Glass Formulation and Testing for U.S. High-Level Tank Wastes
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Background and Objectives

The Hanford Tank Waste Treatment and Immobilization Plant (WTP) is being constructed to treat roughly 200,000 m^3 of legacy high-level waste (HLW) stored in underground tanks (Figure 1). The HLW will be retrieved from the tanks, separated into a high-volume, low-activity waste (LAW) and a low-volume, high-activity fraction which will be immobilized by vitrification into borosilicate glasses (DOE 2000). Models exist to formulate and qualify HLW glasses during plant startup (Piepel et al. 2008; Vienna and Kim 2008). However, these models are based on a relatively small fraction of the anticipated HLW compositions and with only moderate waste loadings in glass. A multi-year program is being conducted by researchers from the Catholic University of America (CUA), the Pacific Northwest National Laboratory (PNNL), the Savannah River National Laboratory (SRNL), and the U.S. Department of Energy (DOE) Office of River Protection (ORP) to develop the data and models needed to process the full range of HLW compositions at high waste loadings in glass.

Figure 1. Aerial Photo of WTP Construction Site Taken July 2014, Courtesy of Bechtel National Inc.

Research Approach

The first step in conducting this study was to evaluate the projected waste compositions and divide them into six groups based on their chemistry and glass formulation limiting factors. Kim et al. (2011) categorized the HLW projection in six groups:

- High alumina wastes (limited primarily by nepheline formation on slow cooling) [5205 ton waste oxides, 47 wt% of total waste oxides]
- High iron wastes (limited primarily by spinel accumulation in the melter) [1329 t, 12%]
- Wastes high in Fe, Cr, Ni, and Mn (limited primarily by spinel accumulation in the melter) [2104 t, 19%]

- High Cr and S wastes (limited primarily by salt accumulation in the melter) [1329 t, 12%]
- High P and Ca wastes (limited primarily by phosphate phase formation and melter processing upsets) [997 t, 9%]
- High alkali wastes (limited primarily by chemical durability) [111 t, 1%]

Glass formulation data and models are being collected for each separate group of wastes in order of importance. As the high alumina category contains the largest amount of waste and is projected to produce the largest amount of glass, this category was selected for the first phase of development. Example waste compositions were initially selected and glass formulations were developed and demonstrated in a scaled melter. Initial formulations show Al_2O_3 loading of over 25 wt% is possible. However, melter tests with those compositions resulted in relatively low processing rates (Kim et al. 2008; Matlack et al. 2007). Additional development work identified ways to increase melting rate (Chun et al. 2013; Pierce et al. 2012; Pokorny and Hrma 2012, 2014) and develop faster melting formulations (Matlack et al. 2008) for high waste loading composition with this waste stream.

It was found that the primary concern in formulating an acceptable glass with such high concentrations of Al_2O_3 is avoiding the formation of nepheline (ideally $NaAlSiO_4$) in glasses subjected to simulated canister centerline cooling (CCC) temperature history. If nepheline forms in the canister, the resulting waste form may have chemical durability that is orders of magnitude poorer than that of the starting glass, depending on the glass composition and amount of nepheline (Kim et al. 1995; Li et al. 1997). Li et al. (1997) developed a nepheline discriminator (ND) based on the normalized concentration of SiO_2 in glass:

$$ND = \frac{g_{SiO_2}}{g_{Al_2O_3} + g_{Na_2O} + g_{SiO_2}},$$

where g_i is the i^{th} component mass fraction in glass. Glasses with ND > 0.62 (the boundary of the nepheline primary phase field in the ternary phase diagram) typically do not form nepheline on CCC. No HLW glasses exposed to CCC tested to date form nepheline with ND > 0.62. Figure 2 shows the nepheline fraction as a function of ND for the 149 glasses with high alumina (>8 wt%) and with quantitative or qualitative estimates. The figure shows that several glasses with ND well below 0.62 do not form nepheline. It is these lower ND glasses that have the highest waste loadings for typical high alumina Hanford HLW's. Applying the Li ND constraint would limit the Al_2O_3 loading of Hanford HLW glasses to below 18 wt% while successful glasses have been formulated with as high as 30 wt%.

