Technology Development in Support of Accelerating the Waste Treatment Mission – 16409

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ABSTRACT

The feed for vitrification to produce a nuclear waste glass is a mixture of waste with glass-forming and modifying additives that is charged onto the cold cap that covers 90–95% of the melt surface. The cold cap consists of a layer of reacting molten glass floating on the surface of the melt in an all-electric, continuous glass melter. As the feed moves through the cold cap, it undergoes chemical reactions and phase transitions through which it is converted to molten glass that moves from the cold cap into the melt pool. Multiple overlapping reactions occur within the cold cap. The process involves a series of reactions that generate multiple gases and subsequent mass loss and foaming significantly influence the mass and heat transfers. The rate of glass melting, is greatly influenced by mass and heat transfers, affects the vitrification process and the efficiency of the immobilization of nuclear waste. Therefore, understanding the cold-cap reactions over the temperature range of the conversion process is critical. It also helps to formulate melter feeds for higher production rate, initiation of crystal forming reactions, and chemical reactions that determine the ultimate fate of technetium in the glass melt. Though the flowsheets at each of the two sites is vastly different development and insertion of mature technological chemical processes and mechanical components can have a significant impact on the duration of the treatment mission and hence the total costs.

INTRODUCTION

Background

The U.S. Department of Energy, Office of Environmental Management is responsible for treating and dispositioning about 92 million gallons of highly radioactive and chemically complex liquid waste. Most of this nuclear waste is a by-product of national defense plutonium-production efforts during World War II and the Cold War era. The technology selected for the treatment and stabilization of the Department’s high-level waste is vitrification, which is a thermal and chemical process that converts the waste to glass thereby rendering it into a stable and durable physical form for permanent disposal in a geological repository. Borosilicate glass has been chosen for the immobilization of radioactive elements largely because of the ease of processing, compositional flexibility, and chemical durability. The largest operating waste vitrification plant in the world is the Defense Waste Processing Facility (DWPF) at the Department’s Savannah River Site in Aiken, South Carolina. DWPF began radioactive operations in March 1996 to vitrify 37 million gallons of radioactive liquid waste stored among 51 underground tanks. At the Department’s Hanford Site in eastern Washington, this vitrification technology will also be used to disposition about

56 million gallons of radioactive liquid waste that was historically stored in 177 underground storage tanks. The Waste Treatment and Immobilization Plant (WTP) is currently being built at Hanford to vitrify this waste. Once fully constructed, WTP will surpass the size of DWPF.

The current estimates and glass formulation efforts developed by the contractor for the WTP are conservative vis-à-vis achievable waste loadings. These formulations have been specified to ensure that glasses are homogenous; contain essentially no crystalline phases; are processable in joule-heated, ceramic-lined melters; and meet WTP Contract terms. The overall mission will require the immobilization of tank waste compositions that are dominated by mixtures of aluminum, chromium, bismuth, iron, phosphorous, zirconium, and sulphur compounds as waste-limiting components. The Office of River Protection undertook an extensive investigation focused upon glass formulation improvements and enhancements of operating efficiencies in the vitrification facilities. Glass compositions for these waste mixtures have been developed based upon previous experience and current glass property models. This work has demonstrated the feasibility of increases in waste loading for high-level waste from 19 weight percent) wt% to 58 wt% (based on oxide loading) in the glass depending on the waste stream. It is expected these higher waste loading glasses will reduce the high-level waste canister production requirement by 45 wt% or more. For low-activity waste, significant improvements in formulating glasses for high loading of sodium in waste streams containing high sulphur concentrations have been successful and higher retention of technetium has been achieved. It is expected that low-activity waste-container production will be reduced by 45–55 percent while treatment capacity for secondary liquid wastes warrants re-evaluation.

The current estimates and glass formulations developed for the DWPF are conservative vis-à-vis achievable waste loadings. Through the years of operation the DWPF has seen increasing waste loading but there is still an opportunity for improvements. In the recent past a significant improvement of throughput was realized by the retro-fitting of a bubbler in the melter. This resulted in a doubling of the rate of glass production. However, the improvement came at the cost of a new mass balance for the offgas. The DWPF mission will soon become dominated by sodium, sulphur, mercury, aluminum plus sodium originating from the feed from the Actinide Removal Process (Modular Caustic Unit/ARP input tied to unwashed sludges), and the resulting reality necessitating the use of low-sodium frits.

