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Office of River Protection Advanced Low-Activity Waste Glass Research and Development Plan

November 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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Executive Summary

The U.S. Department of Energy Office of River Protection (ORP) has initiated and leads an integrated Advanced Waste Glass (AWG) 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 Hanford Tank Waste Treatment and Immobilization Plant (WTP) facilities in the context of an optimized River Protection Project (RPP) flowsheet. The fundamental data stemming from this program will support development of advanced glass formulations, key product performance and process control models, and tactical processing strategies to ensure safe and successful operations for both the low-activity waste (LAW) and high-level waste vitrification facilities. These activities will be conducted with the objective of improving the overall RPP mission by enhancing flexibility and reducing cost and schedule.

The purpose of this advanced LAW glass research and development plan is to identify the near-term, mid-term, and longer-term research and development activities required to develop and validate advanced LAW glasses, property-composition models and their uncertainties, and an advanced glass algorithm to support WTP facility operations, including both Direct Feed LAW and full pretreatment flowsheets. Data are needed to develop, validate, and implement 1) new glass property-composition models and 2) a new glass formulation algorithm. Hence, this plan integrates specific studies associated with increasing the Na_2O and SO_3/halide concentrations in glass, because these components will ultimately dictate waste loadings for LAW vitrification. Of equal importance is the development of an efficient and economic strategy for ^{99}Tc management. Specific and detailed studies are being implemented to understand the fate of Tc throughout the WTP flowsheet and the underlying mechanisms that dictate its partitioning between streams within the LAW vitrification facility. These studies are aimed at increasing the single-pass Tc retention in glass and the potential use of high-temperature mineral phases to capture Tc. The Tc-bearing mineral phases would be thermally stable and resistant to Tc release during feed melting reactions or they could serve as alternative waste forms. The LAW glass research and development is focused on reducing the total volume of LAW glass produced and minimizing the impact of (or potentially eliminating) the need for recycle.

Other key activities of the plan include integration of technical support to facility operations and waste qualification activities during both the commissioning process and radioactive operations. This plan discusses the interdependence of these activities with the ORP AWG program to support the full WTP mission. Figure ES.1 shows these key ORP programmatic activities and their interfaces with 1) tank farm operations; 2) WTP facility design, construction, and operations; and 3) waste qualification needs. This plan is a living document that will be updated to reflect key advancements and mission strategy changes as needed.

The research outlined in this report is motivated by the potential for substantial economic benefit (e.g., significant reduction in glass volume) that will be realized when advancements in LAW glass formulation, model development, and efficient ^{99}Tc management strategies are implemented.

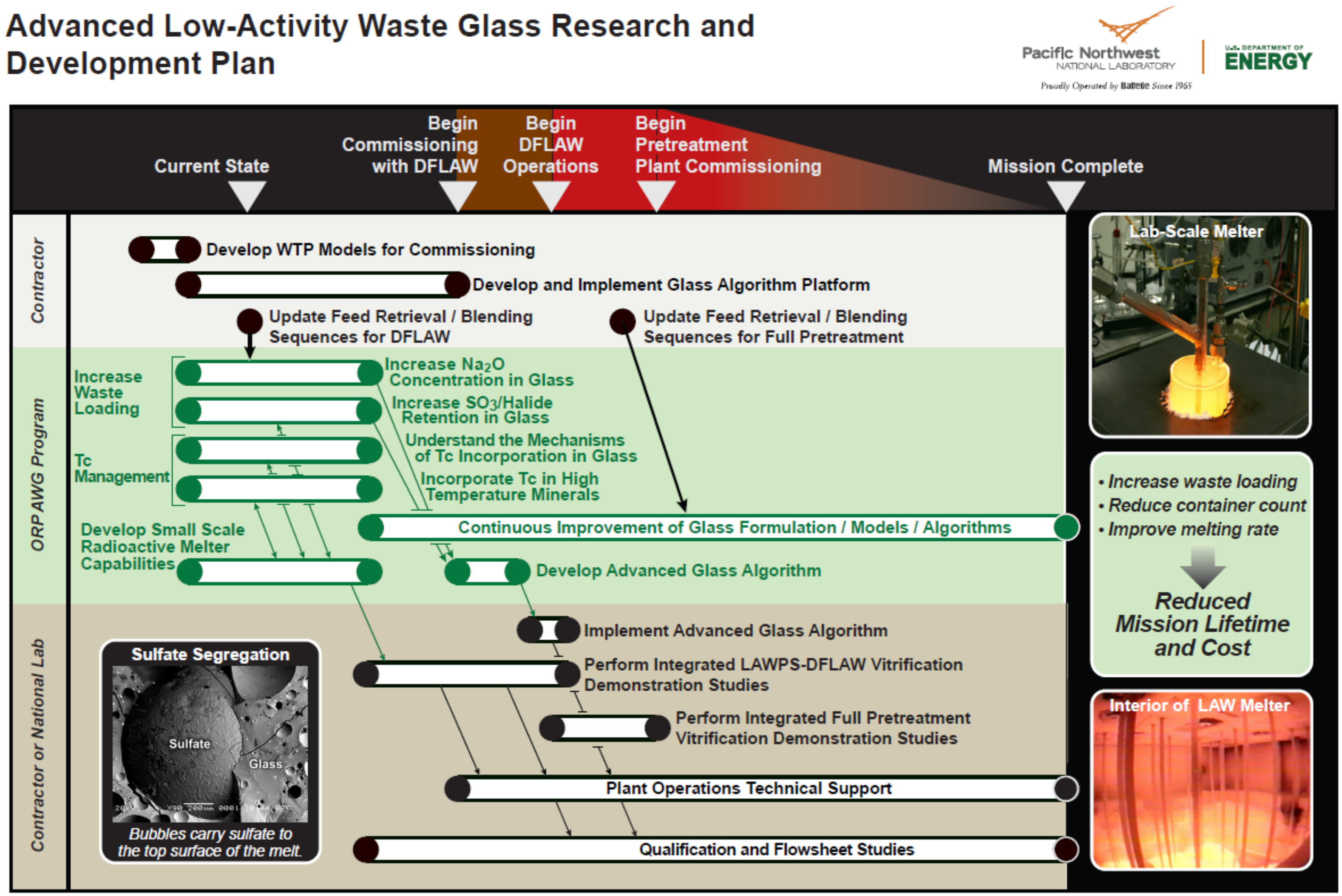

Figure ES.1. Advanced Low-Activity Waste Glass Research and Development Plan to Support the WTP Mission

Acknowledgments

The authors gratefully acknowledge the financial support of the U.S. Department of Energy, Office of River Protection, Waste Treatment and Immobilization Plant Federal Project under the direction of Albert Kruger. The authors thank Albert Kruger, Renee Russell, Dawn Wellman, Brad Johnson, Wooyong Um, and Tongan Jin for their thorough reviews, constructive feedback, and in-depth discussions associated with the development of this plan. The authors are also grateful for the significant contributions of relevant work performed and reported by the Vitreous State Laboratory of the Catholic University of America under the direction of Professor Ian Pegg. The graphics contributions from Ted Tanasse and technical editing by Matt Wilburn are greatly appreciated.

Acronyms and Abbreviations

AWG	Advanced Waste Glass
BNI	Bechtel National, Inc.
CFF	cross flow filtration
CRV	concentrate receipt vessel
CUA	The Catholic University of America
DFLAW	Direct Feed Low-Activity Waste
DOE	U.S. Department of Energy
DST	double-shell tank
EGCR	experimental glass composition region
EMF	Effluent Management Facility
ETF	Effluent Treatment Facility
EWG	Enhanced Waste Glass
HASQARD	Hanford Analytical Services Quality Assurance Requirements Document
HLW	high-level waste
IDF	Integrated Disposal Facility
ILAW	immobilized low-activity waste
IX	ion exchange
LAW	low-activity waste
LAWPS	Low-Activity Waste Pretreatment System
LERF	Liquid Effluent Retention Facility
LSM	laboratory-scale melter
MCC	multiple component constraint
MFPV	melter feed preparation vessel
MFV	melter feed vessel
MOF	metal organic framework
ORP	Office of River Protection
PAF	porous aromatic framework
PCT	Product Consistency Test
PNNL	Pacific Northwest National Laboratory
RLSM	radioactive laboratory-scale melter
RPL	Radiochemical Processing Laboratory
RPP	River Protection Project
SBS	submerged bed scrubber
SCC	single component constraint
SEAB	Secretary of Energy Advisory Board
SLAW	Supplemental Low-Activity Waste
SRNL	Savannah River National Laboratory
SwRI	Southwest Research Institute
VHT	Vapor Hydration Test

VSL	Vitreous State Laboratory
WESP	wet electrostatic precipitator
WRPS	Washington River Protection Solutions
WTP	Hanford Tank Waste Treatment and Immobilization Plant
WWFTP	WRPS Waste Form Testing Program

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1.0 Introduction

The federal facilities located on the Hanford Site, in southeastern Washington State, have been used extensively by the U.S. government to produce nuclear materials for the U.S. strategic defense arsenal. Currently, the Hanford Site is under the stewardship of the U.S. Department of Energy (DOE) Office of Environmental Management. A large inventory of radioactive mixed waste resulting from the production of nuclear materials has accumulated, including high-level mixed waste stored in 177 underground single- and double-shell tanks (DSTs) located in the Central Plateau of the Hanford Site.[a] 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 borosilicate glass products (DOE 2000).

