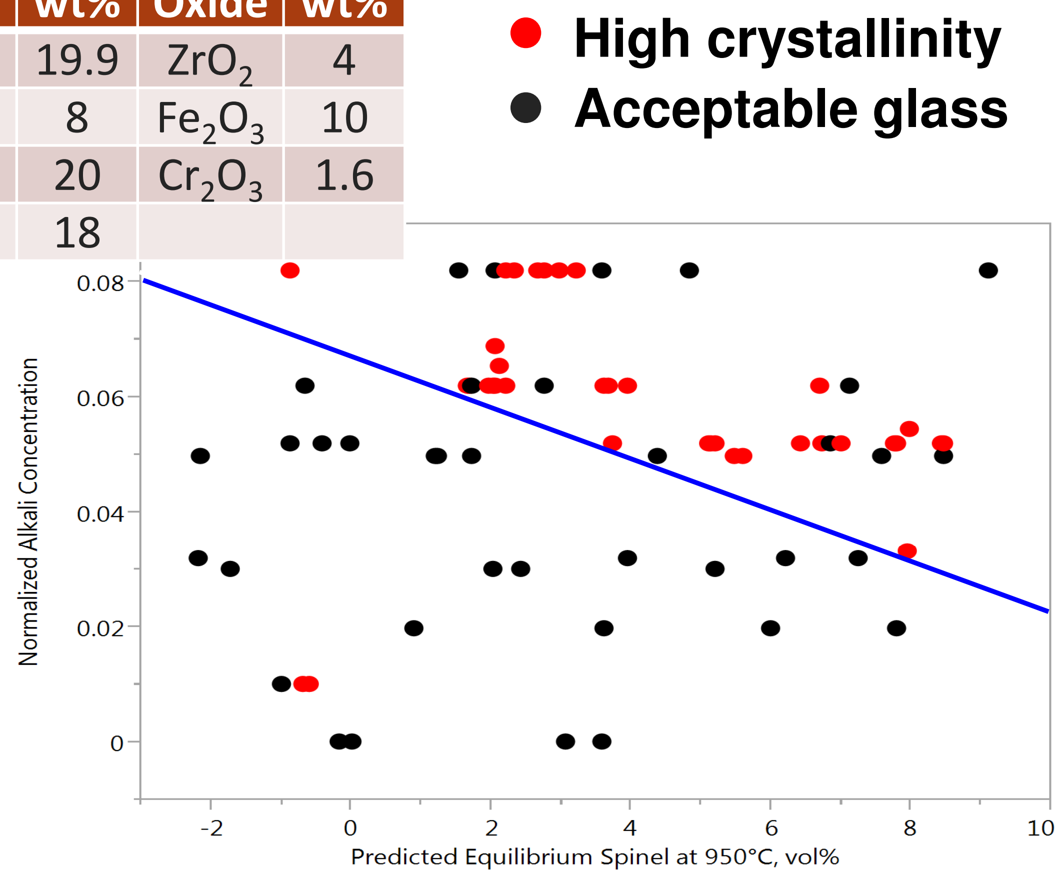
- 45 of the 94 glasses contained sufficient crystallinity to make characterization problematic
- Generally glasses with high alkali and high predicted spinel fraction formed high crystallinity (two exceptions likely don't form spinel)



Oxide	wt%	Oxide	wt%
Al_2O_3	19.9	ZrO_2	4
B_2O_3	8	Fe_2O_3	10
SiO_2	20	Cr_2O_3	1.6
Na_2O	18		

