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| **Statement of Work** |
| **Experimental Characterization and Mathematical Modeling of Batch-to-Glass Conversion Processes for Nuclear Waste Vitrification** |

The INL is a U.S. Department of Energy National Laboratory operated by Battelle Energy Alliance.



Manual: Procurement

## REVISION LOG

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# INTRODUCTION

## Background

Battelle Energy Alliance (BEA) is the current management and operating contractor for the Department of Energy (DOE) located at Idaho National Laboratory (INL). At the Hanford Site in the United States, 213 000 m3 of nuclear waste will be separated into a low-activity waste (LAW) and high-level waste (HLW) fractions, to be processed by vitrification at the Waste Treatment and Immobilization Plant (WTP) (xxxx *et al.*, 2019). The U.S. DOE is implementing a phased approach to the waste treatment and is currently commissioning and starting up two 10 m² Joule-heated electric melters, which will vitrify the LAW fraction of Hanford waste under the direct-feed low-activity waste (DFLAW) configuration (xxxx *et al.*, 2024). In the DFLAW process, the Tank-Side Cesium Removal facility removes radioactive cesium and strontium from the LAW, which is then directly sent to the LAW vitrification facility, bypassing the pretreatment facility. DOE is also considering the potential implementation of direct-feed HLW (DFHLW). For DFHLW, the pretreatment facility could also be bypassed, meaning that ultrafiltration and caustic leaching operations might either not be performed or be replaced by interim pretreatment methods, such as in-tank leaching and settling. These adjustments are likely to affect glass formulations and waste loadings, and will impact downstream vitrification operations.

Unlike many other vitrification facilities around the world that process waste feeds of nearly uniform composition, such as those from commercial nuclear fuel reprocessing, the WTP is slated to process approximately 55,000 distinct waste feed compositions over several decades. Simulants of these feeds have shown a broad range of behaviors during melting. Additionally, new glasses and feed formulations are continually being developed as part of the Enhanced Waste Glass program (xxxxx *et al.*, 2021). Therefore, ensuring high processing rates, steady melter operation, and preventing operational issues and potential runoffs during the processing of the various (DF)LAW and (DF)HLW melter feeds is critical to the success of Hanford’s cleanup mission. Consequently, a significant amount of research has been devoted in recent years to better understand the glass melting process, including experimental analysis and mathematical modeling of batch-to-glass conversion (xxxxx *et al.*, 2023).

Despite this significant progress, BEA’s understanding of the various waste glass melting phenomena is not yet complete. Pressing issues are the radiative heat transfer between the molten glass and the reacting batch, the relationship between the feed composition and primary foaming, or the characterization of the early stages of the melting process and its relation to Tc retention, and the investigation of melter refractory wear by corrosion and spalling (affects melter reliability and lifetime). New challenges and opportunities have also been identified to support the WTP startup and efficient operation, such as the investigating batch-to-glass conversion characteristics of high-iron, high-chromium melter feeds that exceed the current upper limit for glass crystal content for the WTP (1 vol.% at

950 °C). These issues require BEA to conduct further research to improve the efficiency of the vitrification process at the WTP.

## Purpose / Objectives

The Subcontractor shall research the understanding of the cold cap behavior during waste glass melting. This work shall assist with the WTP melter startup and operation.

## Anticipated Benefits

BEA will be able to reduce the costs and shorten the life cycle of the cleanup process at the Hanford Site in Washington.

# APPLICABLE CODES AND REFERENCES

xxxxx, xxxxx, xxxxx, xxxxx, xxxxx, xxxxx, xxxxx, xxxxx, xxxxx, xxxxx, xxxxx, xxxxx Conversion kinetics during melting of simulated nuclear waste glass feeds measured by dissolution of silica. Journal of Non-Crystalline Solids. 579 (2022) 121363.

xxxxx, xxxxx, xxxxx, xxxxx, xxxxx, xxxxx, xxxxx, xxxxx, xxxxx Conversion degree and heat transfer in the cold cap and their effect on glass production rate in an electric melter. International Journal of Applied Glass Science, 14 (2023) 318-329.

xxxxx, xxxxx, xxxxx, xxxxx Challenges with vitrification of Hanford High-Level Waste (HLW) to borosilicate glass – An overview. Journal of Non-Crystalline Solids: X, (2019) 100033.

