Development of High Waste-Loading HLW Glasses for High Bismuth Phosphate Wastes, VSL-12R2550-1, Rev. 0

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

**P.O. Box 450
Richland, Washington 99352**

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Final Report

Development of High Waste-Loading HLW Glasses for High Bismuth Phosphate Wastes

prepared by

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Test Plan: Improving Processing Characteristics of High Waste-Loading HLW Glasses for High Bismuth Phosphate Wastes, VSL-12T2550-1, Rev. 0

This report describes the results of testing specified by the above Test Plan. The work was performed in compliance with the quality assurance requirements specified in the Test Plan. Results required by the Test Plan are reported. The test results and this report have been reviewed for correctness, technical adequacy, completeness, and accuracy.

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TABLE OF CONTENTS

SECTION 1.0 INTRODUCTION	7
1.1 Test Objectives.....	8
1.2 Quality Assurance.....	9
SECTION 2.0.....	10
2.1 Compositions of High Bismuth Phosphate Wastes	10
SECTION 3.0.....	12
3.1 Glass Fabrication	12
3.2 Glass Compositional Analysis	12
3.3 Crystallinity in Glass Samples after Isothermal Heat Treatment.....	12
3.4 Foaming of Glass Sample during Canister Centerline Cooling.....	13
3.5 Viscosity	13
3.6 Electrical Conductivity	13
3.7 Product Consistency Test (PCT).....	14
3.8 Toxicity Characteristic Leaching Procedure (TCLP)	14
SECTION 4.0 GLASS FORMULATION APPROACH	15
SECTION 5.0 RESULTS AND DISCUSSION.....	19
5.1 Glass Formulations for Waste Batch 2394	19
5.2 Glass Formulations for Waste Batch 4098	20
5.3 Glass Formulations for Waste Batch 4006	21
SECTION 6.0 CONCLUSIONS.....	24
SECTION 7.0 REFERENCES.....	26

List of Tables

Table 1	Compositional Summary (wt% Oxide Basis) of the Bi-Limited Waste and the Candidate Wastes Selected.	T-1
Table 2	Compositional Summary (wt% Oxide Basis) of the HLW Simulants.	T-2
Table 3	HLW Canister Centerline Cooling Temperature Profile [13].	T-3
Table 4	Target Compositions of HLW Glasses Previously Developed for Bi-Limited Waste [1, 3].	T-4
Table 5a	Target and XRF Analysis of Glass Compositions for Waste Batch 2394 (wt%).	T-5
Table 5b	Target and XRF Analysis of Glass Compositions for Waste Batch 4098 (wt%).	T-7
Table 5c	Target and XRF Analysis of Glass Compositions for Waste Batch 4006 (wt%).	T-11
Table 6a	Characterization of Glass Samples for Waste Batch 2394.	T-15
Table 6b	Characterization of Glass Samples for Waste Batch 4098.	T-16
Table 6c	Characterization of Glass Samples for Waste Batch 4006.	T-18
Table 7	Viscosity and Electrical Conductivity of Selected Bi-P Glass Melts.	T-20
Table 8	Normalized 7-Day PCT Element Releases for Selected Bi-P HLW Glasses.	T-21
Table 9	TCLP Element Releases from Selected Bi-P HLW Glasses.	T-22