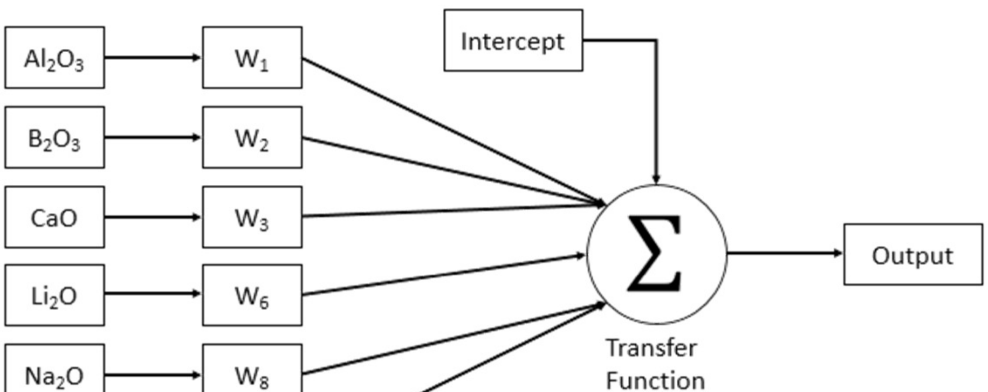


Task 1: Status and Plan

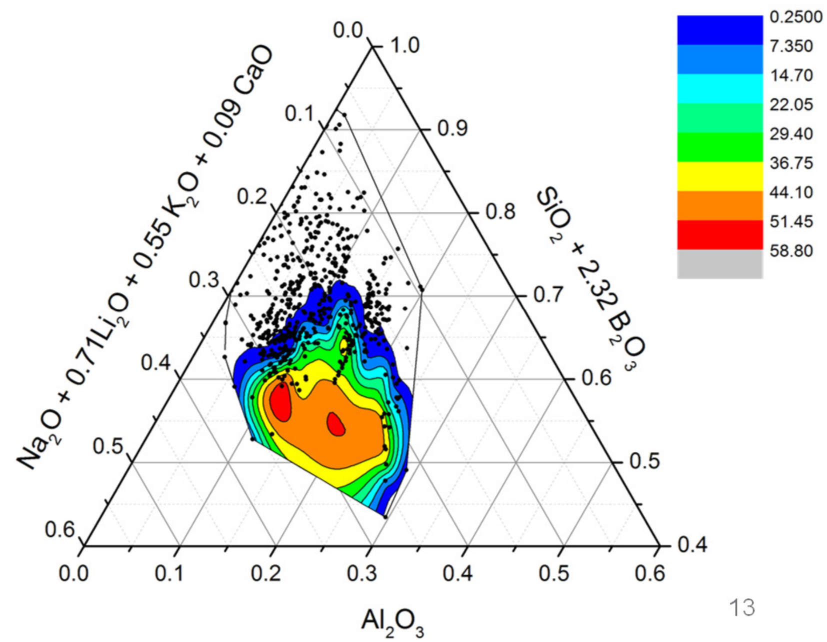
- 45 acceptable compositions have been melted and are currently being characterized:
  - composition
  - viscosity, conductivity, and crystallinity (C) versus temperature
  - PCT, TCLP, and C for both quenched and CCC samples
- Data will be evaluated and reported
- A second phase of testing is currently planned
- Final property-composition models will be fitted to experimental data for use in mission planning, composition control, and waste form qualification
- The same process will be performed for other composition regions

Task 2: Model Forms

- Experimental data has shown composition effects on nepheline precipitation are relatively complicated functional forms
  - a minimum of Al_2O_3, B_2O_3, CaO, Li_2O, Na_2O, and SiO_2 (potentially Fe_2O_3, MgO, and K_2O)
  - highly non-linear behavior
- Two modeling approaches found to be most likely to succeed – neural network (NN) and modified submixture (SM)



$$Transfer\ Function = TanH\left[\frac{1}{2} * \left(Intercept + \sum Weighted\ Input\right)\right]$$



