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The Office of River Protection Cold Cap and Melt Dynamics Technology Development and Research Plan

April 2016

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U.S. DEPARTMENT OF ENERGY

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Executive Summary

The U.S. Department of Energy (DOE) is building the Hanford Tank Waste Treatment and Immobilization Plant (WTP) at the Hanford Site in southeastern Washington State to remediate 55 million gallons of radioactive waste that is being temporarily stored in 177 underground tanks. The WTP is being constructed 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. The cost and schedule of treatment is highly dependent on the waste loading in glass and the rate of glass production. Increasing the rate of glass processing, particularly when coupled with increased waste loadings, will reduce the overall mission life of the WTP facilities.

The DOE Office of River Protection (ORP) has an integrated program focused on advanced glass formulations and process control models as they relate to waste loading, melting rate, and facility operations. Although higher waste loadings are desired and achievable, this must be done without negatively affecting the melting rate, which could decrease the overall waste throughput for the vitrification facility. Therefore, the integrated ORP program includes efforts to understand the batch-to-glass conversion process, the cold cap behavior, and melt dynamics under various processing conditions as a function of melter feed make-up (i.e., waste plus glass forming chemicals that targets a specific glass composition).

Although many factors influence the rate at which the incoming melter feed is converted to a molten glass product, perhaps the least understood is the complex series of reactions within the cold cap and the dynamics of the cold cap. Therefore, melting rates are being studied to develop a fundamental understanding of the batch-to-glass conversion process. In particular, studies are focusing on those reactions that highly influence the rate of melting. For example, one key phenomenon to understand is the formation, stability, and behavior of the foam layer that develops between the primary heat source (molten glass pool) and the cold cap, where all of the complex reactions are occurring. This foam layer can act as a thermal barrier (insulator) that impedes heat transfer into the cold cap, reducing the melting rate. A fundamental understanding of these key phenomena will lead to strategic methods to minimize (or eliminate) the potential negative impacts during facility operations as well as serve as the knowledge base with respect to the fate of Tc which is largely determined by 700 – 800°C in the cold cap. Figure ES.1 shows the ORP programmatic activities as they are related to this cold cap and melt dynamics research and development plan. This plan is a living document that will be updated to reflect key advancements and mission strategy changes as needed.

This plan identifies ongoing, near-, mid-, and longer-term research and development activities required to develop a more fundamental understanding of the complex series of reactions that govern melting rate and the dynamic behavior of the cold cap under various operating conditions. The plan describes analytical techniques that are currently being used or are being developed to provide key material property data (as function of temperature and heating rates) as input data to 1-D and 3-D modeling efforts. The current approach is to develop an integrated mathematical model that can describe the overall melting process for such complex systems and can be used in conjunction with the glass composition – property models not only to maximize waste loading, but to improve melting rate as well. This will ultimately decrease the cost of Hanford tank waste management by reducing the schedule for tank waste treatment and reducing the amount of HLW and LAW glass for storage, transportation, and disposal.

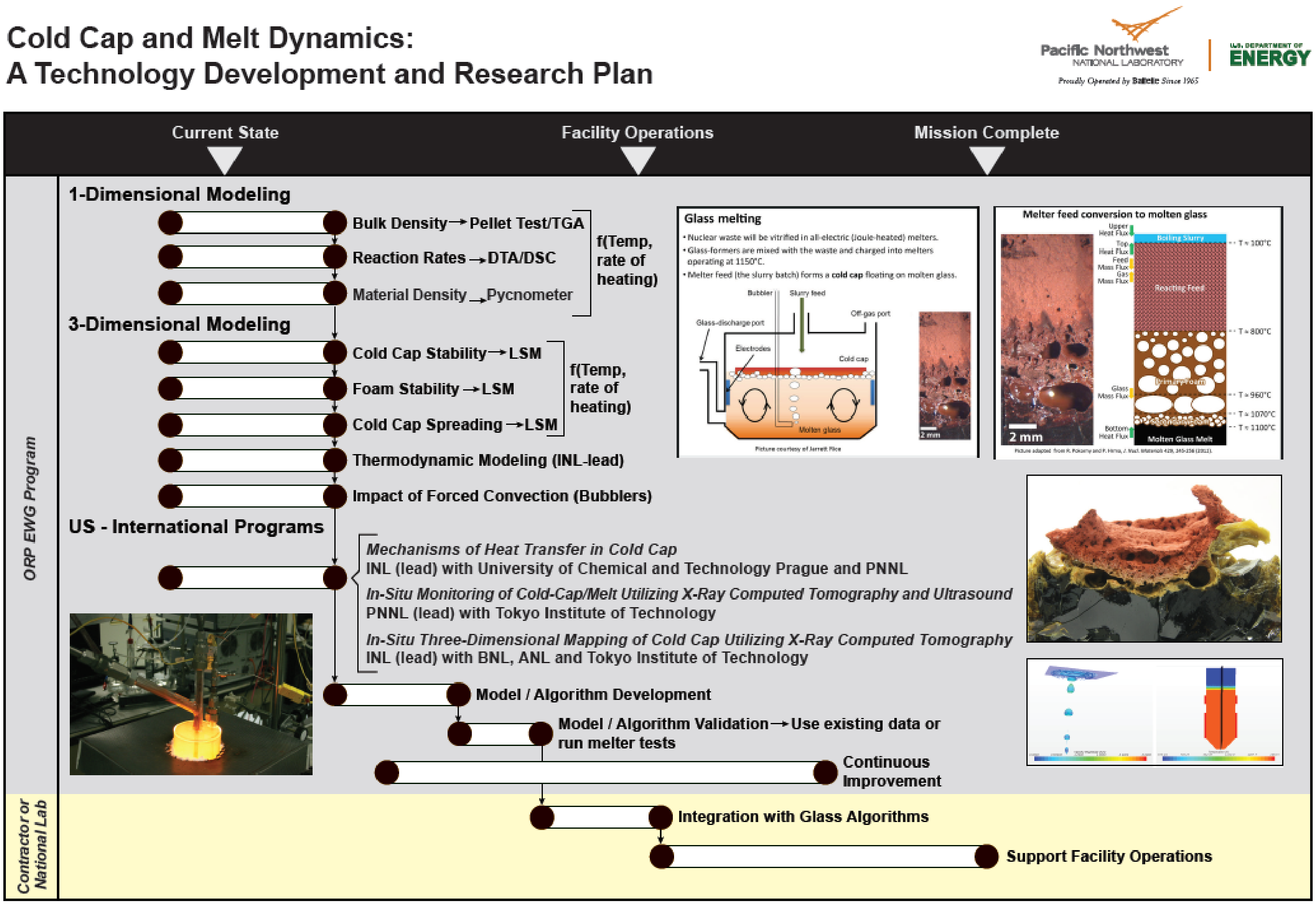

Figure ES.1. Cold cap and melt dynamics research and development plan to support the WTP mission.

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 Director, William F. Hamel. The authors thank Albert Kruger, Dawn Wellman, Jaehun Chun, 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

APS	Advanced Photon Source
EWG	Enhanced Waste Glass (program)
CFD	computational fluid dynamics
CT	computed tomography
CUA	The Catholic University of America
DOE	U.S. Department of Energy
DSC	differential scanning calorimeter
GFC	glass-forming chemical
HLW	high-level waste
IHLW	immobilized high-level waste
ILAW	immobilized low-activity waste
LAW	low-activity waste
LSM	laboratory-scale melter
ORP	Office of River Protection
PNNL	Pacific Northwest National Laboratory
RPP	River Protection Project
RSM	research-scale melter
SAXS	small X-ray scattering
SEAB	Secretary of Energy’s Advisory Board
SSRL	Stanford Synchrotron Radiation Lightsource
UCT	University of Chemistry and Technology (Prague)
VSL	Vitreous State Laboratory
WTP	Hanford Tank Waste Treatment and Immobilization Plant
XAFS	X-ray absorption fine structure

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1.0 Introduction

About 55 million gallons of mixed hazardous waste is currently stored in underground tanks at the U.S. Department of Energy (DOE) Hanford Site in the southeastern Washington State. The Hanford Tank Waste Treatment and Immobilization Plant (WTP) is being constructed 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. The ILAW product will be disposed in an engineered facility on the Hanford Site while the IHLW product is designed for acceptance into a national deep geological disposal facility for high-level nuclear waste. The ILAW and IHLW products must meet a variety of environmental protection requirements to be accepted for disposal.

To support this effort, the DOE Office of River Protection (ORP) has assembled a cadre of technical expertise in 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, 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 (UCT) Prague, with independent technical oversight provided by Alfred University and Vanderbilt University. ORP has developed and implemented an integrated Enhanced Waste Glass (EWG) program[1] that spans several key technical areas, including (but not limited to)

- enhanced 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.

The ORP EWG program provides 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 EWG program will support development of enhanced 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. These activities will focus on improving the overall RPP mission, namely providing maximum operational flexibility and reducing cost.

An important focus area for the EWG program are the challenges associated with HLW and LAW immobilization, which include the efficient processing or conversion of the waste into glass (melting rate) and the incorporation of key chemical components into the melt and glass during vitrification (which

[1] Note that recent ORP research and development plans (Peeler et al. 2015a, b) inadvertently used the term “advanced” instead of “enhanced”.

ultimately dictates waste loading). These two key terms (melting rate and waste loading), when combined with operational efficiency or availability of the vitrification facility, determine the amount of waste being processed per unit time (or waste throughput) as illustrated by Figure 1.

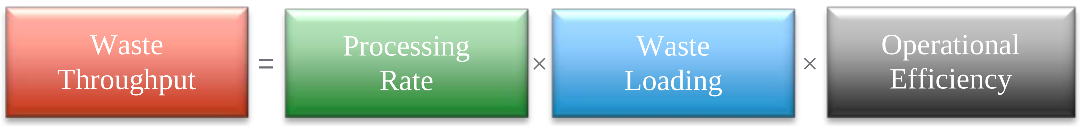

Figure 1. Factors determining waste throughput for WTP vitrification facilities.

The purpose of this cold cap and melt dynamics glass research and development plan is to identify the ongoing, near-term, mid-term, and longer-term research and development activities aimed at developing a fundamental understanding of the dynamic behavior of the cold cap and other factors that influence the overall melting rate for both HLW and LAW production. A fundamental understanding of the melt dynamics and cold cap behavior will lead to improvements in glass processing rates. Understanding cold cap behavior over a range of processing conditions will also provide a technical foundation for minimizing or preventing upset conditions or off-normal melter behavior, increasing operational efficiency. The research outlined in this plan is motivated by the potential for substantial economic benefit (reduced overall mission life) from implementing critical processing strategies developed under the cold cap / melt dynamics portion of the ORP EWG program.

This plan discusses the interdependence of the EWG program research activities with other critical process operations to support the full RPP mission. For example, there are challenges not only in improving our understanding of the physical and chemical behavior of melter feed, molten glass, and solid glass, and the transitions between these states, but also in understanding how this behavior affects other processing concerns such as Tc/halide/SO_3 volatility or molten salt accumulation during the vitrification process. Research and development plans for the other key focus areas have been issued (Peeler et al. 2015a, b; Matyas et al. 2014).

2.0 Benefit to WTP and Motivation for Research

In the simplest terms, the primary objective of the cold cap and melt dynamics research is to achieve a fundamental understanding of the cold cap behavior and melt dynamics under various processing conditions as a function of melter feed composition. This fundamental understanding could advance the current mathematical model of the cold cap and ultimately enable its integration into a full 3-D model of the melter. As mentioned, a fundamental understanding of the melt dynamics and cold cap behavior will lead to improvements in glass processing rates and provide a technical foundation for minimizing or preventing upset conditions or off-normal melter behavior, increasing operational efficiency resulting in a reduced overall mission life for WTP.

