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Advanced High-Level Waste Glass Research and Development Plan

July 2015

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U.S. DEPARTMENT OF ENERGY

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

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Richland, Washington 99352

Executive Summary

The U.S. Department of Energy Office of River Protection (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 quality requirements. The integrated ORP program is focused on providing a technical, science-based foundation from which key decisions can be made regarding the successful operation of the Hanford Tank Waste Treatment and Immobilization Plant (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 low-activity waste (LAW) and high-level waste (HLW) vitrification facilities with an appreciation toward reducing overall mission life.

The purpose of this advanced HLW glass research and development plan is to identify the near-, mid-, and longer-term research and development activities required to develop and validate advanced HLW glasses and their associated models to support facility operations at WTP, including both direct feed and full pretreatment flowsheets. This plan also integrates technical support of facility operations and waste qualification activities to show the interdependence of these activities with the advanced waste glass (AWG) program to support the full WTP mission. Figure ES-1 shows these key ORP programmatic activities and their interfaces with both WTP facility operations and qualification needs. The plan is a living document that will be updated to reflect key advancements and mission strategy changes.

The research outlined here is motivated by the potential for substantial economic benefits (e.g., significant increases in waste throughput and reductions in glass volumes) that will be realized when advancements in glass formulation continue and models supporting facility operations are implemented. Developing and applying advanced glass formulations will reduce the cost of Hanford tank waste management by reducing the schedule for tank waste treatment and reducing the amount of HLW glass for storage, transportation, and disposal.

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 may 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, reduced leaching/washing requirements, and improved melting rates provides a system-wide approach to improve the effectiveness of the WTP process.

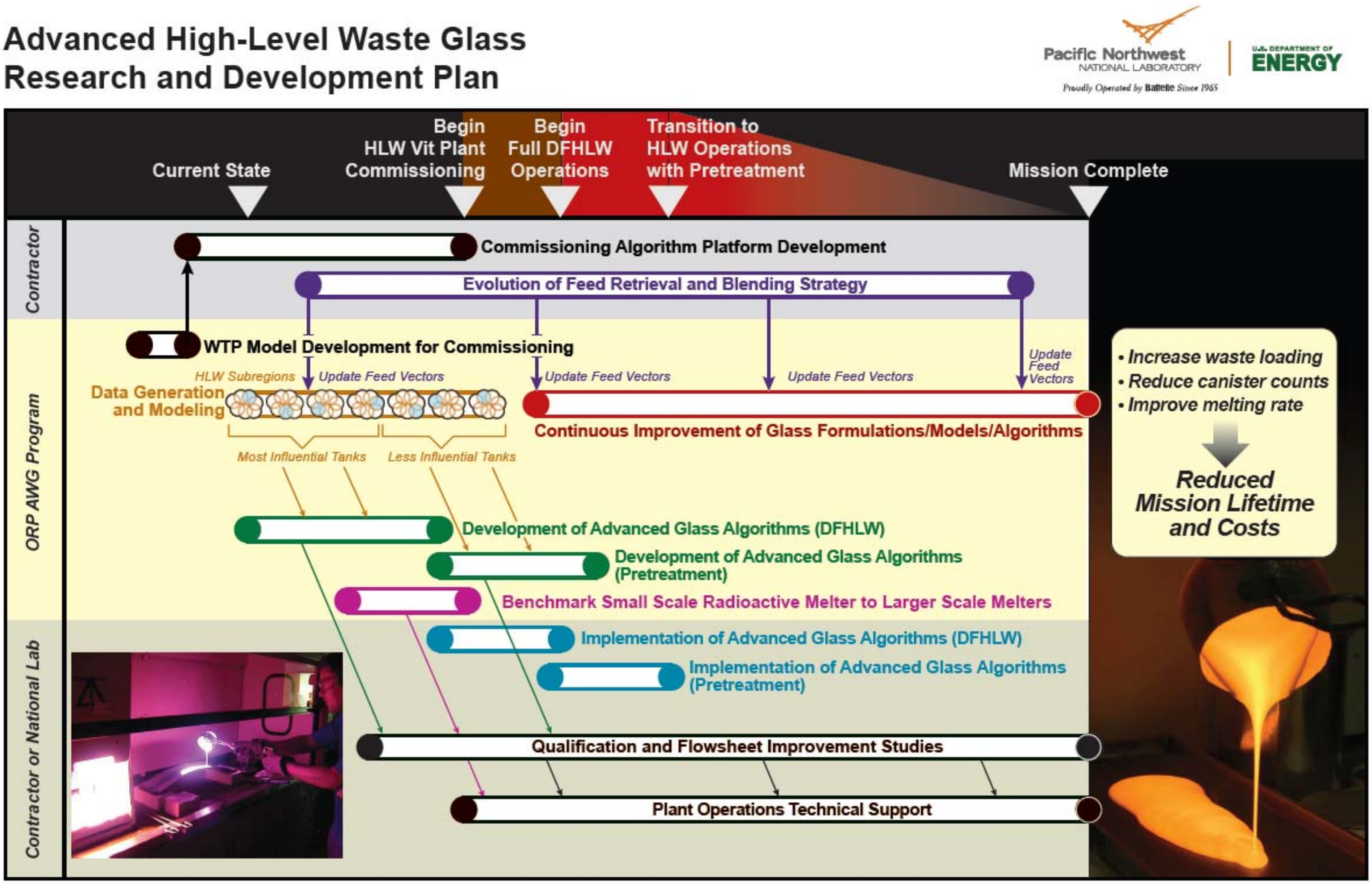

Figure ES-1. Advanced High-Level Waste Glass Research and Development Plan to Support the WTP Mission

Acknowledgments

The authors gratefully acknowledge the financial support of Albert Kruger of the U.S. Department of Energy, Office of River Protection, Waste Treatment and Immobilization Plant Federal Project. The authors thank Albert Kruger, Dong-Sang Kim, Dawn Wellman, and Joe Westsik for their thorough reviews, constructive feedback, and in-depth discussions associated with the development of this plan. The graphics contributions from Ted Tanesse and technical editing by Matt Wilburn are greatly appreciated.

Acronyms and Abbreviations

AWG	Advanced Waste Glass
BNI	Bechtel National, Inc.
CCC	canister centerline cooling
CUA	The Catholic University of America
DFHLW	direct feed high-level waste
DOE	U.S. Department of Energy
DWPF	Defense Waste Processing Facility
EGCR	experimental glass composition region
HLW	high-level waste
HTWOS	Hanford Tank Waste Operations Simulator
IEWO	Inter-Entity Work Order
IHLW	immobilized high-level waste
ILAW	immobilized low-activity waste
LAW	low-activity waste
MT	metric tons
NLDC	National Laboratory Directors' Council
ORP	Office of River Protection
PCT	product consistency test
PNNL	Pacific Northwest National Laboratory
PUREX	plutonium uranium reduction extraction
REDOX	reduction oxidation
QGCR	qualified glass composition region
RPP	River Protection Project
RSM	Research-Scale Melter
SEAB	Secretary of Energy Advisory Board
T_L	liquidus temperature
VSL	Vitreous State Laboratory
WTP	Hanford Tank Waste Treatment and Immobilization Plant

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1.0 Introduction

About 55 million gallons of high-level mixed waste is currently stored in underground tanks at the U.S. Department of Energy (DOE) Hanford Site in the State of Washington. Bechtel National, Inc. (BNI) is constructing the Hanford Tank Waste Treatment and Immobilization Plant (WTP) to separate the tank waste into high-level waste (HLW) and low-activity waste (LAW) fractions, which will then be vitrified respectively into immobilized low-activity waste (ILAW) and immobilized high-level waste (IHLW) borosilicate glass products (DOE 2000). The ILAW product will be disposed in an engineered facility on the Hanford Site while the IHLW product is designed for acceptance into a deep geological disposal facility for high-level nuclear waste. The ILAW and IHLW products must meet a variety of requirements with respect to protection of the environment before they can be accepted for disposal.

