Development of High Alumina Glass Property Data for Hanford High-Level Waste Glass Models – 16231

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ABSTRACT

Roughly half of the projected Hanford high-level waste batches will have waste loadings limited by relatively high concentration of Al_2O_3. Individual glasses have been formulated and tested to demonstrate that it is possible to increase the loading of these high-Al_2O_3 wastes in glass by as much as 50%. To implement such increases in waste loading in the Hanford Tank Waste Treatment and Immobilization Plant, the impact of composition on the properties of high-Al_2O_3 waste glasses must be quantified in the form of validated glass property-composition models. To collect the data necessary for glass property-composition models, a multi-phase experimental approach was developed. In the first phase of the study, a set of 46 glass compositions were statistically designed to most efficiently backfill existing data in the composition region for high-Al_2O_3 (15 to 30 wt%) waste glasses. The glasses were fabricated and key glass properties were tested:

- Product Consistency Test (PCT) on quench (Q) and canister centerline cooled (CCC) samples
- Toxicity Characteristic Leaching Procedure (TCLP) on Q and CCC samples
- Crystallinity as a function of temperature (T) at equilibrium and of CCC samples
- Viscosity and electrical conductivity as a function of T

The measured properties of these glasses were compared to predictions from previously existing models developed over lower Al_2O_3 concentration ranges. Areas requiring additional testing and modeling were highlighted.

INTRODUCTION

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. Under the current baseline process, the HLW will be retrieved from the tanks, separated into a high-volume, low-activity waste (LAW) and a low-volume, HLW fractions which will be vitrified into borosilicate glasses.[1] Models currently exist to formulate and qualify HLW glasses during plant startup.[2, 3] However, these models are based on a relatively small fraction of the anticipated HLW compositions and with only modest waste loadings in glass. A multi-year program initiated and lead by the U.S. Department of Energy (DOE) Office of River Protection (ORP) is being conducted by researchers from the Pacific Northwest National Laboratory (PNNL), the Catholic University of America (CUA), the Savannah River National Laboratory (SRNL), and ORP to develop the data and models needed to process the full range of HLW compositions at high waste loadings in glass.[4]

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:[5]

- High alumina wastes (limited primarily by nepheline formation on slow cooling) [5205 metric ton (t) waste oxides, 47 wt%]
- 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 are being collected and models developed for each separate group of wastes because the composition subregion and some of the property-composition models are expected to differ noticeably for each group. Because 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 melter tests achieved Al_2O_3 loading of over 25 wt%, however processing rates during testing were relatively slow.[6, 7] Additional development work identified ways to increase melting rate [8, 9, 10, 11, 12, 13] and develop faster melting formulations [14] for this waste stream.

To process glasses at the WTP, glass property-composition models must be used to ensure glass compositions processed meet all the property constraints with sufficient confidence.[2, 3] Current models cover a composition region extending to only 13 wt% Al_2O_3.[2] To expand the models, a matrix of glasses with systematic variation in composition in the desired composition region is formulated using statistical design methods and the glasses will be characterized and the data used to fit new glass property- composition models.

RESULTS

A composition region was defined using estimates of high-alumina waste compositions and existing high-alumina glass data. The composition boundaries are listed in Table 1. In addition to single-component concentration limits, three multiple-component limits were specified. Limits of $Fe_2O_3 + Al_2O_3 \leq 30$ wt% and $ZrO_2 + Al_2O_3 \leq 30$ wt% were used to avoid unreasonably high combined concentrations of refractory components unlikely to be experienced in real waste glasses. Also, predicted viscosity at 1150°C was limited to the range 0.5 to 20 Pa·s. The composition region defined by these limits was represented by ~40,000 vertices. Modern experimental design methods were used to select 45 of the vertex glass compositions to augment the roughly 22 existing compositions in the same region. In addition, a centroid composition was included, which is listed in Table 1. The selected glass compositions are shown graphically in Figure 1.

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

Each of the 46 compositions was fabricated by (i) batching the appropriate amounts of oxide and carbonate precursors, (ii) 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, (iii) quenching on a stainless plate, and (iv) grinding and remelting for one hour. Some of the compositions did not make glasses suitable for further characterization (see examples in Figure 2). Of 46 matrix compositions: 34 formed a glass suitable for further characterization, 2 compositions formed a segregated salt, 3 formed nepheline (on quenching), and 7 grossly crystallized (usually with spinel). 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 acceptable glasses.