To support this effort, the DOE Office of River Protection (ORP) has assembled a cadre of technical expertise regarding vitrification technologies for the WTP from an international collaborative team composed of Pacific Northwest National Laboratory (PNNL), The Catholic University of America (CUA), Savannah River National Laboratory (SRNL), Idaho National Laboratory, Washington State University, Rutgers University, Tokyo Institute of Technology, the University of Sheffield, the Department of Chemistry at the University of Ottawa, 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, and halogen retention in glass
- nepheline formation in glass
- crystal-tolerant glass formulations
- melting rate enhancements.

This integrated ORP Advanced Waste Glass (AWG) program is focused on providing a technical, science-based foundation for making key decisions regarding the successful operation of River Protection Project (RPP) mission facilities, including the waste qualification process. The fundamental data stemming from the ORP program will support development of advanced glass formulations, key product performance and process control models, and tactical processing strategies to ensure safe and successful operations for the LAW and HLW vitrification facilities. The focus of these activities will be on improving the overall RPP mission, namely providing maximum operational flexibility and reducing cost.

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[a] High-level mixed waste consists of both radioactive and hazardous waste components regulated under the Resource Conservation and Recovery Act. See http://www3.epa.gov/epawaste/hazard/wastetypes/mixed.htm. It should also be noted that retrieval of waste from 10 of the 177 tanks has been declared complete and retrieval of waste from an additional 4 tanks was nearing completion at the time this document was issued.

The purpose of this advanced LAW glass research and development plan is to identify the near-term, mid-term, and longer-term research and development activities required to support RPP mission planning and facility operations, including both Direct Feed LAW (DFLAW) and full pretreatment flowsheets. This plan discusses specific studies aimed at increasing Na_2O and SO_3/halide concentrations in glass, because these components will ultimately dictate waste loadings for LAW vitrification. The ability to increase the waste loading will reduce the overall ILAW glass volume produced and thereby increase waste throughput.

Of equal importance is the management of ^{99}Tc, which has low (roughly 20% to 70%) single-pass retention in glass during LAW vitrification (Matlack et al. 2011). 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.

This plan discusses the interdependence of these research activities within the ORP AWG program as they relate to critical process operations and qualification needs to support the full RPP mission. The research outlined in this plan is motivated by the potential for substantial economic benefit that will be realized from implementing advancements in 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 (Peeler et al. 2015, *Advanced High-Level Waste Glass Research and Development Plan*; Matyas et al. 2014, *Road Map for Development of Crystal-Tolerant High Level Waste Glasses*) or are being developed (i.e., cold cap behavior and melt dynamics) in parallel with this effort.

2.0 Current Technology Status

Section 2.1 discusses the current LAW glass models and associated waste loading constraints. Section 2.2 discusses the issue of ^{99}Tc management and the impact of recycle on both the DFLAW and full pretreatment flowsheets.

2.1 LAW Glass Models and Waste Loading Constraints

The WTP has developed glass property-composition models to formulate compositions and qualify LAW glasses for disposal (Piepel et al. 2007). The glass property-composition models are used to predict various process (such as viscosity, electrical conductivity, and sulfate solubility) and product performance (durability) properties and are critical to support facility operations and waste form qualification efforts. The glass property-composition 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). The LAW data and models developed by BNI are based on glasses that target modest waste loadings for commissioning rather than focusing on maximum achievable waste loadings.

With respect to post-commissioning operations, the compositional region of interest for LAW vitrification is less complicated than the multiple HLW compositional regions because LAW is dominated by sodium salts with smaller (but influential) concentrations of sulfur, phosphate, halide, and potassium. As a result, the loading of LAW in glass has been found to be limited by two factors (Muller et al. 2004; Kim and Vienna 2012; Vienna et al. 2013; Muller et al. 2010):

- alkali content of the glass (primarily Na_2O, but also K_2O in some wastes), which if too high causes poor chemical durability in general and more specifically fails the current WTP contract constraints for the Product Consistency Test (PCT) and the Vapor Hydration Test (VHT) responses (DOE 2000)
- salt formation in the melter that is promoted by excessive SO_3 concentration and to lesser extents Cr_2O_3, Cl, F, and P_2O_5.

To support facility operations, Muller et al. (2004) have refined a LAW glass formulation approach (referred to as the glass formulation correlation). This approach uses the Na^+:SO_4^{-2} ratio of the waste to interpolate between reference glasses (Muller et al. 2004; Kim and Vienna 2012; Matlack et al. 2006a), all of which met both process and product performance acceptance criteria and were processed successfully up to pilot scale.

Kim and Vienna (2012) provide a set of waste loading constraints that are used to determine the target waste loading for LAW glasses. As an example, consider Figure 1, which is used to determine the acceptable concentration of Na_2O in the glass using the "Na_2O-SO_3-K_2O rules" as defined by Muller et al. (2004).[b] The maximum Na_2O content in the glass must be at or below 21 wt% or the Na_2O plus 0.66 times the K_2O concentration must be at or below 21.5 wt% in glass—both constraints due primarily to the data availability in the high-alkali region of waste compositions (e.g., high Na^+:SO_4^{2-} ratio). The rules indicate that the SO_3 concentration in glass must be at or below 0.77 wt% to avoid the formation or accumulation of a salt layer on the surface of the melt pool. In addition, the "Na_2O-SO_3-K_2O rules" state that the Na_2O concentration must be at or below the value of 35.875 wt% minus 42.5 times the SO_3 wt% in glass. This set of rules essentially establishes upper limits on both Na_2O and SO_3 for the final glass product, which, as previously mentioned, for most feed vectors dictates the maximum waste loading for ILAW glass.[b] The current glass formulation algorithm (Kim and Vienna 2012) uses the chemical compositions of waste and individual additives and the melter process parameters as input data, all with associated uncertainties, and calculates the volume of waste to be transferred from the waste receipt vessel to the melter feed preparation vessel (MFPV), the volume of process water to be added, the mass of each additive for addition to the MFPV, the composition of resulting glass, and the predicted properties, all with associated uncertainties. The glass property-composition models (Piepel et al. 2007) are used to confirm that the resulting glass to be produced will satisfy all the process and performance requirements after accounting for the uncertainties and to generate the production records. The additive masses are determined using glass-formulation rules (Muller et al. 2004) described above.

[b] It should be noted that other rules are in place with respect to Cl-F-SO_3 as well as Cr_2O_3-K_2O-P_2O_5. When considered holistically, these rules ultimately determine the maximum concentrations of key components that limit waste loading. Please refer to Kim and Vienna 2012 for more details.