DISCUSSION

High-level waste (HLW) streams bearing elevated concentrations of alumina represent as much as 47 wt% of the total waste oxides. The addition of relatively small concentrations of Al_2O_3 to borosilicate glasses generally enhances the durability of the waste form (through creation of network-forming tetrahedral Na^+-[AlO4/2]-pairs). However, nepheline ($NaAlSiO_4$) formation, which partially depends on the Al_2O_3 content, can severely deteriorate the chemical durability of the glass. Representative 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 [1, 2]. Additional development work identified ways to increase melting rate [3, 4, 5 & 6] and develop faster melting formulations [7] 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 [8, 9]. Li et al. [9] developed a nepheline discriminator (ND) based on the normalized concentration of SiO_2 in glass:

$$N_{Si} = \frac{g_{SiO_2}}{g_{SiO_2} + g_{Al_2O_3} + g_{Na_2O}} \leq 0.62$$

Where N_{S_i} = normalized silica concentration

g_i = 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 1 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. Applying the Li ND constraint would limit the Al_2O3 loading of Hanford HLW glasses to below 18 wt% while successful glasses have been formulated with as high as 30 wt%.

While the discriminator excludes glasses prone to nepheline precipitation upon CCC, it also excludes a number of glasses with N_{Si} as low as 0.47 with no nepheline. It is within this compositional region that high-waste-loaded Al-based glasses exist but currently cannot be accessed.

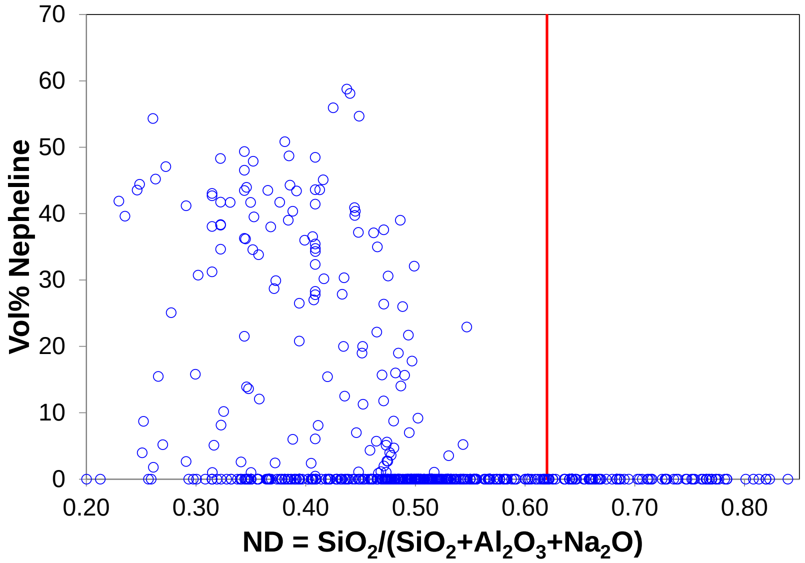

Figure 1. Nepheline Volume Percent after CCC Heat Treatment vs. Nepheline Discriminator for WTP HLW Glasses [10].

Developing an alternative approach or model that removes the conservatism (i.e., allows access to broader compositional envelope) while (a) protecting against nepheline formation after slow cooling or (b) defining a threshold of nepheline formation that does not produce an unacceptable glass, is critical to the HLW Advanced Waste Glass (AWG) program and WTP operations. McCloy et al. [11] 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 (gi) 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.

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. 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.

Several forms of composition constraints remain to be assessed and may include both thermodynamic indicators such as the location of the glass within various composition submixtures as well as kinetic parameters such as viscosity at a given temperature and non-parametric models. Only after investigating a number of such constraints and comparing them to the current database will the final constraint be determined. Development of an alternative constraint for nepheline formation could also be based on a graded approach. Three approaches are currently being considered under the HLW AWG program for control of nepheline in IHLW for Hanford are:

1. Control the glass composition so that no nepheline (or other detrimental phase) forms during CCC. This is the most conservative and easiest approach as it only requires the ability to predict whether nepheline will form during CCC.
2. Control the glass composition so that the fraction of nepheline that forms during CCC will not cause the product consistency test (PCT) response of CCC glass to fail constraints with sufficient confidence. This approach is less conservative and more difficult as it requires the ability to predict the fraction of nepheline to form on CCC and the PCT response of the resulting waste form.
3. Control the glass composition so that the fraction of nepheline that forms throughout the canister will not cause the canister average glass PCT response to fail constraints with sufficient confidence. This approach is least conservative and most difficult as it requires the ability to predict the fraction of nepheline to form on CCC and the PCT response of the resulting waste form.

The composition region of acceptable glasses with very high alumina loading is limited and there are currently insufficient data to develop the qualified glass composition region (QGCR) for high-loaded, high-alumina glasses or a transition path from high-loaded, high-alumina glasses to other high-waste-loaded glasses with different limiting components.

CONCLUSIONS

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. [12]. The only difference in the formulation approach is what constraint is used to limit the risk of nepheline formation in canistered glass waste form. 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 Al2O3 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.

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