To support this effort, the DOE Office of River Protection (ORP) has requested 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, Rhenish-Westphalian Technical University, the 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
- Model development and implementation in support of facility operations
- SO_3, Tc, I, and halide retention in glass
- Nepheline formation in the final glass waste form
- Crystal-tolerant glass formulation
- Melting rate enhancements.

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.

The research outlined in this glass research and development plan is motivated by the potential for substantial economic benefits (e.g., significant reductions in glass volumes and canister counts) that will be realized when advancements in glass formulation continue and models supporting facility operations are developed, validated, vetted, and implemented to support glass formulation and facility operations.

This plan focuses on the technical areas of advanced HLW glass formulation, data generation, and model development supporting glass algorithm revisions and implementation, and melter testing.[1] Research and development plans for the other key focus areas have either been issued (Matyas et al. 2014) or are being developed in parallel with this effort.

2.0 Benefit to the River Protection Project

In simple terms, the objective of the HLW Advanced Waste Glass (AWG) program is to develop the fundamental technical basis for increasing waste loading for WTP HLW glasses through an investigation of glass formulations and property relationships. Although increased waste loading can significantly reduce canister counts, a broader goal of the integrated ORP program is to reduce overall mission life and cost for the River Protection Project (RPP) facilities as a whole. Mission life will be dictated not only by the waste loading that can be achieved during operations but also by melting rate and facility attainment.[2] These factors ultimately dictate the amount of waste being processed per unit time (referred to as waste throughput), which is directly related to the overall facility mission life.[3]

Development of advanced glasses also has the potential for additional significant benefits to the WTP flowsheet. For example, the ability to target higher waste loadings for certain components (e.g., Al_2O_3 and Cr_2O_3) would have significant impacts on decisions within pretreatment. If Al_2O_3 concentrations can increased in glass above current WTP requirements, then the degree of Al dissolution required (via caustic leaching) in pretreatment may be reduced or eliminated for certain waste campaigns. Elimination of caustic leaching can also address the erosion/corrosion concerns in filtration process vessels (UFP-1 and UFP-2) and reduce the risk associated with precipitation of aluminum salts during the filtration process. Oxidative leaching to remove Cr_2O_3 during pretreatment carries the risk of transporting fissile materials with the dissolved Cr to LAW. Implementation of advanced glasses that can tolerate higher Cr_2O_3 concentrations can minimize or eliminate the need for oxidative leaching and thus reduce the associated risk.

Therefore, not only can the HLW AWG program reduce canister counts and overall mission life, but could reduce or eliminate specific pretreatment unit operations, have significant positive impacts on erosion/corrosion and precipitation issues, and influence the Na_2O management within the WTP flowsheet. Implementation of advanced glass would open up processing options (e.g., Direct Feed HLW) that would not exist otherwise. The objective of the HLW AWG program to increase waste loading is

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[1] Although the ORP program encompasses both HLW and LAW advanced glass work, separate research and development plans are being developed for advanced LAW glass formulation and Tc/SO_3/halide retention and cold-cap reactions/melting rate studies.

[2] Facility attainment is considered the percentage of time the HLW vitrification facility is operational or on-line. Although critical with respect to determine waste throughput, operational efficiencies (e.g., impacted by downtime for scheduled maintenance, unexpected idling times, etc.) are outside the scope of the AWG program.

[3] This statement assumes that waste feed delivery, pretreatment, and/or products and secondary waste handling are not rate limiting.

being integrated with efforts to improve melting rate, reduce leaching requirements, and increase LAW throughput, which provides a system-wide improvement of the RPP flowsheet.

3.0 Current Technology Status

The WTP has developed glass property-composition models to formulate compositions and qualify HLW glasses (Piepel et al. 2008) for disposal. These models are based on data from crucible-scale tests with simulants, crucible-scale tests with actual waste, and scaled melter tests with simulants collected under the BNI contract to design, construct, and commission the WTP (DOE 2000). Because the scope of the BNI contract was limited to operating the plant for only a few months with a wastes (equating to approximately 60 canisters of IHLW) from four waste tanks that were to be set aside for initial plant operation (AZ-101, AZ-102, AY-102/C-106, and AY-101/C-104, three of which were high iron wastes), the data and resulting models only cover a fraction of the HLW glass compositions needed for the entire Hanford Site mission. In addition, the data and models developed by BNI are based on glasses that target waste loadings only moderately above the contract minimum rather than focusing on maximum achievable waste loadings. There are significant compositional gaps between the currently qualified HLW regions and those regions that will be needed to support the full vitrification mission.

Prior to discussing the compositional gaps in more detail, a discussion of two key terms used throughout this document is warranted. The first term is *experimental glass composition region* (EGCR), which refers to a composition region of glasses that has been (or will be) experimentally explored through fabricating glasses and measuring their properties. Ideally, an EGCR will be broader than the compositions that the HLW facility plans to process such that compositions that satisfy all process- and product-quality related constraints can be identified. To accomplish that, the EGCR has to encompass glass compositions that fail one or more constraints in order to define acceptability boundaries. The experimental data collected on glass compositions covering the EGCR provide the basis for developing property-composition models that can (1) discriminate between glass compositions that satisfy or fail the specific requirements, and (2) adequately predict glass properties of compositions that satisfy all requirements. The second term, *qualified glass composition region* (QGCR), refers to the subset of the EGCR where all processing and product quality constraints are satisfied with sufficient confidence, after accounting for applicable uncertainties.

3.1 HLW Compositional Gaps

As previously mentioned, the existing WTP HLW QGCR (compositional region associated with commissioning) is focused on glasses for wastes identified in the BNI contract that are primarily high in Fe_2O_3 and marginally exceed contract minimum waste loadings. Figure 1 conceptually contrasts the full mission Hanford HLW EGCR with the current WTP HLW EGCR (commissioning only). The commissioning EGCR is a small subset of the full compositional region over which WTP plans to process HLW. In fact, the full Hanford EGCR is large enough to necessitate division into composition subregions (represented by the gold circles) as shown in Figure 2 by the composition of the waste (e.g., high-iron, -alumina, -sulfate, -chrome, -soda, and -bismuth concentrations).