xxxxx, xxxxx, xxxxx, xxxxx, xxxxx, xxxxx, xxxxx (2020). Simplified melting rate correlation for radioactive waste vitrification in electric furnaces. *Journal of the American Ceramic Society*, *103*(10), 5573-5578.

xxxxx, xxxxx, xxxxx, xxxxx, xxxxx, xxxxx, xxxx, xxxxx, xxxxx, xxxxx, xxxxx (2021). Melting rate correlation with batch properties and melter operating conditions during conversion of nuclear waste melter feeds to glasses. *International Journal of Applied Glass Science*, *12*(3), 398-414.

xxxxx, xxxxx, xxxxx, xxxxx, xxxxx Hanford low-activity waste vitrification: A review, Journal of Hazardous Materials, Volume 461 (2024) 132437.

xxxxx, et al. Enhanced Hanford Low-Activity Waste Glass Property Data Development: Phase 2. United States: N. p., 2021. PNNL-28838, EWG-RPT-021, doi:10.2172/1813429.

# SCOPE

## Work to be Performed

The Subcontractor shall perform the following tasks:

* + 1. Investigate early stages of HLW and LAW glass batch melting, formation of transient glass-forming melt, and exploring ways for the minimization of primary foam.
    2. Develop the advanced cold cap model and its implementation in the integrated computational-fluid-dynamics (CFD) model.
    3. Perform experimental investigation and analysis of refractory corrosion.
    4. Determine the effects of glass-forming additives and reducing agents on the Tc/Re retention during vitrification of LAW and HLW.

## Task 1*.* Investigation of Early Batch Melting Stages, Transient Melt Formation, and Minimization of Primary Foaming

In this task, the Subcontractor shall investigate how the batch-to-glass conversion processes, including primary foaming, are related to the melter feed composition. This will involve the investigation of conversion processes of feeds with a high content of chromium oxide and spinel-forming oxides. Using x-ray diffraction (XRD), x-ray fluorescence (XRF), and leaching tests, the Subcontractor shall evaluate the fraction and composition of glass-forming melt and crystal phases as functions of temperature and batch thermal history. Using viscometry and composition-property models, the Subcontractor shall assess the effect of transient melt viscosity on the primary foam formation/stability and help understand the relationship between feed composition and feed processability during melting.

Developing robust methods for designing melter feeds and glass compositions is essential to support ongoing improvements and modifications to the WTP flowsheet, including the potential bypass of the waste pretreatment facility. In the past, substantial effort was invested in developing and refining mathematical models for enhanced waste glass formulations that meet or exceed baseline WTP requirements, such as viscosity, electrical conductivity, and chemical durability. However, less attention has been given to the formulation of the melter feed itself— specifically, to the chemical form and particle size of glass-forming and modifying additives, which have a significant impact on the feed-to-glass conversion process during melting.

In addition, enhanced waste glass formulations have been recently explored to increase the waste loading in (DF)HLW glasses. For some of these glasses, particularly those high in Fe and Cr, waste loading is limited by the formation of spinel crystals. To prevent excessive crystallization in the melter and related settling issues, a glass formulation limit of 1 vol.% of crystals at 950 °C has been

established for the WTP. However, bubbled melters have demonstrated the capability to tolerate a higher fraction of crystals. During tests in the DM100 melter at Vitreous State Laboratory (VSL), no issues with glass discharge were reported, even after extended idling with feeds containing high spinel and eskolaite crystal contents (xxxxx, 2009), suggesting that the 1 vol.% crystallinity constraint might be relaxed. However, two of these tests reported the formation of bridging cold caps, which led to feeding interruptions, the need for manual cold cap dislodging, and reduced melting rates. These issues may be more closely related to feed conversion kinetics than to the higher glass crystallinity.

## Task 2. Develop the Advanced Cold Cap Model and its Implementation in the Integrated CFD Model

In this task, the Subcontractor shall continue modeling efforts across several areas. The “melting rate correlation” (MRC) equation, which relates the melting rate of both HLW and LAW feeds to the melter operating conditions and feed properties (xxxxx *et al.*, 2020, 2021), underpins the methodology. Following this first step, a detailed cold cap model was developed that considers both the heat transfer in the cold cap and the feed-to-glass conversion kinetics (xxxx *et al.*, 2022). By coupling this cold cap model with a CFD model developed at INL for the Joule-heated glass melter, the vitrification process of four HLW and LAW melter feeds was successfully simulated (xxxxx *et al.*, 2023).