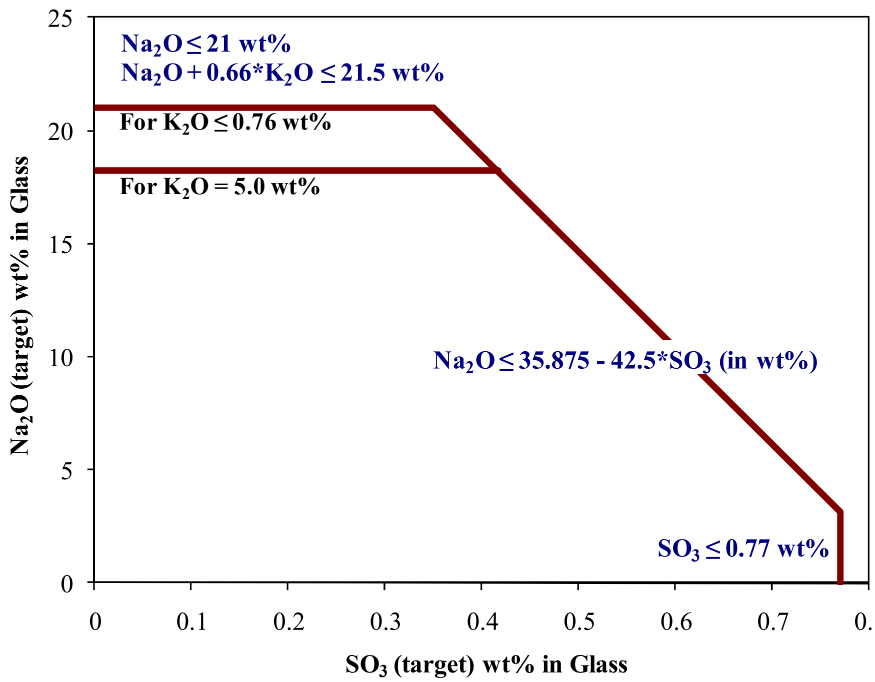

Figure 1. Schematic of Current WTP Glass Formulation Rules for Na_2O-SO_3 with Bounding K_2O Concentrations. Two horizontal lines represent Na_2O upper limits for expected K_2O concentration extremes.

More recent formulation activities have expanded the compositional envelope over which LAW glasses can be processed, leading to enhancements in both alkali and sulfur loading. These relatively new advanced formulations with high waste loadings have been developed by CUA and PNNL in support of ORP (Matlack et al. 2005a, 2005b, 2006b, 2006c, 2007, 2009; Muller et al. 2010; Vienna et al. 2004; Kim et al. 2011). Muller et al. (2012) and Vienna et al. (2013) have summarized these data. The basic conclusions of these studies are that loadings for low-activity wastes in glass can be increased significantly over what would be allowed by current WTP LAW constraints (e.g., application of the rules as shown in Figure 1). Examples of the gains made in recent studies include the following:

- LAW sulfur loadings of 1.5 wt% (as SO_3) were successfully processed in small-scale melters (see Matlack et al. 2006c, 2007, 2009), which is roughly double the 0.77 wt% allowed by the current WTP LAW composition region (Kim and Vienna 2012).
- LAW soda loadings of 24 wt% have been achieved (Muller et al. 2010; Vienna et al. 2013) compared to the 21 wt% maximum in the current WTP LAW composition region (Kim and Vienna 2012).

Though glass formulations, composition constraints, and property-composition models are available to support commissioning, there are significant cost savings and process flexibility gains to be realized through optimization of the waste loading in LAW glass formulations based on advanced formulation rules and constraints. As a result of the ORP AWG testing program, a new (but still preliminary) set of LAW glass formulation rules have been developed (Vienna et al. 2013). For example, Figure 2 compares the results of the advanced LAW glasses with the commissioning glasses on the alkali-SO_3 wt% concentration plot (similar to Figure 1). The ability to target Na_2O or SO_3 concentrations up to ~24% and 1.5%, respectively, will significantly influence waste loading targets for facility operations and ultimately glass volumes produced relative to the current commissioning (or baseline) glass formulation algorithm.

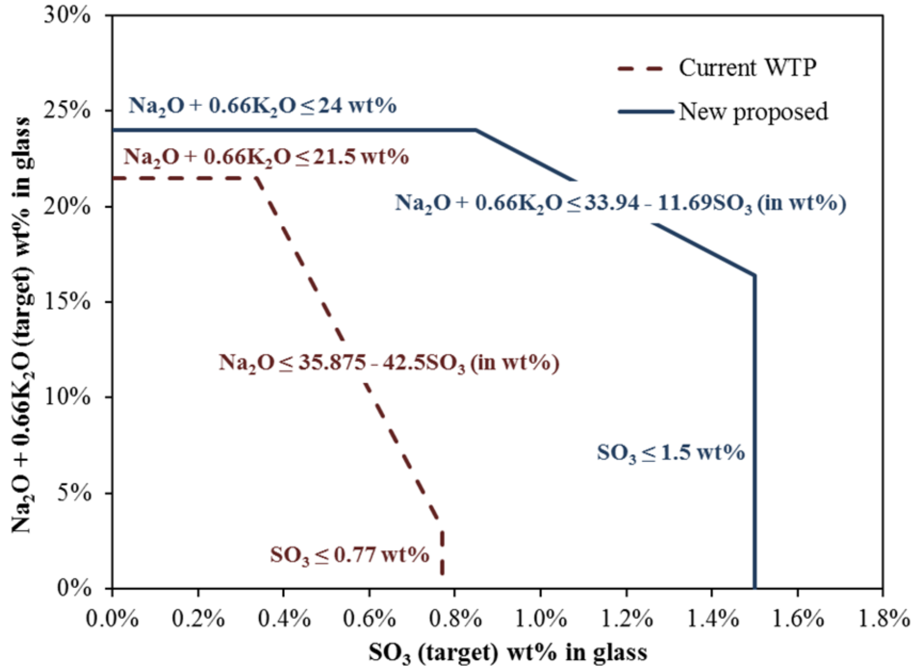

Figure 2. Comparison of Alkali and SO_3 Loadings of Advanced Formulations and Formulations Based on the WTP Baseline Glass Formulation Rules (Kim 2013)

2.2 Tc Management

^{99}Tc is a long-lived radionuclide and is a significant fission product from nuclear reactors. Over 50 years of nuclear materials production at Hanford, approximately 29,700 Ci (DOE 2012) have been accumulated. The primary chemical form of ^{99}Tc found in Hanford tank waste is the pertechnetate anion (TcO^{4-}), with a +7 oxidation state, although a significant (2% to 25%) fraction of the ^{99}Tc may be present as soluble non-pertechnetate species such as Tc(I) carbonyl compounds (Rapko 2014). In the WTP baseline flowsheet, ^{99}Tc will not be removed from the aqueous waste during pretreatment. The soluble ^{99}Tc is expected to partition to the LAW stream and a smaller, insoluble fraction of the Tc is expected to partition to the HLW stream. Previous studies (Mann et al. 2001, 2003; DOE 2012) have shown that, due to its long half-life and high mobility, ^{99}Tc is a major dose contributor to the Integrated Disposal Facility (IDF) performance assessment.

Technetium is also one of the more volatile radionuclides whose retention in LAW glass under the high temperature conditions during vitrification can vary depending on feed composition, Tc chemistry, and melter operating parameters. Based on the current LAW full pretreatment flowsheet (Figure 3 provides a high-level schematic), the fraction of Tc that volatilizes from the glass melter is captured in the off-gas treatment system. The off-gas condensates containing most of the captured Tc are recycled back to the WTP pretreatment facility, where they are combined with fresh LAW and recycled to the LAW stream to increase the overall retention of Tc in the LAW glass. A negative impact of this off-gas recycle strategy is to disproportionately increase the sulfur and halides in the LAW and Supplemental LAW (SLAW) feed and thereby increase the volume of LAW glass produced and increase either the required SLAW capacity or the mission duration. Therefore, it clearly benefits the overall RPP flowsheet to develop technologies for implementing chemistries that enhance halide incorporation into the LAW glass melt or that can efficiently manage Tc without recycling the off-gas stream.

With respect to Tc partitioning between the LAW and HLW flowsheets, Pajunen and Leung (2002) evaluated the need for Tc separation in the WTP. For flowsheet options that do not deploy leaching and washing, a significantly larger fraction (roughly 50%) of the Tc will be sent to the HLW vitrification plant (Place 2005). Peeler et al. (2015) discuss the recent advanced HLW glass formulations, which have shown significant improvements in Cr_2O_3 and Al_2O_3 concentrations and could serve as the basis for eliminating the need for solids leaching in pretreatment.