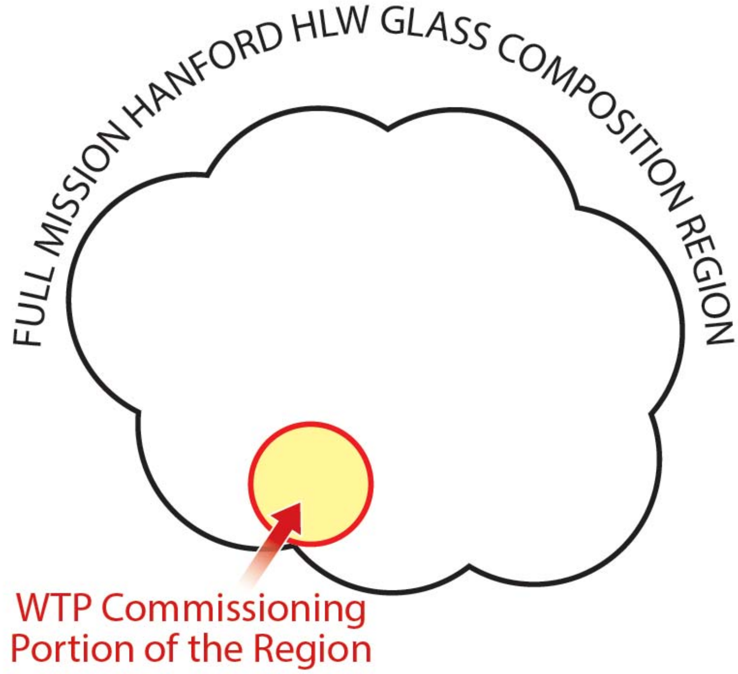

Figure 1. Two-Dimensional Conceptual Representation of the Full Hanford HLW EGCR

Figure 2. Conceptual Representation of the Full Hanford HLW EGCR Divided into Subregions of Like-Glass Compositions (as gold circles)

Figure 1 demonstrates the compositional gaps between the current WTP HLW QGCR and those regions that will be needed to support the full vitrification mission. Without additional data and revised glass models, WTP operations would be bound by the current compositional limits over which the existing WTP models are valid. This is the basis for the HLW AWG program and its objective to expand the compositional region over which HLW glasses can be processed—including the advanced waste glasses that will allow higher waste loadings.

3.2 Initial HLW Glass Formulation Advancements

Initial advancements in HLW glass formulations focused on increasing waste loadings over current WTP contract limits through glasses developed by CUA (Matlack et al. 2005a, 2007a, 2008, 2009a, 2010a, 2010b, 2011, 2012a, 2012b; Kot et al. 2011; Gan et al. 2009) and by PNNL (Kim et al. 2008 and 2011; Schweiger et al. 2008 and 2011; Rodriguez et al. 2011; McCloy et al. 2010). The resulting data were summarized by Muller et al. (2012) and Vienna et al. (2009 and 2013).

These studies conclude that loadings for specific wastes in glass can be increased significantly over the loadings allowed by the current WTP constraints or the existing WTP EGCR for which models exist, while still meeting both process and product performance requirements. Examples of the gains made in these initial studies include the following:

- HLW glasses have been formulated with 26 wt% Al_2O_3 (Matlack et al. 2008; Kim et al. 2008; Fox and Peeler 2007), which is double the 13 wt% maximum value allowed by the current WTP HLW EGCR (Piepel et al. 2008).
- HLW glasses have been produced with Bi_2O_3 concentrations ranging from approximately 3 to 16 wt% (Vienna et al. 1996; Crum et al. 1997; Matlack et al. 2007a; Vienna et al. 2009; McCloy and Vienna 2010), which is roughly 13 times the maximum value of 0.3 wt% in the current WTP EGCR.
- HLW glasses have been formulated with CaO concentrations ranging from approximately 7 to 20 wt% (Matlack et al. 2007a; Vienna et al. 2009; Riley et al. 2011), compared to the 1 wt% limit in the current WTP EGCR.

Scaled melter tests have also demonstrated the ability to process HLW glasses with substantially higher concentrations of key components that can limit waste loading. Processing of various waste streams through scaled melters demonstrates scale-up principles and reduces facility operational risks compared with implementation strictly based on crucible-scale testing. For example, glasses targeting 26 wt% Al_2O_3 were not only produced at crucible scale, but scaled melter tests were performed with high Al concentration feeds, demonstrating the feasibility of processing these advanced glasses (Matlack et al. 2008; Kim et al. 2008).

The coverage of experimental data for the full Hanford HLW EGCR is sparse and most studies have focused on the high waste-loading boundaries with limited studies within a specific EGCR. Figure 3 conceptually illustrates how the current data (red dots) are distributed over the full Hanford HLW glass composition region. Glasses produced along these high waste-loading boundaries are primarily based on single-component maxima. These boundary glasses can possess either acceptable or unacceptable properties with respect to their related process or performance constraints. Thus, due to the multi-dimensional compositional aspects of these glasses, coverage across each compositional subregion will be required.

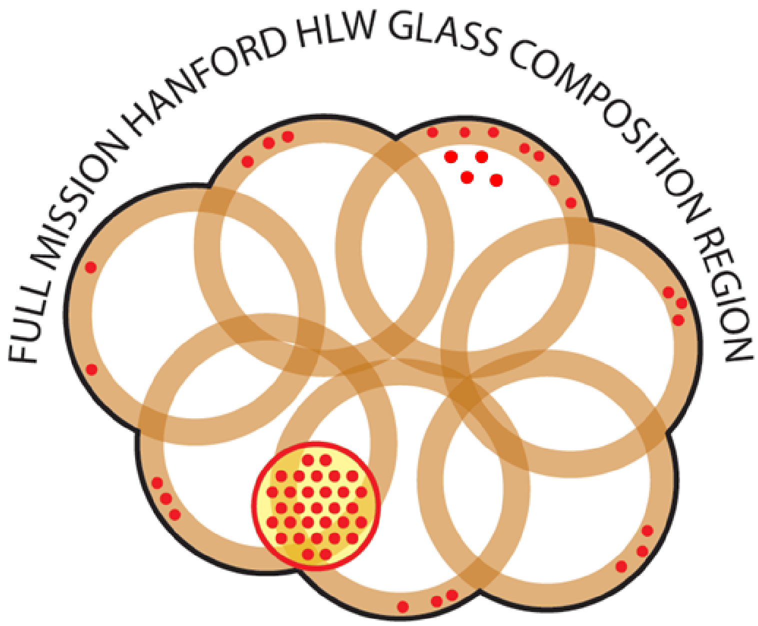

Figure 3. Distribution of Current HLW Glass Property-Composition Data Shown on the Full Hanford HLW EGCR (each red dot conceptually represents test compositions and the yellow region is the current WTP EGCR)

As Figure 3 shows, there is ample data (red points) coverage in the current WTP EGCR (highlighted in yellow region) with limited test data in the other EGCR subregions that cover the full WTP processing region. Therefore, a primary focus of the integrated HLW AWG program is to fill (and integrate) those subregions with experimental data from which new models can be developed and implemented to support facility operations for the entire mission.