The validity of the MRC equation will be tested using data from the processing of DFLAW and (DF)HLW melter feeds in the continuous laboratory-scale melter (CLSM) operated at Pacific Northwest National Laboratory. These processing data will be used both to validate the MRC equation and to evaluate the applicability of the CLSM for estimating melting rates in large-scale production melters. In the CFD-cold cap modeling, the Subcontractor shall continue analyzing the radiative thermal conductivity of molten glass and implement a radiative conductivity model into the integrated melter model. Additionally, the Subcontractor shall further develop cold cap models for newly formulated DFHLW feeds.

## Task 3. Perform Experimental Investigation and Analysis of Refractory Corrosion

The Subcontractor shall conduct research by performing static and dynamic (rotating vessel) corrosion tests to (1) provide the corrosion rate as a function of temperature, and (2) support the development of a corrosion model based on diffusion-limited refractory dissolution and provide data for its validation. To support the development and validation of the corrosion model and evaluate the diffusion coefficients of major K-3 components (Al2O3 and Cr2O3) in molten glass, corrosion rate data will be complemented by measurements of saturated concentrations of Al2O3 and Cr2O3 in the test glasses, as well as other relevant glass and refractory material properties, including density, viscosity, or surface tension.

The Subcontractor shall design an experimental procedure to investigate spalling. Spalling typically results from thermal shocks experienced by the refractory and is typically caused by differences in thermal expansion between the bulk refractory and the corroded refractory at the interface. To investigate spalling, refractory samples will be periodically immersed in the melt and then exposed to a low temperature. Samples will be embedded in epoxy resin after the test, sectioned and examined using image analyzer. Changes in the refractory material microstructure will be evaluated using polarizing microscopy and SEM-EDX. Thermo-mechanical analysis of the refractory and the glass will be conducted to assess the mechanical stresses induced by the differences in the thermal expansion coefficients of the Monofrax K-3 refractory and the adjacent glass layer at the glass-refractory interface or of the interface spinel layer. The Subcontractor shall also continue supplying refractory coupons for corrosion testing at PNNL and SRNL.

## Task 4. Determine Effects of Glass-Forming Additives and Reducing Agents on the Retention of Rhenium and Technetium during Vitrification of LAW and HLW

One of the most challenging components of many defense and commercial nuclear wastes, including Hanford LAW, is technetium-99 (Tc). Not only is Tc water soluble and highly mobile in the environment, the 99Tc half-life (2.1×105 years) is more than four orders of magnitude longer than that of other radionuclides, such as 99Sr and 137Cs, making it the major source of glass radiation over thousands of years. In previous studies, it was found that for a fixed glass composition, the rate at which Tc or rhenium (Re) is incorporated into the glass-forming melt can be enhanced by proper selection of glass forming and modifying additives (GFMAs). For example, increasing sucrose content accelerates the denitration process, reducing the fraction of the salt phase and increasing the driving force for Tc/Re diffusion into the glass- forming melt at temperatures below 700 °C, before volatilization begins. Additionally, we found that the Re retention was consistently higher, by up to 25%, in glasses produced from LAW feeds where the nominal alumina source, kyanite, was replaced with gibbsite or boehmite. While this improvement is attributed to the formation of nanocrystalline alumina, the exact mechanism of this phenomenon is not yet understood.

In this task, the Subcontractor shall continue investigating the effect of feed composition on the Re/Tc retention by analyzing factors controlling Re/Tc diffusion from the oxyanionic salt melt into the transient glass-forming melt. Specifically, for the alumina source effect, the Subcontractor shall examine the formation and dissolution of nanocrystalline alumina by XRD and nuclear magnetic resonance (NMR) as a function of temperature and analyze its effect on the Tc/Re retention. For the sucrose effect, the Subcontractor shall test the hypothesis that higher sucrose content reduces the molten salt phase fraction, thereby increasing the driving force for Re diffusion into the glass-forming melt. This will involve analyzing Re retention in feeds with varying soluble salt fractions and evaluating

the effect of molten salts on Re retention. Additionally, the Subcontractor shall investigate the effect of silica particle size, which has recently been observed to influence Re retention.