Glass models developed by the WTP project for commissioning of the facilities (Piepel et al. 2007 [LAW] and Piepel et al. 2008 [HLW]) were incorporated into algorithms for plant operation (Kim and Vienna 2012 [LAW] and Vienna and Kim 2014 [HLW]). These models did not target the full range of Hanford tank wastes nor were they meant to allow for optimized waste loading. More recent glass property collection has targeted a broader range of waste compositions and sought to determine optimal waste loadings (Matlack et al. 2005, 2006a, 2006b, 2007, 2010; Kim et al. 2003, 2008, 2011; and Muller et al. 2012 for example). The formulations were developed for individual waste compositions and showed waste loading improvements of 25 to 50 relative percent, depending on the waste composition. Vienna et al. (2013) compiled the data and developed a series of glass property models and formulation rules that would allow for the prediction of glass to be produced during the life of the mission. The 2013 models were applied to prediction of mission life by Jenkins et al. (2013) and DOE (2014), demonstrating significant improvements in waste loading and diminished value of time consuming and technically challenging pretreatment options. This development work continues and will result in an updated set of formulation rules and models scheduled for 2016, followed by a set of glass property models and glass formulation algorithms suitable for plant operation (see Peeler et al. 2015 a, b for detailed plans).

However, the current glass models do not evaluate melting rate or glass production rates. To address this issue, a mathematical model of the cold cap is being developed together with a computational fluid dynamics (CFD) melter model. Coupling the mathematical cold cap and CFD melter models with the glass models will enable decisions regarding targeting optimal feed and glass compositions to evaluate both waste loading and melting rate—two primary factors that determine waste throughput for both the HLW and LAW vitrification facilities. Therefore, the cold cap and melt dynamic research aims to integrate the aspect of melting rate into the mission life equation to holistically assess the primary technical aspects that can be influenced by strategic glass formulation efforts. Developing the coupled cold cap/melter model is thus going to be a significant step forward towards the understanding of the waste vitrification at a fundamental level and towards its optimal control.

3.0 Research and Development Objectives

The research and development objectives of this plan are as follows:

1. Summarize the status and technical maturity of the mathematical modeling efforts to simulate or approximate the complex series of reactions within the batch-to-glass conversion process
2. Define the key features of the cold cap that ultimately dictate or control the batch-to-glass conversion process or melting rate
3. Summarize the impact of forced convection (bubbling) on melting rate and how it has been incorporated into the current cold cap model
4. Identify the near-, mid-, and longer-term research and development activities aimed at continuing to improve the status or understanding of the dynamic behavior of the cold cap and other factors that influence the overall melting rate
5. Demonstrate how the output of this program supports WTP facility operations

4.0 Cold Cap and Melt Dynamics: A General Discussion

The general process to convert nuclear waste to a stable glass product starts with adding GFCs to a specific waste composition. The waste contains 40 to 60 elements forming water-soluble salts, amorphous gels, and crystalline materials. Vienna and Kim (2014) describe a preliminary IHLW glass algorithm and

Kim and Vienna (2012) describe a preliminary ILAW glass algorithm, which are used to determine not only the types of GFCs to add to the HLW and LAW, respectively, but also the amount (which dictates waste loading) to generate a melter feed that will yield a product that meets both melter processing and glass product performance constraints. Once the appropriate glass formers have been added, the slurry melter feed is transferred to a high-temperature melter, where it is converted into a molten liquid state and then poured into stainless steel canisters, where it forms a solid glass product.

Immobilizing HLW and LAW into a borosilicate waste form presents two major challenges, as previously discussed: (1) minimizing the number of HLW canisters and LAW containers produced (waste loading) and (2) maximizing the rate of production (melting rate). As shown in Figure 1, improvements to both of these key terms (waste loading and melting rate) will ultimately reduce the overall mission life for WTP. Peeler et al. (2015a, b) describe the ORP activities focused on enhanced HLW and LAW glass formulations and process control models as they are related to waste loading. The significant impacts of those activities are expected to have on minimizing the volume of glass produced and ultimately stored. Although higher waste loadings are desired and achievable, this must be done without negatively affecting the melting rate, which could decrease the overall waste throughput for both the HLW and LAW vitrification facilities.

Figure 2 is a schematic of the melting process for nuclear waste vitrification based on Pokorny and Hrma (2014) and Pokorny et al. (2014). The melter feed (composed of waste and GFCs) is transferred to the melter, where it forms a floating layer of reacting feed called the cold cap. In commercial melters, the cold cap or batch (with minimum moisture) is typically spread in a layer of uniform thickness over the entire surface area of the melt. However, in nuclear waste vitrification, the melter feed or slurry contains ~40% to 60% water and typically covers 90% to 95% of the melt surface under steady-state conditions.

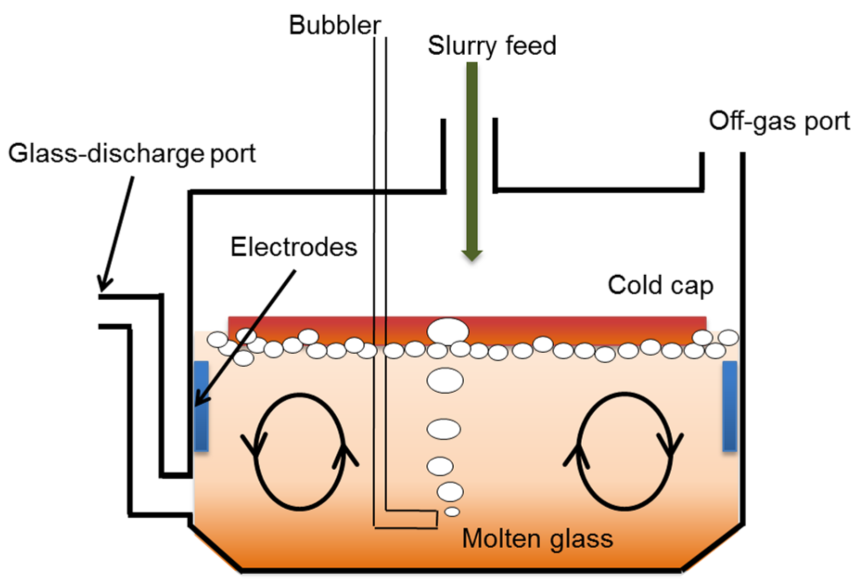

Figure 2. Schematic of the melting process for nuclear waste vitrification (based on Pokorny and Hrma 2014 and Pokorny et al. 2014).

Inside the cold cap, the dry feed is progressively heated and undergoes a series of complex reactions until it is ultimately converted into silicate melt. Figure 3 is a schematic of the cold cap showing the primary layers, approximate boundary temperatures, and heat fluxes from the plenum space (Q_U) and from the molten glass pool (Q_B). Given the melter feed is charged as a slurry, part of the cold cap is covered with a boiling suspension or slurry (nominally at 100°C), while other areas are dry with temperatures above 100°C. Just under the cold cap surface lies the primary reaction layer, which is characterized by open porosity. This primary reaction layer is where most of the complex reactions associated with batch-to-glass conversion processes occur. The feed reactions form gases, liquids, and solid intermediate phases, but the open porosity of the primary reaction layer allows reaction gases to escape to the melter plenum and ultimately flow downstream into the melter off-gas system via the melter off-gas port.

As discussed by Pokorny and Hrma (2014), a foam layer separates the primary reaction layer in the cold cap from the molten glass. This foam layer consists of up to three sub-layers: (1) primary foam, (2) gas cavities, and (3) secondary foam. The primary foam is generated at temperature, T_P, at which an initial glass-forming melt connects and the open porosity closes, trapping evolving gases. Because of the high viscosity of the melt, the buoyant motion of the primary bubbles is slower than the downward motion of the melt. Therefore, the primary bubbles descend until, at the cavity temperature (T_C), the bubbles coalesce and merge into large cavities. These cavities are trapped between the regenerating primary foam and a secondary foam that is produced primarily through reduction-oxidation (redox) reactions and the release of dissolved gases from the molten glass. These gases ascend from the melt below and create the secondary foam layer. The formation and stability of the foam layers impede heat transfer from the primary energy source (molten glass pool) into the cold cap, which in turn dictates the rate of batch-to-glass conversion or melting rate.

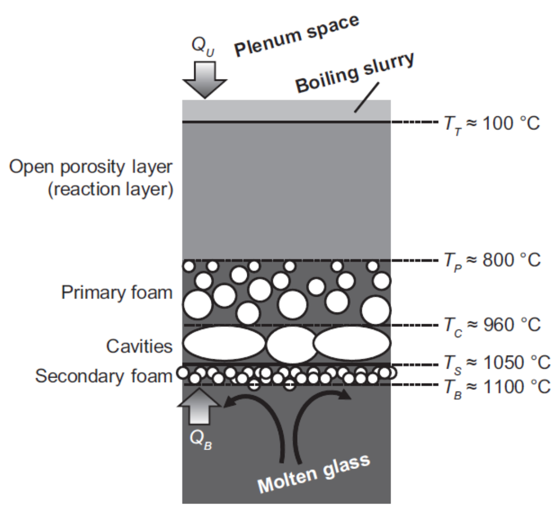

Figure 3. Schematic cold cap formation with slurry feeding (from Pokorny and Hrma 2014).

Cold cap dynamics and the formation and stability of the various layers depend on many factors, including feed rate, melter operating conditions, thermal profiles within the melt pool (natural convection), and the use of bubblers (forced convection). Bubblers added to nuclear waste melters (directly under the cold cap) have been shown to significantly influence melting rate (e.g., Matlack et al. 2008). Section 5.1.4 provides a more detailed discussion on bubblers and their influence on melting rate. Bubblers increase melting rate by increasing the melt pool convection, which minimizes or eliminates the formation of secondary foam and large cavities. Understanding the complex reactions within the cold cap as they relate to compositional changes to the melter feed, adds significant values in terms of optimizing the GFCs for a given waste stream with respect to melting rate.

As previously mentioned, the batch-to-glass conversion process is a series of complex reactions. The total number of reactions is perhaps unquantifiable, with up to 60 chemical components in the melter feed, and identifying each specific reaction in such a complex system would be intractable. However, a small number of apparent reactions and physical factors (amount of foaming, total conversion heat, etc.) control the overall conversion (or melting) rate of the melter feed to a glass product. Therefore, one objective of the ORP EWG program is to develop a phenomenological or apparent kinetic model as a reasonable approximation for the overall rate of batch-to-glass conversion as described by Pokorny et al. (2015).

5.0 Modeling: Current Status

Glass batch melting has been investigated, by experiments and modeling, to gain insight into the process and to assist in furnace design and development (Kuhn 2002). Most of the modeling literature pertains to fuel-fired furnaces and to a lesser degree electric melters. Even the most recent mathematical modeling efforts (Moukarzel and Kuhn 2003; Feng et al. 2008; Abbassi and Khoshmanesh 2008; Yen and Hwang 2008) rarely model the batch conversion process, and instead merely assume a uniform inlet velocity with a prescribed temperature boundary at the batch-melt interface while ignoring gas bubbles under the batch pile. As pointed out by Choudhary (2002), the modeling of phenomena in the batch melting subdomain still represents a relatively weak link in the glass furnace model effort. Since the batch melting process influences the velocity and temperature fields inside the melter, melter models cannot reliably predict the melting rate without an adequate model for the batch melting process. Several studies have developed simplified 1-D or 2-D models for the batch piles charged into a gas-heated furnace (Mase and Oda 1980; Viskanta and Wu 1984; Ungan and Viskanta 1984; Hrma 1982; Schill 1982a, b).

However, vitrification of radioactive wastes occurs almost exclusively in joule-heated or induction-heated electrical furnaces. As Pokorny and Hrma (2012) point out, the simplest case for mathematical modeling of batch melting assumes that a particle of batch or melter feed moves down through the cold cap. This assumption greatly simplifies the mathematical treatment and, at a sufficient distance from the cold cap edges, leads to a 1-D modeling concept for the melting process. Further simplifications or assumptions are needed for a 1-D model because of the complexities associated with batch-to-glass conversion process. These complexities include water evaporation, gas evolution, melting of salts, borate melt formation, reactions of borate melt with molten salts and amorphous solids, formation or precipitation of intermediate crystalline phases or solids, formation of a continuous glass-forming melt, growth and collapse of primary foam, secondary foam formation and accumulation at the bottom of the cold cap, and dissolution of residual solids.