To accomplish this, a phased approach is being pursued. Rather than attempting to fill the EGCRs of multiple subregions in one step, the subregions will be prioritized based on the estimated impacts on total HLW glass volume likely to result from immobilizing each subregion of wastes or potential impacts to pretreatment decisions. Kim et al. (2011) used the HTWOS 2009 baseline model predictions (Vienna et al. 2009) to determine the fraction of glass that was limited by specific constraints for a set of wastes estimated based on a feed vector by Certa et al. (2008). The results of that study are summarized in Figure 4 and highlighted below (the fraction of glass limited by each factor given parenthetically):

- High Al_2O_3 wastes that are limited by nepheline formation and spinel (46%)
- High Fe_2O_3 wastes (with and without significant Cr_2O_3, MnO, and NiO) forming spinel and other crystals (24%)
- High Cr_2O_3 and SO_3 wastes that are subject to data range constraints but prone to salt formation are potential eskolaite formation (20%)

- High P_2O_5 and P_2O_5+CaO wastes that are limited by phase separation and potential process upsets (9%)
- High Na_2O wastes limited by data range constraints but prone to poor durability (1%).

The high-alumina (Al_2O_3) subregion was selected for the initial phase of the HLW AWG study because it makes up roughly 50% of the waste (see Figure 4), represents the highest potential for reduction in overall glass volume, and will provide input to decisions regarding leaching efficiency requirements. The high Fe_2O_3 and spinel-limited wastes are the basis for the current WTP models, but additional work is being performed to address spinel formation and potential accumulation in melters under a specific research and development plan (Matyas et al. 2014 – discussed in more detail in Section 5.2). The chromium and sulfur subregion could significantly affect pretreatment decisions (e.g., oxidative leaching of Cr_2O_3) and will likely require extensive melter testing to evaluate composition effects on salt accumulation in the melter. Hence, this subregion was identified as a key region for which testing should be initiated as soon as possible. The next subregions will be selected based on ORP priorities, which will likely be related to the timing of batches to be delivered to the WTP and the impact to the overall mission.

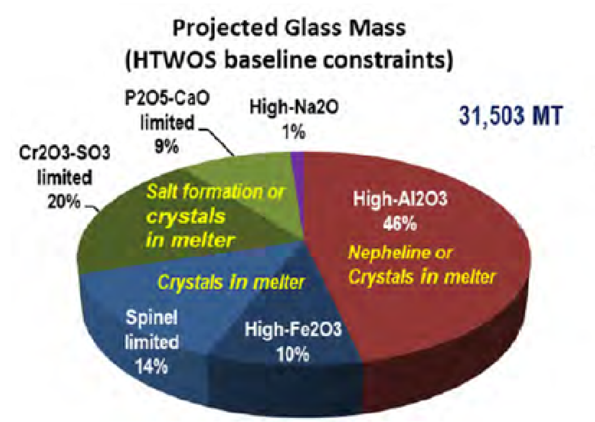

Figure 4. Distribution of HLW Glass by Limiting Factors (Kim et al. 2011)

Kim et al. (2011) point out that the composition region of successful glasses with very high alumina loading is limited (or the coverage of the high-alumina subregion is sparse). Current data are insufficient for developing the QGCR for high-loaded, high-alumina glasses or for developing a transition path from high-loaded, high-alumina glasses to other high-waste-loaded glasses with different limiting components (i.e., transition from one QGCR to the next, which is represented by the overlapping subregions in Figure 5). To accomplish that, a series of test matrices needs to be developed to cover the compositional subregions of interest and intermediate transitions. The data resulting from these matrices will provide the technical basis for defining acceptable processing regions from which advanced models can be developed and implemented. Figure 5 conceptually shows a composition subregion (e.g., high Al_2O_3 glasses) being filled by a test matrix (or series of matrices) represented by the blue dots.

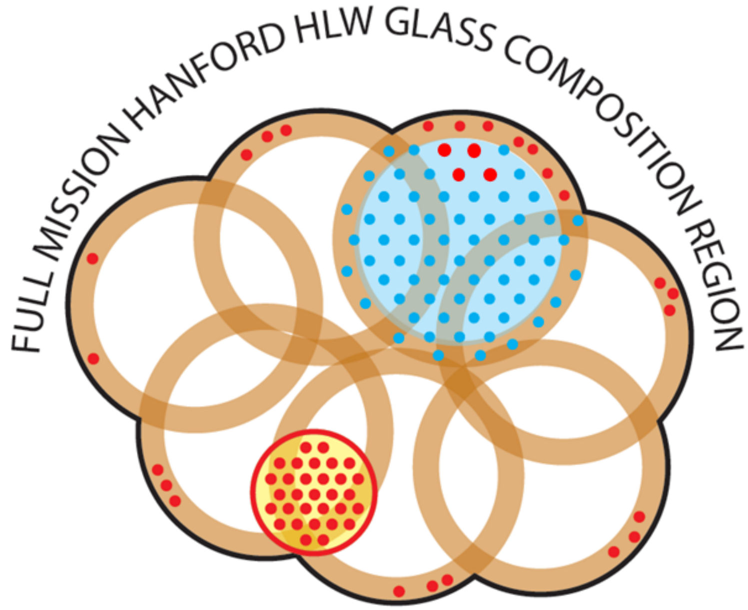

Figure 5. Glass Composition Data Shown Conceptually on the Full Hanford HLW EGCR (each red dot representing an existing test glass composition) with New Composition Data Required to Fill a Single Subregion (shown in blue dots)

A primary objective of the integrated HLW AWG program is to fill in (and integrate) each subregion with experimental data from which new models can be developed and implemented to support facility operations for the entire mission.

4.0 Motivation for Continued Research for HLW

Vienna et al. (2013) used a preliminary set of advanced models and constraints developed on limited data and compared glass volumes that would be expected to be produced using the current WTP models and constraints (commissioning based) for a series of feed vectors or clusters. The advanced models and constraints were used to indicate the potential impact on glass volume estimates and were not intended for use in plant operation or waste form qualification activities.

Kim et al. (2011) performed an analysis of two compositional feed vectors ("2008" from Certa et al. 2008 and "2011" from Certa et al. 2011) which identified 20 clusters for each feed vector. The maximum waste loadings were estimated for each of the 20 clusters from each feed vector using the sets of constraints for the qualified WTP algorithm constraints (Vienna and Kim 2014), the Hanford Tank Waste Operations Simulator (HTWOS) 2009 constraints (Vienna et al. 2009), and the HTWOS 2010 constraints (McCloy and Vienna 2010).

Figure 6 (from Vienna et al. 2013) compares the different model and constraint sets on estimated glass volumes that may be produced. Implementing the advanced glass models (recognizing that models are preliminary and do not address uncertainties at this point) would significantly reduce the volume of HLW glass produced due to the ability to target higher waste loading for a broad range of waste streams. The current WTP baseline (commissioning) constraints and models would lead to approximately 2.5

times the amount of glass compared to an approach based on the use of advanced models. This provides the motivation to develop and implement advanced glass models and constraints.