Task 2: Preliminary Data Set

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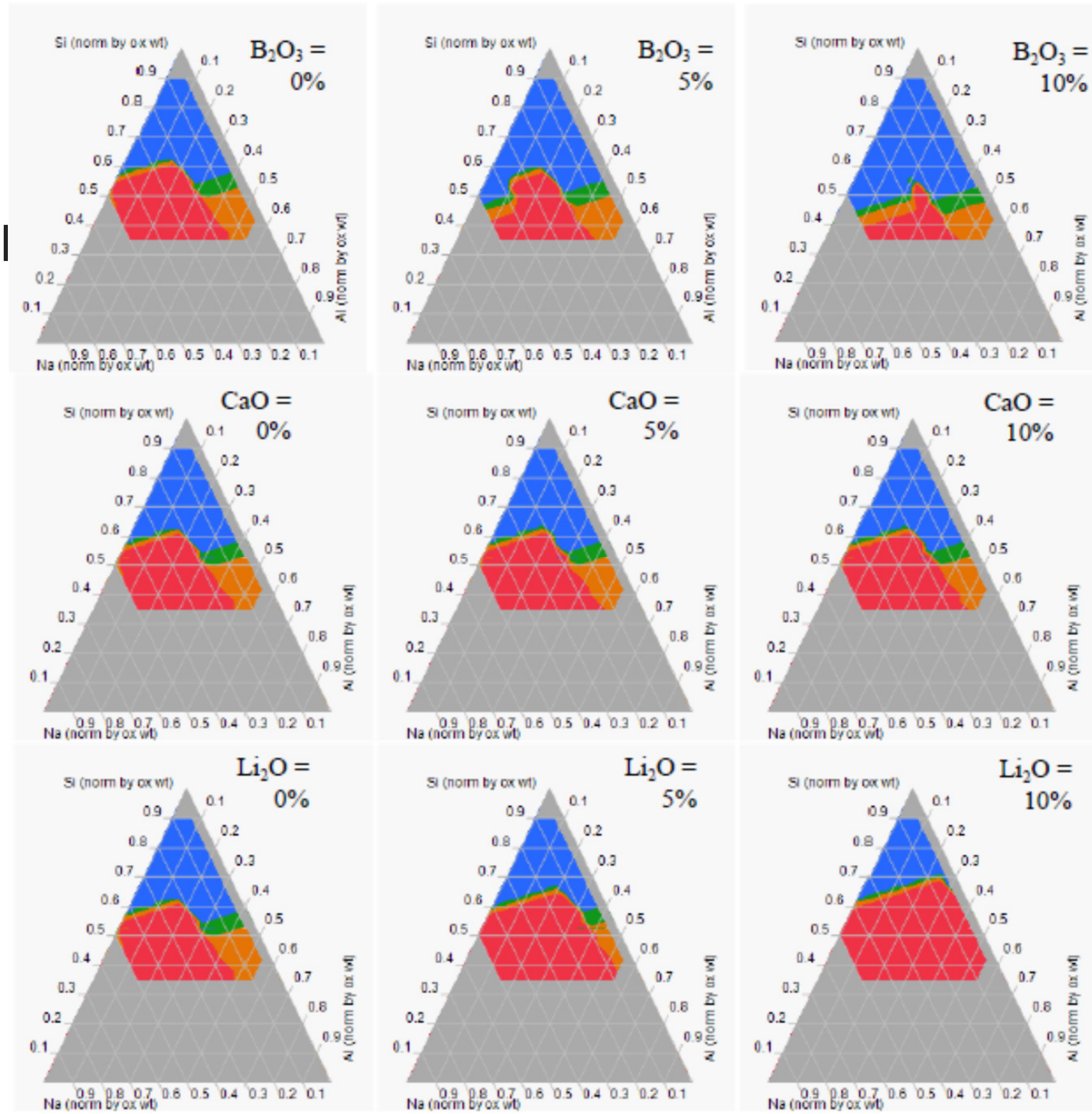
- 629 compositions
- 6 cooling profiles
- Binary (Y/N) data for all 629
- Quantitative or qualitative nepheline fraction for 149

Component	Min	Max
Al_2O_3	0	39.00
B_2O_3	0	28.65
Bi_2O_3	0	16.37
CaO	0	18.20
Cr_2O_3	0	2.97
Fe_2O_3	0	19.95
K_2O	0	24.07
Li_2O	0	9.14
MnO	0	5.59
Na_2O	2.00	39.00
P_2O_5	0	9.00
SiO_2	17.44	60.00
SrO	0	3.00
TiO_2	0	2.12
ZnO	0	2.00
ZrO_2	0	16.00

