Advances in the Glass Formulations for the Hanford Tank Waste Treatment and Immobilization Plant – 15053

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ABSTRACT

The Department of Energy-Office of River Protection (DOE-ORP) is constructing the Hanford Tank Waste Treatment and Immobilization Plant (WTP) to treat radioactive waste currently stored in underground tanks at the Hanford site in Washington. The WTP that is being designed and constructed by a team led by Bechtel National, Inc. (BNI) will separate the tank waste into High Level Waste (HLW) and Low Activity Waste (LAW) fractions with the majority of the mass (~90%) directed to LAW and most of the activity (>95%) directed to HLW. The pretreatment process, envisioned in the baseline, involves the dissolution of aluminum-bearing solids so as to allow the aluminum salts to be processed through the cesium ion exchange and report to the LAW Facility. There is an oxidative leaching process to affect a similar outcome for chromium-bearing wastes. Both of these unit operations were advanced to accommodate shortcomings in glass formulation for HLW inventories. A by-product of this are a series of technical challenges placed upon materials selected for the processing vessels.

The advances in glass formulation play a role in revisiting the flow sheet for the WTP and hence, the unit operations that were being imposed by minimal waste loading requirements set forth in the contract for the design and construction of the plant. Another significant consideration to the most recent revision of the glass models are the impacts on resolution of technical questions associated with current efforts for design completion.

INTRODUCTION

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 sulfur 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 HLW from 19 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 HLW canister production requirement by 45% or more. For LAW, significant improvements in formulating glasses for high loading of sodium in waste streams containing high sulphur concentrations have been successful. It is expected that LAW container production will be reduced by 45-55%

The waste itself contains 40−60 elements existing as water-soluble salts, amorphous gels, and crystalline minerals. Conversion to glass proceeds over a wide range of temperatures spanning formation of a molten salt phase that reacts with feed solids, turning them into intermediate products and ultimately the glass-forming melt [1-3]. It has been demonstrated [4-7], feeds with glass beads (frit) may produce extensive foaming, both in low-viscosity frit that sinters early and in feeds with high-alkali wastes that attack frit particles at low temperature, causing early sintering and subsequent foaming similar to foam glass manufacturing [8]. More than 200 000 m^3 of nuclear waste will be vitrified at the Hanford Site over the coming decades [9]. Hence, using raw materials (minerals and chemicals) for glass-forming and glass-modifying additives provides flexibility that allows optimization of feed for both different types of wastes and a stable fast-melting cold cap. Our glass program seeks an understanding of the spectrum of physicochemical properties from feed to molten glass and their role in the melter waste-processing rates. The fruits of our efforts will guide strategies for efficient operations in the WTP [10] that will significantly shorten the life cycle of the cleanup process at the Hanford Site.

METHODS

The ORP effort on glass formulation and melter testing data have resulted in the first major revision of the WTP glass models. These models have suggested that significant increases in waste loading in high-level waste (HLW) and low-activity waste (LAW) glasses [11] are possible over current system planning estimates. The data (although limited in some cases) were evaluated to determine a set of constraints and models that could be used to estimate the maximum loading of specific waste compositions in glass. In the near term, these models and constraints are being used to estimate the likely HLW and LAW glass volumes that would result pending the outcome of the extensive current glass formulation studies. It is recognized that some of the models are preliminary in nature and will change in the coming years. In addition, the models do not currently address the prediction uncertainties that would be required before they could be used in plant operations. The models and constraints are only meant to give an indication of rough glass volumes and are not intended to be used in plant operation or waste form qualification activities. The current research program is in place to develop the data, models, and uncertainty descriptions for that purpose.

Models to constrain the composition and loading of high-level waste (HLW) glasses include models to control the amount of spinel in the melter (c_{Sp}), the sulfur tolerance of the melter feed, nepheline formation in canister-cooled glass, viscosity of the melt, product consistency test (PCT) response, and liquidus temperature (T_L) of zirconia-containing phases. Also contained in the model are component concentration limits for model validity, chromium tolerance, and phosphate tolerance.

Models to constrain the composition and loading of LAW glasses include models to control the sulfur tolerance of the melter feed PCT response, Vapor Hydration Test (VHT) response, and viscosity. Also contained in the model are component concentration limits for model validity, as well as the chromium, halide, phosphate, and alkali tolerance.

DISCUSSION

The first step in conducting our HLW 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. [12] categorized the HLW projection in six groups:

- High alumina wastes (limited primarily by nepheline formation on slow cooling),
- High iron wastes (limited primarily by spinel accumulation in the melter),
- Wastes high in Fe, Cr, Ni, and Mn (limited primarily by spinel accumulation in the melter),
- High Cr and S wastes (limited primarily by salt accumulation in the melter),
- High P and Ca wastes (limited primarily by phosphate phase formation and melter processing upsets), and
- High alkali wastes (limited primarily by chemical durability).