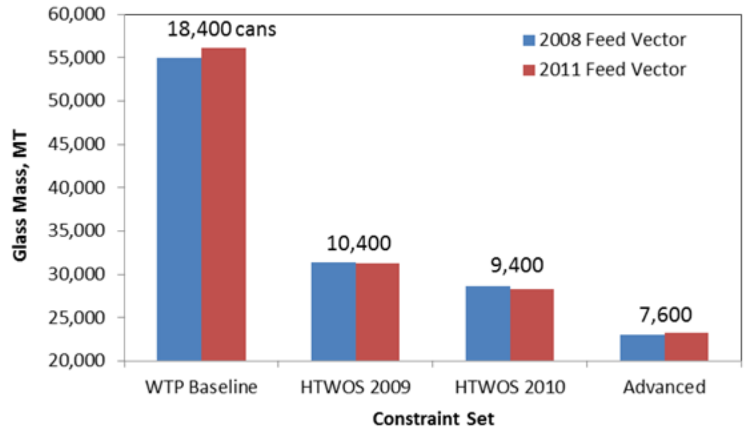

Figure 6. Comparison of Estimated Glass Masses Based on Various Model and Constraint Sets (from Vienna et al. 2013)

5.0 Data Needs: Current and Future Research

Four key activities provide the technical foundation of the HLW AWG program:

- Develop new composition-property data over the full Hanford HLW EGCR (i.e., fill in known compositional gaps).
- Update or revise the current glass composition-property models and constraints (Piepel et al. 2008) to incorporate the new glass composition-property data.
- Update the preliminary HLW glass formulation algorithm (Vienna and Kim 2014) with the new HLW glass composition-property models and constraints.
- Demonstrate effective glass processing in scaled melter tests (both simulant and radioactive) for glass compositions across each region within the full Hanford HLW EGCR.

Prior to discussing current and future HLW AWG program activities, it would be beneficial to describe how the HLW AWG program integrates or supports future facility operations including commissioning, plant operations, qualification, and flowsheet studies. Although there are obviously additional technical scopes that support these functions, this advanced HLW glass research and development plan focuses on the glass formulation, model development, and melter testing needed to complete the tank waste cleanup mission for HLW. Figure 7 is a schematic of the HLW AWG research and development plan. The plan is divided into three primary sections: (1) key RPP milestone activities (HLW vitrification plant commissioning, direct feed high-level waste [DFHLW] operations, pretreatment plant commissioning, and mission completion); (2) AWG program scope (data, model, algorithm development and implementation); and (3) contractor or national laboratory related activities (plant operations, operational technical support, waste feed qualification, and flowsheet studies).

The plan reflects the current status of having models and algorithms developed to support HLW vitrification facility commissioning as part of ongoing BNI activities to develop a platform for implementing the algorithms to support facility operations. The cornerstone of the HLW AWG program is the development and validation of advanced HLW glasses and their associated models to support facility operations at WTP under both DFHLW and pretreatment feed flowsheets. These models are required for three primary purposes:

1. To support vitrification plant operations to ensure processable batches and acceptable glass compositions are produced.
2. To support waste feed prequalification to evaluate melter feed properties, drive decisions on pretreatment operations, and evaluate vitrification process effectiveness.
3. To support RPP mission planning, including optimization of the mission from a waste feed delivery strategy, waste pretreatment requirements, and mission life/cost estimation.

The following subsections provide a high-level overview of the major HLW AWG programmatic activities (Figure 7) and how successful outcomes will support the transition from the current technology state to mission complete status. Key markers with which the HLW AWG program elements are aligned include WTP commissioning, post-commissioning operations (e.g., DFHLW), implementation of full pretreatment operations (as required), plant operations technical support, and actual waste process testing in the form of qualification or pre-decisional flowsheet studies.

The plan is not intended to set policy for the DOE. It does not identify facilities in which various activities will be performed nor does it reflect actual dates by which certain facility operations would be initiated or completed. Although not the focus of this document, this plan does integrate technical support of facility operations and waste qualification activities to show how these activities are interdependent with the advanced waste glass program to support the full WTP mission.

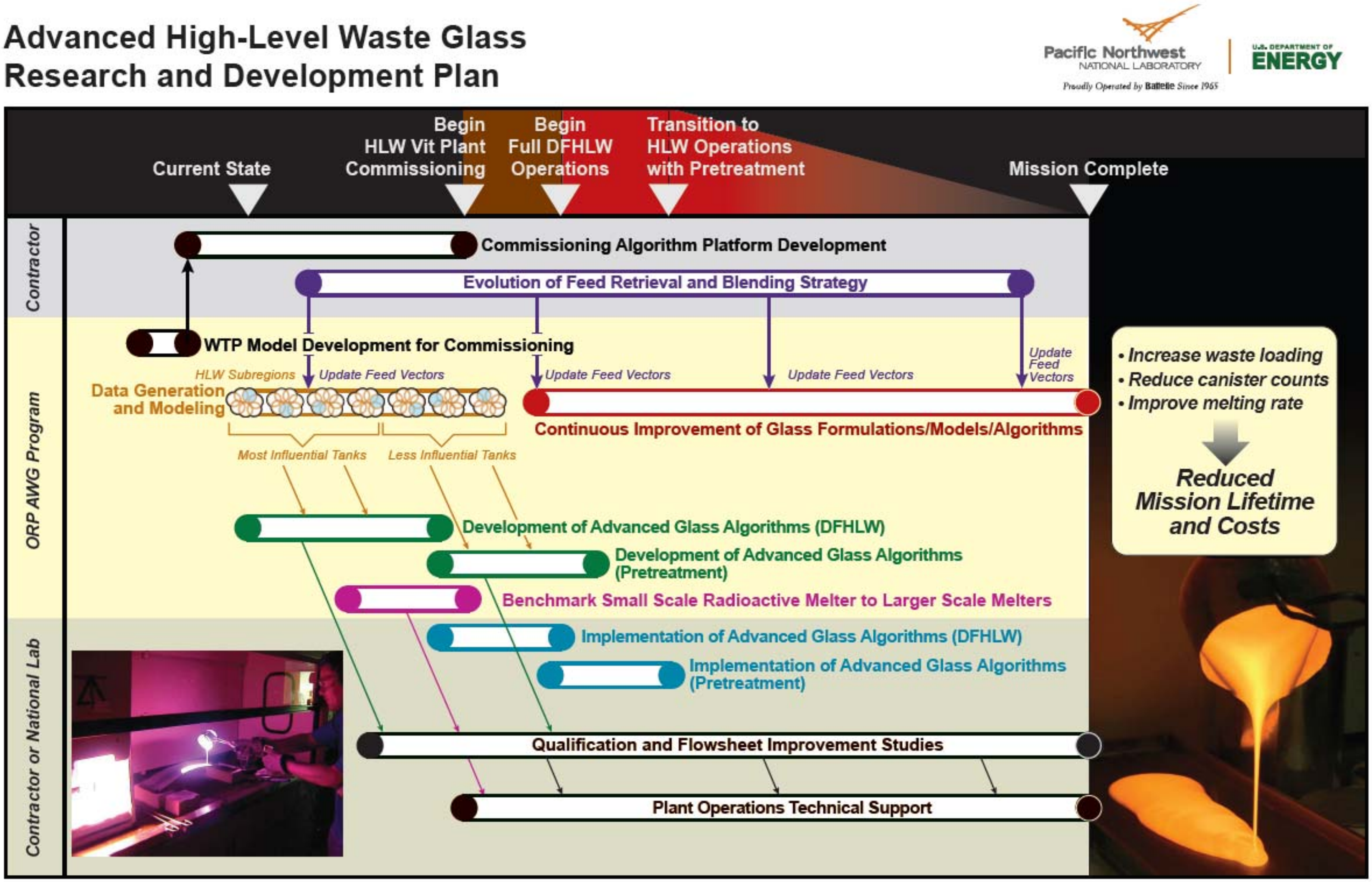

Figure 7. Advanced High-Level Waste Glass Research and Development Plan to Support the WTP Mission