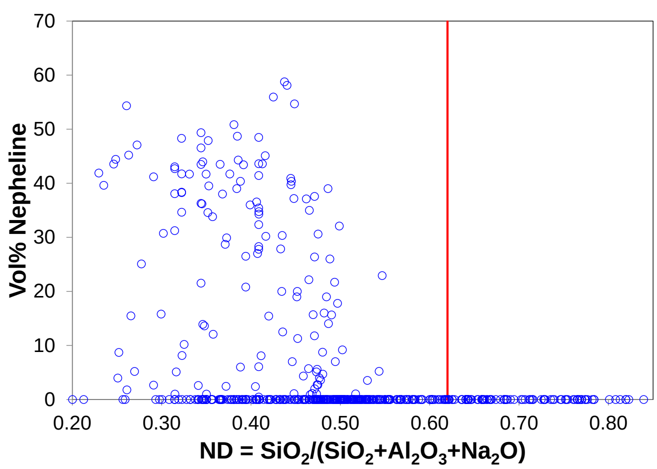

Figure 2. Amount of nepheline measured in simulated HLW glasses exposed to CCC temperature histories as a function of ND.

Therefore, a two-fold strategy has been developed:

1) Develop data on glasses with systematic composition variation across the composition region of interest and fit models to each property of interest.
2) Develop an improved modeling approach to predict nepheline formation with less conservatism.

Both efforts are underway and the initial results are reported in the following subsections.

<u>Initial Results: Glass Property Data with Systematic Composition Variation</u>

A composition region was defined using estimates of high-alumina waste compositions and existing high-alumina glass data. The composition boundaries and additional constraints are described in Table 1. In addition to single-component concentration limits, limits of 30 wt% for Fe_2O_3 + Al_2O_3 and ZrO_2 + Al_2O_3 were used to avoid unreasonably high combined concentrations of refractory components unlikely to be experienced in real waste glasses and a viscosity range between 0.5 and 20 Pa·s at 1150°C. The composition region defined by these boundaries was represented by over 40,000 extreme vertices. Modern experimental design methods were used to select the most suitable 44 glass compositions to back fill the roughly 22 existing compositions in the same region in addition to a centroid (also listed in the table). The selected glass compositions are shown graphically in Figure 3.

Table 1. Component concentration boundaries defining the experimental region of interest, wt%