List of Figures

Figure 1	Cross sections of glass CCC samples of Waste Batch 2394.	F-1
Figure 2a	SEM image of HL WBi2394-3 heat treated at 950°C.	F-2
Figure 2b	SEM image of HL WBi2394-3 heat treated at 900°C.	F-2
Figure 2c	SEM image of HL WBi2394-3 heat treated at 850°C.	F-3
Figure 2d	SEM image of HL WBi2394-3 heat treated at 800°C.	F-3
Figure 3a	SEM image of HL WBi2394-4 heat treated at 950°C.	F-4
Figure 3b	SEM image of HL WBi2394-4 heat treated at 900°C.	F-4
Figure 3c	SEM image of HL WBi2394-4 heat treated at 850°C.	F-5
Figure 3d	SEM image of HL WBi2394-4 heat treated at 800°C.	F-5
Figure 4	Total amount of crystalline phases (vol%) after isothermal heat treatment of HWBi2394-3 (45 wt% waste loading, blue open circles) and HWBi2394-4 (40 wt% waste loading, red open squares).	F-6
Figure 5	Cross sections of glass CCC samples of Waste Batch 4098.	F-7
Figure 6a	SEM image of HL WBi4098-6 heat treated at 950°C.	F-10
Figure 6b	SEM image of HL WBi4098-6 heat treated at 900°C.	F-10
Figure 6c	SEM image of HL WBi4098-6 heat treated at 850°C.	F-11
Figure 6d	SEM image of HL WBi4098-6 heat treated at 800°C.	F-11
Figure 7a	SEM image of HL WBi4098-7 heat treated at 950°C.	F-12
Figure 7b	SEM image of HL WBi4098-7 heat treated at 900°C.	F-12
Figure 7c	SEM image of HL WBi4098-7 heat treated at 850°C.	F-13
Figure 7d	SEM image of HL WBi4098-7 heat treated at 800°C.	F-13
Figure 8	Total amount of crystalline phases (vol%) after isothermal heat treatment of HWBi4098-7 (45 wt% waste loading, blue open circles) and HWBi4098-6 (40 wt% waste loading, red open squares).	F-14
Figure 9	Cross sections of glass CCC samples of Waste Batch 4006.	F-15
Figure 10a	SEM image of HL WBi4006-6 heat treated at 950°C.	F-18
Figure 10b	SEM image of HL WBi4006-6 heat treated at 900°C.	F-18
Figure 10c	SEM image of HL WBi4006-6 heat treated at 850°C.	F-19
Figure 10a	SEM image of HL WBi4006-6 heat treated at 800°C.	F-19
Figure 11	Total amount of crystalline phases (vol%) after isothermal heat treatment of HWBi4006-4 (45 wt% waste loading, blue open circles) and HWBi4006-6 (40 wt% waste loading, red open squares).	F-20
Figure 12a	SEM image of HL WBi4006-7 heat treated at 950°C.	F-21
Figure 12b	SEM image of HL WBi4006-7 heat treated at 800°C.	F-21
Figure 13a	SEM image of HL WBi4006-4 heat treated at 950°C.	F-22
Figure 13b	SEM image of HL WBi4006-4 heat treated at 900°C.	F-22
Figure 13c	SEM image of HL WBi4006-4 heat treated at 850°C.	F-23
Figure 13d	SEM image of HL WBi4006-4 heat treated at 800°C.	F-23

List of Abbreviations

ANL-LRM	- Argonne National Laboratory-Low Activity Waste Reference Material
ASME	- American Society of Mechanical Engineers
CCC	- Canister Centerline Cooling
DCP-AES	- Direct Current Plasma Atomic Emission Spectroscopy
DWPF-EA	- Defense Waste Processing Facility-Environmental Assessment
HLW	- High Level Waste
HTWOS	- Hanford Tank Waste Operations Simulator
NIST	- National Institute of Standard and Technology
ORP	- Office of River Protection
PCT	- Product Consistency Test
QARD	- Quality Assurance Requirements and Description
RPP	- River Protection Project
SEM/EDS	- Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy
TCLP	- Toxicity Characteristic Leaching Procedure
VGF	- Vertical Gradient Furnace
VSL	- Vitreous State Laboratory
WTP	- Hanford Tank Waste Treatment and Immobilization Plant
XRF	- X-ray Fluorescence Spectroscopy

SECTION 1.0 INTRODUCTION

The processing rate of High Level Waste (HLW) at the Hanford Tank Waste Treatment and Immobilization Plant (WTP) depends on the waste loading in the HLW glass and the glass production rate. Both the waste loading and production rate have been the focus of on-going work for the Office of River Protection (ORP) performed at the Vitreous State Laboratory (VSL). Glass formulation development work at VSL has demonstrated the feasibility of increases in waste-loading from about 25 wt% to 33-50 wt% (based on waste oxide loading) in the glass for various waste streams [1]. Glass formulations and glass-forming additive blends were also developed for selected waste streams to maximize processing rates while maintaining high waste loadings and acceptable glass properties [2].