5.1 Data Generation to Fill HLW Glass Compositional Gaps

This activity is focused on expanding the glass compositional region over which acceptable glasses can be fabricated and processed through the WTP using a phased approach that prioritizes the potential impacts to glass volumes, support of near-term RPP decisions, and readiness for the most likely initial batches of waste to be treated. This phased approach is conceptually shown as "rings" on the data generation and modeling activity in the plan (Figure 7). Each ring represents a different EGCR that would be evaluated through a series of test matrices. The data being generated for each ECGR are based primarily on crucible-scale tests with simulants to be augmented with melter tests and actual waste sample testing. These data ultimately serve as the basis from which key composition-property models will be developed or updated to support future mission planning as well as plant operation.

The initial stage of the phased HLW AWG approach is to evaluate specific EGCRs associated with high Al- and Cr-containing glasses, as they are primary drivers for the degree of leaching that may be required for what is projected to be a large fraction of the wastes to be processed at the WTP (see Figure 4). Selection of the next EGCR to be evaluated could be dictated by future decisions regarding changes to the commissioning tanks or feed retrieval and/or blending strategies based on ORP priorities. Any revisions to the Waste Feed Delivery Plan (West et al. 2012) or System Plan (DOE 2014) may drive decisions on the sequencing or priority of subregions that should be evaluated. It is recognized that the waste feed composition for plant commissioning is not yet known. Once the initial feed composition is determined, the development of models covering the composition space to be processed will become a high priority.

5.1.1 High Al_2O_3 Glasses

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^+-[$AlO_{4/2}$]-pairs). However, nepheline ($NaAlSiO_4$) formation, which partially depends on the Al_2O_3 content, can severely deteriorate the chemical durability of the glass. Numerous studies have assessed the potential for devitrification in various high Al_2O_3 concentration HLW glasses and its impact on durability (e.g., Spilman et al. 1986; Kim et al. 1995; Li et al. 1997; Riley et al. 2011; Fox et al. 2007; Matlack et al. 2008). These studies generally agree that the impact of devitrification on durability depends on the type and extent of crystallization.

The combination of high Al_2O_3 and high Na_2O concentrations, coupled with lower SiO_2 concentrations as waste loadings increase, can lead to the formation of nepheline. Li et al. (1997) indicated that sodium alumino-borosilicate glasses are prone to nepheline crystallization if their compositions projected on the Na_2O-Al_2O_3-SiO_2 ternary are within or near the nepheline primary phase field in the Na_2O-Al_2O_3-SiO_2 phase diagram.

A nepheline discriminator (Li et al. 1997) was shown to limit the risk of nepheline formation in waste glasses at the Defense Waste Processing Facility (DWPF) (Fox et al. 2007) and is the basis used in the current WTP HLW glass formulation algorithm (Vienna and Kim 2014):

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

Where N_{Si} = normalized silica concentration
g_i = i-th component mass fraction in glass

Figure 8 compares N_{Si} to the volume percent of nepheline in WTP project glasses after being heat-treated to simulate the canister centerline cooling (CCC) profile. This plot shows that the nepheline discriminator is conservative for these glasses. 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.

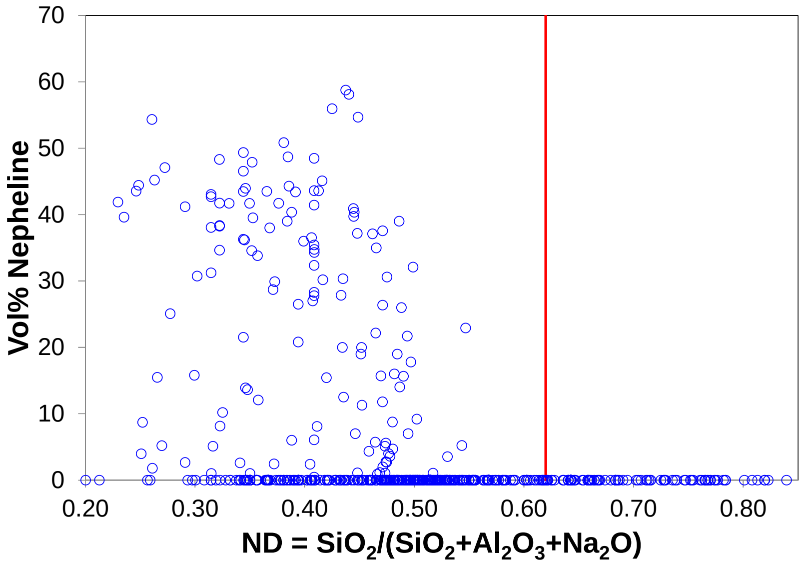

Figure 8. Nepheline Volume Percent after CCC Heat Treatment vs. Nepheline Discriminator for WTP HLW Glasses (Vienna and Kim 2014)

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 AWG program and WTP operations. Several forms of composition constraints will 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 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. To fill in this compositional subregion, a test matrix (or series of matrices or one/multi-component change-at-a-time designed studies) will be developed (conceptually shown in Figure 5).

PNNL has developed and is currently fabricating and characterizing an initial series of HLW glasses focused on increasing the Al_2O_3 concentration in HLW glass. This initial series of glasses is based on both a statistically designed set of glasses as well as supplemental studies involving one-at-a-time, two-at-a-time, and three-at-a-time component changes. Given the focus on Al_2O_3, all of the test glasses have targeted Al_2O_3 concentrations between 15 and approximately 35 wt% Al_2O_3. Preliminary results suggest that glasses with up to 31 wt% Al_2O_3 can be fabricated without forming nepheline on slow cooling.[4] While this result is promising, the technical challenges of avoiding nepheline formation, its potential impact on waste-form-affecting properties, and the ability to clearly isolate or segregate those glasses that do and do not form nepheline in a multi-dimensional compositional region is complex and is still being evaluated. The challenge appears to be the development of a model or series of compositional constraints that can differentiate the multi-component glasses that will and will not form nepheline on slow cooling. This concept is reflected in the plan (Figure 7) as updating specific models after data from specific EGCRs are obtained, leading to development of advanced glass formulation algorithms. Although not summarized here, the Vitreous State Laboratory (VSL) at CUA is also working on advanced high Al_2O_3 glasses (Kot et al. (2013), Kot et al. (2014a), Kot et al. (2014b)).