## Work Excluded

Execution of the CFD model is outside the scope of this work.

## Requirements

None

## Place of Performance

The place of performance of the Subcontractor shall primarily be offsite at the Subcontractor’s location.

## Interfaces

None

## Miscellaneous

* + 1. **Quality Assurance**

The Subcontractor shall exercise diligence in their efforts for this task. As expected for research laboratories, there are basic requirements for quality assurance; this includes, but is not limited to, the calibration of balances and optical imaging equipment, checking of thermocouples against a known standard or reference, and acquiring reproducible results that can be verified by another researcher following identical laboratory processes.

If a formal quality assurance program exists at the Subcontractor’s location, the process shall be made available for review to BEA. Otherwise, experimental efforts shall be described in sufficient detail in reports and communication with sponsors and quality-affecting equipment, such as balances and mass flow monitors, shall have calibration records to show diligence to basic quality-affecting issues for this task.

## Technical Requirements

The Subcontractor’s expertise in glass chemistry is essential for developing and validating BEA’s models.

# DELIVERABLES

The Subcontractor shall provide the following deliverables:

1. Frequent communication (at least weekly) via email and/or voice communication to BEA and its partners.
2. Monthly progress reports for each of the four tasks outlined in section 3.1. Reports shall be delivered to BEA personnel at INL and the DOE client. Reports shall be one to two pages in length and include a short summary of highlights, accomplishments, and any difficulties and/or problems encountered.
3. Timely reviews and input on research directions performed by the WTP glass science team.
4. Attend project meeting in-person (at least once per year) to discuss project progress and deliverables.
5. A published manuscript and/or report that describes the effect of aluminum source on the Re/Tc retention during LAW feed melting.
6. A submitted manuscript and/or report that describes the relationship between the primary foaming and the transient melt viscosity, fraction, and the particle size of undissolved solids.

# SCHEDULE AND MILESTONES

The Gantt chart shows the tasks, milestones, and schedule for this subcontract.

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| **Task 1 - Investigation of Batch-to-Melt Conversion, Transient Melt Formation, and Minimization of Primary Foaming** | | | | | | | | | | | | | | | | | | | | | | | | |
| Analysis of batch-to-glass conversion and minimization of primary foaming  High crystal content glasses - effect of composition and crystal content on the feed processability |  |  | | | | | | | | |  | | | | | | | | | | | |  |  |
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Cooperation with INL and PNNL on the development of advanced cold cap model and on the Integrated CFD

**Task 2 - Collaboration with INL and PNNL on the Development of the Advanced Cold Cap Model**

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Validation of MRC using CLSM melter data

**Task 3 - Analysis of Refractory Corrosion**

**Task 4 - Effect of glass-forming additives and reducing agents on the Tc/Re retention**

Experimental analysis of refractory corrosion as a function of velocity, temperature, and glass composition Evaluation of spalling - experimental characterization and numerical analysis

M3.1

Development of mathematical model for refracotry wear

M4.1

The table below lists the required deliverables, due dates, and deliverable type.

Effect of Al-sources on Re retention

Effect of feed composition and silica particle size on Re retention

M4.2

|  |  |  |
| --- | --- | --- |
| **Deliverable** | **Due Date** | **Type** |
| Monthly progress reports to the BEA Technical Point of Contact (TPOC). | Due on the last day of each month | [Monthly Progress Measure (Regular)] |
| Attend in-person project meeting | 5/31/2025 | [Annual Progress Measure (Regular)] |
| Submitted journal manuscript and/or report describing the effect of Al- source on the Re/Tc retention during LAW feed melting. | 12/31/2025 | [Annual Progress Measure (Regular)] |
| Submitted journal article manuscript and/or report describing the relationship between the primary foaming and the transient melt viscosity, fraction, and the particle size of undissolved solids. | 2/28/2026 | [Annual Progress Measure (Regular)] |

# COMPLETION CRITERIA AND FINAL ACCEPTANCE

Documentation of the research results shall be provided in the form of journal manuscripts and/or reports. Draft journal articles shall be submitted for review and comment to BEA personnel and to the DOE client before submitting to the journal. Final acceptance will be determined by the BEA TPOC. The publication of the approved report or manuscript in the journal will complete the deliverable and the documentation of the task.

# APPENDICES

None

# ATTACHMENTS

None