The WTP's overall mission will require the immobilization of tank waste compositions that are dominated by mixtures that include aluminum, chromium, bismuth, iron, phosphorus, zirconium, and sulfur compounds as waste-limiting components. The development work for the WTP baseline has focused on early HLW feeds, all of which are limited by iron. However, in order to develop the basis for the balance of the WTP mission, ORP has specified representative waste streams that are limited by other key components, for testing that was conducted previously at VSL [1]. The loadings of these wastes in HLW glass were expected to be limited by bismuth, chromium, aluminum, and aluminum plus sodium. Glass formulations that meet all processing and product quality requirements for each of these waste streams were developed with waste loadings ranging from 33 to 50 wt%, which far exceed the minimum, and approach or meet the maximum levels specified by ORP [1]. The testing also identified new risks associated with those waste types.

For the Bi-limited waste, an HLW glass formulation with 50 wt% waste loading was successfully developed and tested [1]. This glass contains 6.71 wt% of Bi_2O_3 , which suggests that a 70% reduction in glass volume is achievable when compared to the WTP contract minimum of 2 wt% Bi_2O_3 when the waste loading is limited solely by Bi_2O_3 . The maximum waste loading for the bismuth-limited waste was primarily limited by the crystallization of spinel and phosphate. In addition, however, crucible melts of high-bismuth glasses were observed to foam upon heat treatment using the WTP HLW canister centerline cooling (CCC) curve [1]. Such an occurrence during cooling of actual HLW canisters would be highly undesirable and could therefore represent a significant risk associated with processing of high bismuth/phosphorus wastes.

Subsequent testing was conducted at the crucible scale and on the HLW pilot melter (DM1200) to determine the nature, cause and extent of glass foaming when processing a high bismuth waste stream. Test results confirmed that the foaming behavior observed in crucible scale tests also occurred at larger scale under conditions prototypical of those at WTP [3]. The test results also demonstrated a compositional dependence of foaming for high-bismuth glasses,

identifying phosphorus and chromium as contributors to the observed foaming, while bismuth was found to play no significant role, even though it is a major glass component [3]. Based on the test results, several methods were identified as potentially effective to mitigate the foaming observed during CCC. All of the previous work was conducted with a single high Bi-P waste composition and therefore testing of other potential high Bi-P HLW feeds to the WTP is required to assess whether similar foaming behavior is observed for those waste streams and whether similar mitigation approaches are effective.

It is worth noting that the foaming behavior observed in the high Bi-P waste occurred during cooling of the melt, unlike the case of more traditional foaming behavior that is observed during glass melting for which a substantial amount of literature is available. It is common to observe the foam development during batch melting and glass fining processes. In nuclear waste glasses, foaming can occur as the result of reduction of multivalent oxides with increasing melt temperature [4, 5]. As demonstrated in numerous studies, foaming can also occur during the batch reactions as raw materials are converted to glass melt [6] or during fining in the later stage of glass production, as for example in the case of decomposition of sulfate dissolved in glass melts [7]. However, as documented previously [3], for the WTP high Bi-P melts, foaming did not occur during feed to melt conversion or as a result of increasing melt temperature. The foaming phenomenon that is the subject of this work is observed during controlled *cooling* of the melt according to the temperature profile that simulates the WTP HLW centerline canister cooling curve [1, 3]. Consequently, a different mechanism is apparently responsible for this type of foaming, as described previously [3].

This report presents results from tests with new glass formulations that have been developed for several high Bi-P HLW compositions that are expected to be processed at the WTP that have not been tested previously. WTP HLW feed compositions were reviewed to select waste batches that are high in Bi-P and that are reasonably distinct from the Bi-limited waste that has been tested previously [1, 3]. Three such high Bi-P HLW compositions were selected for this work [8]. The focus of the present work was to determine whether the same type of issues as seen in previous work with high-Bi HLW [1, 3] will be seen in HLW with different concentrations of Bi, P and Cr and also whether similar glass formulation development approaches would be successful in mitigating these issues. New glass compositions were developed for each of the three representative Bi-P HLW wastes and characterized with respect to key processing and product quality properties and, in particular, those relating to crystallization and foaming tendency.

1.1 Test Objectives

As described in the Test Plan for this work [8], the primary objectives of the work were to: select high Bi-P HLW compositions that are expected to be processed at the WTP that have not been tested previously; develop high waste loading glass formulations that meet the necessary processing and product quality requirements for each of the three selected high Bi-P WTP HLW streams; investigate the extent of foaming observed during CCC with these new waste compositions; and investigate glass formulation methods to mitigate such foaming.