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

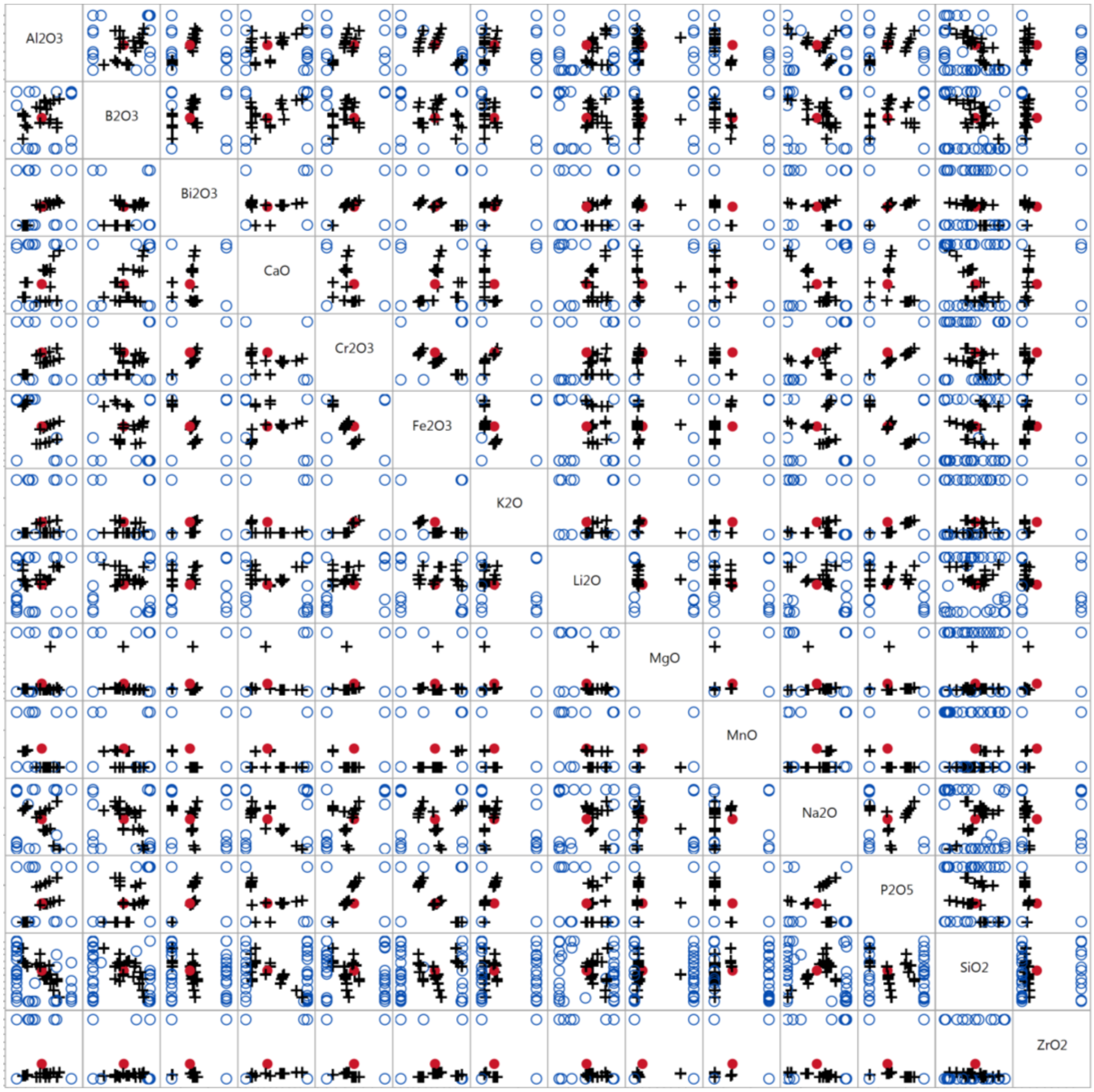

Figure 3. Scatterplot matrix showing existing glasses (+), matrix centroid (●), and design points (○)

Each of the 45 compositions were fabricated by batching the appropriate amounts of oxide and carbonate precursors, melting in a Pt-alloy crucible with a tight fitting lid, for one hour at a temperature corresponding to a viscosity of 4 Pa·s, quenching on a stainless plate, grinding and remelting for one hour. Some of the compositions did not make glasses suitable for further characterization (see examples in Figure 4). As one of the main purposes of the test matrix was to develop data to better define the boundary between good and bad glasses at the composition extremes, it is not surprising that some of the matrix compositions did not form an acceptable glass. Of 45 matrix compositions: 33 formed a glass suitable for further characterization, 2 compositions formed a segregated salt, 3 formed nepheline, and 7 grossly crystallized (usually with spinel).

(a) salt segregation *(b) nepheline formation* *(c) gross crystallization*

Figure 4. Photographs of typical unsuccessful matrix compositions.

Each of the unsuccessful compositions was systematically varied in composition until a successful glass was fabricated for full characterization. The result was 94 individual compositions, 45 acceptable glasses, 12 with salt separation, 4 to 6 with nepheline, and 45 with gross crystallinity. A set of compositional rules were developed to successfully separate the acceptable glass forming region from each of the three other regions. The 45 compositions that formed glasses are currently being characterized for the following properties: viscosity, electrical conductivity, and equilibrium crystallinity as functions of temperature; product consistency test response, toxicity characteristic leaching procedure response, and phase assemblage of both quenched and CCC samples; and chemical composition.