Pokorny et al. (2012, 2014, 2015) and Hrma et al. (2012) have developed a preliminary 1-D cold cap model that addresses heat transfer issues within the cold cap, incorporates the dynamic behavior of the foam layer through which heat is transferred from the melt pool into the cold cap, and demonstrates how the foam layer affects glass production rates. The initial model was developed for a situation where natural convection due to temperature differences in the melt pool causes flow in the melt pool and a boiling slurry covers the top surface of the cold cap. The model calculates the temperature distribution within the cold cap by splitting the cold cap into four regions: (1) the reacting feed layer, (2) the primary foam layer, (3) cavities, and (4) the secondary foam layer. Material properties as function of temperature and composition are needed as initial inputs into this preliminary 1-D model. Therefore, a primary focus of the ORP cold cap and melt dynamics research is to generate the material property data, as discussed in subsequent sections of this plan.

Recent efforts (Pokorny et al. 2015) have been made to advance the initial cold cap model to account for the influence of forced convection (e.g., use of bubblers just under the cold cap) on production or melting rates. The progressive development of the preliminary 1-D model and the acquisition of the required input parameters are discussed in more detail in the next few sections.

Before discussing the continual development of the cold cap model and its integration into a 3-D melter model, it would be beneficial to describe how the activities of this program integrate or support future facility operations. Figure 4 is a schematic of the ORP cold cap and melt dynamics research and development plan. The plan is divided into two primary sections: (1) key ORP related activities (e.g., testing to supply key modeling inputs, model development and validation) and (2) contractor or national laboratory related activities (e.g., integration of melting rate model and 3-D melter model with existing glass algorithm to facility support operations). Although there are obviously additional technical scopes that support HLW facility operations (refer to Peeler et al. 2015a), this research and development plan focuses on those key activities that will allow for the continued development and provide the critical inputs for a mathematical model describing melting rate as a function of composition under various melter operating conditions.

With respect to the current ORP activities, the plan reflects the current status of using a preliminary 1-D cold cap model as the basis for continuous improvements. Key focal areas include (1) material property information as a function of temperature and heating rates, (2) cold cap and foam formation and stability as a function of temperature and heating rates, (3) defining and understanding critical mechanisms of heat transfer that control the batch-to-glass conversion process, and (4) in situ and 3-D mapping of cold caps using advanced analytical techniques such as X-ray computed tomography (CT) and ultrasound. Ultimately, the cold cap or melting rate model will be integrated into a 3-D model for the entire melter system to support facility operations.

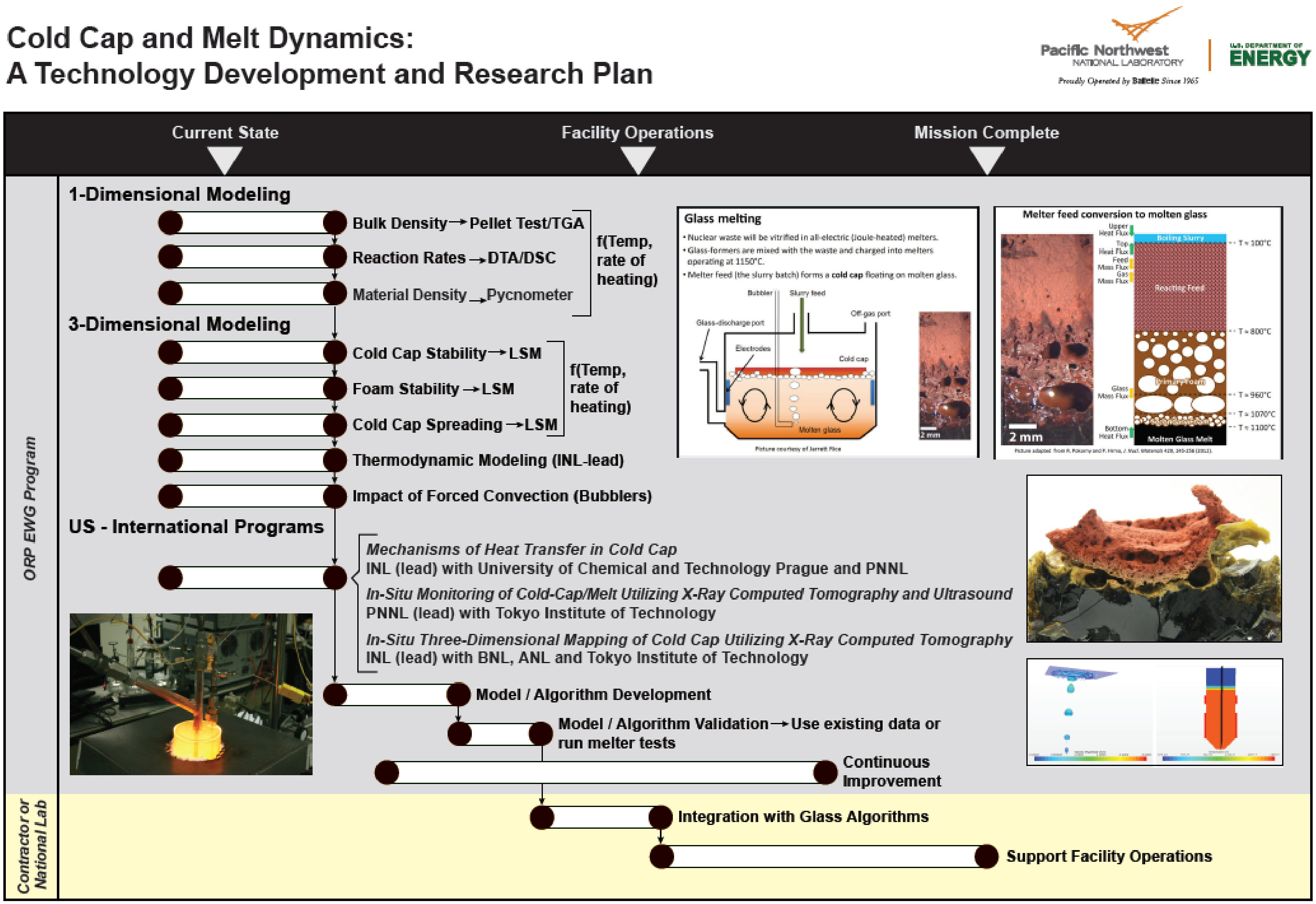

Figure 4. Cold cap and melt dynamics research and development plan to support the WTP mission.

5.1 One-Dimensional Cold Cap Model

Pokorny et al. (2012, 2014, 2015) describe a preliminary 1-D mathematical model for the cold cap in a melter for HLW vitrification, based on the schematic shown in Figure 3. The glass batch or melter feed is a heterogeneous mixture of multiple solids including GFCs and is fed onto the pool of molten glass, creating a cold cap. The 1-D model views the cold cap under a steady-state condition as a blanket of uniform thickness that receives uniform heat fluxes from both the molten glass below and the plenum space above; temperature, velocity, and extent of conversion are functions of the position along the only vertical coordinate. The 1-D mathematical model simulates this process by solving the differential equations for mass and energy balances with appropriate boundary conditions and constitutive relationships for material properties.

Under optimal steady-state conditions, each particle of the melter feed travels down through the cold cap. As the particle approaches the molten glass pool, the temperature increases, causing the particle to respond. As a result, feed properties such as density, dissolution rates of solids, and reaction kinetics, change with the vertical position within the cold cap. In other words, as the batch-to-glass conversion progresses, the temperatures, velocities, and extent of feed reactions are functions of a single variable: the position along the vertical coordinate with the origin located at the cold cap bottom.

Pokorny and Hrma (2012) describe multiple overlapping reactions that produce gases (H_2O, CO_x, NO_x, and O_2), liquids (molten salts and glass-forming melts), and intermediate phases or solids that occur during the melting process. Within the cold cap, the individual phases move with different velocities. Thus, for simplicity, the initial 1-D model treats the reacting mixture as consisting of just two phases: (1) the condensed phase (all solids and liquids) and (2) the gas phase. Each phase exchanges mass and energy with the other phase.

To solve energy (heat) and mass balance equations, material properties as functions of temperature and composition are needed. These properties such as heat conductivity and bulk density are parameters in the mass and energy balance equations, which, when coupled with boundary conditions, can describe heat transfer, chemical reactions, phase transitions, and other processes in the cold cap. These material properties can be measured on specific simulated melter feeds as described by Pokorny et al. (2012, 2014, 2015) and Hilliard and Hrma (2015). The following subsections describe some of the analytical techniques being used to determine the critical materials properties that provide inputs to the 1-D model for melting rate. Note that the research and development activities are focused on providing key data that can be used to improve the current 1-D cold cap model and ultimately develop a 3-D model for the melter to assess melting or production rate.

5.1.1 Bulk Density and Porosity

As mentioned, bulk density and porosity are key input parameters for any model to adequately describe the dynamics of the cold cap and potential impacts on heat transfer. Hilliard and Hrma (2015) and Pierce (2015) described details of the volume expansion tests (also referred to as the pellet test) from which bulk density and porosity data can be determined and represented as functions of temperature and heating rate for mathematical modeling. In general, a pellet of known composition, mass, and dimensions (approximately 13 mm in diameter by 6 mm high) is produced using a die tool and hydraulic press, by pressing dried (homogeneous) melter feed. The pellet is then placed in a furnace on an alumina plate. With a camera mounted in front of a viewing window on the furnace, the pellet is heated at a selected rate from room temperature to 1100°C to 1200°C. Photographs are taken at pre-determined intervals as the pellet contracts, expands, and ultimately collapses. A computational imaging of each photograph determines pellet profile area and volume. Figure 5 shows a series of photographs of the general batch-to-glass conversion process as a function of temperature.

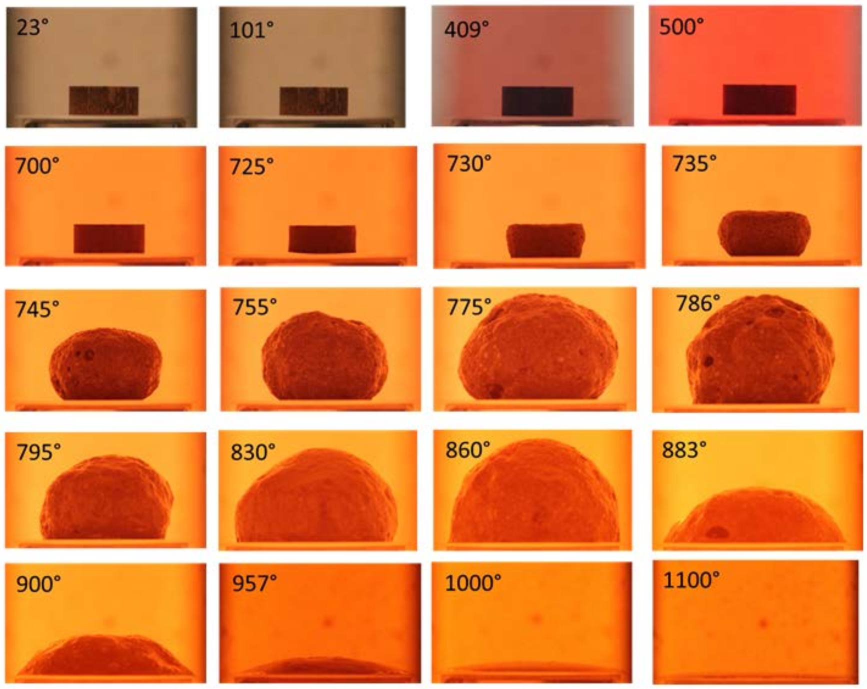

Figure 5. Volume expansion as a function of temperature for an advanced melter feed pellet.[1]

Density of the melter feed is estimated by pellet expansion data and from loose-batch data reported by Hrma et al. (2010). Figure 6 shows normalized profile area data (based on the pellet test) for a given melter feed as a function of heating rate. Pellet volume remains essentially unchanged through approximately 700°C, even though initial reactions occur and batch gases are evolving. These gases can still escape through open pores in the reaction layer. At approximately 700°C, the melter feed starts to shrink, with a low-temperature minimum normalized area (and thus volume) occurring around 800°C. Above 800°C, the glass-forming melt becomes interconnected and open pores turn into bubbles while gases continue to evolve—primary foam formation. As the temperature increases, the melt (or pellet) expands due to foam formation and eventually collapses between 900°C and 1000°C due to coalescence of bubbles into large cavities and rapidly decreasing melt viscosity. Henager et al. (2011) and Hilliard and Hrma (2015) describe the geometrical exercise of computing the pellet's normalized area as a function of temperature into the pellet's volume and porosity.