Glass Family	#	Lab	Heat Treatment	Ref for Glass Compositions	Ref for Crystal Measurement
EM	30	SRNL	DWPF CCC	(Johnson and Edwards 2009)	unpublished
SRNL-JB	18	SRNL	DWPF CCC	unpublished	unpublished
SRNL-JB02	20	SRNL	DWPF CCC	unpublished	unpublished
HWI-ALS	13	VSL	DWPF CCC	(Matlack et al. 2010b)	(Matlack et al. 2010b)
HWI-Al	8	VSL	WTP CCC	(Matlack et al. 2010a)	(Matlack et al. 2010a)
IWL-SLC	7	PNNL	WTP CCC	(Kim et al. 2011)	(Kim et al. 2011)
IWL-HAC	10	PNNL	WTP CCC	(Kim et al. 2011)	(Kim et al. 2011)
NE3	29	SRNL	DWPF CCC	(Fox and Edwards 2009)	(Rodriguez et al. 2011)
NP2	25	SRNL	DWPF CCC	(Fox and Edwards 2008)	(Rodriguez et al. 2011)
HWI-Al	15	VSL	WTP CCC	(Matlack et al. 2008)	(Rodriguez et al. 2011)
HLW-E-Al	14	VSL	WTP CCC	(Matlack et al. 2007a)	(Rodriguez et al. 2011)
PNNL-Al-24-X	13	PNNL	WTP CCC	(Rodriguez et al. 2011)	(Rodriguez et al. 2011)
HLW-E-ANa	13	VSL/PNNL	WTP CCC	(Matlack et al. 2007a)	(Rodriguez et al. 2011)
HLW-E-ANa-X	24	PNNL	WTP CCC	(Rodriguez et al. 2011)	(Rodriguez et al. 2011)
A	6	PNNL	WTP CCC	(Hrma et al. 2010)	(Rodriguez et al. 2011)
HAL	19	PNNL/SRNL	WTP CCC	(Kim et al. 2008)	(Rodriguez et al. 2011)
NP	20	PNNL	WTP CCC	(Li et al. 1997)	(Li et al. 1997)
NEPH	12	SRNL	DWPF CCC	(Peeler et al. 2005)	(Rodriguez et al. 2011)
NEPH2	27	SRNL	DWPF CCC	(Peeler et al. 2006)	(Rodriguez et al. 2011)
NEPH3	16	SRNL	DWPF CCC	(Fox et al. 2006)	(Rodriguez et al. 2011)
DZr	24	PNNL/SRNL	INEEL CCC	(Crum et al. 2002)	(Riley et al. 2001)
US	44	PNNL/SRNL	DWPF CCC	(Fox et al. 2008)	(Fox et al. 2008)
CVS1, CVS2	121	PNNL	HWVP CCC	(Hrma et al. 1994)	(Hrma et al. 1994)
CVS3	39	PNNL	HTM CCC	(Vienna et al. 1996b)	(Vienna et al. 1996b)
EM09	22	PNNL	950°C, 24h	(McCloy et al. 2010)	(McCloy et al. 2010)
SB5NEPH	40	SRNL	950°C, 24h	(Fox et al. 2007)	(Rodriguez et al. 2011)

Task 2: Neural Network

- Probability of formation is predicted
- Al_2O_3, B_2O_3, CaO, Li_2O, and SiO_2 included in model
- 6.6% misclassification rate for model data set, 6.3% misclassification rate for validation data set
- Complicated equation and methods for quantifying prediction uncertainty