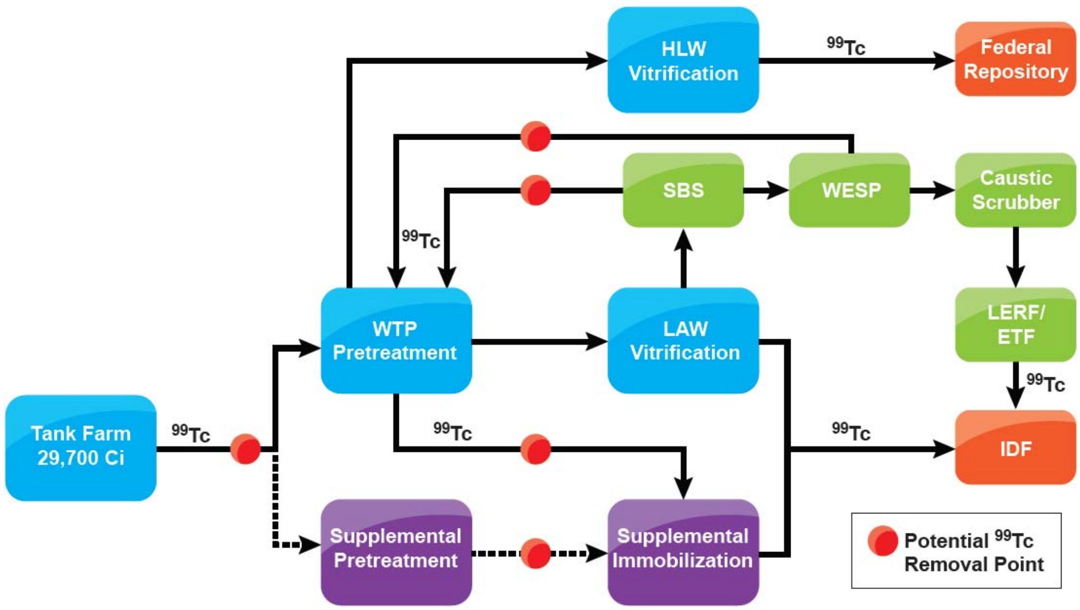

Figure 3. Schematic of Tc Partitioning within WTP Full Pretreatment Flowsheet

Prior to full pretreatment coming online, DOE is considering implementing a DFLAW flowsheet. In that flowsheet, LAW supernatant will be processed through the LAW Pretreatment System (LAWPS), where solids and Cs will be removed via filtration and ion exchange processes, respectively (see Figure 4 for a schematic). Although the flowsheet is not fully mature, current plans are to transfer the decontaminated salt solution to the LAW vitrification facility, where glass formers will be added, the waste will be vitrified and poured into containers, and the melter off-gas will be treated. The off-gas treatment will generate a liquid effluent that will be evaporated in the Effluent Management Facility (EMF), with the evaporator bottoms recycled to the LAW facility or directed back to the DST system in the tank farm. An assumed split between the concentrated recycle streams exiting EMF is 85% to LAW vitrification (directly to the concentrate receipt vessel [CRV]) and 15% back to the DSTs. Regardless of the ultimate split, the impact of the recycle on LAW vitrification disproportionately increases the sulfur and halides in the LAW feed. This is especially true if the condensate batches are accumulated and dumped into the CRV instead of metering a constant volume to blend with LAW. In this situation the volume of LAW glass produced would increase and result in the potential need for additional corrosion control strategies in the tank farms. Again, it clearly benefits the overall RPP flowsheet to develop technologies for implementing chemistries that enhance halide incorporation into the LAW glass melt or that can efficiently manage Tc without recycling the off-gas stream.

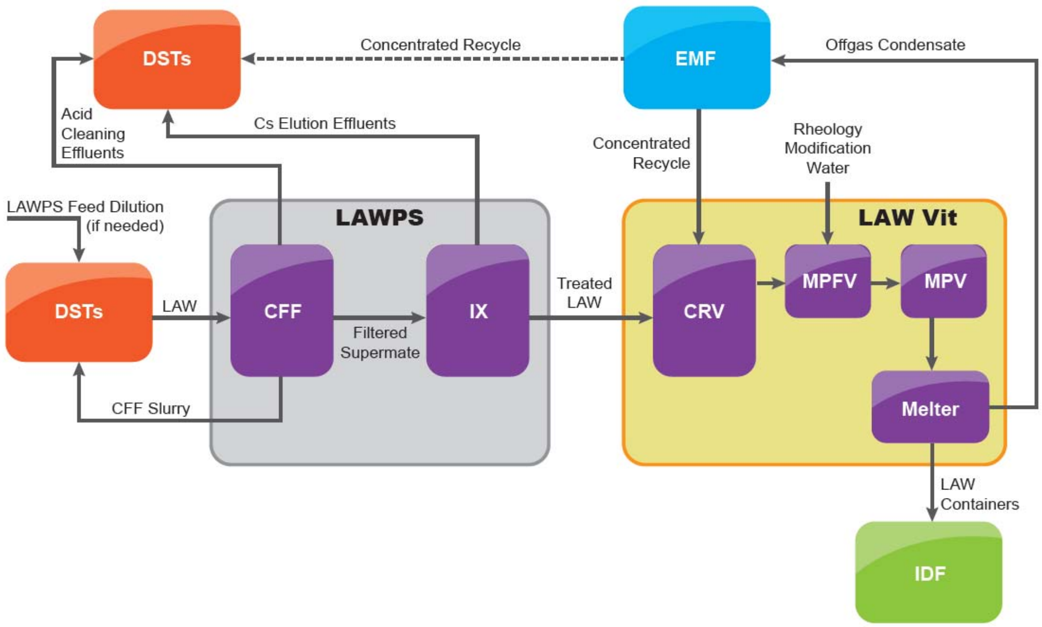

Figure 4. Schematic of the Proposed DFLAW Flowsheet

3.0 Motivation and Benefit to the River Protection Program

In simple terms, the objective of the LAW AWG program is to increase the waste loading in LAW glass, which can lead to a significant reduction in the glass volume produced from the RPP mission through 1) advanced LAW glass formulations and 2) technologies to achieve high Tc retention in glass without recycling off-gas solutions. With respect to advanced glass formulations, a primary focus is the ability to increase the concentration of key components (such as Na_2O, SO_3, halides (primarily F and Cl), and K_2O) that limit waste loading in glass while still meeting both process and product performance requirements. Developing and implementing the technologies to increase Tc retention without off-gas recycle, either by increasing single-pass retention or by separating Tc from off-gas and recycling Tc only, will be key to effective Tc management plans for various pretreatment and supplemental LAW scenarios.

Kim (2013) illustrated the potential impact by estimating the glass mass reduction that could be achieved if the waste loading enhancements indicated by more recent studies were to be realized. This will require future efforts to expand the glass property-composition models and to update the glass formulation algorithm over those currently in place to support commissioning. Kim (2013) compared the projected glass masses using the 2012 LAW WTP glass formulation algorithm (Kim and Vienna 2012) and a preliminary set of advanced glass formulation rules using both conservative and optimistic halide constraints for a given set of projected LAW feed compositions.[c]

The LAW stream that served as the basis for the Kim (2013) study contained a total of 70,580 metric tons of sodium (Na), which was partitioned between the WTP LAW vitrification facility and the SLAW

[c] Kim (2013) assumed that all of the glass property constraints were met at the waste loading determined by the glass formulation rules and halide constraints that were applied without considering compositional uncertainties.

treatment facility at approximately 37% and 67%, respectively. The results suggested that the average sodium loading in glass would increase from 11.9 wt% Na_2O to 19.7 wt% and the number of LAW glass containers would decrease by approximately 38% (from approximately 135,000 containers to approximately 82,000 containers) if the enhancements in waste loading as indicated by recent glass formulation studies and scaled melter tests could be achieved. Figure 5 compares the projected number of containers produced using the current WTP baseline constraints with the number projected if the advanced formulation rules were to be implemented (with the optimistic halide constraints). In addition, Peeler et al. (2015) discussed the recent advanced HLW glass formulations, which have shown significant improvements in Cr_2O_3 and Al_2O_3 loadings and could serve as the basis for eliminating the need for solids leaching in pretreatment. If the solids leaching is eliminated from pretreatment, the waste Na mass will decrease (estimated to be 50,580 metric tons), resulting in a significant reduction in LAW glass volume. Figure 5 also compares the projected number of containers to be produced if the solids leaching is not performed using the current WTP and advanced glass formulation rules.