5.1.2 High Cr_2O_3 Glasses

A preliminary study on increasing Cr_2O_3 concentrations in HLW glass was recently completed by VSL (Matlack et al. 2014). The study focused on developing glass formulations for a blended HLW stream from tanks SY-101 and SY-102, which has high concentrations of Cr_2O_3 (4 wt%) and Al_2O_3 (44 wt%) coupled with a relatively high concentration of Na_2O (24 wt%). A series of glasses were developed, fabricated at the crucible scale, and characterized to determine the optimum concentrations of CaO, Li_2O, and K_2O, together with B_2O_3 and Na_2O, to manage crystallization of spinel and nepheline-like phases while maintaining acceptable product quality and processability. After reviewing all of the crucible scale data, VSL selected a 45% waste-loaded glass (referred to as HLW-HCr-16) that targets 1.82 wt% Cr_2O_3 and 19.82 wt% Al_2O_3 to process through a scaled melter. Measured physical property results of the HLW-HCr-16 crucible-scale glass indicated that the glass would be processable in the

[4] J Kroll, *EWG – Nepheline Glasses*, presentation to B Hamel and A Kruger, DOE-ORP, April 7, 2015 (unpublished work).

DM-100 melter and would produce a durable product. The 1.82 wt% Cr_2O_3 target in glass is well above the current 0.5 wt% Cr_2O_3 WTP contractual limit.

Both VSL and PNNL (using the Research-Scale Melter (RSM)) demonstrated that this high Cr_2O_3 glass could be processed in pilot-scale melters. At VSL, characterization of the resulting melter glass confirmed crucible-scale test results demonstrating an acceptable glass product targeting 45% waste loading (1.82 wt% Cr_2O_3) could be achieved, which is more than triple the waste loading corresponding to the current WTP contract minimum for this Cr-limited waste. The melter test also demonstrated that processing rates can be increased by nearly 100% over the current WTP HLW baseline requirement using advanced formulations in combination with optimization of melt pool bubbling. While this single composition was successfully processed through scaled melters, more data and melter testing are needed within the high Cr EGCR to support model development and facility operations for the full range of Hanford Site high Cr_2O_3 wastes.

5.2 Crystal Tolerant Glasses

The major factor limiting waste loading for many waste compositions in glass melters is the settling of crystalline materials. The most common crystalline phases that can accumulate in continuous melters vitrifying high-level radioactive wastes are spinel, RuO_2, and their combination. The formation of crystals within the melter may impede processing or could potentially lead to melter failure. A review of the WTP HLW melter design and operating strategy identified crystal accumulation in the pour-spout riser as the most likely failure mode due to crystallization. However, it is not currently known how much of each type of crystal can be tolerated in a melter without causing processing problems or limiting the melter lifetime. A conservative limit on crystallinity was adopted by the DWPF that specifies the spinel liquidus temperature must be less than 1050°C to avoid crystals (noble metals and their oxides excluded) in the melter (Edwards et al. 2006). This conservative approach has been confirmed by recent sampling after an extended period of melter idling (Fox et al. 2014). The WTP has constrained the glass composition to produce less than 1 vol% of spinel crystals at 950°C ($T_{1\%}$) (Vienna and Kim 2014).

Recent HLW AWG studies have targeted the development of glasses with higher crystal content (>1 vol% at 950°C), and some of these glasses have been successfully processed in scaled melters (Matlack et al. 2009a; Matyas et al. 2010). For example, a series of glasses was formulated by VSL that exhibited crystallization of spinel, chromium oxide (eskolaite), or a mixture of spinel and chromium oxide phases over a range of relatively high crystal contents from 1.6 – 4.2 vol% at 950°C (Matlack et al. 2009a). These five glass compositions were successfully processed through the DM100 and characterization of the resulting glasses demonstrated acceptable product quality. Successful processing of these glasses provides the initial basis from which one could transition from a 1 vol% to 2 vol% at 950°C processing limit and with each successive set of experimental results the risks associated with changing this constraint grow diminishingly small or insignificant. To support this effort, the AWG program will continue to evaluate the technical basis for controlling crystal settling and accumulation during melter processing prior to replacing the current 1 vol% at 950°C WTP constraint. To allow for increased HLW loading, an improved understanding of the composition effects on spinel formation, settling, and accumulation is required.

Matyas et al. (2013) provided details on an empirical modeling approach that is intended to predict the crystal accumulation rate in the WTP glass discharge riser and melter bottom as a function of glass composition, time, and temperature. When coupled with an associated operating limit (e.g., the maximum tolerable thickness of an accumulated layer of crystals), this model could then be integrated into the process control algorithms to formulate crystal-tolerant HLW glasses targeting high waste loadings while still meeting process-related limits and melter lifetime expectancies. The model is expressed as:

$$h = \sum_{i=1}^{q} h_i g_i + t \sum_{i=1}^{q} s_i g_i$$

Where	H	=	height of spinel sludge layer (μm)
	h_i	=	i-th component coefficient (μm)
	g_i	=	i-th component mass fraction in glass
	T	=	time (h)
	s_i	=	i-th component time coefficient (μm/h)
	Q	=	number of components in the model

Currently, this model only covers the effects of a few glass components in a narrow composition region around a reference glass composition and it has not been validated with a complete EGCR study or scaled melter tests. It is not ready for implementation or as a replacement to the current WTP crystal constraint. The model is also considered too premature to support development of advanced glasses that could lead to increased waste loading for specific waste streams. Matyas et al. (2014) issued a research and development plan outlining an integrated ORP program to mature this model to the degree needed for implementation.

Laboratory testing and melter modeling have also demonstrated that crystal fraction and crystal size are far better predictors of potential melter failure caused by spinel buildup than T_L or $T_{1\%}$ constraints (Hrma et al. 2003; Hrma and Vienna 2003; Hrma 2010). Crystal size is the main factor that determines the rate of settling of individual crystals, such as those of spinel. The HLW AWG program is considering an alternative approach based on this premise. Based on the work by Hrma, the ability to predict the viscosity of the glass, crystal fraction, and particle size as functions of composition and temperature should allow one to compute the accumulation rate of spinel or other particle agglomerates.

5.3 HLW Glass Models and Algorithms

The benefits of the research described above will be realized in the WTP facilities through the development of glass models and process control algorithms based on the data generated within the EGCRs. Glass property-composition models relate the physical and chemical properties of glass (which are key to the processing and compliance of waste glasses) to glass composition. These models are used to estimate the amount of waste glass to be produced by a range of different treatment options and scenarios during system planning. These models will also guide waste treatment and blending decisions, glass-forming chemical selection, glass formulation, and waste form compliance demonstration during waste treatment.

As new composition-property data become available, glass models will be updated as needed (refer to Figure 7). One of the first integration steps is to ensure that the WTP models developed (Piepel et al. 2008) to support WTP commissioning are still applicable to current or future commissioning strategies. More specifically, the current WTP commissioning models were developed to formulate compositions and qualify HLW glasses assuming specific tanks were used. Since some of those tanks may not be available for commissioning, the HLW AWG program will work with the contractors to ensure that the existing models are valid for any planned changes. If not, new models will need to be developed or waste loadings will need to be reduced over current contractual agreements. If the commissioning models are updated or revised, the preliminary HLW glass formulation algorithm (Vienna and Kim 2014) will also need to be updated with new HLW glass property-composition models and constraints.

The HLW AWG program is currently focused on post-commissioning facility operations. That is, given that the current WTP models only cover a limited compositional region, the data generated from the phased subregion approach will need to be developed, vetted, and implemented (converted into the algorithm platform) to support post-commissioning facility operations. In fact, this research and development plan (Figure 7) reflects the implementation of DFHLW (limited or no pretreatment of wastes) after commissioning. If DFHLW becomes a reality; data, models, and glass algorithms to support its implementation will be needed.