Task 2: Submixture

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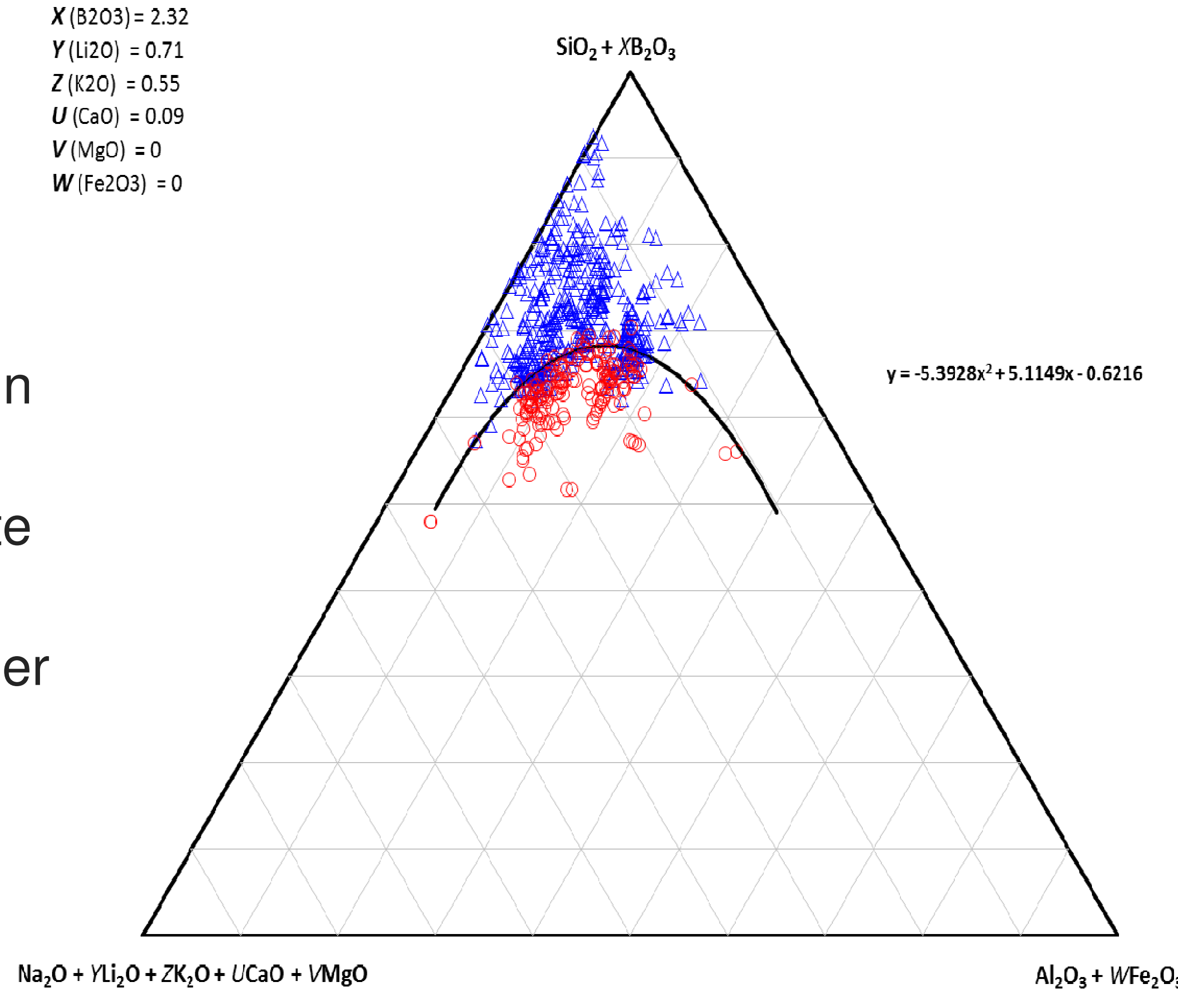
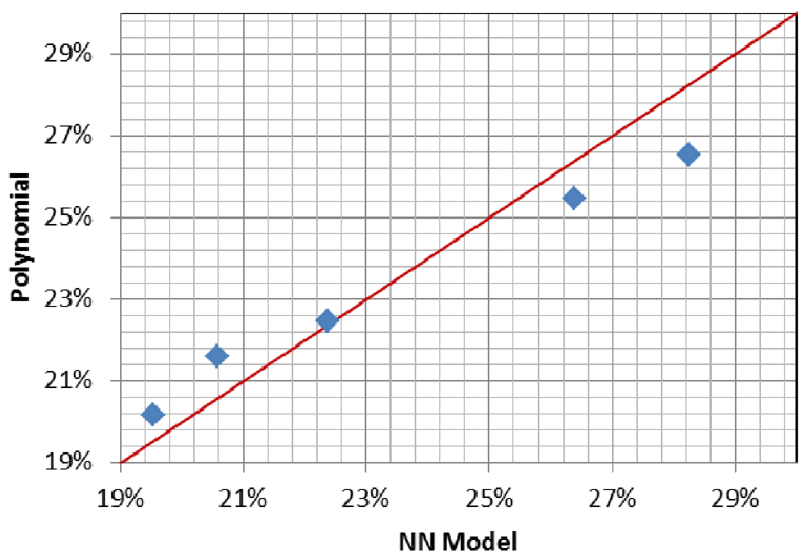
- Polynomial function separates compositions that form nepheline from those that don't
- Al_2O_3, B_2O_3, CaO, K_2O, Li_2O, and SiO_2 included in model
- 15% misclassification rate (2% false negatives)
- Simple function, but higher misclassification rate