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[1] From B VanderVeer, P Hrma, Z Hilliard, D Peeler, and M Schweiger, Comparison of High Level Waste Glass Feeds Containing Frit and Glass Forming Chemicals, *WM Symposia 2016*, March 2016, Phoenix, AZ, Paper No. 16154 (in press)**.**

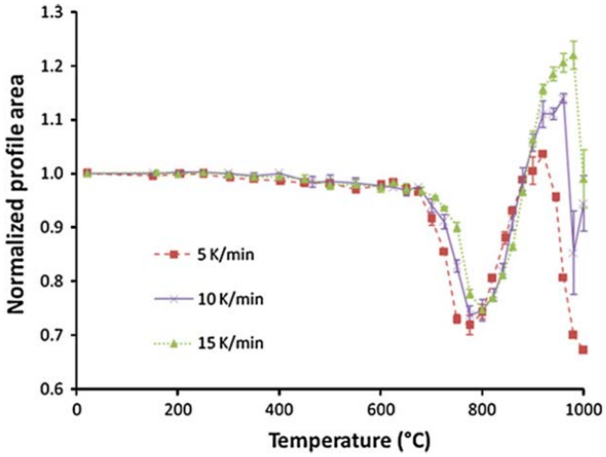


Figure 6. Normalized melter-feed area versus temperature measured at different heating rates.

Figure 7 provides similar information from the pellet test but identifies two critical temperatures: T_P (primary foam temperature) and T_M (primary foam collapse temperature). More specifically, as the temperature rises above T_P (which depends on the feed composition and its time-temperature history or heating rate), the feed starts to expand (or void volume increases). This indicates the temperature where the initial glass melt begins to trap evolved gases and primary foam formation begins. As the temperature increases, expansion continues until the gas-phase released exceeds its accumulation (e.g., maximum void volume), at which point the volume decreases until a bubble-free melt is formed at the primary foam collapse temperature (T_M).

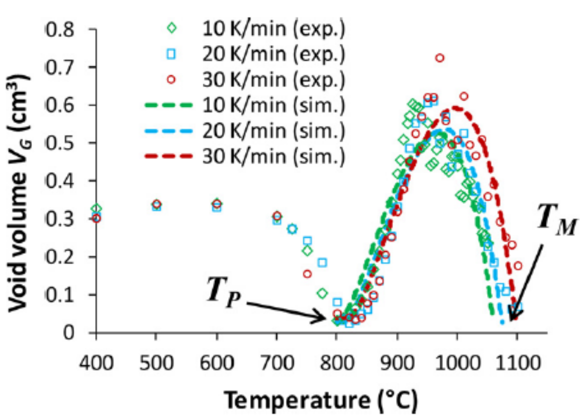


Figure 7. Gas phase volume versus temperature for various heating rates.

Determining the bulk density and porosity requires additional information about the conversion process. Based on previous discussions, batch-to-glass conversion is a kinetic process of colossal complexity. The material properties associated with this process, such as bulk density and heat conductivity, change in response to the changes in fractions, configurations, and chemical composition of the phases present. These parameters cannot be measured directly, which drives the use of various analytical techniques to gather such data. Hilliard and Hrma (2015) define bulk density as a function of temperature as $\rho_b(T) = m(T)/V(T)$; where mass (m) and volume (V) are functions of temperature. Based on the pellet test data, m(T) can be determined based on the pellet's initial mass (m_o) and the mass loss fraction for a given temperature (f (T)) – or m(T) = m_o[1 – f (T)]. The mass loss fraction as a function of temperature can be determined by thermogravimetric analysis. Figure 8 shows an example of the mass loss and mass loss rate for a simulated HLW feed from which bulk density can be determined.

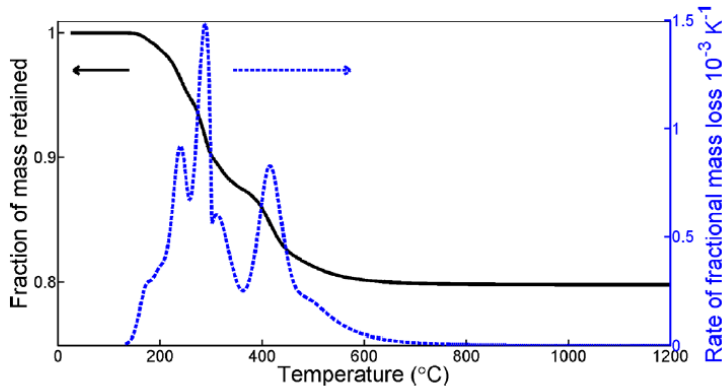


Figure 8. Mass loss and mass loss rate from an HLW feed heated at 10 K/min (from Hilliard and Hrma 2015).

Porosity, ϕ, is slightly more challenging to determine, but represents the ratio of the gas-phase volume, V_V, to the pellet volume V (or $\phi = V_V/V$). Hilliard and Hrma (2015) write this expression in terms of bulk density, ρ_B, and the material density (i.e., density of condensed phase; the gas phase is not included):

$$\phi(T) = 1 - (\rho_B(T)/\rho(T)) \quad (1)$$

5.1.2 Reaction Rates / Degree of Conversion

Figure 9 shows the mass loss fraction and the corresponding rate of gas-phase production together with the degree of conversion (inset) from Pokorny and Hrma (2012) for a given melter feed. As expected, the peaks shift to higher temperatures and the peak heights generally decrease as the rate of heating increases. Unfortunately, hardly any natural or industrial mixture has as many components or undergoes as many reactions as melter feeds during vitrification of nuclear wastes. Thus, at this stage, there has been no attempt to assess the mechanisms of individual gas-evolving reactions (both successive and simultaneous) from solid and liquid components, which include the release of chemically bonded water, reactions of nitrates with organics, and reactions of molten salts with solid silica.

However, assuming that the reactions are independent, a kinetic reaction model was developed to simulate the multiple gas-evolving reactions that occur during heating of an HLW melter feed. Although most of the gas-evolving reactions are completed at temperatures below 600°C, even at the fastest heating rates, the small shift of the reaction-rate peaks influences the melting rate by affecting the rate of foaming. Indeed, as Figure 6 shows, the extent of foaming increases as the heating rate increases.

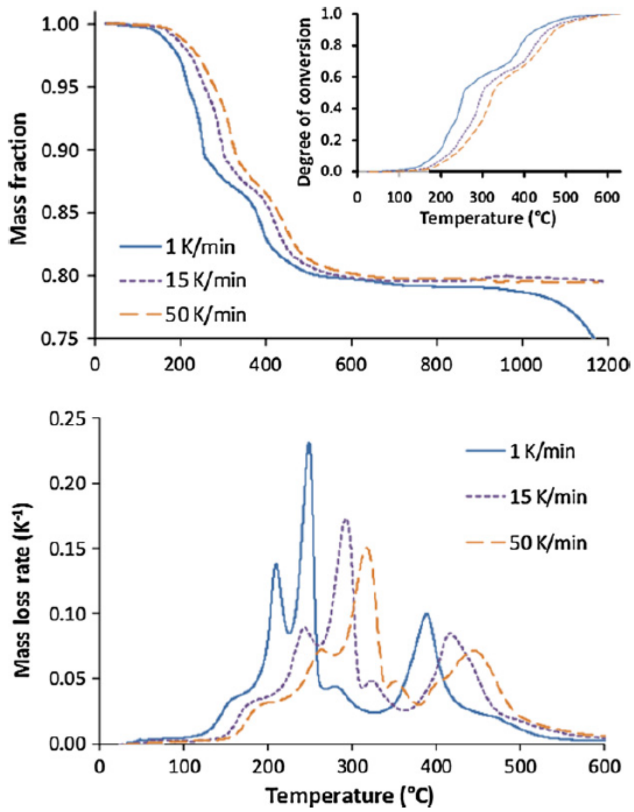


Figure 9. Melter feed mass loss, degree of conversion based on mass changes (inset), and mass loss rate versus temperature and heating rate (from Pokorny and Hrma 2012).

5.1.3 Heat Capacity

The effective heat capacity of the melter feed, c_p^{Eff}, is measured with a differential scanning calorimeter (DSC) (see Figure 10). The peaks on the effective-heat-capacity curves are associated with endothermic reactions, such as the release of bonded water or decomposition of carbonates. The c_p^{Eff} is the sum of the specific heat, c_p, and the reaction heat (Chun et al. 2013), that is,

$$c_p^{Eff} = c_p + \Delta H \mathrm{d}\alpha_H/\mathrm{d}T \quad (2)$$

where ΔH is the total reaction heat (J kg^{-1}) and α_H is the degree of conversion related to reaction heat. Following the reactions at ~600°C, c_p^{Eff} is assumed to have nearly a constant value of 1100 J kg^{-1} K^{-1} (because the DSC machine used is imprecise at higher temperatures). Clearly, the total heat necessary for the batch-to-glass conversion depends on the composition of the feed, especially on its free and bonded water content.

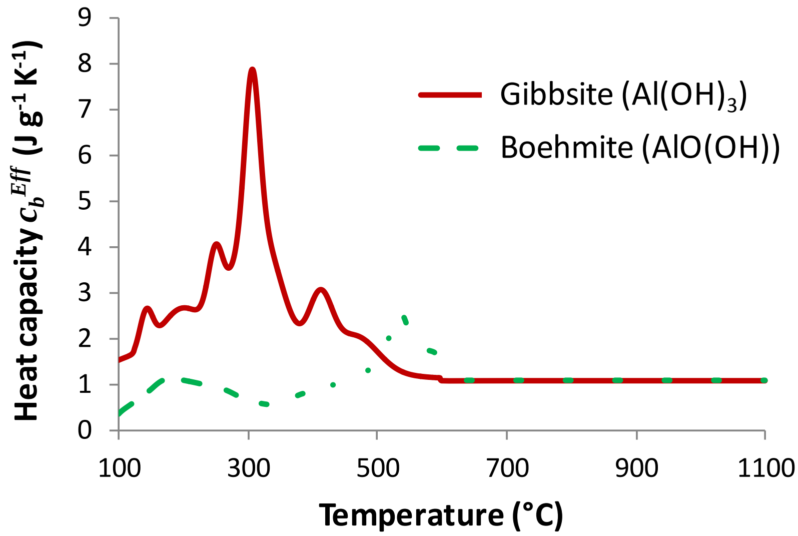


Figure 10. Effective heat capacities versus temperature for melter feeds with gibbsite ($Al(OH)_3$) (solid line) and boehmite (AlO(OH)) (dashed line) heated at 20 K min^{-1} (from Pokorny and Hrma 2014).

5.1.4 Impact of the Foam Layer

The equations for the preliminary 1-D model described by Pokorny and Hrma (2011, 2012) were numerically solved by the finite difference method, which allowed the temperature field within the cold cap to be calculated and the behavior of the cold cap under different boundary conditions to be evaluated. The input data for this preliminary model were obtained from feed melting crucible studies and literature data. The preliminary 1-D model was effective in performing sensitivity analysis of the effects of key parameters on the cold cap behavior, such as estimating the cold cap thickness at various heat fluxes from the molten glass and plenum space. The sensitivity analysis also provided insight into the phenomenon of batch foaming and its significant effect on the batch-to-glass conversion process and melting rate. Pokorny and Hrma (2011, p. 10.1) suggested that "for a reliable prediction of melting rate as a function of feed properties and melter conditions; future work has to focus on the behavior of the foam layer at the bottom of the cold cap and the heat transfer through it."