1.2 Quality Assurance

This work was performed according to the quality assurance program that is in place at VSL. That program is compliant with applicable criteria of 10 CFR 830.120; Office of Civilian Waste Management DOE/RW-0333P, Quality Assurance Requirements and Description (QARD) Revision 20; the American Society of Mechanical Engineers (ASME) NQA-1, 2004; and DOE Order 414.1 C, Quality Assurance. The requirements of DOE/RW-0333P were applicable to the following specific aspects of this work:

- Crucible melt preparation of HLW glasses;
- Analysis of HLW crucible melt glasses;
- PCT of HLW glasses.

The program is supplemented by a Quality Assurance Project Plan for ORP work [9] that is conducted at VSL. Test and procedure requirements by which the testing activities are planned and controlled are also defined in this plan. The program is supported by VSL standard operating procedures that were used for this work [10].

SECTION 2.0 WASTE COMPOSITIONS

Glass formulation work performed previously at VSL for high bismuth phosphate wastes focused on waste compositions provided by WTP [11] and ORP [1]. The WTP Project supplied waste feed compositions that were from dynamic flow-sheet modeling runs using the WTP Dynamic Model (Gensym G2) for initial waste delivery scenarios. These scenarios involved the blending of various waste types (e.g., bismuth phosphate waste) in selected WTP tanks (e.g., C-104). Some of these wastes contained moderately high concentrations of bismuth and phosphate. In contrast, the Bi-limited waste provided by ORP contained considerably higher concentrations of these components (i.e., 12.91 wt% Bi_2O_3 and 9.60 wt% P_2O_5). Glass formulations with high waste loadings have been successfully developed and tested for wastes from both sources [1, 11]. The present work investigated other high Bi-P HLW compositions that are expected to be processed at the WTP that have not been tested previously.

The WTP HLW feed compositions from the WTP System Plan, Rev 6 [12] were used as the source of high Bi-P HLW compositions for this work. A review of the WTP HLW feed composition data [11] was conducted to select the waste compositions for glass formulation development. This section summarizes the results of the review and the high Bi-P waste compositions selected for glass formulation development.

2.1 Compositions of High Bismuth Phosphate Wastes

Within the River Protection Project (RPP), the Hanford Tank Waste Operations Simulator (HTWOS) is a dynamic computer model that tracks the waste through storage, retrieval, feed staging and treatment processes. The HTWOS output provides WTP feed vectors, which include information on feed compositions, quantities and dates. The HTWOS baseline case for the WTP System Plan, Rev 6 feed compositions was the basis for the selection of high Bi-P waste compositions to be tested in this work.

The HTWOS compositional data were converted from units of kg to wt% oxides for the present evaluation. A review of the HTWOS data shows that the WTP will process 4106 batches of HLW glass for the overall mission [12], each with its own waste feed and glass composition. The Bi_2O_3 and P_2O_5 concentrations in the WTP HLW streams range from 0.04 wt% to 11.95 wt% and 0.59 wt% to 13.00 wt%, respectively. These values can be compared with 12.91 wt% Bi_2O_3 and 9.60 wt% P_2O_5 found in the Bi-limited waste provided previously by ORP [1]. Many of the HTWOS batches with high Bi or P contents are also high in other components that are potentially waste-loading limiting; such streams were therefore not selected for the current work. For example, many waste batches with high Bi_2O_3 (or P_2O_5) concentrations also include SO_3 in very high concentrations such that the SO_3 will be the waste loading limiting component instead of Bi_2O_3 (or P_2O_5); one such case is waste batch number 4077, which

contains 12.09 wt% P_2O_5 and 3.56 wt% SO_3 but this waste was not chosen because the HLW glass formulation is expected to be limited by SO_3 .

Based on the above review, three waste compositions from the HTWOS output were selected for this work: Waste Batch Number 2394, 4006, and 4098. These composition are listed without the minor oxides (i.e., < 0.1 wt%) in Table 1, which also includes the Bi-limited waste composition previously studied for comparison. As seen in Table 1, the compositions of the selected wastes show considerable differences from the original Bi-limited waste [1]. With the exception of P_2O_5 in Batch 4098, the concentrations of Bi_2O_3 and P_2O_5 in the selected wastes are generally lower than the respective values found in the Bi-limited waste. However, the ratio of Bi_2O_3 to P_2O_5 (Table 2) spans a wide range around that for the original Bi-limited waste. In addition, the waste loadings in HLW glasses for the selected wastes are still expected to be limited by Bi_2O_3 or P_2O_5 . Furthermore, Cr_2O_3 , which has been identified as the primary oxide that caused foaming in earlier tests [3], is present at similar or higher concentrations when compared to that found in the original Bi-limited waste. Finally, MnO , which is present in all of these wastes (up to 6.82 wt% in Batch 4006), also may have important effects on foaming behavior in these glass melts. In contrast, MnO is absent from the original Bi-limited waste.