The outcomes of the major (i.e., Al, Fe, and S) HLW property-composition relationships have been reported previously [13-16]. Additional work on sulphur and chromium in HLW glass processing have been completed and reported [17, 18]. A significant fraction of the projected HLW feed batches to the WTP HLW vitrification facility will have relatively high concentrations of phosphorus and glasses produced with relatively high- bismuth and phosphate concentrations show frequent occurrence of phosphate crystals. Currently, there is an effort underway to understand the roles of calcium and phosphate and their interactions in leading to crystallization processes. The justification is tied to the previous efforts being only to spinel crystallization in glasses.

During our work to support the revision of the baseline glass model for LAW we came to appreciate [11] the need for exploration and quantification of the role of what we labeled “minor components” on overall waste loading in the glass. In parallel the 2012 Tank Utilization Assessment (TUA) [19] employed the current baseline WTP LAW glass models [20] to evaluate scenarios in which the WTP and second LAW facilities are coupled but with finite second LAW capacity. These scenarios resulted in a significant increase in the amount of LAW glass produced as well as extensive idling of the High Level Waste (HLW) facility. The primary cause appears to be the buildup of halides, and to lesser extent sulfates, in the recycle stream, which leads to reduced waste loading in the LAW glass. The reduced waste loading increases the glass volume, which reduces the waste processing rate through the second LAW facility, which in turn holds up operation of the WTP HLW facility. The TUA calculations assume the same WTP baseline LAW glass models for both the WTP facility and the second LAW facility. Previous assessments showed that use of these models in the WTP allowed the WTP contract LAW loadings to be met. However, those assessments focused on the performance of the WTP and included secondary LAW treatment only as a simple “black-box” with infinite capacity for “excess” LAW. In view of the LAW glass development work performed for ORP, it is likely that revised glass models would provide higher waste loadings than the baseline WTP models, which could potentially mitigate the highly undesirable consequences found in the 2012 TUA projections. Such a revision would build upon relevant data with the meeting the identified design basis input Quality Assurance requirements that have been collected since the development of the baseline models, as well as the targeted collection of new data to both fill data gaps and to validate the new models. This work has been reported [21] and it’s anticipated that revisions of the enhanced glass models will commence in the near future.

CONCLUSIONS)

It is recognized that some of the model elements are preliminary in nature and will change in the coming years. In addition, the models do not currently address the prediction uncertainties that would be needed before they could be used in plant operations. Work is currently underway or planned to address a number of the constraints that were advanced to safely produce waste form compliant with the WTP baseline for startup. Included among these are the high Cr_2O_3 and SO_3 wastes that are subject to data range constraints but prone to salt formation and potential eskolaite formation, the one-volume percent spinel crystal in the melt (T1%), the nepheline discriminator that was imposed to avoid nepheline formation in the HLW product and has limited Al-loading, high Fe_2O_3 wastes (with and without significant Cr_2O_3, MnO, and NiO), the concentration limits of SO_3 of 0.5 wt%, 3.2 wt% Bi_2O_3 and 2.5 wt% P_2O_5 in glass as constrained by model-validity regions. The 2013 Tank Utilization Assessment [22] employed the revised (i.e., enhanced) ORP HLW and LAW glass models [11] to evaluate a number of operational scenarios. The results of which project a vastly different set of assumptions and feed vectors can be entertained and that the WTP capacity is increased and mission duration lessened. Table I offers a tabular representation of projected mission outcomes possible.

Table I. Mission Impacts with ORP High Waste Loading HLW and LAW Glasses

	BNI/WTP Baseline Models	2008 TUA* Baseline	2013 TUA Baseline	2013 TUA w/ caustic and oxidative leaching eliminated
HLW Canisters	18,400	14,838	8,223	13,534
LAW Containers	145,000	91,400	79,465	65,151
Total Canisters & Containers	163,000	106,238	87,688	78,685

*The "2008 models" were altered BNI Baseline Models in anticipation of our work.

The most significant conclusion that could be drawn, is aside from the impacts on design completion for vessels utilized in baseline operations for caustic leaching or the criticality safety items associated with oxidative leaching, is that coupling the enhanced HLW and LAW glass models allows for the conclusion that the WTP LAW Facility is properly sized to address treatment of the Hanford tank waste mission.

ACRONYMS

BNI Bechtel National, Inc.
ORP Office of River Protection
TUA Tank Utilization Assessment
WTP Hanford Tank Waste Treatment and Immobilization Plant

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