To address this issue, Pokorny et al. (2014, 2015) revised the 1-D cold cap model to include a functional representation of the primary foam behavior and to account for a dry cold cap surface. That study computed the melting rate as a response to dependence of the primary foam collapse temperature on the heating rate and melter operating conditions, including the effect of bubbling (forced convection) on the cold cap bottom and top surface temperatures, as discussed in the next section.

5.1.5 Impact of Forced Convection (Bubblers) on the Cold Cap

The introduction of bubblers in waste glass melters has significantly increased the melting rate (Perez et al. 2005; Matlack et al. 2008, Matlack and Pegg 2013), for the following reasons:

1. Bubbling generates powerful forced convection in molten glass that greatly exceeds natural convection driven by buoyancy (see also Section 5.4). This causes velocity and temperature gradients below the cold cap to become steeper. As the temperature at the cold cap bottom rises, more heat is delivered to the cold cap, producing more glass per unit time and area.
2. Large bubbles from bubblers sweep away the insulating secondary foam layer from beneath the cold cap, further increasing the transferred heat.
3. With strong bubbling, the cavity layer, into which the primary foam gas is released, can be displaced together with secondary foam, exposing the primary foam to the upwelling hot glass. Primary foam then collapses faster, allowing more heat to be delivered to the cold cap.
4. Feed can be stirred into the melt at the edges of vent holes that open above the bubblers, exposing a fraction of the feed to high temperatures at which batch reactions are rapid and gases are quickly released if the viscosity is low enough.
5. Bubblers can increase the temperature above the cold cap by bringing hot gas to the plenum space and by exposing the plenum space to the hot melt in the vent holes. The augmented heat flux to the cold cap from the plenum space helps increase melting rate.

With respect to modeling, bubbling changes the boundary conditions for the top and bottom surfaces in the cold cap. Under bubbling conditions, Pokorny et al. (2014) suggested that the rate limiting or critical batch-to-glass conversion process is the progress of growth and collapse of the primary foam. This requires reexamining the concept of uniform melting temperature, typically used in literature, in favor of relating the cold cap bottom temperature to the growth and collapse of primary foam as the terminal conversion process.

The kinetics of primary foam evolution and decay has been studied using volume expansion experiments with the feed, and can be expressed in the form of the gas-phase balance (Pokorny et al. 2015):

$$\frac{\mathrm{d}V_G}{\mathrm{d}t} = R_E - R_C \tag{3}$$

where V_G is the volume of gas in the foam (in the case of monitoring the volume a feed pellet), $\mathrm{d}V_G/\mathrm{d}t$ is the rate of change in the pellet void volume, t is the time, R_E is the gas generation rate (leading to foam expansion), and R_C is the gas release rate to the atmosphere (governing foam collapse). Three sources of foam expansion exist: residual batch gases, thermal expansion of existing gases, and oxygen generation from redox reactions. On the other hand, the gas release rate is controlled by the thinning of the liquid films that separate the foam bubbles, leading to coalescence (internal collapse) and opening the foam cells to the atmosphere. The main factor that destabilizes the films separating bubbles from one another and from the atmosphere is the decrease in viscosity caused by increasing temperature. Figure 7 shows the results of the kinetic model fit.

Implementing the dynamic behavior of the foam layer into the cold cap model could allow the melting rate to be estimated as a function of measured feed properties and cold cap boundary conditions (which has to be supplied by the full 3-D melter model, Section 5.4).

5.1.6 Effectiveness of Current Model

The estimates for the melting rate and cold cap temperature profile reasonably agree with data from laboratory-scale and pilot-plant studies (Pokorny et al. 2014, 2015). Figure 11 shows the simulated dependence of melting rate on cold cap bottom temperature T_B, calculated for T_T values between 200°C and 400°C to cover the possible range of cold cap surface temperatures. The results show that the melting rate strongly increases with increasing T_T and T_B, reaching up to ~2500 kg m^{-2} day^{-1}. This agrees well with experimental observations that report faster melting rates for higher melter operating temperatures and increased bubbling, as both of these effects increase the temperature directly at the cold cap/molten glass interface (cold cap bottom) (Pokorny et al. 2014). According to pilot-plant data, bubbling increased the melting rate to as high as 2200 kg m^{-2} day^{-1} (Matlack et al. 2010). A better comparison will be provided once the cold cap model is implemented into the melter model, as only the coupled model can provide the correct boundary conditions, T_T and T_B (i.e., the temperatures at plenum space/cold cap and cold cap/molten glass interfaces).

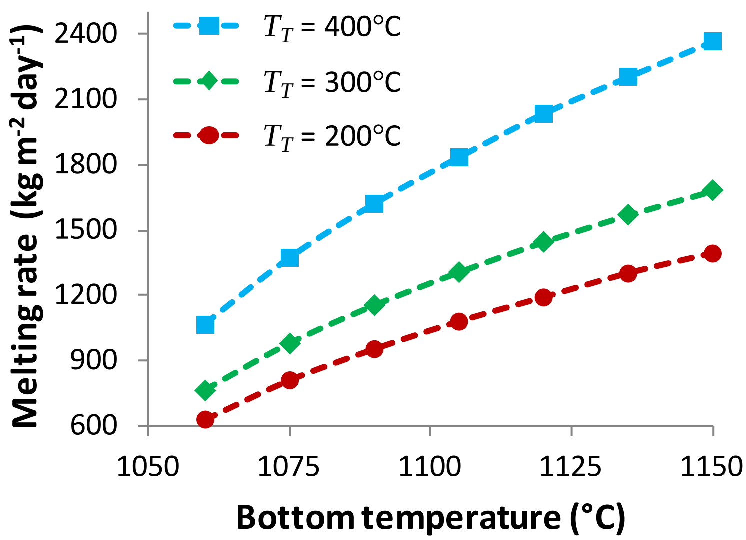


Figure 11. Melting rate versus cold cap bottom temperature, T_B, for various values of cold cap top temperature, T_T.

Figure 12 shows the cold cap temperature profile in a laboratory-scale melter (LSM; see Figure 13), together with the simulated temperature profile. Because the temperature profile in the LSM cold cap was only measured after quenching, it had to be adjusted to the profile during melting. This was done by assuming that the primary foam layer thickness shrank by 60%. The small difference in the measured and simulated temperature profile was likely caused by additional melting and feed compaction during sample quenching.

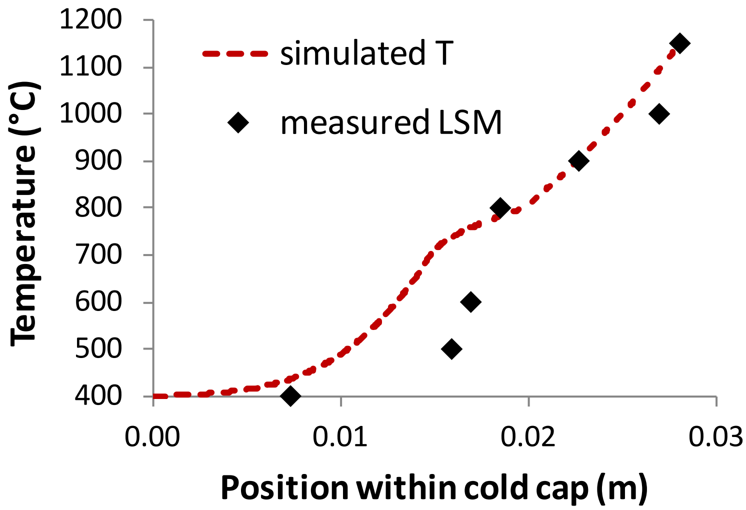


Figure 12. Comparison of the simulated temperature profile with the profile measured in a cold cap produced in the laboratory-scale melter.

Although the model predictions for the melting rate and cold cap temperature profile reasonably agree with data from laboratory-scale and pilot-plant studies, the model still has limitations:

- The 1-D cold cap model represents the major part of the 3-D cold cap reasonably well as long as the velocity field inside the cold cap remains one-dimensional. However, this may not be the case around vent holes and fissures in the cold cap, which often occur in current melters when there is strong bubbling from bubblers.
- At this point, the model still rests on data obtained for a particular waste stream, denoted as A0 (a simplified, high-Al HLW feed). Validating the model for other HLW or even LAW feeds is essential to ensure the best possible functionality of the combined cold cap-melter model.

Several scopes are being performed under the current program to address these issues. The validity of the 1-D cold cap model is being tested by LSM experiments (see Section 5.2.1) and feed and cold cap rheology studies (Section 5.2.2). Additionally, the material properties described in Section 5.1 are currently being measured for other HLW feeds. These data will be used to validate the model across a broad range of different HLW (and possibly LAW) melter feeds.

5.2 Three-Dimensional Modeling

As discussed in the previous section, the research has currently focused on developing a 1-D reactive-transport model for melting in a non-actively bubbled melter (see Pokorny and Hrma 2014) or actively-bubbled melter (Pokorny et al. 2015). This model relies on data such as the conversion enthalpy of the feed, the temperature at the bottom of the cold cap, the fraction of heat flux to the cold cap from above, and the foaminess of the feed. Although the model results reasonably agree with both laboratory- and pilot-scale experimental data, the model uses several simplifying assumptions, including the assumption that the melting of the feed in the cold cap can be described as a 1-D process. Additional work is thus ongoing to validate and extend the 1-D model to a pseudo 3-D model. In such a 3-D model, the 1-D model will be used to predict the melting rate and other cold cap properties as a function of position and time, using the appropriate boundary conditions provided by the 3-D melter model. The following subsections provide a high-level overview of the key technical areas the integrated program is focused on as the 1-D model evolves to a more complex, dynamic 3-D model.

5.2.1 Laboratory-Scale Melter: Cold Cap and Foam Stability

Temperature distribution within the cold cap is a key parameter that influences when and where key reactions occur. Ultimately, these reactions lead to the formation of the primary reaction zone and the foam layer (primary, cavities, and secondary) and thus play a key role in defining the melting rate of a given melter feed. Because it is impractical to directly measure the temperature field within the cold cap of a large melter, an indirect method has been developed that can map the textural features of the cold cap as a function of height or position. These textural features can then be used to correlate the temperature distribution within the cold cap using heat-treated feed samples of nearly identical structures at known temperatures. This temperature profile can then be compared to the mathematically simulated profile generated by a cold cap model.

Figure 13 shows the LSM that is currently being used to assess thermal profiles within the cold cap as well as the formation and stability of the cold cap—including the primary reaction layer and the foam layers. The LSM is a fused-silica crucible that simulates the glass heating process by partially submerging the crucible into the furnace hot zone. Because the LSM lacks a discharge port for molten glass, the furnace is periodically adjusted to maintain a constant cold cap, which is observed through the top of the transparent crucible. In general, 100 to 200 g of crushed glass (targeting the composition of the melter feed) is placed in the bottom of the crucible and heated to 1100°C to 1200°C. Once a molten glass forms, the melter feed is pumped into the crucible at a fixed charging rate (e.g., 7.5 mL min^{-1}). The slurry or melter feed is continuously fed to the crucible for a given time (~30 to 45 minutes depending on feed rate) while raising the furnace to maintain a constant cold cap (i.e., keeping the cold cap just outside the primary heat source). The feed nozzle is cooled by 10°C chiller water. The off-gas passes through the off-gas condensate column with an exhaust port vented to a fume hood. After the test, the feed pump is turned off and the crucible is removed (while at temperature) from the furnace and rapidly cooled by quenching on a large copper block. Once cool, portions of the cold cap can be obtained and analyzed.