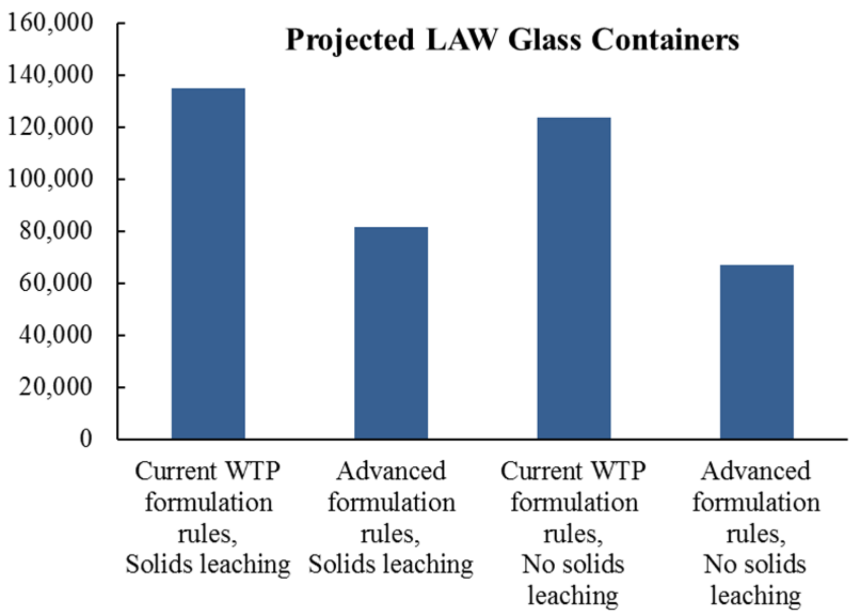

Figure 5. Comparison of Predicted LAW Glass Containers Using Current WTP Formulation Rules and Advanced Glass Formulation Rules for Solids Leaching and No Leaching Cases

4.0 Data and Research Needs

Prior to discussing specific LAW AWG program activities (current and future), it is beneficial to describe the key aspects of the program and how they are integrated and support future facility operations, including commissioning, plant operations, qualification, and flowsheet studies. There are obviously additional technical scopes that support future facility operational functions. However, this advanced LAW glass research and development plan focuses on glass formulation, model development, ^{99}Tc management, and melter testing needed to complete the tank waste cleanup mission for LAW.

Figure 6 is a schematic of the LAW AWG research and development plan. The plan is divided into four primary sections: 1) key RPP milestone activities (e.g., commissioning of WTP with DFLAW,

DFLAW operations, pretreatment plant commissioning and operations, and mission completion), 2) contractor-related activities associated with implementing the LAW glass formulation algorithm and developing/updating feed retrieval and blending strategies, 3) ORP AWG program scope (data generation, advanced glass property-composition models and glass formulation algorithm development and implementation, scaled-melter tests, and continuous improvement), and 4) contractor- or national laboratory-related activities (implementation of an advanced glass formulation algorithm, integrated flowsheet demonstrations, waste feed qualification, plant operations, and operational technical support).

The plan reflects the current status of having glass property-composition models and a glass formulation algorithm developed to support LAW vitrification facility commissioning (Kim and Vienna 2012). In addition, the plan shows the ongoing BNI activity to develop a platform for implementing the LAW glass formulation algorithm to support facility operations.

There are two cornerstones of the LAW AWG program:

1. Develop and validate advanced LAW glasses with higher waste loadings and associated glass property-composition models and uncertainty expressions to support WTP facility operations under both DFLAW and pretreatment feed flowsheets.
2. Develop a fundamental understanding of Tc retention and behavior to support strategic and economical ^{99}Tc management.

Sections 4.1 and 4.2 provide a more detailed discussion of these two cornerstone technical areas and how successful outcomes will support the transition from the current technology state to mission-complete status. However, in context of a general description of the overall plan, these two cornerstone areas will depend on crucible-scale simulant testing to systematically cover the LAW glass compositional region(s) of interest. These crucible-scale simulant tests will provide additional data from which LAW glass property-composition model updates or revisions can be made in addition to providing insight into key mechanistic factors affecting Tc retention. Small- and large-scale melter testing with simulants will also be required to demonstrate scale-up from the crucible tests. Crucible- and small-scale melter tests with actual waste will also be required to validate simulant testing with respect to key process and product performance properties. Key markers with which the LAW AWG program elements are aligned include WTP commissioning, post-commissioning operations, 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.

This 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 its focus, this plan does integrate technical support of facility operations and waste qualification activities to show how these activities are interdependent with the AWG program to support the full WTP mission.

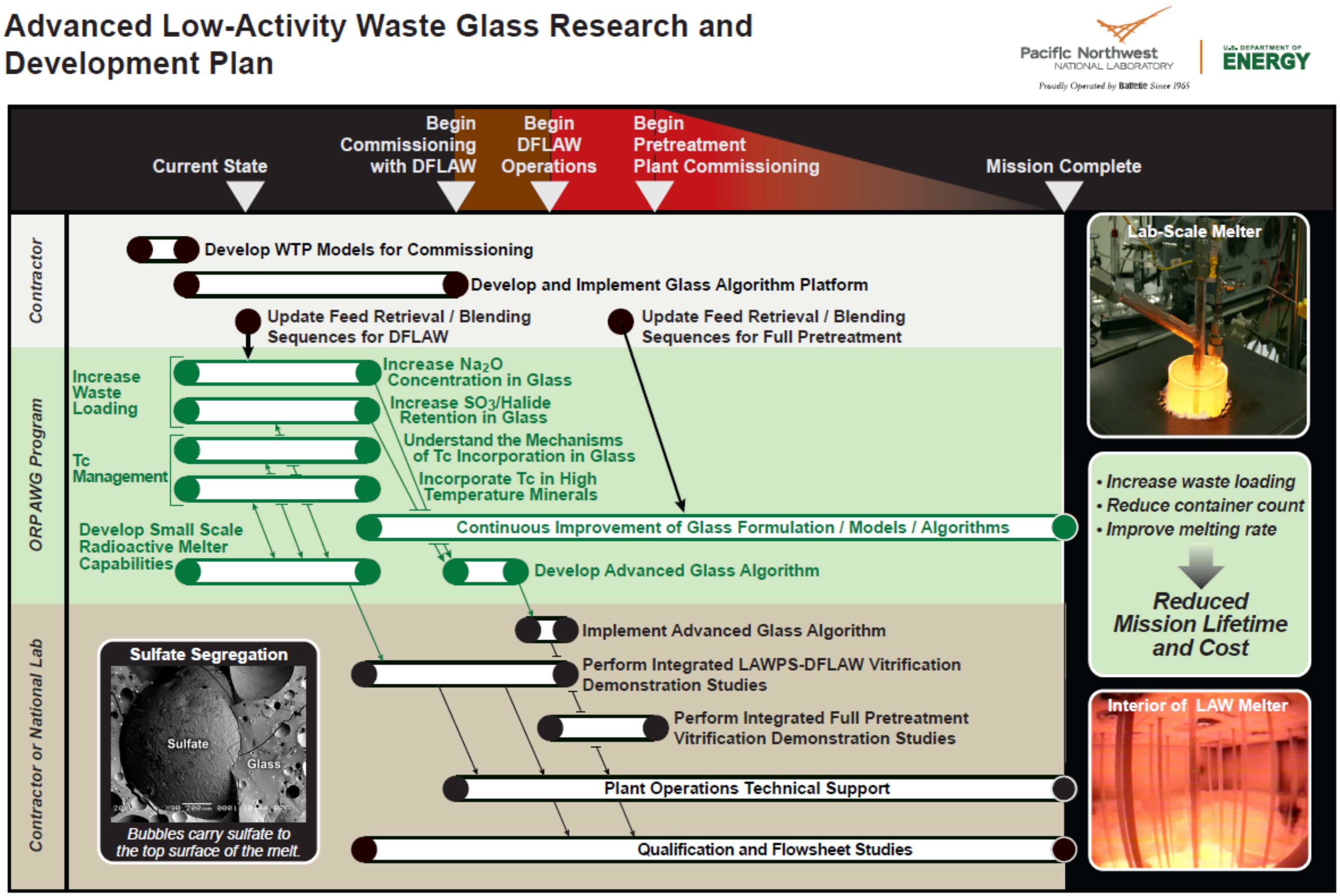

Figure 6. Advanced Low-Activity Waste Glass Research and Development Plan to Support the WTP Mission

4.1 Glass Property-Composition Data, Models, and Advanced Formulations for LAW Glasses with Higher Waste Loadings

Section 4.1.1 discusses approaches for generating LAW glass property-composition data to support fitting glass property-composition models. Section 4.1.2 discusses approaches for developing advanced LAW glass formulations with higher waste loadings.