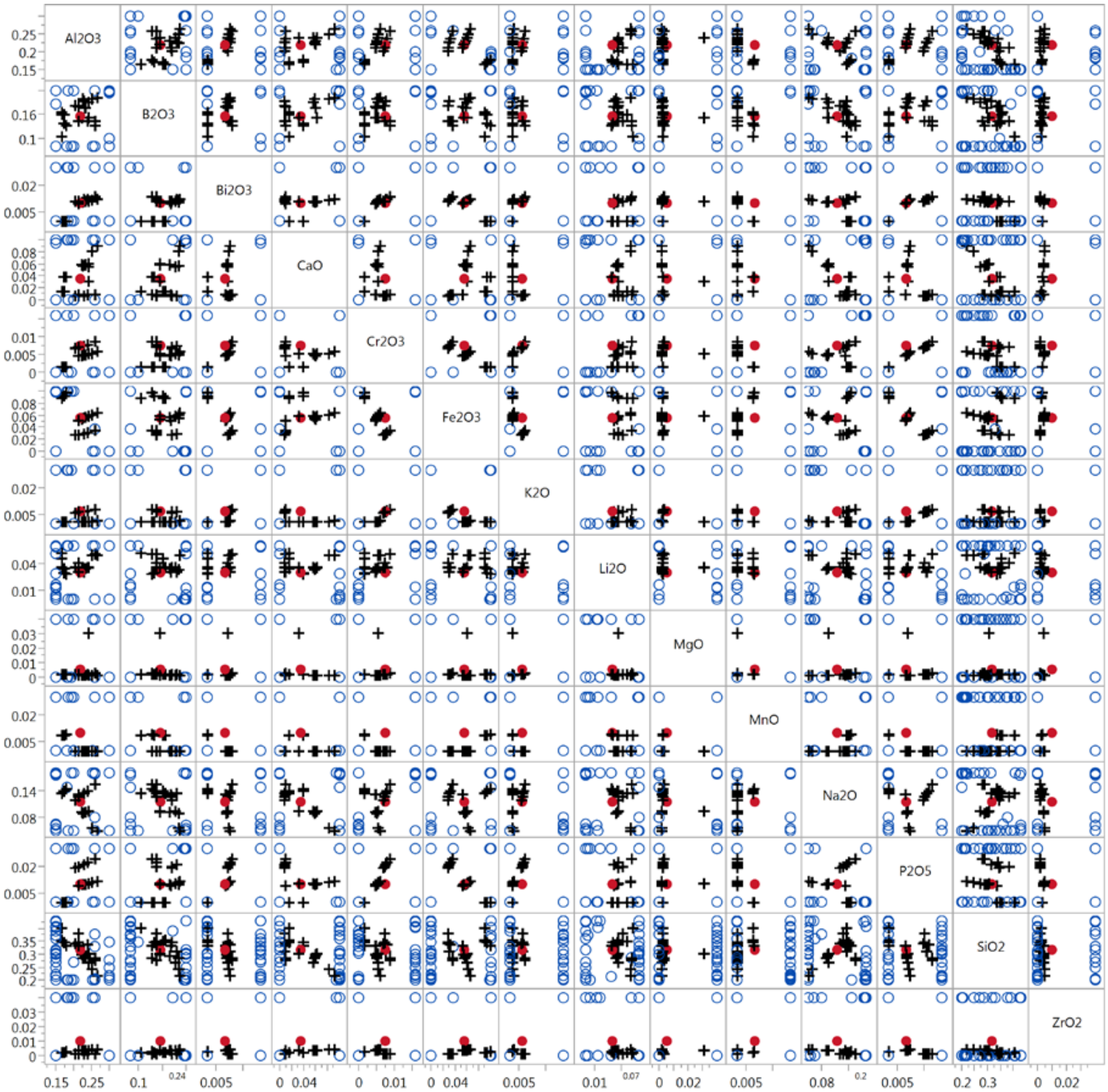

Figure 1. Scatterplot matrix showing existing glasses (+), matrix centroid (●), and design points (○)

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

Figure 2. 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, 46 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 46 compositions that formed glasses were characterized for the following properties: (i) viscosity, electrical conductivity, and equilibrium crystallinity as functions of temperature, (ii) PCT response, TCLP response, and phase assemblage of both Q and CCC samples, and (iii) chemical composition. The viscosity, PCT, and CCC crystallinity results are reported here.

The viscosity of test glasses was measured over a range of temperatures and interpolated to 1150°C using the Vogel-Tamman-Fulcher equation. The resulting η_{1150} ranged from 0.33 to 65 Pa·s. This range was broader than the range predicted using models fitted to low-alumina high-level waste glass composition region confirming that extrapolation of the existing models is not appropriate for this data set. The range well covers the range of values anticipated in plant operation of 2 to 8 Pa·s. No distinct trends were identified between the composition of glasses and the ability to predict their viscosity. Alkali, alkaline-earth, and boron oxides reduce viscosity of these glasses and silicon, zirconium, and aluminum oxides increase viscosity, similar to the effects seen in previous studies.