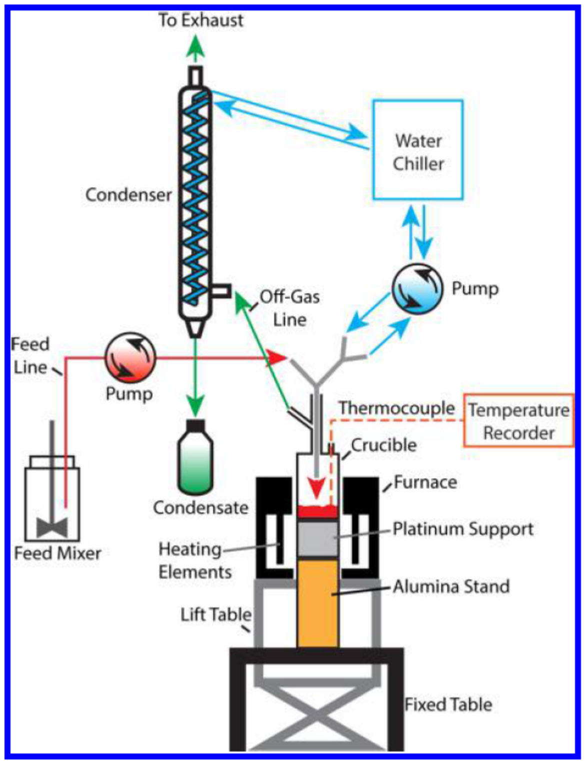


Figure 13. Schematic of the laboratory-scale melter.

Figure 14 shows an example cross-section of a cold cap obtained from an LSM test (see Dixon et al. 2015 for more details). Figure 14a clearly shows the transition of unreacted or dried melter feed through the primary reaction layer (portion of sample containing bubbles and voids) to the glass product (black glass at bottom). Figure 14b is an enlarged, polished subsample (insert from Figure 14a) of the cold cap showing the transition of primary reaction layer to the foam layer.

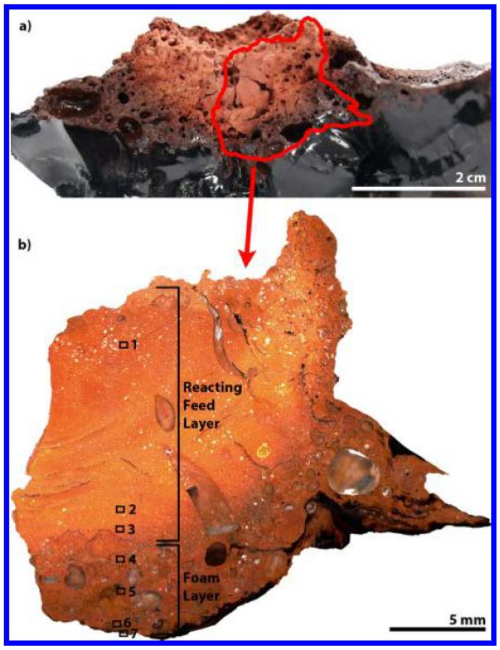


Figure 14. Example of cold cap cross-section obtained from LSM (from Dixon et al. 2015).

The LSM platform has been used to assess the effect of charging rate on the cold cap structure (Dixon et al. 2013), comparing the cold cap features with heat-treated feed samples (Dixon et al. 2014), and determining the temperature distribution within the cold cap (Dixon et al. 2015). The LSM also will be used to assess the stability of the cold cap and foam layers for different melter conditions (e.g., bubbling or non-bubbled) and feed compositions. All of this information is critical for the successful development of the 3-D model.

5.2.2 Feed and Cold Cap Rheology

One of the most important assumptions of the cold cap model is that the feed in the cold cap moves downward, allowing the conversion to be modeled as a 1-D process. To confirm this hypothesis, and to understand the spreading of the slurry and formation of the cold cap in melters of various scale, the rheology of the melter feed is studied. While initial rheology studies focused on the viscosity of the feed above 750°C (Marcial et al. 2014), current work focuses on measuring the yield stress and viscosity of the feed across the whole temperature region, including the slurry fed into the melter.

The initial results (Figure 15) show that the rigidity of the slurry feed strongly increases with decreasing water content. This demonstrates that the slurry feed has to spread over the cold cap surface before a significant portion of the water is evaporated. Further testing is focusing on the rheology properties (viscosity, yield stress, creep testing) of melter feed after the slurry dries.

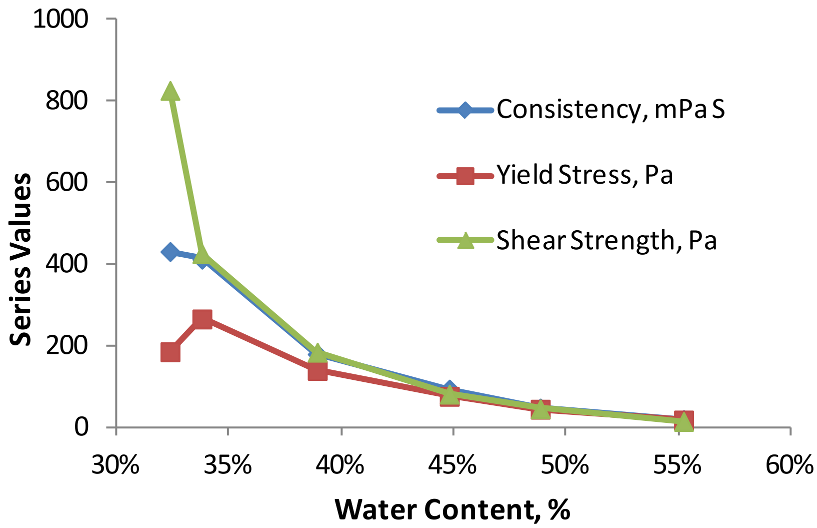


Figure 15. Yield stress, shear strength, and consistency of slurry feed at different water content.

5.3 U.S. – International Programs

5.3.1 Mechanisms of Heat Transfer

Understanding the heat transfer into the incoming feed is crucial to reliably predicting melting rate and cold cap behavior. The UCT Prague is focusing on several issues related to heat transfer:

- **Cold cap formation and slurry water evaporation.** This task is studying water evaporation and slurry spreading. Pokorny et al. (2014) recently reviewed literature for the heat flux from the plenum space gas (combined conduction, convection, and radiation). According to Trier (1987), the heat supplied to the batch in commercial melters operating at 1400°C to 1600°C is typically ~45 to 80 kW m^{-2}. In a waste glass melter equipped with plenum heaters (e.g., the joule-heated melter at the Defense Waste Processing Facility in Aiken, SC), the plenum space temperature ranges from 700°C to 900°C and the heat transfer from plenum space directly to the cold cap is ~30 kW m^{-2} (the rest of the heat for melting comes from the electrodes). Without plenum heaters and at a plenum space temperature of ~500°C, it was argued that the heat flux from plenum is approximately Q_U = ~10 kW m^{-2}. However, the heat flux necessary to evaporate the water and heat the dry feed to 400°C is, at melting rate of 1500 kg m^{-2} day^{-1}, ~80 kW m^{-2}. Thus, the heat flux from the plenum space represents only 15% of the flux needed. Understanding where and how water evaporates is necessary to predict the time-temperature history of the melting feed. This work will be also supported by a study of the rheological impacts, which will help to understand the spreading of the water slurry on the cold cap surface.

- **Heat transfer in the foam layer.** The heat transfer into the cold cap through the foam layer determines the rate of melting. However, precise simulation of the heat transfer is a daunting task. To simplify the problem, the current cold cap model uses the kinetics of foam evolution and collapse, experimentally measured in the laboratory (see Section 5.1). This simple approach takes advantage of the fact that the measured foam evolution and collapse is related to the amount of heat transferred into the foaming batch during the experiment. However, a more in-depth study of the heat transfer in the foam layer is underway, which if successful could replace or complement the current foam kinetics model. This model will use the statistical morphology of bubbles obtained from X-ray tomography (see Section 5.3.2) and numerical heat transfer models for two-phase media.

5.3.2 In Situ Monitoring of Cold-Cap/Melt with X-Ray Computed Tomography

X-ray CT is capable of mapping the 3D bulk of a sample by capturing 2D X-ray images of the sample at various angles. Phases of various densities can be spatially resolved if the collection time is short enough compared to time scales associated with density variation within the sample. X-ray CT of reacting feeds can provide detailed and unique information about the stages of foaming occurring and the morphology of the melt (see Figure 16).

Data from X-ray tomography provides insight into the topology of bubble distribution within the foaming feed at various temperatures. Six different glass formulations were sent to the Tokyo Institute of Technology for X-ray tomography to examine batch reactions during heating. Batches of A19-original feed were used to study the effects of quartz particle size. The A19 modified feeds (designated A19-0 to A19-9) were formulated to study the foam dynamics for different final melt viscosities.

For the study performed above a joule-heated furnace with a rotating stage allowed for the capture of X-ray CT images of pellets heated at 10°C min^{-1}. These pellet tests in the X-ray CT-equipped furnace are analogous to the pellet tests performed at PNNL and monitored by camera to give surface area and volume approximations. The images collected by Yano (2015) can be used to verify the volumes calculated at PNNL, as well as to characterize bubble size distributions.

Professor Yano will use computational software to characterize the distribution of bubbles in the reacting feeds at various temperatures. As discussed in Yano 2015 and Johnson et al. 2014, the void distribution of X-ray CT constructions can be calculated to a fine precision with available software. Knowledge of the sizes and distribution of these bubbles can give information on heat transfer into the cold-cap, as in Wang and Penn 2008, and thus melting rate.

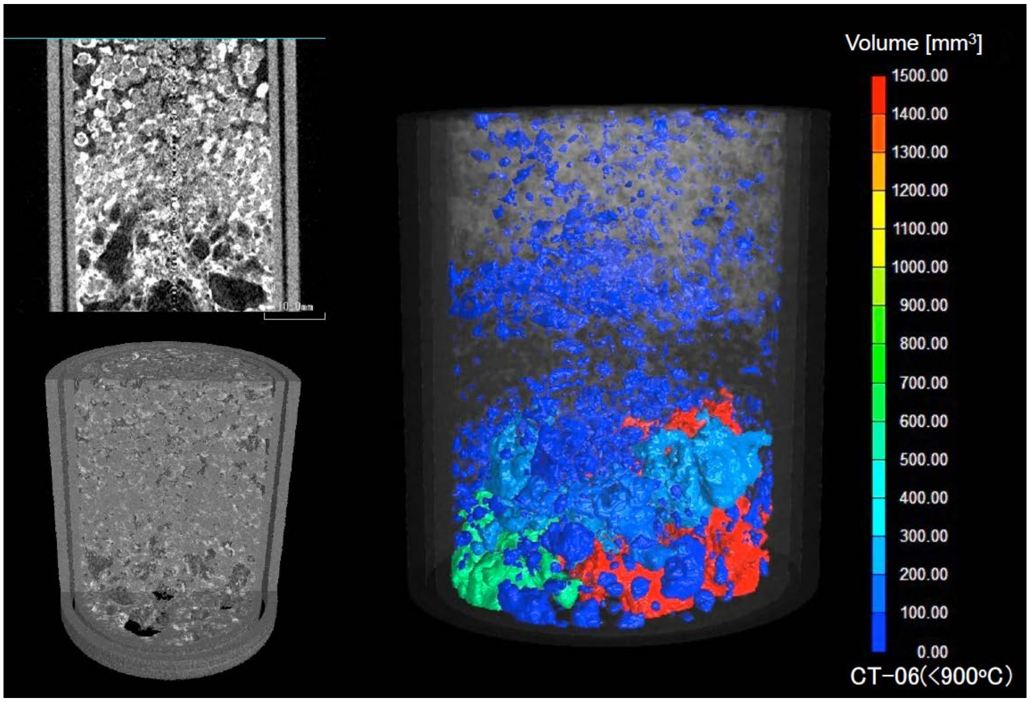
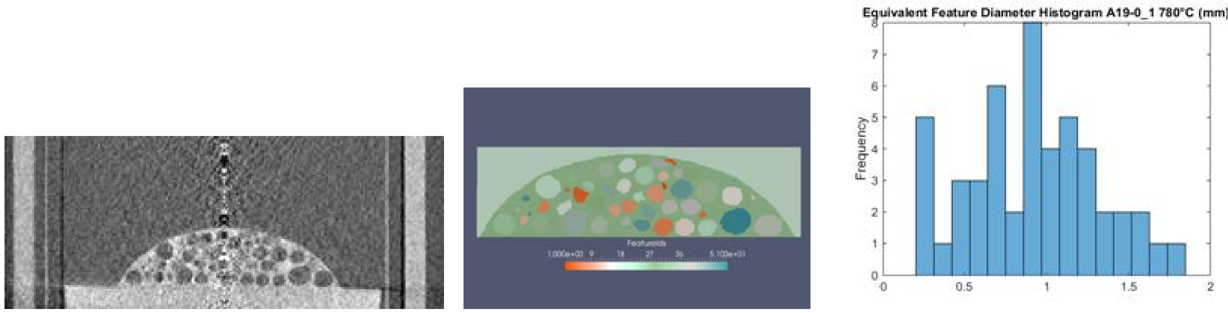


Figure 16. Computationally resolved bubble morphology in a quenched cold cap. Taken from Yano 2015.