The waste compositions in Table 1 include the radioactive components UO_3 and ThO_2 . These oxides are omitted from the HLW simulants for developing and testing glass formulations; the renormalized compositions after omission of UO_3 and ThO_2 are given in Table 2. Also given are the ratios of Bi_2O_3 and P_2O_5 to the respective WTP contract limit and the ratio of Bi_2O_3 to P_2O_5 .

SECTION 3.0 EXPERIMENTAL METHODS

3.1 Glass Fabrication

Glass formulated for each of the high bismuth phosphate waste simulants was prepared from reagent grade or higher purity chemicals. The starting materials were batched and blended before loading into a platinum-gold crucible (1 liter). The typical batch size is 400 g of glass.

The loaded crucible was placed inside a Deltech furnace and melted at 1200°C for 2 hours. Mixing of the melt was enhanced mechanically using a platinum stirrer. The glass melt was quenched at the end of 120 minutes by pouring it onto a graphite plate. The glass was subsequently processed for various measurements.

3.2 Glass Compositional Analysis

The compositions of the prepared glasses were determined using X-ray fluorescence (XRF) spectroscopy. Selected glasses were analyzed for their boron and lithium contents with direct current plasma atomic emission spectroscopy (DCP-AES), as described below.

Powdered samples of the fabricated glasses (–200 mesh) were analyzed with a PANalytical Axios mAX-Advanced XRF spectrometer. The spectrometer was calibrated over a range of glass compositions using standard reference materials traceable to National Institute of Standard and Technology (NIST), as well as waste glasses including the Argonne National Laboratory-Low Activity Waste Reference Material (ANL-LRM), the Defense Waste Processing Facility-Environmental Assessment (DWPF-EA) Glass, and Hanford WTP glasses. Analysis by XRF provides data for most glass components of interest except lithium and boron, which were represented by their target values or analyzed for selected glasses by DCP-AES.

Powdered glass samples for DCP-AES analysis were subjected to microwave-assisted total acid dissolution in Teflon vessels. Twenty milliliters (ml) of a 1:5 mixture of concentrated HF:HNO₃ mixture was diluted to 50 ml before use in dissolution. The resulting solutions were analyzed by DCP-AES.

3.3 Crystallinity in Glass Samples after Isothermal Heat Treatment

Glass samples (5 g each) were melted in platinum-gold crucibles with tight fitting covers at a temperature of 1200°C for 1 hour before a 70 hour isothermal heat treatment at a specific temperature between 800°C and 950°C. At the end of the heat-treatment period, the glass samples were quenched by contacting the outside of the crucibles with water. This quenching froze in the

phase assemblage present in the melt at the heat-treatment temperature. The heat-treated samples were prepared for Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy (SEM/EDS) examination to determine the nature and the volume fraction of crystalline phases. In order to obtain a representative measure of the overall crystal fraction in the sample, the heat-treated glass was ground and sieved (-18 mesh or ≤ 1 mm) before SEM/EDS analysis using a JEOL JSM-5910LV SEM with INCAEnergy 300 system.

3.4 Foaming of Glass Sample during Canister Centerline Cooling

The prepared HLW glasses underwent CCC heat treatment according to the CCC temperature profile provided by the WTP Project [13] (see Table 3). As is the case for isothermal heat-treatment, the glass samples (40 gram for each CCC experiment) in platinum alloy crucibles were maintained at a pre-melt temperature of 1200°C for 1 hour before initiation of CCC treatment. The samples recovered after CCC heat treatment were sectioned perpendicular to the surface, polished, and optically scanned. The digital images thus acquired were inspected on a computer monitor for signs of foam development.