Initial Results: Nepheline Model Development

The ND, currently used to avoid nepheline precipitation is too conservative to allow for glasses with Al_2O_3 concentrations above 18 wt% with typical Hanford high-alumina wastes. McCloy et al. (2011) proposed an approach to reduce the conservatism using a parameter related to the optical basicity (OB) of the glass melt. This approach did reduce some of the conservatism, but still limited the potential loading of high alumina wastes in glass. A new approach to limiting the nepheline precipitation on CCC is clearly needed to optimize waste loading in glass. In this study we have investigated two approaches: 1) a neural network model (NN) and 2) an extended submixture model.

The NN model approach was selected because of its ability to represents complex non-linear interactions between melt components. A model comprised of a network with a single layer and three nodes, all using the hyperbolic tangent (TanH) activation function was developed. These nodes are classified as the hidden layers of the model. A series of modeling experiments explored the effects of many different glass descriptors, including OB, normalized concentrations of SiO_2 (ND), Na_2O, and Al_2O_3, and the unnormalized mass fractions (g_i) of Al_2O_3, B_2O_3, CaO, Fe_2O_3, K_2O, Li_2O, MgO, Na_2O, and SiO_2. It was determined that the normalized component concentrations and OB were not as effective in predicting nepheline formation as the unnormalized oxide concentrations.

A data set of 629 glasses with six different heat treatment methods was used to train and validate the model. Ideally, a data set with a single heat treatment method (CCC for WTP) is preferred as other heat treatments may show different nepheline formation results. However, it was determined that there is insufficient data (149 of 629 glasses) to develop the NN model if restricted to only the CCC for WTP heat treatment data. As this is a preliminary model, it was decided to include all the data to develop the model and collect additional data with the single heat treatment for final model fitting in the future.

Efforts were made to create a quantitative prediction model for the nepheline fraction in glass, but there were not a sufficient number of data points to create an accurate model. As a result, a binary response (i.e., nepheline forms or not) was modeled. The initial NN model developed to predict the probability of nepheline formation as a function of glass composition is a relatively complex mathematical form of the concentrations of Al_2O_3, B_2O_3, CaO, Li_2O, and SiO_2. A set of SiO_2-Na_2O-Al_2O_3 ternary diagrams are shown in Figure 5 to demonstrate the predicted compositional effects. Validation of the model to a 20% subset of the data not used in model fitting showed a roughly 7% misclassification rate with more than half of the misclassifications in the conservative direction.

Application of this model to projected Hanford high-alumina waste compositions showed that formulations with Al_2O_3 concentrations as high as 28 wt%. This model is significantly less conservative than the ND or the ND+OB constraints while still reducing the risk of formulating a glass prone to nepheline precipitation. However, its complex mathematical form and difficulty in quantifying the uncertainties in prediction make it difficult to directly implement in plant operations.

The second modeling approach was to expand on the ternary submixture approach of Li et al. (1997) by adding other influential components to the submixture. Based on the results of the NN model development and some scoping tests an empirical submixture model was derived. The ternary end members of the submixture were $SiO_2+xB_2O_3$, $Na_2O+yLi_2O+zK_2O+u$CaO$+v$MgO, and $Al_2O_3+wFe_2O_3$. The parameters *x*, *y*, *z*, *u*, *v*, and *w* were then empirically fit to best separate glasses that form nepheline from those that don't. It was determined that *v* (MgO) and *w* (Fe_2O_3) did not have a significant effect, while all other parameters did. Figure 6 shows the resulting submixture. This initial model shows a higher misclassification rate than the NN model (15%), the polynomial was adjusted so that only 2% of the glasses were predicted not to form nepheline and actually did form nepheline (i.e., non-conservative misclassification).

