Waste Treatment & Immobilization Plant, a Leader in the International Glass Community – 16003

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ABSTRACT

The U.S. Department of Energy (DOE), Office of River Protection (ORP) is constructing the Tank Waste Treatment and Immobilization Plant (WTP) [1] to treat radioactive waste currently stored in underground tanks at the Hanford Site in Washington State. The WTP that is being designed to separate the tank waste into high-level waste (HLW) and low-activity waste (LAW) fractions with the majority of the mass (approximately 90 percent) directed to LAW and most of the activity (greater than 95 percent) directed to HLW. The pretreatment process, envisioned in the baseline, involves the dissolution of aluminum bearing solids 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. These two unit operations were advanced to accommodate shortcomings in glass formulation for HLW inventories.

A significant consideration to the most recent revision of the glass models is the extensive collaboration developed, funded, managed, and coordinated from the ORP. The current effort includes researchers at the Pacific Northwest National Laboratory, Idaho National Laboratory, Savannah River National Laboratory, Brookhaven National Laboratory, Catholic University of America, Washington State University, Rutgers University, Institute of Chemical Technology Prague, University of Ottawa, Tokyo Institute of Technology, The University of Adelaide, and University of Sheffield. Independent technical evaluation having been solicited from faculty of Alfred University and Vanderbilt University.

These advances in glass chemistry generate a need to revisit the feed vectors, flowsheet, and the unit operations driven by minimal waste loading requirements set forth in the contract for the design and construction of the plant. The current status and plans for the immediate future of glass chemistry are the subject of the primary concern to successfully completing our clean-up mission at Hanford.

INTRODUCTION

Background

Current estimates and glass formulation efforts developed by the contractor for the WTP are conservative vis-à-vis achievable waste loadings [2]. 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 ORP 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 that these higher waste loading glasses will reduce the HLW canister production requirement by 45 percent or more. For LAW, 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 LAW container production will be reduced by 45 to 55 percent while treatment capacity for secondary liquid wastes warrants re-evaluation.

The feed for vitrification to produce a nuclear waste glass is a mixture of waste with glass-forming, and modifying additives that are charged onto the cold cap that covers 90 to 95 percent 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 rates, initiation of crystal forming reactions, and chemical reactions that determine the ultimate fate of technetium in the glass melt.
Vitrification of technetium-containing radioactive waste is the preferred process, since technetium can be immobilized in glass together with the rest of radionuclides. Unfortunately, a significant fraction of technetium is escaping during the vitrification process into offgas. Technetium is one of the most difficult contaminants to address at the Hanford Site because of its complex chemical behaviour in tank waste, volatility in high-temperature immobilization processes (i.e., vitrification), and high mobility in the soils adjacent to the disposal environments. Past performance assessment studies have shown that technetium-99 would be the primary dose contributor to the performance in disposal activities of immobilized LAW over the period of thousands and tens of thousands of years. However, only the portion of technetium not immobilized in borosilicate glass are seen to give rise to unacceptable outcomes by performance assessment studies. ORP undertook an effort for sufficient understanding of the technetium chemistry to ensure near stoichiometric inclusion in the glass matrix.
HLW melters are projected to operate in an inefficient manner as they are subjected to artificial constraints, such as minimum liquidus temperature (T_L) or maximum equilibrium fraction of crystallinity at a given temperature. These constraints substantially limit waste loading, but were imposed [currently below 1 vol% ($T_{0.01}$),

nominally below 1,050°C] to prevent clogging of the melter with spinel crystals [(Fe, Ni, Mn, Zn)(Fe, Cr)$_2$O$_4$]. In the melter, the glass discharge riser is the most likely location for crystal accumulation during idling because of low glass temperatures, stagnant melts, and small diameter. However these constraints were developed for nonagitated (i.e., nonbubbled) melters with bottom electrodes. Work to-date is on track to demonstrate that there is no greater risk to the melter by moving to 2 vol% with a benefit of a reduction of the mission by circa 20 percent.

DISCUSSION

To support this effort, the DOE Office of River Protection has engaged the technical expertise regarding vitrification technologies for the WTP from an international collaborative team including the Pacific Northwest National Laboratory (PNNL), The Catholic University of America (CUA), Savannah River National Laboratory (SRNL), Idaho National Laboratory (INL), Washington State University, Rutgers University, Tokyo Institute of Technology, University of Ottawa, University of Sheffield, and the University of Chemistry and Technology Prague with independent technical oversight provided by Alfred University and Vanderbilt University. ORP has developed and implemented an integrated program that spans several key technical areas, including (but not limited to):

- Advanced waste glass formulations for both HLW and LAW
- Glass property-composition model development and implementation in support of mission planning and facility operations
- SO_3, Tc, I, and halide retention in glass
- Nepheline formation in the final glass waste form
- Crystal-tolerant glass formulation and demonstrating safe operations with tolerance for crystalline materials in the melt
- Melting rate enhancements
- Materials chemistry to enhance the durability of secondary waste from vitrification

In addition to the key technical areas bulleted above, this integrated ORP program is focused on providing a technical, science-based foundation for making key decisions regarding the successful operation of WTP facilities. The fundamental data stemming from this program will support development of advanced glass formulations, key process control models, and tactical processing strategies to ensure safe and successful operations for both the LAW and HLW vitrification facilities with a focus on reducing overall mission life.