3.5 Viscosity

The melt viscosity (η) was measured using a Brookfield viscometer with a platinum/rhodium spindle and crucible. The relative torque of a rotating spindle immersed in molten glass was measured as a function of rotational velocity. Measurements were performed in the temperature (T) range of 950-1250°C. To facilitate comparison, the data were interpolated to standard temperatures (e.g., 1150°C) using the Vogel-Fulcher equation:

$$\ln \eta = A/(T-T_0) + B,$$

where A , B , and T_0 are fitting parameters. The equipment was calibrated at room temperature using standard oils of known viscosity and then checked at high temperatures using a National Institute of Standards and Technology (NIST) standard reference glass (SRM 711). Both precision and accuracy of the viscosity measurements are estimated to be within ± 15 relative%.

3.6 Electrical Conductivity

The electrical conductivity (σ) of the glass melt was determined by measuring the resistance of the melt as a function of frequency using a calibrated platinum/rhodium electrode probe attached to an Agilent 4294A impedance analyzer. Measurements were performed over similar temperature ranges to those employed for the melt viscosity measurements. The results were analyzed using an equivalent circuit model to obtain the DC electrical conductivity. To facilitate comparison, the electrical conductivity data were then interpolated to standard temperatures (e.g., 1150°C) using the Vogel-Fulcher equation:

$$\ln \sigma = A/(T-T_0) + B,$$

where A , B , and T_0 are fitting parameters. Estimated uncertainties in the electrical conductivity measurements are ± 20 relative%.

3.7 Product Consistency Test (PCT)

The product consistency test (PCT; ASTM C 1285) was used to evaluate the relative chemical durability of glasses by measuring the concentrations of the chemical species released from 100-200 mesh crushed glass (75-149 μm) to the test solution (de-ionized water in this case). PCT tests on the HLW glasses were performed at 90°C for 7 days, in accordance with the current WTP contract requirement. The ratio of the glass surface area to the solution volume for this test is about 2000 m^{-1} (typically, 10 g of 100-200 mesh glass is immersed in 100 ml of deionized water). All tests were conducted in triplicate, in 304L stainless steel vessels, and in parallel with a standard glass included in each test set. The internal standard was the DWPF-EA glass.

3.8 Toxicity Characteristic Leaching Procedure (TCLP)

The TCLP tests were performed at VSL using SW-846 Method 1311, which employs leaching of crushed glass ($< 3/8''$) in a sodium acetate buffer solution for 18 hours at 22°C with constant end-over-end agitation. 100 grams of glass was leached in 2 liters of TCLP extract, according to the extraction method for non-volatiles. The surface area to volume ratio for this test is about 20 m^{-1} , which is about two orders of magnitude lower than that in the PCT. The leachates were analyzed by DCP-AES according to VSL standard operating procedures.

SECTION 4.0

GLASS FORMULATION APPROACH

A series of glass formulations were developed and tested for each of the three high Bi-P HLW waste streams listed in Table 1. The primary objective was to achieve high waste loadings for each of the HLW simulants while controlling crystallization and the melt foaming during cooling that has been observed in previous studies [1, 3]. A total of 24 new glasses were designed, fabricated, and characterized in the present work and the results were analyzed to select recommended formulations for each of the three new HLW streams.

Results obtained from previous testing of WTP HLW high Bi-P glasses [1, 3] were used to guide the present formulation development work. Those studies showed that the waste loading was typically limited by melt foaming during CCC heat treatment and by crystallization of spinel/phosphate phases at 950°C [1, 3]. The glass formulation HLW-E-Bi6 with 50 wt% waste loading of the original bismuth-limited waste was developed in the first of those studies [1] (Table 4). However, it was noted that HLW-E-Bi6 displayed signs of unusual melt foaming during CCC heat treatment which was not well understood at the time [1]. That glass exhibited about 1.8 vol% of spinel and phosphate after heat treatment at 950°C and relatively slow melt rates in DM100 melter tests [1]. In a subsequent investigation [3], the foaming tendency of HLW-E-Bi6 during cooling was confirmed in one-third scale pilot melter tests on the DM1200 melter system [3].