Additionally, 2-D images through a cross-section of the melting pellet were provided for each formulation at 20°C increments from 600°C to 1040°C. The images were manually thresholded to capture features of interest, then processed by software to obtain statistics to characterize bubble topology (Guillen et al. 2016). The formulation A19-0_1 at 780°C gives an example of this process. Figure 17a shows the original image obtained from X-ray tomography. Figure 17b provides an enhanced image to identify features of interest. Figure 17c shows the feature statistics, in this case, the equivalent diameter of the bubbles. Additional statistics being obtained include total pellet volume, porosity, and bubble morphology as a function of temperature. These statistics will be used to compare the melting behavior of the different glass formulations as a function of temperature. An integrated experimental-computational approach is being used to produce statistically induced, realistic instantiations that represent the actual parameters and their distributions (Groeber et al. 2008). As mentioned above, this information can help generate heat transfer and melt rate models. In the case of a dynamic system, bubble formation from generated gases may be able to be distinguished from residual gases moving down the cold cap (see Section 5.3.1). The sensitivity and uncertainty of model parameters on conversion rate will be quantified.



(a) (b) (c)

Figure 17. X-ray CT image of A19-0 glass at 780°C: (a) original image, (b) enhanced image, and (c) bubble size statistics.

Further work with X-ray CT technology may give more valuable information. Dynamic imaging of systems that can be approximated as two phases is possible in real time, as in Myers et al. 2011. With suitable assumptions about the division of phases, water flowing through glass beads was resolved into a "4-D" reconstruction that mapped the flow of water in the sample in three dimensions across time (the 4^{th} dimension). Such a technique may be suitable for imaging bubblers operating under a cold cap. This would provide real-time information on the action of the bubblers without the distortion caused by quenching. This may provide the type of data on bubble motion that is called for in Section 5.4.

5.3.3 Three-Dimensional Mapping of Cold Cap Using X-Ray Computed Tomography and Beamline Technology

Understanding the morphology of the cold cap can greatly inform models, which can in turn help to predict and improve the glass production rate of the waste glass melter. The foam layer, especially its interface between the cold cap and the glass melt, is especially important and obscure. This interface is assumed to occur at the glass melt viscosity at which the foam bottom is ripped from the foam layer by the convective current in the melt pool. The temperature at the foam-melt interface is a key characteristic needed for an adequate mathematical model of the feed-to-glass conversion within the cold cap. Unfortunately, this layer proves too evanescent to be captured by quenching the cold cap even by the LSM. As a result of its evanescence, the foam layer in a quenched crucible is not representative of the foam layer in the active cold cap.

The solution to the foam-melt interface problem is to use X-ray CT to image the foam layer in an operating melter, preferably an LSM. The work done already by Yano shows that foaming in pellet tests can be satisfactorily captured *in situ*. What remains is to adapt this technique to a LSM-type melter. While an LSM is similar in diameter to the furnace equipment already used by Yano, modifications will be needed. Principally, the X-ray CT source and detector would have to rotate around the furnace (rather than allow the contents of the furnace to rotate), which would have to remain stationary due to the complexities of the feed nozzle, the air bubbler, thermocouples and off-gas system that attaches to it. If these requirements be accommodated, direct measurement of the foam layers, cavities, and air bubbles possibly could be imaged during the melter operation.

X-ray absorption fine structure (XAFS) can be used to monitor the motion of glass melts in real-time as well. The convection of the glass melt is similarly an important factor in understanding the flow of heat in models of the melter. Okamoto et al. 2013 observed a melt using X-ray projections (not CT), monitoring an energy specific to a Ru tracer that was added to the glass. The elemental sensitivity of this technique allowed the Ru to be imaged as it settled to the bottom of the glass melt over time. Tracers may similarly be used to monitor convection in the glass melt in an LSM, which could provide important data that might improve the melter model. Similarly, the elemental distribution of some elements could be tracked through the cold cap and melt across time, providing a deeper understanding of the incorporation of troublesome elements such as Tc.

Future studies using small X-ray scattering (SAXS) are being planned to investigate inhomogeneities in the glass, especially the presence of particulate phases. The feed (a combination of tank waste and finely powdered glass additives mixed together in a water-based slurry) is charged into the melter on the top of the molten glass, where it forms the cold cap. Research has been ongoing for several years to characterize the cold cap by measuring chemical reaction processes, melt connectivity temperature, foaming (void fraction expansion), volume expansion of cold cap, heat capacity, and viscosity of reacting components. The melt from the cold cap is not fully homogenized, since it contains dissolving solids (quartz particles). Mixing in the melt pool promotes homogenization by exposing the melt to velocity gradients that allow diffusion to smooth concentration differences. Insufficient homogeneity can cause crystallization, phase separation, and uneven dissolution in an aqueous environment. The effects on glass durability are especially important for nuclear waste compositions that are diverse, have maximum waste loading, and have minimum residence time in the melter. Nuclear waste glasses have not undergone a thorough investigation of the final product to determine homogeneity. It is important that homogeneity be determined for evaluating various glass melting technologies, such as joule-heated melters and hot and cold crucible melters of various scales, with or without bubblers, to determine the effect of each technology. A homogeneous glass product is necessary to prevent unacceptable levels of corrosion of the material in a waste repository.

Experiments have been conducted at the Stanford Synchrotron Radiation Lightsource (SSRL) in collaboration with scientists at Lawrence Berkeley National Laboratory and the Advanced Photon Source (APS). The experiments at SSRL were performed with radioactive samples that included technetium, whereas the APS experiments were conducted on non-radioactive glass samples. The SSRL experiments identified and quantified the oxidation state of radioactive ^{99}Tc in a series of simulated nuclear waste glasses. Additionally, these studies used chemometric modeling to investigate the localized structure of the Tc in the glasses. At APS, XAFS was performed to identify the oxidation states of Fe, Zn and Zr and x-ray fluorescence mapping was conducted to identify the presence of phase separation. The data is being analyzed and evaluated. Well characterized reference materials were obtained from the National Institute of Standards and Technology and the Smithsonian for use in calibrating the data. These initial results will be used to inform future studies. Additional glass compositions are being identified for examination. Different software and training are required for XAFS versus SAXS data analysis. There are plans for thermodynamic modeling studies to compare predicted with measured glass compositions.

5.4 Three-Dimensional Melter Model

Idaho National Laboratory is leading the effort to develop a high-fidelity heat transfer model of a joule-heated ceramic-lined melter to better understand the complex, inter-related processes occurring with the HLW and LAW melters. The glass conversion rates in the cold cap layer depend on promoting efficient heat transfer from the melt pool to the cold cap. A CFD model of the melter is being developed to investigate the processes affecting melt rate (Guillen and Beers 2015). Prior modeling studies have shown that the thermal convection currents within the melt pool due to joule heating supplied by the electrodes are substantially altered by forced air bubbling (Matlack et al. 2002, Hodges et al. 2012). In practice, heat transfer is augmented by inserting air bubblers into the molten glass. Increased melting rates result from improved heat transfer from the glass pool to the cold cap. Adding bubblers increases glass circulation within the melt pool and agitates the melt surface to break up insulating foam layers in the cold cap. Heat from the molten glass is continually supplied to the cold cap/glass interface, where it is used to drive the cold cap reactions (Pokorny et al. 2015). Bubbling also increases heat transfer to the plenum, which provides heat to the cold cap from the atmosphere above.

Knowledge of the bubble characteristics in the molten glass is needed to accurately model the flow and heat transfer within the melter. Specifically, modeling of the bubbling directly relates to the convective heat transfer effects of the melter. Larger bubbles breaking the liquid surface create waves and disturbances at the glass-cold cap interface, which distributes heat more rapidly through convection.

However, the computational simulations must be validated to provide confidence in the solutions. Experimental data from laboratory- and pilot-scale tests are being used to inform and validate the model. A validation hierarchy has been developed wherein the melter physics are decoupled into smaller systems to validate individually, then built up methodologically from unit problems to benchmark cases to subsystem cases to the complete system (Guillen and Abboud 2016). The strategy behind this tiered approach is to assess how accurately the computational results represent the real world system (Oberkampf and Trucano 2000). For example, test cases have substituted molten glass for a simulant liquid with similar density and viscosity at room temperature to study mixing through bubbling as an isolated effect without considering the heat transfer dynamics. Figure 18 illustrates the formation of large bubbles that detach from the orifice and rise to the free surface. In the full-scale melter, this disruption of the free surface by bubbling will affect the convective heat flux into the cold cap layer. The simulation results are compared to experimental data obtained by the Vitreous State Laboratory (VSL) at the CUA. The data that is provided by the experiments is the projected area of the bubbles at the liquid surface. The results are shown in Figure 19, where the experimental data with its standard deviation is plotted with X's and the simulation data is plotted with circles. For all cases performed at various nozzle depths and bubble flow rates, simulation data is agreeable with experimental data within the standard deviation reported. This result validates that the volume of fluid method should be sufficient for continued use in the melter simulations.

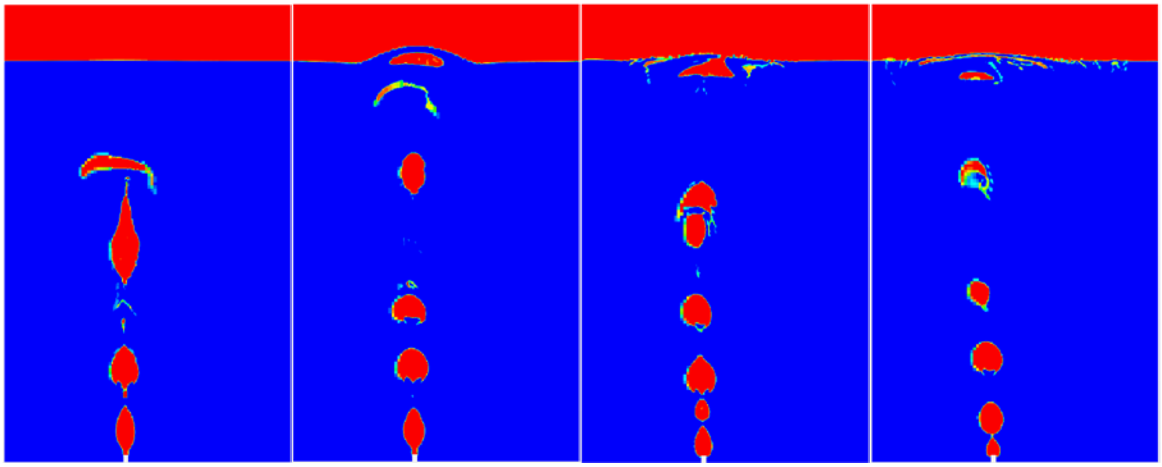


Figure 18. Injected bubbles rising towards the free surface; red represents volume fraction of air.

Another test case is simulating the DM100 melter to assess the modeling software's fidelity to predict the thermal gradients produced by ohmic heating. CFD modeling is being used to understand the system's heat transfer dynamics and to provide insight to optimize the process. The first iteration of the small DM100 melter was built with a negligible mass of air bubbling, such that the ohmic heating is a dominant force over any convective currents in the system. As part of the validation procedure, the mass flow of air bubbling will be ramped up in accordance with prior studies by VSL to compare the thermal gradients at different bubbling rates.