One objective of this program is to expand the Hanford Site LAW and HLW glass database and property-composition models to cover the balance of the tank waste treatment and immobilization mission. Because of the variability in the waste compositions to be vitrified, there is no single HLW or LAW glass formulation; rather, compositional envelopes for both HLW and LAW glasses will be needed. The effort to expand the glass compositional regions over which acceptable glasses can be fabricated and processed through the WTP will continue to be supported by crucible-scale tests with simulants, crucible-scale tests with actual waste, scaled melter tests with simulants, and scaled melter tests with actual waste.

Of equal importance is the management of ^{99}Tc, which has low (roughly 20% to 70%) single-pass retention in glass during LAW vitrification [3]. The current baseline approach to achieve higher Tc retention is to recycle Tc captured in the off-gas stream. However, recycling the off-gas also increases the SO_3 and halide concentrations in the melter feed and consequently decreases the loading of waste coming from the tank farm. Therefore, specific and detailed studies are being performed to understand the behavior of Tc throughout the WTP vitrification process (including potential recycle) and eventually to develop strategies for efficient management of Tc.

The interdependence of these research activities within the ORP Advanced Waste Glass (AWG) program as they relate to critical process operations and qualification needs to support the full River Protection Project (RPP) mission. Our research is motivated by the potential for substantial economic benefit that will be realized from implementing advancements in HL glass, LAW glass formulation and strategies for efficient and economic ^{99}Tc management. Research and development plans for the other key focus areas have either been issued [4, 5 & 6] or are being developed (i.e., cold cap behavior and melt dynamics) in parallel with the experimental effort.

Successful deployment of post-commissioning glass property-composition models and related glass formulation algorithm will hinge on a critical interface with the tank farm operations contractor. The retrieval and blending strategies, tank sequencing, and any planned waste treatment (e.g., at- or in-tank treatment) unit operations will ultimately define the envelope of the feed compositions coming to the LAW vitrification facility. The impact of potential retrieval and blending strategies on various feed composition scenarios may be reflected in the output of the system planning models or tools as they aim to gain insight into the overall impacts to the overall facility mission life. Ensuring the AWG program is aligned with tank farm and/or pretreatment operational strategies is paramount for successful post-commissioning facility operations.

As the mission progresses toward completion, glass formulation activities should be focused on continuous improvements and should remain highly integrated with flowsheet development efforts to ensure downstream operations can be supported by the best available formulations, glass property-composition models, and glass formulation algorithm aimed at increasing waste loading.

CONCLUSIONS

ORP has implemented an integrated program to increase the loading of Hanford tank wastes in glass while meeting melter lifetime expectancies and process, regulatory, and product performance requirements. The integrated ORP program is focused on providing a technical, science-based foundation for making key decisions regarding the successful operation of the WTP facilities. The advanced glass research and development program has identified the near-, mid-, and longer-term research and development activities required to develop and validate 1) advanced HLW and LAW glasses, 2) advanced property-composition models and uncertainty expressions, and 3) an advanced glass algorithm to support facility operations at WTP, including both direct feed and full pretreatment flowsheets.

Our LAW AWG program is motivated by the potential for substantial economic benefit (e.g., significant reductions in glass volume) that will be realized when advancements in glass formulation, property-composition models supporting facility operations, and efficient ^{99}Tc management strategies are implemented. These activities will reduce the cost of the RPP mission by shortening the schedule for tank waste treatment and decreasing the amount of LAW glass that is permanently disposed of onsite in a shallow subsurface disposal facility, IDF. Additionally, the ability to minimize or even eliminate the need for off-gas recycle is significant not only from a vitrification perspective, but for other unit operations including pretreatment and tank farm operations.

Four key activities have been identified that serve as the foundation for the HLW AWG program:

1. Develop new composition-property data over the full Hanford HLW compositional region of interest.
2. Update or revise the current glass composition-property models and constraints to incorporate the new glass property-composition data.
3. Update the HLW glass formulation algorithm with the new HLW glass composition-property models and constraints.
4. Demonstrate effective glass processing in scaled melter tests for glass compositions across the full WTP compositional envelope.

Developing and applying the advanced glass formulations will reduce the cost of Hanford tank waste management by reducing the cost of fabrication, storage, transportation, and disposal of the HLW glass. Additional benefits will be realized if advanced glasses are developed that demonstrate more tolerance for key components in the waste (such as Al_2O_3, Cr_2O_3, SO_3 and Na_2O) above the currently defined WTP constraints. Tolerating these higher concentrations of key waste loading limiters can reduce the burden on (or even eliminate the need for) leaching to remove Cr and Al and washing to remove excess S and Na from the HLW fraction. Advanced glass formulations may also make direct vitrification of the HLW fraction without significant pretreatment more cost effective. Finally, the advanced glass formulation efforts seek not only to increase waste loading in glass, but also to increase glass production rate. When coupled with higher waste loading, ensuring that all of the advanced glass formulations are processable at or above the current contract processing rate leads to significant improvements in waste throughput (the amount of waste being processed per unit time),which could significantly reduce the overall WTP mission life. The integration of increased waste loading, elimination or reduction of leaching/washing requirements, and improved melting rates provides a system-wide approach to improve the effectiveness of the WTP process. Additionally, it could be envisioned that another outcome of the AWG work can be a direct feed to HLW vitrification. Eliminating the introduction of tank waste solids to the Pretreatment Facility could vastly reduce the burden of completion of the design of that facility.

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