Based on these observations, the origin of the foaming during melt cooling was investigated in a series of crucible melt tests [3]. The results of those tests showed that there was synergetic effect between P and Cr in gas generation which is believed to be due to the chemical affinity between Cr^{6+} and P^{5+} . Phosphorus and chromium form poly ions containing both P and Cr that are closely related to the pyrophosphate and linear polyphosphate ions with P and Cr both in tetrahedral coordination. In this group of phosphochromates, one, two, three, or four of the O atoms of a PO_4 group can be shared with tetrahedral CrO_4 groups. Therefore, formation of the phosphochromate species in the P-rich HLW glass would probably stabilize Cr^{6+} and result in a higher $\text{Cr}^{6+}/\text{Cr}^{3+}$ ratio. In a simple homogeneous system, the redox equilibrium will normally shift towards the more reduced direction with *increasing* temperature. The available phase equilibrium data and experimental data suggest that two factors that involve heterogeneous reactions change this outcome [3]: 1) the solubilities of chromate within phosphate and phosphate within borosilicate; and 2) the competition for chromium between phosphochromate and spinel. Considering the strong affinity of trivalent chromium for the spinel lattice, it is not surprising that as the temperature is *decreased*, phosphochromate, after, and possibly even before, being separated from phosphate-rich domains would be *reduced* to Cr^{3+} in order to be accommodated by the more favorable spinel structure [3]. This mechanism can be summarized by the following reactions [3]:

where m indicates a melt phase, xl a crystalline phase, Sp a spinel crystal, and g a gas phase. A simple dimer type of phosphochromate is chosen to represent the proposed Cr and P poly ions in both reactions. Sodium pyrophosphate is chosen in the first reaction to match the same dimer configuration. In the second reaction, as Cr^{6+} is reduced to Cr^{3+} , it is assumed that all sodium atoms associated with this phosphochromate remain with phosphate to form a less polymerized orthophosphate. Cr^{3+} will then react with appropriate available divalent cations (such as Ni^{2+}) to form spinel crystals. Stoichiometrically, each mole of Cr_2O_3 generated will be accompanied by 1.5 moles of O_2 . A simple estimation shows that for a glass with a density of 2.6 g/cm^3 at 1100 K (833°C), $0.5 \text{ wt\%}$ Cr_2O_3 in the glass will release an amount of gas equal to approximately 10 times the melt volume. Even under the assumption that only 10% of the Cr exists as phosphochromate at high temperature (before CCC cooling), the gas volume released will equal that of the glass melt [3].

The above discussion captures what appear to be the essential features of the foaming mechanism. However, a glass melt being subjected to CCC would evolve as an interrelated system. For example, the liquidus of the spinel phase will likely be influenced by the stability of Cr^{6+} in phosphochromate. As more Cr^{3+} becomes available, the spinel liquidus will move to a higher temperature in response. Nevertheless, the same general behavior would be expected.

Based on these results, several possible methods for mitigating the foaming observed on CCC were suggested [3]:

- Suppression of Cr^{6+} with a reductant or glass chemistry.
- Reduction of glass melt viscosity to facilitate release of gas bubbles.
- Formation of other competing phosphate species.

Suppression of Cr^{6+} will reduce the amount of oxygen gas that would be generated due to reduction of hexavalent chromium. In principle, this could be accomplished through the use of reductants or by decreasing the optical basicity of the host glass melt by, for example, decreasing the levels of alkalis such as sodium or potassium. However, this approach may cause unfavorable crystallization and high viscosities due to lack of flux.

A glass melt of considerably lower viscosity, especially at temperatures where the reduction reaction takes place, would possibly facilitate the escape of oxygen gas bubbles. However, considering the steep temperature dependence of melt viscosity and the adverse effects of very low melt viscosity on melter refractory corrosion, this route may have limited practical value.

The third option is aimed at creating direct competition with Cr^{6+} for the available phosphorus in the waste glass. The strategy is then to tie up the phosphorus that could otherwise

interact with Cr^{6+} to form detrimental phosphochromate species. Chemical additives that can effectively bond to phosphorus, such as aluminum, may also act to suppress Cr^{6+} in glass. This approach for mitigation of foaming was emphasized and demonstrated to be quite effective in the previous work [3] and was also employed in the present study.