Five representative Hanford high-alumina HLW composition estimates were selected to evaluate the impacts of using the two preliminary models developed in this study. Glasses were formulated for each of the five waste compositions so that the full range of required glass processing and product quality constraints are met using methods described by Vienna et al. (2013). The only difference in the formulation approach is what constraint is used to limit the risk of nepheline formation in canistered glass waste form. Table 2 lists the Al_2O_3 concentrations in each optimum formulation and Figure 6 compares the results from the NN and submixture models. Both the NN and submixture models allow for higher Al_2O_3 concentrations than the current ND constraint. The maximum Al_2O_3 concentration is roughly 6.5 relative percent higher for the NN model than for the polynomial model. The average Al_2O_3 concentrations for the NN (23.4) and submixture (23.2) models are 40 relative percent higher than the ND constraint (16.7). So either the NN or submixture model approach can significantly reduce the conservatism of the ND constraint.

The next step is to develop data in the composition region of highest uncertainty in predicted probability of nepheline formation and most applicability to Hanford high-alumina HLW glass compositions and use that data to improve the models for nepheline formation. A matrix with one-, two-, and three-component variations was statistically designed. The data is being collected with the same and appropriate CCC temperature history and quantitative fraction of nepheline formed. This data set will be used to improve the models and evaluate new modeling approaches.