The PCT normalized boron responses of glasses ranged from 0.19 to 20.8 g/m^2 -- well covering the upper limit value of 8.35 g/m^2.[15] Extrapolation of previous PCT response models to prediction of the response for these glasses showed significantly different composition effects. Most notably, the previous models [16] fit to glasses with lower alumina concentration (≤ 20 wt%) under predicted the PCT responses to these glasses and the under-prediction increased with increased Al_2O_3 concentrations (Figure 3). The trend shows significant and increasing under-prediction of PCT responses for glasses with Al_2O_3 concentrations above 20 wt%. This suggests that the effect of alumina on PCT response is highly non-linear. At low concentrations Al_2O_3 will decrease PCT response, at mid concentrations it will have relatively small effect, and at high concentrations it will increase PCT response. This non-linear trend is consistent with effects previously reported.[17, 18, 19]

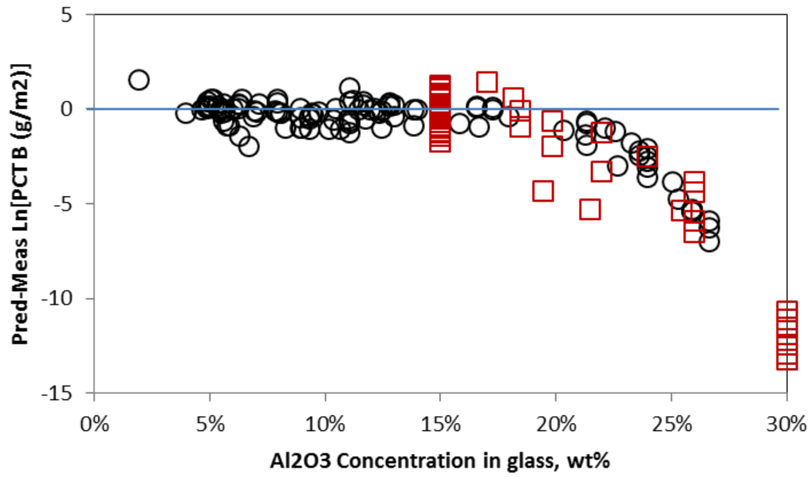

Figure 3. Comparison of the measured and predicted Q glass natural logarithm PCT boron response for test glasses as a function of Al_2O_3 concentration in glass. Glasses from this study (□) *and from [20]* (○).

All but five of the matrix glasses formed some crystals on simulated CCC heat treatment. For most of the glasses, relatively small concentrations (< 10 vol%) of crystals (typically spinel, eskolaite, or transition metal silicates) formed. However, some glasses over 20 vol% of aluminosilicates (e.g., nepheline and eucryptite) formed. This latter set of glasses showed substantial impacts of CCC heat treatment on both PCT and TCLP responses. Figure 4 compares the logarithm PCT responses for quenched and CCC glasses. It's clear from the plot that glasses that precipitated nepheline and/or eucryptite showed significant increases in PCT responses. All other glasses, some of which have over 20 vol% of other crystalline phases, did not show significant deviation between quenched and CCC PCT responses.

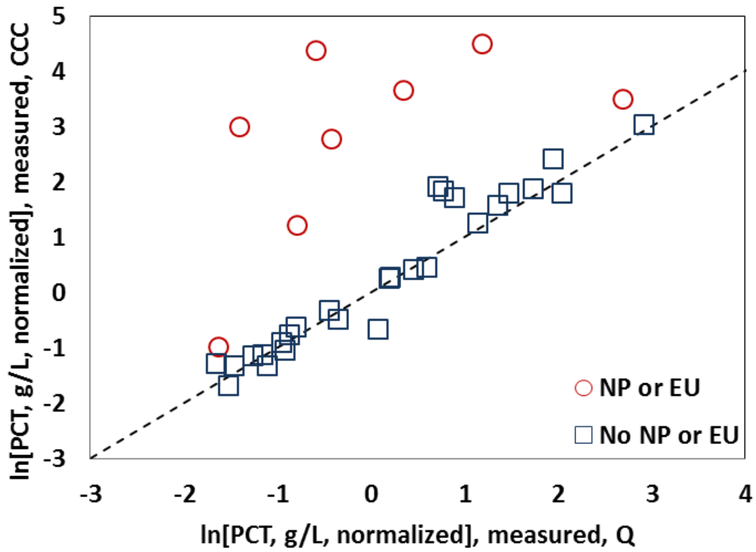

Figure 4. Comparison of the PCT responses for Q and CCC glass samples.

The impact of composition on the formation of alumino-silicates was determined to be a significant focus of future testing. An initial study resulted in the development of a submixture model to predict nepheline formation during canister centerline cooling.[21]

The details of the glass compositions and test results are being complied and will be reported separately.

SUMMARY AND DISCUSSION

A matrix of 46 glasses was statistically designed to backfill existing high-alumina Hanford HLW glass compositions. The glasses were fabricated and key glass properties were tested. Twelve of the original compositions did not form glasses suitable for full characterization due to crystallization or salt separation. A series of 48 scoping glasses were developed to define the boundaries between “good” and “bad” glasses and to formulate modified compositions for the 12 original glasses. The resulting 46 glass test matrix (34 original matrix glasses plus 12 modified glasses) were fabricated and tested. The measured properties of these glasses are compared to predictions from previously existing models developed over lower Al_2O_3 concentration ranges. It was found that the effect of Al_2O_3 on PCT response cannot be extrapolated to high concentrations studied in this test as shown in Figure 3. The effect of CCC heat treatment on PCT response is relatively small except for those glasses precipitating alumino-silicate minerals (specifically nepheline and eucryptite). Viscosity is better predicted by existing models. This study completes the first phase of a multi-phase experimental and modeling program. A matrix is being designed for the second phase of testing.

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