4.1.1 Generating LAW Glass Property-Composition Data

The general approach for generating property-composition data to support developing property-composition models and uncertainty expressions is to 1) specify an experimental glass composition region (EGCR) of interest, and 2) use statistical experimental design methods and software as well as actively designed LAW glass formulations to adequately cover the EGCR with test compositions for which LAW glass properties will be measured. The first step of specifying an EGCR is to identify LAW glass components (e.g., oxides and halides) whose proportions affect one or more glass properties of interest. Then, an EGCR is specified by lower and upper bounds on single components (referred to single component constraints, SCCs) and lower and/or upper bounds on linear functions of two or more components (referred to as multiple-component constraints, MCCs). The resulting EGCR specified by the SCCs and MCCs is in general a polyhedron in q-1 dimensions, where q is the number of LAW glass components whose proportions (e.g., mass fractions) sum to one.

Two sets of glass formulation constraints are currently used in the Hanford Tank Waste Operations Simulator to estimate the amount of glass that will be produced at Hanford. These are the LAW glass formulation constraints developed for WTP (Kim and Vienna 2012) and the "ORP 2004" constraints developed based on glass formulation with initial higher-sulfate loading (Hamel et al. 2003). These glass formulation constraints were designed for glasses that were not optimized for full potential with respect to achieving higher waste loadings. However, subsequent efforts by ORP to enhance the WTP LAW vitrification system resulted in glass property data for a significant number of LAW glasses with high waste loadings. The CUA compiled the existing data on these LAW glasses and evaluated the data gaps that need to be filled (Muller et al. 2012). In addition, Vienna et al. (2013) showed two distinct composition subregions for the existing LAW dataset: 1) the current WTP region with lower waste loadings, and 2) the LAW AWG region with higher waste loadings.

Two viable options are being pursued to generate additional data to fill in compositional gaps within the higher-waste-loading subregion and to ensure data are available to bridge the gap between the two subregions. The first option is to use a single EGCR that would cover both the current WTP and the advanced ORP compositional regions. The second option is to focus on the advanced LAW EGCR without ties to the current WTP subregion with lower waste loadings. Currently, the PNNL LAW AWG program is focused on the higher-loaded subregion (Piepel et al. 2015), while the CUA testing program is attempting to bridge the gap between the two regions (Muller et al. 2014, 2015a). Based on the results of these data generation efforts, decisions will be made on the approach for future testing with both simulants and actual waste samples.

4.1.2 Approaches for Developing Advanced LAW Glass Formulations

The current WTP LAW glass formulation approach (Kim and Vienna 2012) is to use glass formulation rules (Muller et al. 2004; Kim and Vienna 2012) that specify the waste loading and glass composition and then apply the glass property-composition models (Piepel et al. 2007) to confirm that the formulated glass meets all the processing and performance requirements. However, this may not be the best approach for advanced glass formulations to achieve the maximum possible waste loading. Therefore, the following approaches are being considered under the LAW AWG program.

- **Approach 1:** Develop and apply advanced glass formulation and halide rules that produce a predefined glass composition for a given waste. Glass property-composition models and their corresponding uncertainties will then be used to ensure that property constraints are met. This is the same approach as the current WTP LAW glass formulation approach (Kim and Vienna 2012), except that advanced glass-formulation rules as well as advanced glass property-composition models would be used.
- **Approach 2:** Apply glass composition optimization using glass property-composition models and their corresponding uncertainties along with glass performance and processing constraints. This is the same approach as the current WTP HLW glass formulation approach (Vienna and Kim 2014), except that advanced glass property-composition models would be used.
- **Approach 3:** Develop and apply advanced glass formulation and halide rules that define the maximum waste loading for a given waste and formulate the "optimized" glass composition using advanced glass property-composition models and their corresponding uncertainties at the determined waste loading. This approach is a hybrid of Approaches 1 and 2.

Each of these approaches requires 1) glass property-composition models capable of predicting the key properties related to processing and product performance for the region of glass compositions to be processed, and 2) expressions for calculating the uncertainties in property predictions throughout the composition region. Properties currently envisioned to be modeled include viscosity at 1150°C, electrical conductivity at 1150°C, PCT, VHT response, sulfur solubility (or salt formation) (see Vienna et al. 2014; Muller et al. 2015a), phase stability during cooling, and potentially materials corrosion (see Muller et al. 2015b) and melting rates. With respect to the advanced LAW glass property-composition models and glass formulation algorithm, they are required for three primary purposes:

1. To support vitrification plant operations by ensuring processable batches and acceptable glass compositions are produced.
2. To support waste feed qualification by assessing melter feed properties, drive decisions on pretreatment operations, and evaluate vitrification process effectiveness.
3. To support RPP missing planning and optimization, considering the waste feed delivery strategy, waste pretreatment requirements, and mission life/cost estimation.

4.2 Research Needs for ^{99}Tc Management

Scope associated with Tc management is focused on increasing the single-pass Tc retention in glass to the extent that minimizes the negative impact of recycle on LAW glass volumes produced. The LAW AWG program is also focused on incorporating Tc from the off-gas stream (or potentially the LAW feed streams directly) into a high-temperature Tc-bearing phase that could be recycled to the melter or serve as a separate waste form (Duncan 2012; Taylor-Pashow et al. 2013, 2014; Banerjee et al. 2015[d]).

It should be mentioned that in addition to the two focus areas of the ORP AWG program, there is an EM-International Project investigating zirconium-metal organic framework (MOF) and similar structures (e.g., PAF: porous aromatic framework) for removal of ^{99}Tc from liquid waste. The objectives of that research are to 1) demonstrate the chemical stability, high selectivity, and kinetics of such a material for ^{99}Tc removal and 2) determine the optimal material properties and physical form (bulk powders, pellets, fibers, gels, magnetic core-shell nanoparticle, etc.) for which the MOF should be commercially manufactured.

Laboratory experiments have shown that Zr-MOF and PAF are exceedingly effective in sequestering specific targeted ionic species from radioactive liquids. The salts formed from Zr-MOF sequestration process have been shown to be thermally stable at temperatures from 300°C to 900°C and in highly alkaline environments. The addition of a Zr-MOF to the aqueous material at the submerged bed scrubber (SBS) of the WTP LAW vitrification facility would remove ^{99}Tc from the process stream for subsequent treatment and permanent disposal as low-level solid radioactive waste. This work does include the possible competitions offered by the other components anticipated in the SBS material. Use of the Zr-MOF as a "molecular sieve-like" material at the Hanford Effluent Treatment Facility would allow for the non-elutable sequestration of ^{99}Tc and the subsequent encapsulation in, for example, cement-based materials. This method of permanent immobilization of ^{99}Tc in a solid waste form should give rise to a performance assessment for the Hanford IDF that would allow for a significantly enhanced performance in the permanent disposal of ^{99}Tc as low-level radioactive solid waste.

The following subsections discuss two general research areas of the ORP LAW program to develop technologies that can eliminate the need for recycling the off-gas stream for Tc management and the potential approaches for implementing those technologies, if successfully developed and demonstrated.

4.2.1 Mechanism of ^{99}Tc Incorporation into Glass Melt

The nominal value of ^{99}Tc retention (single-pass) in LAW glass used in the current ILAW glass formulation algorithm is 43% (Kim and Vienna 2012). Recent small-scale melter tests at the Vitreous State Laboratory (VSL) of the CUA with seven representative LAW glass feeds spiked with Tc-99m showed that the single-pass technetium retention varied from 18% to 66% depending on the feed composition. The baseline cases are shown in Figure 7, based on results from Matlack et al. (2010, 2011).