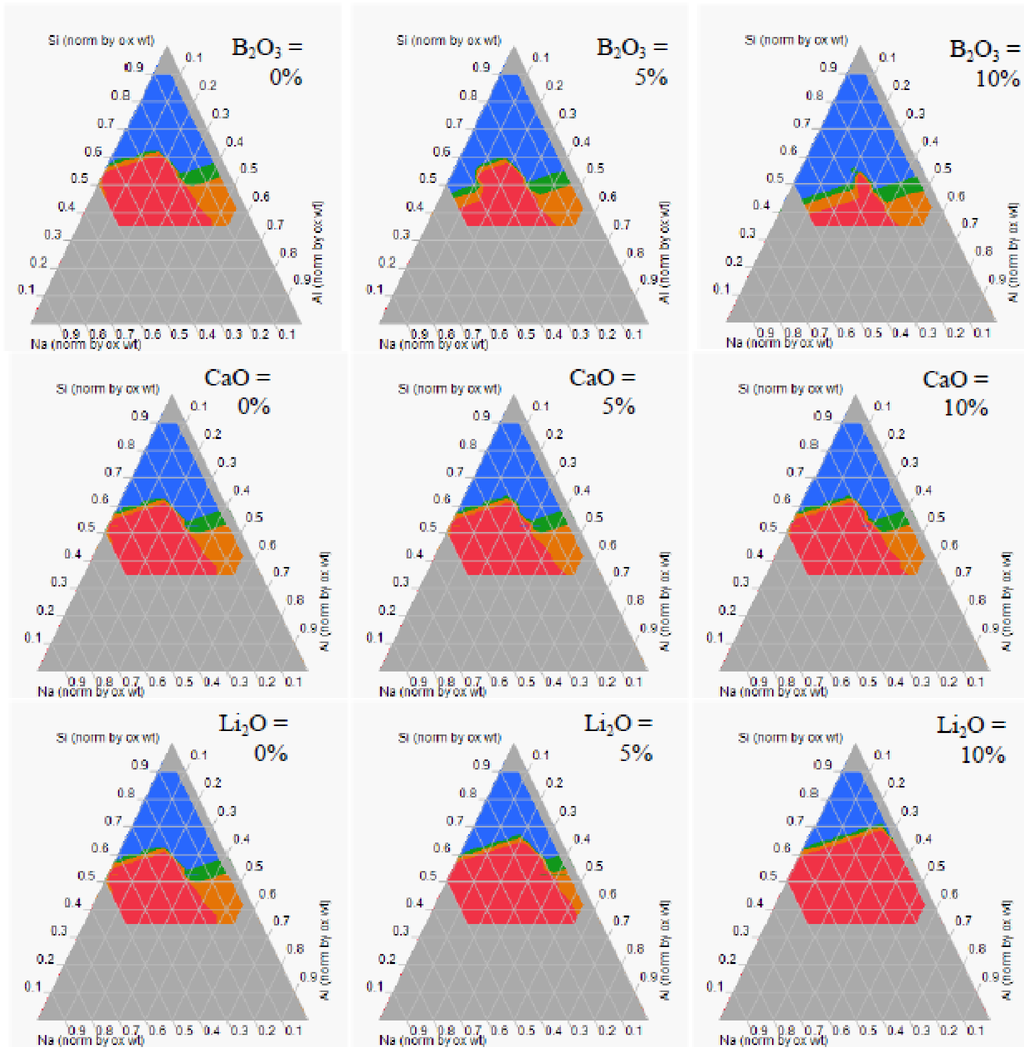

Figure 5. Nepheline formation regions at different concentrations of B_2O_3, CaO, and Li_2O [blue – low probability (0-5%), red – high probability (50+%), and orange (27-50%) and green (6-27%) are intermediate probabilities]

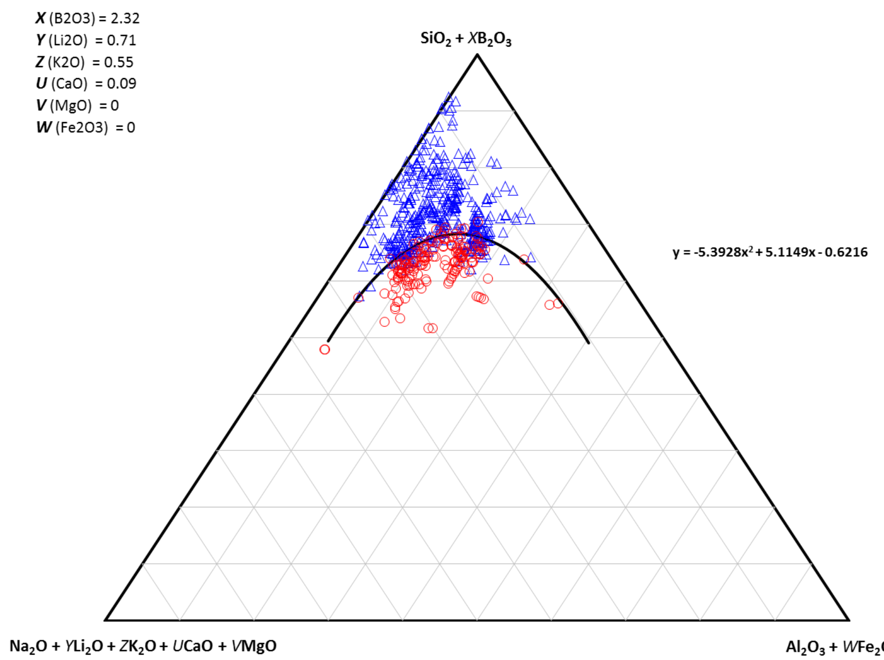

Figure 6. Submixture showing glasses which form nepheline (○) and those that do not form nepheline (Δ) separated by a second order polynomial.

Table 2. Projected maximum Al_2O_3 concentration in representative high-alumina Hanford HLW estimates. Each glass simultaneously meets a series of glass processing and product quality related constraints.

Waste Estimate	ND	NN	Submixture
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

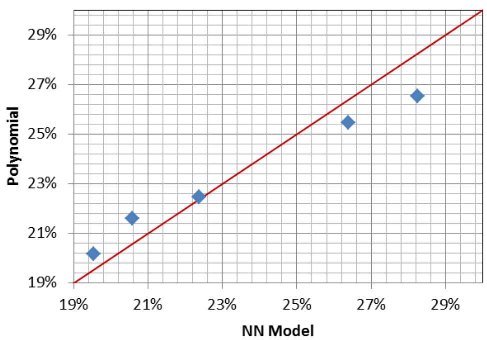

Figure 7. Maximum Al_2O_3 concentrations in glasses formulated from five representative Hanford high-alumina HLW estimates. Each glass simultaneously meets a series of glass processing and product quality related constraints.

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