Task 2: Impacts on Projected Waste Loading

- 5 representative Hanford high-Al HLW composition estimates selected
- Glasses formulated for each waste to simultaneously meet a range of processing and product quality requirements with only the nepheline constraint varied
- Maximum Al_2O_3 content in glass increase ~40% for the new models compared to the ND
- None of the preliminary models can obtain the 30 wt% Al_2O_3 obtained experimentally → more work is needed

Waste	ND	NN	SM
A	16.1	19.6	20.2
B	17.7	28.2	26.5
C	17.0	22.4	22.5
D	15.7	20.6	21.6
E	17.2	26.4	25.5
Ave	16.7	23.4	23.2



Task 2: Experimental Study

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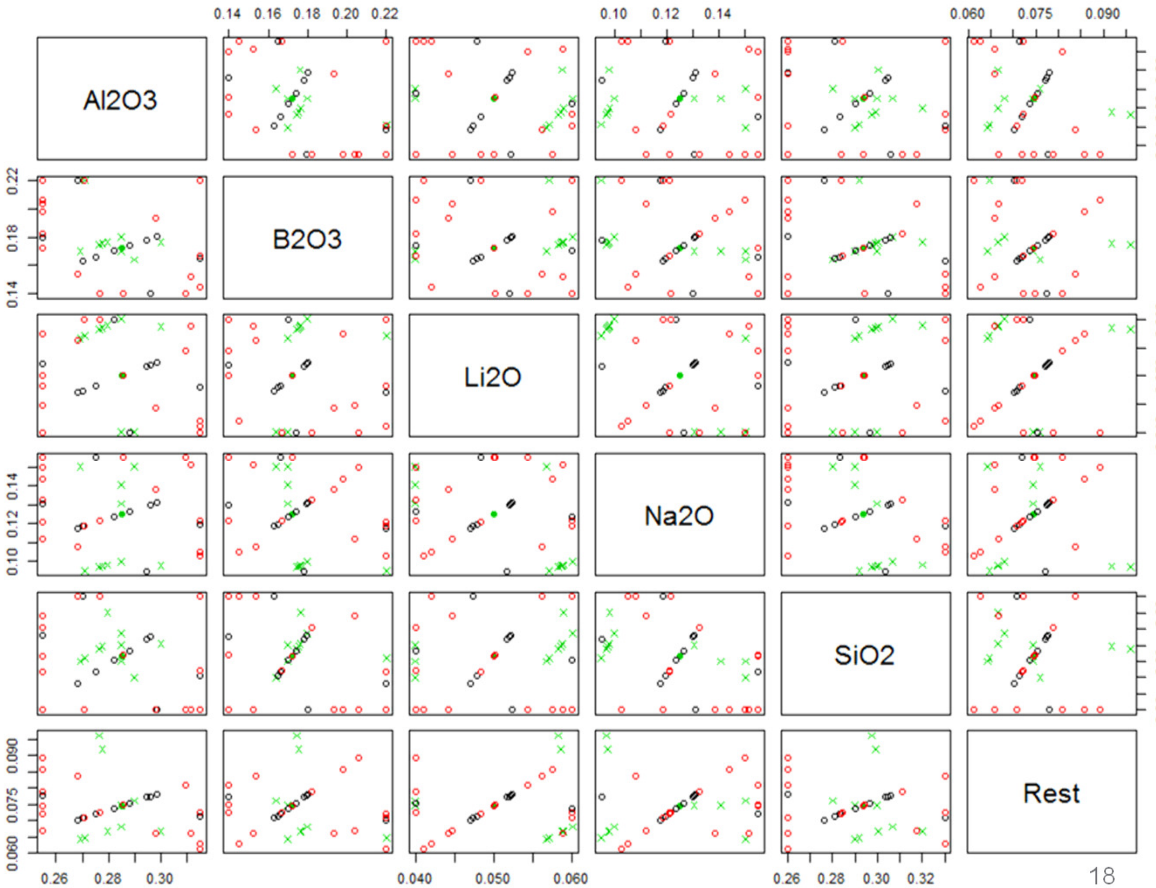
- Preliminary study of 14 glasses based on average Hanford high-Al waste with one-component-at-a-time change ($27<Al_2O_3<30$ wt%)
  - only 2 compositions formed nepheline (high Na_2O and low SiO_2)
- A second matrix of 30 glasses was designed to vary 2 and 3 components-at-a-time
- Glasses all to be heat-treated according to WTPCCC quantitative crystallinity measured
- Glass testing underway