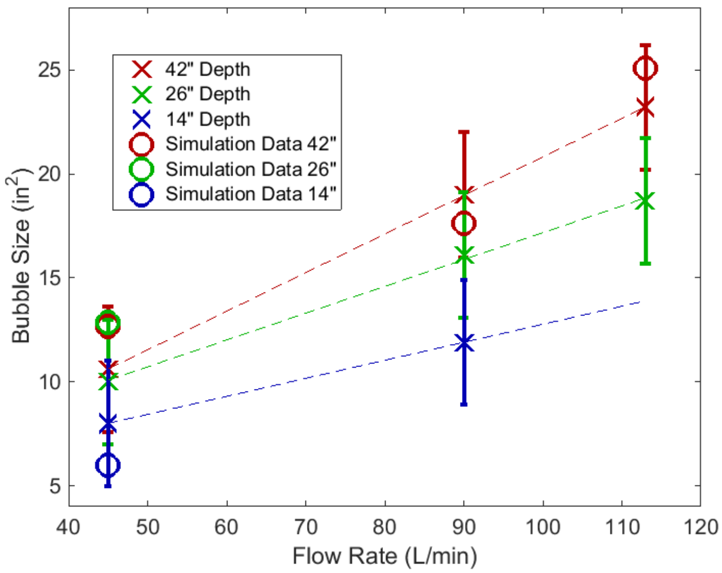


Figure 19. Comparison of projected bubble surface area in simulations to experiments.

Figure 20 shows several properties of the small-scale melter near startup in a centerline slice that is in-line with the electrode locations. Figure 20a shows the voltage in melter that is applied from the side electrodes. In this case with no bubbling, a constant 30.7 V is applied across the electrodes. Figure 20b shows the corresponding current field in the melter. The current field is symmetrical in the plane shown, and does not penetrate into the plenum region. The joule heating provided to the molten glass should be directly proportional to the current field. Figure 20c shows the molten glass, cold cap, and plenum regions of the melter in red, green, and blue, respectively. Figure 20d shows the temperature, the plenum, and molten glass regions are initialized to typical experimentally measured values, and the cold cap region is initialized with a temperature gradient consistent with an experimental study (Dixon et al. 2015). In this early stage of the simulation, the molten glass temperature is nearly constant, and heat from the cold cap region starts to cause temperature gradients in the nearby plenum.

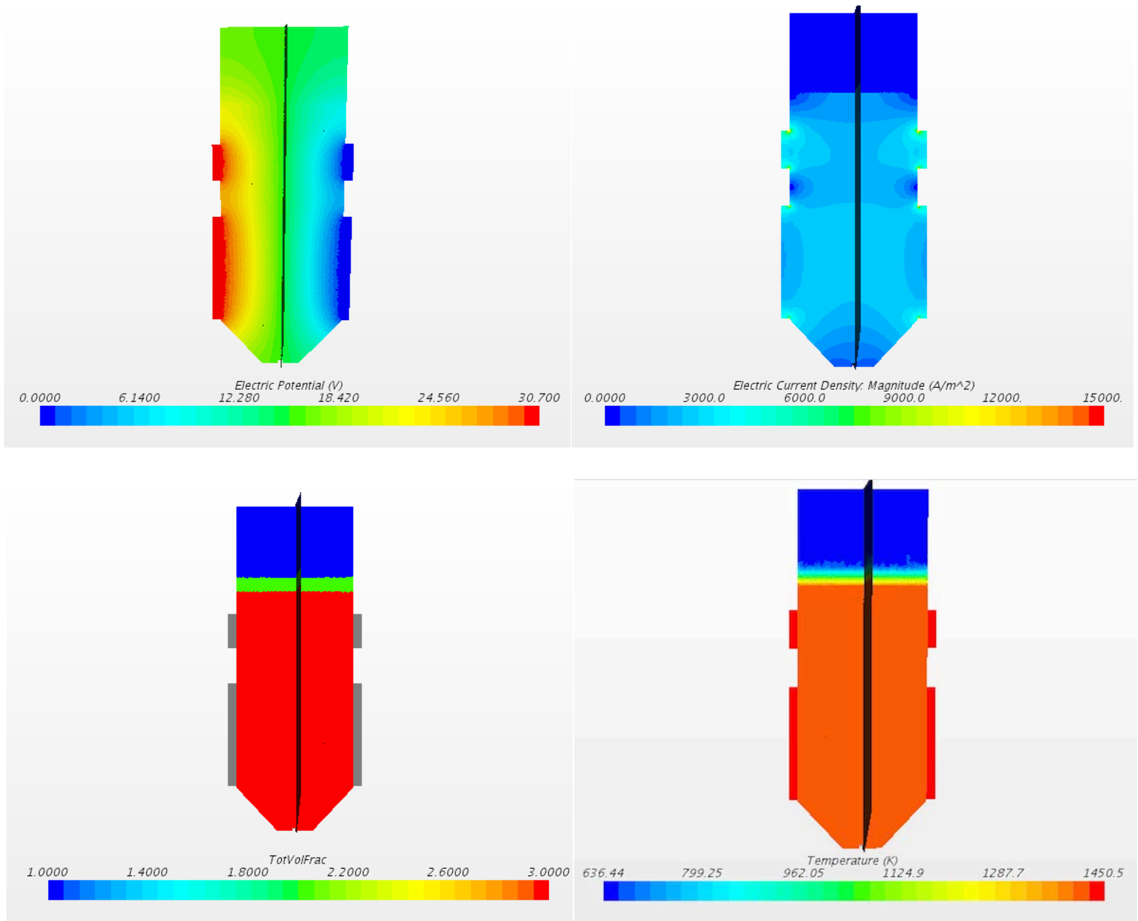


Figure 20. Images of (a) electric potential, (b) electric current, (c) volume fraction, and (d) temperature for the DM100.

The results from these two tests are part of the larger validation hierarchy that is planned for the study. Figure 21 shows a current layout of the validation hierarchy, which is built in increasing levels of complexity to model separate, mixed, and integral effects. The inert bubbling case is a part of the unit tests for the problem, and the simplified DM100 case is part of the benchmark cases. The validation hierarchy also contains efforts (discussed previously) to better describe the cold cap for incorporation into the melter model. At the top of the hierarchy is the long-term goal for the full WTP model. Prior to building this model, the subsystem DM100, research-scale melter (RSM), and complete system DM1200 need to be validated to provide confidence in the overall WTP melter model.

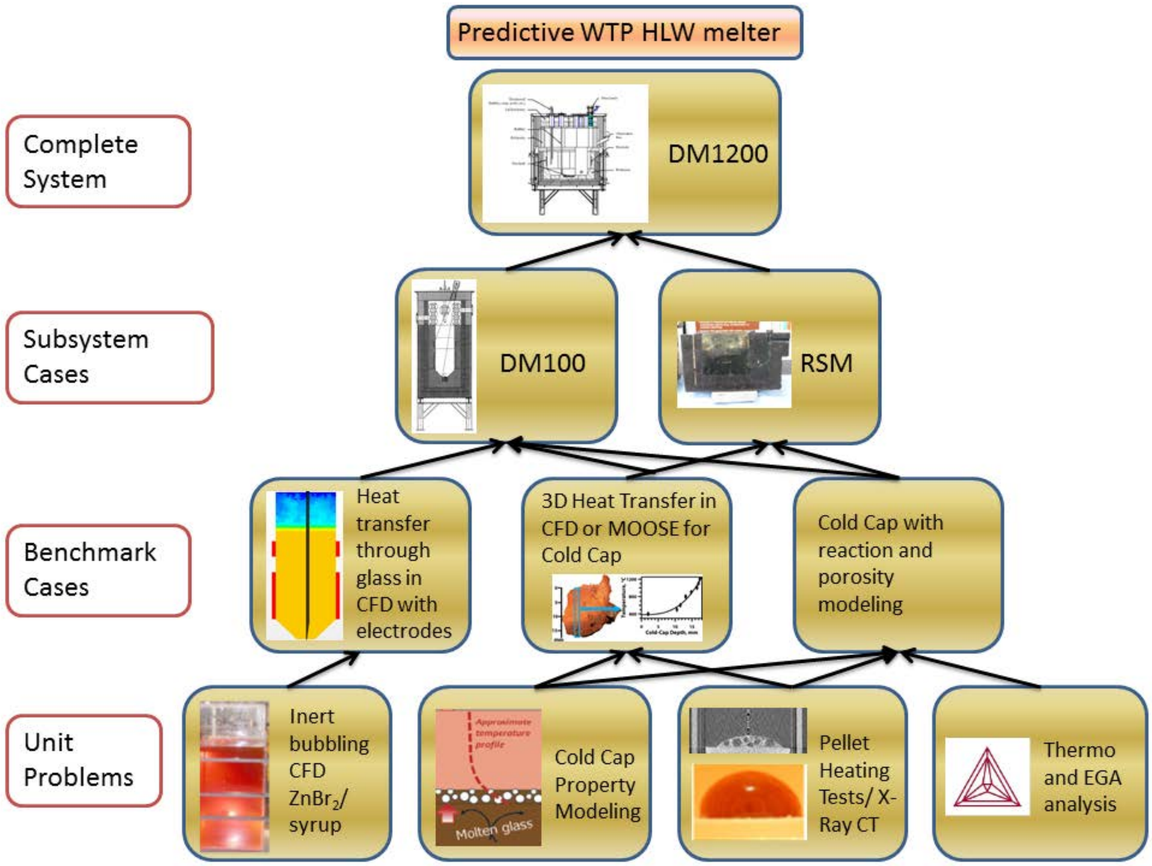


Figure 21. Melter model validation hierarchy.

6.0 Summary

DOE is building the WTP at the Hanford Site to remediate 55 million gallons of radioactive waste that is being temporarily stored in 177 underground tanks. The WTP will separate the tank waste into HLW and LAW fractions, which will then be vitrified respectively into ILAW and IHLW borosilicate glass products. The cost and schedule of treatment is highly dependent on the waste loading in glass and the rate of glass production. Increasing the rate of glass processing, particularly when coupled with increased waste loadings, will reduce the overall mission life of the WTP facilities.

ORP's EWG program is focused on advanced glass formulations and process control models as they relate to waste loading, melting rate, and facility operations. Although higher waste loadings are desired and achievable, this must be done without negatively affecting the melting rate, which could decrease overall waste throughput for both the HLW and LAW vitrification facilities. Therefore, the ORP program includes efforts to understand feed-to-glass conversion process, the cold cap behavior, and melt dynamics under various processing conditions and as a function of melter feed make-up.

Although many factors influence the rate at which the incoming melter feed is converted to a molten glass product, perhaps the least understood is the complex series of reactions that occur within the cold cap and the dynamics of the cold cap. Therefore, melting rate studies are being performed to develop a fundamental understanding of the batch-to-glass conversion process. In particular, studies are focusing on those reactions that highly influence the rate of melting. For example, one of the key phenomena to understand is the formation, stability, and behavior of the foam layer that develops between the primary heat source (molten glass pool) and the cold cap, where all of the complex reactions are occurring. This foam layer can act as a thermal barrier (insulator) that impedes heat transfer into the cold cap, reducing the melting rate. A fundamental understanding of these key phenomena will lead to strategic methods to minimize (or eliminate) the potential negative impacts during facility operations. Figure 4 in Section 5.0 shows the ORP programmatic activities as they relate to the cold cap and melt dynamics research and development plan. This plan is a living document that will be updated to reflect key advancements and mission strategy changes as needed.

The plan identifies ongoing, near-, mid-, and longer-term research and development activities required to develop a more fundamental understanding of the complex series of reactions that govern melting rate and the dynamic behavior of the cold cap under various operating conditions. Analytical techniques that are currently being used or are being developed are providing key material property data (as function of temperature and heating rates) as input data to 1-D and 3-D modeling efforts. The current approach is to develop an integrated mathematical model that could be used to describe the overall melting process for such complex systems, which can be used in conjunction with the glass composition – property models not only to maximize waste loading, but to improve melting rate as well. This will ultimately decrease the cost of Hanford tank waste management by reducing the schedule for tank waste treatment and reducing the amount of glass for storage, transportation, and disposal.

For perspective, the advancements and successes of the integrated ORP EWG 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 EWG program stated:[1]

> "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."

[1] 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.

"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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