5.4 Flowsheet Integration

Successful deployment of post-commissioning models and related glass algorithms will hinge on a critical interface with the tank farm operating 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 compositional envelope of the feed vectors coming to the HLW vitrification facility. The impact of potential retrieval and blending strategies on various feed vector 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 facility mission life. These types of key inputs are represented in the plan as a decision point (albeit likely a series of decision points) labeled “Update Feed Vectors.” Ensuring the HLW AWG program is aligned with tank farm and/or pretreatment operational strategies is paramount for successful post-commissioning facility operations.

In addition to the DFHLW flowsheet, the research and development plan (Figure 7) also shows the subsequent implementation of the full pretreatment flowsheet. With the potential for the advanced glass formulation work to change the requirements for waste leaching and washing unit operations, integration between the HLW AWG program and key Hanford contractors is critical to ensure glass formulation efforts have the latest feed vector information that could influence compositional subregions.

Although the plan shows a series of HLW AWG programmatic activities to support both the DFHLW and pretreatment flowsheets, continuous improvement of glass formulations, model development, and glass algorithms will be required to support subsequent operations. As the mission progresses toward completion, glass formulation activities should be highly integrated with flowsheet development efforts to ensure downstream operations can be supported by the best available formulations, models, and algorithms aimed at increasing waste loading.

5.5 Scaled Melter Tests

The task of benchmarking a small scale radioactive melter to larger scale melter testing is aimed at reducing operational risk to ensure effective glass processing can be demonstrated in scaled melters—not just produced in the laboratory. Numerous melter campaigns have been performed at VSL (using the DM-series of melters) and PNNL (using the RSM and Laboratory-Scale Melter) to demonstrate the feasibility of processing certain waste streams, obtaining off-gas information such as split factors for halides or simulants of various radionuclides, and obtaining production rate information using various bubbling conditions. These scaled melter tests provide critical information to assess potential recycle streams that must be managed, provide production rate information that feeds mission planning efforts, and identify potential processing issues with specific waste streams.

Although critical to supporting mission-essential data, the larger-scaled melter tests are time consuming and expensive as they require significant volumes of simulated feed to be produced, significant resources to conduct the tests, and a large volume of sampling, analysis, data reduction, and waste disposal. An objective of the HLW AWG program is to develop and benchmark a continuously fed, small-scale radioactive melter to the larger-scale systems. PNNL is currently scoped with implementation of the Radioactive Laboratory Scaled Melter (RLSM) in the Radiological Processing Laboratory (RPL) to support Tc retention studies for LAW vitrification.[5] A separate plan is being developed for the Tc retention program but in general this scope is focused on developing a fundamental, science-based understanding of the factors (both chemical and physical) that affect Tc retention or volatilization. The RLSM will also provide information on cold cap behavior and melting rates not only for LAW but for HLW as well.[6]

The small radioactive melter will be used to support future operations and evaluations of potential flowsheet changes prior to making implementation decisions, minimizing cost to DOE. This system will provide an additional platform for determining off-gas split factors, identifying potential processing issues (e.g., foaming, feed rheology and cold cap behavior, etc.), and providing feedback on production rates for various waste streams using actual wastes.

6.0 Summary

ORP has implemented an integrated program to expand the Hanford Site LAW and HLW glass databases and property-composition models to cover the balance of the Hanford Site tank waste treatment and immobilization mission. The primary effort to expand the glass compositional region over which acceptable glasses can be fabricated and processed through the WTP is supported by crucible-scale tests with simulants, crucible-scale tests with actual waste, and scaled melter tests with simulants.

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.

[5] The RPL is permitted to receive Hanford tank farm wastes.

[6] Implementing a RLSM in RPL's Shielded Analytical Laboratory (SAL) would be integrated with a platform or test bed for the evaluation and demonstration of technologies to support HLW tank waste operations and processing as well as gain critical insight into WTP facility operations. The integrated platform would be a modular unit consisting of unit operations to support filtration, oxidative leaching, caustic leaching, ion exchange, and melt behavior studies. The integrated platform could also be used to support waste qualification efforts.

4. Demonstrate effective glass processing in scaled melter tests for glass compositions across the full WTP compositional envelope.

A glass research and development plan has been developed that presents a comprehensive, integrated assessment of these key technology-related activities needed to complete the tank waste cleanup mission. The core HLW AWG activities are central to the research and development plan and serve as the technical basis for commissioning and subsequent facility operations, including decisions regarding DFHLW, pretreatment, waste qualification, and support facility operations. The cornerstone of the HLW AWG program is the development and validation of advanced HLW glasses and their associated models to support facility operations at WTP under both DFHLW and pretreatment feed flowsheets. These models are required for three primary purposes:

1. To support vitrification plant operations to ensure processable batches and acceptable glass compositions are produced.
2. To support waste feed prequalification to evaluate melter feed properties, drive decisions on pretreatment operations, and evaluate vitrification process effectiveness.
3. To support RPP mission planning, including optimization of the mission from a waste feed delivery strategy, waste pretreatment requirements, and mission life/cost estimation.

This plan is motivated by the potential for continued advancements in glass formulation that will lead to substantial economic benefits (e.g., significant reductions in glass volumes and canister counts) associated with the WTP mission. 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 may 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, reduced leaching/washing requirements, and improved melting rates provides a system-wide approach to improve the effectiveness of the WTP process.

For perspective, the advancements and successes of the integrated ORP AWG program have been recognized by the Secretary of Energy's Advisory Board (SEAB). In a 2014 report on technology development for Environmental Management it was stated (SEAB 2014):

> "Successful past examples of the sorts of technology development of the character that should be pursued include: the improvement of glass waste loading and the ability to accept a wider range of waste constituents… A presentation to us by the National Laboratory Directors' Council (NLDC) shows that past advances in these areas have achieved a disproportionate return on

investment. We agree with their assertion that significant gains can be achieved by a program that is focused on advancing novel ideas."

In addition, an external and independent review of the ORP AWG program stated (LaCourse 2014):[7]

"The extensive work carried out under DOE-ORP funding covered a wide range of topics, but was well-focused on those aspects of melting and properties that are critical to success of the waste vitrification process. The goals/ objectives relative to production increases and enhanced compositions have generally been reached or exceeded. Importantly, the reports indicate that the researchers and administrators recognize that there is much left to do regarding the newer compositions and changes to the melt process. My review of more recent literature published by DOE indicates that much of the required work is already in progress.

As an educator it is of further interest that results of both past and projected studies may prove valuable in general glass science and education and, in specific areas, the glass industry as a whole. The DOE sponsored work on chemical durability has already impacted the field, and there is reason to believe that advances in our understanding of melt redox, viscosity (non-Newtonian), electrical conductivity and thermal conductivity will be spurred by this work. Efforts should be made to assure that results/data are easily accessible by academic and industrial researchers."

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[7] The external and independent review was led by Dr. W.C. LaCourse, Kruson Distinguished Professor of Glass Science, New York State College of Ceramics, Alfred University.

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