A major finding from the VSL small-scale melter tests was the beneficial effect of reducing agents on Tc retention, especially Fe(II) oxalate. Figure 7 also shows that the addition of iron(II) oxalate to seven baseline feeds with nominal sugar addition increases the Tc retention for all feeds except for AZ-102 (LAWE10H), which had highest baseline Tc retention (66%). The major factors responsible for these varied Tc retention values, including the mechanism responsible for the effect of reducing agents and the unexpected negative effect of iron(II) oxalate for AZ-102 feed, are not currently known. Therefore, a primary focus of the LAW AWG research and development plan is to develop a fundamental

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[d] Banerjee D, PK Thallapally, D Kim, MJ Schweiger, and AA Kruger. 2015. *Removal of TcO_4^- Ions from Solution: Materials and Future Outlook*, in preparation.

understanding of the mechanism(s) of Tc retention into (or escape from) the cold cap during melting of LAW glass feeds. With a firm grasp on the fundamental mechanistic drivers, alternative processing conditions and melter feed chemistry may be developed to increase ^{99}Tc single-pass retention in glass.

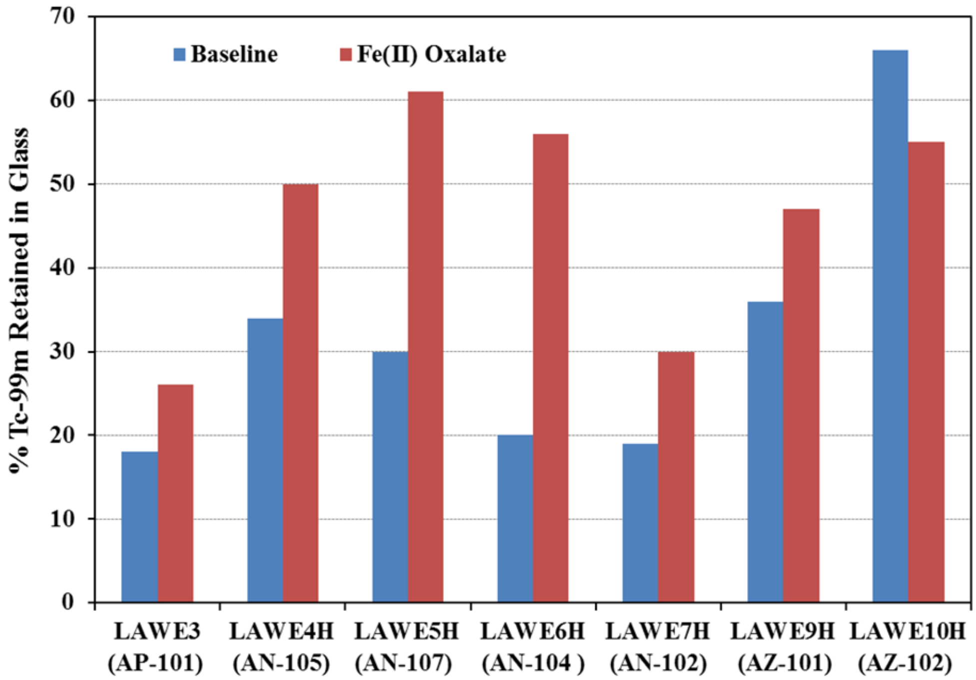

Figure 7. Effect of Iron(II) Oxalate on Tc-99m Retention in Glass during Melting of Seven Representative LAW Glass Feeds. DM-10 tests performed at VSL (Matlack et al. 2010, 2011)

To evaluate if the solubility of Tc in glass can affect its retention in glass, a vacuum-sealed fused silica ampoule setup was used to measure the solubility of Re and ^{99}Tc in a representative LAW glass (McCloy et al. 2012; Soderquist et al. 2014). The measured solubility at 1000°C was 3000 ppm mass for Re (used as surrogate for Tc) (McCloy et al. 2012) and 2000 to 2800 ppm mass for ^{99}Tc (Soderquist et al. 2014). Considering that the projected concentration of ^{99}Tc in LAW glass is ~3 ppm mass on average (Soderquist et al. 2014), solubility is not a factor that will affect Tc retention in LAW glass. Therefore, if technologies can be developed to eliminate or minimize Tc volatility during cold-cap reactions, Tc retention should dramatically increase.

The experiments performed at PNNL to measure the solubility of Re and ^{99}Tc also yielded additional information that can be helpful for the research activities to increase the ^{99}Tc retention in glass described in Section 4.2. The results have been published for the topics that include the structural role of Re and ^{99}Tc in LAW glass (Goel et al. 2013; Gassman et al. 2014), Re mass balance from a Re solubility test (Kim and Schweiger 2013), and characterization of Re and ^{99}Tc salt phases formed on glass melt surface (Riley et al. 2013; Soderquist et al. 2015[e]).

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[e] Soderquist CZ**,** EC Buck, JS McCloy, MJ Schweiger, and AA Kruger**.** 2015. "Formation of Technetium Salts in Hanford Low Activity Waste Glass." *Journal of Nuclear Materials* (submitted).

A series of studies (Jin et al. 2014, 2015) is being performed to understand the mechanism of Re/Tc retention into (or escape from) the cold cap during melting of LAW melter feeds. The studies are focused on developing a fundamental understanding of the mechanistic drivers for Tc partitioning, which will serve as the basis for developing alternative processing conditions or potential additives that will increase ^{99}Tc retention. The three sets of tests are summarized here:

- AN-102 and AZ-102 feeds that showed extreme difference in Tc retention (as shown in Figure 7) were selected for the first set of tests, with results published in Jin et al. (2015). A preliminary conclusion was that the different compositions of the salt phase formed during the major feed-to-glass conversion reactions occurring at ≤700°C are responsible for the large difference in Re (surrogate for Tc) retention observed in both the scaled melter tests (Figure 7) and the crucible melts (Jin et al. 2015). However, details on how different salt compositions affect Re incorporation during feed-to-glass conversion reactions are not fully understood. Crucible studies using simplified feeds containing four to five of the most critical components to simulate the characteristics of each feed are currently being performed to understand the effects of different salt compositions on Re partitioning and retention.
- The second set of tests is investigating the effect of sulfate content on Re partitioning and retention in both AN-102 and AZ-102 feeds with varying target concentrations of sulfate. The data are currently being evaluated, with initial results published in Jin et al. (2014). However, the preliminary finding on the reason for the negative effect of sulfate is contrary to what was suggested in a previous study (Kim et al. 2005). Kim et al. (2005) suggested that sulfate promotes volatilization of Re and Tc through enhanced sulfate bubble transport at temperatures above ~800°C. However, the present results suggest that 1) sulfate suppresses incorporation of Re into glass melt below ~800°C, and 2) any sulfate that was not incorporated into glass melt below ~800°C volatilizes without further incorporation into glass. Similar to the first set of tests, it is not understood how (by what mechanism) sulfate suppresses Re incorporation below ~800°C. Crucible studies using simplified feeds are also planned to support this assessment. The preliminary results of this set of tests led to the concept that the negative effect of sulfate may be avoided if sulfate is incorporated in a thermally stable phase (certain composites or minerals) that can survive feed melting reactions below ~800°C. Scoping tests are being performed to assess the feasibility of this concept.
- The third set of tests will investigate the effects of reducing conditions and reducing agents on Tc retention. Although reducing agents appear to have a positive influence on Tc retention for most waste streams, there is a fundamental lack of mechanistic understanding of this effect that was observed from small-scale melter tests at VSL (Matlack et al. 2010, 2011). Similar experimental methods to those used in the first two sets of studies will be applied. However, ^{99}Tc will be used for this set of tests because it is known that Re and ^{99}Tc behave differently when redox reactions are involved because of the different reduction potentials of Re^{7+} and Tc^{7+} (Kim et al. 2005; McKeown et al. 2007; Lukens et al. 2007; Buechele et al. 2012).

4.2.2 Incorporation of ^{99}Tc into High-Temperature Minerals

Another research area being pursued at PNNL is incorporating Tc into high-temperature minerals that are thermally stable and resistant to Tc release during feed melting reactions in the cold cap. The basis for this approach is that various crystalline phases are known to incorporate Tc in their crystal structure, and the syntheses methods for these phases have been reviewed by Luksic et al. (2015).

The spinel family of crystals were identified as the suitable phases that can be precipitated from the off-gas or LAW stream through aqueous reactions at relatively low temperatures e.g., <100°C. In particular, it has been shown that iron minerals (goethite, magnetite, maghemite, trevorite) are good candidate hosts for Tc incorporation (Muller et al. 1964; Khalil and White 1984). Recent tests (Um et al. 2015) have shown that the solid $Fe(OH)_2$(s) can be used as an initial substrate to form spinel phase and can also serve as a reducing agent to reduce Tc(VII) to Tc(IV), which is required for Tc to be incorporated into spinel structure. Currently, test efforts to synthesize Tc-bearing spinel are being performed with a simulated off-gas stream. Once complete, research efforts will transition to precipitation of Tc-bearing spinel directly from simulated LAW, which will be more challenging.