Task 2: Status and Plan

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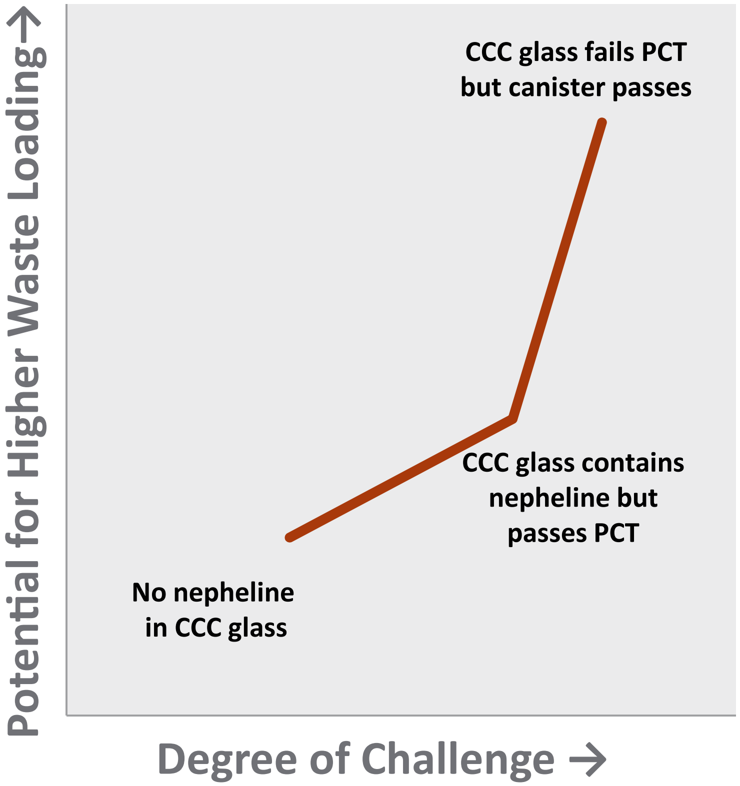
- Two model forms show promise for predicting binary response and allow for a 40% increase in waste loading compared to the ND
- Data collection is underway to supply a consistent set of data to improve the models
- Other modeling approaches are being surveyed including models for fraction of nepheline formed
- Other approaches to limit the impact of nepheline formation are also being investigated



Summary and Conclusions

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- Two tasks are underway to develop glass property-composition models covering the region of Hanford high-Al HLW glasses with high waste loading
- When complete the models will be used for mission planning, composition control, and waste form qualification
- Year 1 results are already showing significant promise for improvements to the Hanford cleanup effort
- This study will continue and will be reported on in the next IAEA CRP meeting

Acknowledgements

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