The general concept for this approach is to incorporate the Tc in a crystalline structure by directly treating the LAW prior to glass former addition or by treating the off-gas stream. In both concepts, the Tc-bearing crystalline phase is synthetically generated and is fed to the LAW melter, where it retains Tc in its structure during complex reactions in the cold cap at relatively low temperatures. Ideally, after the LAW melter feed is converted to a glass, the crystalline structure may melt, releasing Tc into the bulk glass, but at that point Tc will be incorporated into the glass product as Tc solubility will not be limited—thus increasing Tc retention in glass. Alternatively, the Tc-bearing phases formed by treating the off-gas stream could be fed to the HLW melter instead of the LAW melter depending on various pretreatment, DFLAW, and SLAW options. In addition, the Tc-bearing crystals may serve as a final waste form or they could be a host phase that is incorporated into other low-temperature waste forms (Westsik 2009).

4.2.3 Potential Implementation Approaches

The research activities described in Sections 4.2.1 and 4.2.2 are exploratory in that they pursue new ideas or concepts that have potential technical merit, perform scoping tests to evaluate technical feasibility, or design and perform experiments that can improve the understanding of fundamental mechanisms. Although the research is exploratory, it is worth considering in advance potential implementation scenarios, so that more specific goals can evolve as the research progresses and matures. Two potential implementation approaches can be considered:

- **Approach 1:** Increase the single-pass Tc retention to the extent that does not require off-gas recycling. This approach assumes that the off-gas stream containing a low level of Tc (although not completely depleted of Tc) is collected and treated into a separate waste form, such as low-temperature waste forms that are being considered or developed for liquid secondary wastes (Westsik 2009; Pierce et al. 2010; Sundaram et al. 2011). For this approach, it is expected that the single-pass Tc retention needs to be significantly higher than current nominal value of 43% used for WTP (Kim and Vienna 2012) or 18% to 66% according to Matlack et al. (2010, 2011). The required level of retention will depend on the performance of the low-temperature waste form to be developed. The potential methods from this approach may include the following:
  - Feed modifications including redox control, sulfate sequestration, or modification of slurry and glass conversion reactions during early stage of feed melting by certain additives.
  - Incorporation of Tc directly from LAW into a high-temperature mineral phase that can retain Tc during feed melting reactions. The $Fe(OH)_2$(s) is a candidate currently being tested. Other materials or technologies that can have similar potential effect will also be evaluated.

The advantage of this approach is that it does not require any additional process steps other than adding ingredients to the LAW melter feed that can increase Tc retention, as long as these additives do not have major impact on glass formulations. Depending on the success of each method, either one or both methods discussed above may need to be implemented to achieve the required level of single-pass Tc retention. This approach needs to be associated with the low-temperature waste form development efforts and IDF performance assessment to determine the required level of single-pass retention. In addition, implementation of any feed modifications to promote formation of mineral phases prior to the melter will have to also consider any impacts on rheological properties or potential settling to ensure the melter feed can be successfully transferred to and through the melter.

- **Approach 2:** Incorporate Tc from the off-gas stream into a Tc-bearing phase and recycle it to the LAW melter. For this approach, any Tc-bearing phase materials can be effective, e.g., the sorbent and reactant materials being tested at SRNL (Taylor-Pashow et al. 2013, 2014), MOF being investigated at PNNL, and tin(II) apatite (Duncan 2012). A disadvantage of this approach is that it requires additional process steps of collecting and recycling the Tc-bearing phases.

After the methods to increase Tc retention are identified, crucible melting tests to evaluate the method will be performed. If crucible melting tests show encouraging results, laboratory-scale melter tests that use slurry feeding will be performed as discussed in Section 4.3.

4.3 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) 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 operating 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, because they require 1) significant volumes of simulated feed to be produced; 2) significant resources to conduct the tests; and 3) large volumes of sampling, analysis, data reduction, and waste disposal. In addition, the larger-scaled melter tests are not practical to support actual radioactive waste testing. To fill the gap between the crucible tests with dried feeds and scaled-melter tests with slurry feeds, PNNL has developed a laboratory-scale melter (LSM) that is capable of slurry feeding but without glass product discharge (Kim et al. 2012). The LSM has been and is being used for the study of cold cap melting reactions occurring during melting of both LAW and HLW glass feeds (Dixon et al. 2013, 2015). One of the objectives of the LAW AWG program is to develop and benchmark a continuously fed, small-scale radioactive melter to the larger-scale systems. PNNL currently has scope to install the radioactive LSM (RLSM) in the Radiochemical Processing Laboratory (RPL) to support Tc retention studies for LAW vitrification.[f]

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

The RLSM is planned to be used for 1) verifying crucible test results from research efforts described in Section 4.2 (e.g., the methods to increase Tc retention through feed reaction modifications or the effect of Tc-bearing minerals on Tc retention) and 2) collecting off-gas solution from melting of actual LAW mixed with additives under slurry melting conditions. The off-gas stream obtained will be used to test and verify various Tc separation methods discussed in Section 4.2.

The RLSM could also be used to support future facility operations and evaluations of potential flowsheet changes prior to making implementation decisions, minimizing cost to DOE. This melter system will provide an additional platform for determining off-gas split factors, identifying potential processing issues (foaming, feed rheology, cold cap behavior, etc.), and providing feedback on production rates for various waste streams using actual LAW. The RLSM, when coupled with the various upstream unit operations within pretreatment (either LAWPS or full pretreatment), can support waste and waste form qualification efforts and serve as a technical platform for evaluating upcoming or future WTP facility operations.

4.4 Flowsheet Integration

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. These types of key inputs are represented in the plan (see Figure 6) as decision points labeled "Update Feed Retrieval / Blending Sequences." Ensuring the LAW 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.

5.0 Quality Assurance

The work contained herein was and will be performed in accordance with QA-EWG-0001, Enhanced Hanford Waste Glass Models (EWG) Quality Assurance Plan. The EWG project uses the Washington River Protection Solutions (WRPS) Waste Form Testing Program (WWFTP) QA program (QA-WWFTP-001) at the Applied Research level as the basis for performing work which the LAW task described in this report is included. The WWFTP QA program implements the requirements of NQA-1-2008, *Quality Assurance Requirements for Nuclear Facility Applications*, and NQA-1a-2009, *Addenda to ASME NQA-1-2008, Quality Assurance Requirements for Nuclear Facility Applications*, graded on the approach presented in NQA-1-2008, Part IV, Subpart 4.2.

Per ORP, all analytical project work will be performed following the latest "Hanford Analytical Services Quality Requirements Document" (HASQARD). PNNL plans to subcontract to Southwest Research Institute (SwRI) for analytical services which will require HASQARD compliance. PNNL has audited and accepted SwRI services as compliant to the HASQARD requirements and has placed SwRI on the PNNL Evaluated Suppliers List as an acceptable supplier for analytical services in accordance with HASQARD.

6.0 Summary

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 purpose of this advanced LAW glass research and development plan is to identify the near-, mid-, and longer-term research and development activities required to develop and validate 1) advanced 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.

Given that data are needed to develop, validate, and implement new property-composition models and LAW glass-formulation algorithm, this advanced LAW glass research and development plan integrates specific studies associated with increasing the Na_2O and SO_3/halide concentrations in glass, as these components will ultimately dictate waste loadings for LAW vitrification. Of equal importance is the development of a strategy for economical ^{99}Tc management. Specific and detailed studies are being implemented to understand the fate of Tc throughout the WTP flowsheet and the underlying mechanisms that dictate its partitioning. These studies are aimed at increasing the single-pass Tc retention in glass as well as the potential use of high-temperature mineral phases to capture Tc that are thermally stable and resistant to Tc release during feed melting reactions or serve as alternative waste forms. The LAW glass research and development is focused on reducing ILAW glass volumes produced and minimizing the impact of or potentially eliminating the need for recycle.

The research outlined here is motivated by the potential for substantial economic benefit (e.g., significant reductions in glass volume) that will be realized when advancements in LAW 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.

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

"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:[g]

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

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