Based on the above mechanistic understanding of the observed foaming during melt cooling, several new formulations were developed to mitigate such foaming [3]. From that work, two new formulations were recommended, HLW-Bi-F3 and HLW-Bi-F9, which achieve the same waste loading as the earlier HLWE-Bi6 formulation but are free of melt foaming during CCC (Table 3). In addition, vertical gradient furnace (VGF) melt rate screening tests were performed in the development of these new formulations, the results of which indicated that both of the new formulations should show faster melting rates as compared to the original HLWE-Bi6 formulation [3]. HLW-Bi-F9 showed a faster melting rate than HLW-Bi-F3 but exhibited a higher crystal content after heat treatment at 950°C and some what poorer (though still acceptable) 7-day PCT releases. In view of the enormous economic benefits associated with the combination of high waste loading and fast melt rate, HLW-Bi-F9 [3] was used as a model formulation and starting point for the present glass formulation work recognizing, however, that the new waste compositions differ from that of the original bismuth-limited waste. More specifically, the new glass formulation development work was initially weighted toward the compositional space characterized by high boron, high alumina, high Li/Na ratio, and low silica. Of the different glass former additives used in HLW glass formulation, Al_2O_3 , B_2O_3 , Li_2O , and SiO_2 were varied in this work. CaO was not increased because of the tendency for formation of Ca-P phases in compositions with high concentrations of Ca and P. The Na_2O concentration was not increased because previous tests [1, 3] showed that Na_2O was not particularly beneficial in reducing foaming.

Property-composition models were used to support the design of new glass formulations for testing, as is the standard practice at VSL for all glass formulation development work. The property-composition models that were used include melt viscosity, melt electrical conductivity and $T_{1\%}$. PCT and TCLP models were not used because these properties are usually not constraining for HLW glass formulation design. Since there is no model for foaming on CCC, glass formulation development to address this issue used an iterative approach with formulation design guided by past experience and results from the previous set of crucible melts. It should be noted, however, that since many of the new formulations being developed for ORP are compositionally outside the limits of applicability of the current models, the model predictions were part of several inputs into the selection of a glass formulation for testing; i.e., glass compositions were not necessarily rejected for testing solely because one of the models predicted a property value outside of the preferred limits. An iterative approach was used in the development of new glass formulations for the three high-Bi HLW streams because our past experience is that this approach would be more efficient and economical for the present objectives as compared to statistically designed composition matrices; the latter better suited to provide coverage of pre-defined composition spaces for subsequent model development.

After the crucible melt glasses were prepared as described in Section 3, the characterization was done in two steps. The earlier formulation efforts [1, 3] demonstrated that

the waste loadings for high Bi-P waste was typically limited by foaming during CCC and crystallization of spinel and other secondary phases at 950°C [1, 3]. Therefore, in the initial screening step, all glasses formulated in this work were characterized with respect to foaming and crystallization behavior before other properties were measured. If the prepared glass did not meet the processing requirements with regard to foaming and crystallization, measurements were generally not performed for the other properties. During glass formulation development work, equal emphasis was placed on crystallization and foaming because in most cases, once foaming was mitigated, crystallization became the waste loading limiting property. In the selection of candidate glass compositions for further testing, efforts were made to avoid any crystallization at the melt temperature while allowing small amounts of crystals (1 to 2 vol%) at lower temperatures (~950 °C). Glasses that exhibited acceptable crystallization and CCC foaming behavior were identified and characterized in the second step with respect to other properties, including melt viscosity, electrical conductivity and product quality (Product Consistency Test and Toxicity Characteristic Leaching Procedure). The results were then reviewed to select recommended formulations for each of the three new high Bi-P waste streams.

SECTION 5.0 RESULTS AND DISCUSSION

5.1 Glass Formulations for Waste Batch 2394

Waste Batch 2394 has the highest concentrations of Bi_2O_3 and Fe_2O_3 and the lowest concentration of P_2O_5 among the three HLW streams investigated in this work (Table 2). Formulation HWBi2394-1 for Waste Batch 2394 (Table 5a) has 50 wt% waste loading and has 15.2 wt% B_2O_3 , 4 wt% Li_2O and 10.9 wt% Na_2O . This formulation showed minor signs of melt foaming in the cross section of its CCC sample (Figure 1) and about 1.1 vol% spinel crystallization after heat treatment at 950°C (Table 6a). HWBi2394-2 at the same 50 wt% waste loading used more B_2O_3 and Li_2O but no Na_2O as glass forming additives and did not show any signs of melt foaming but contained nearly 2 vol% spinel crystals after 950°C heat treatment (Table 6a). For HWBi2394-3, which is similar to HWBi2394-2 but at a lower waste loading of 45 wt%, crystallization of spinel decreased to about 0.8 vol%. A further reduction in waste loading to 40 wt% in HWBi2394-4 resulted in a similar amount of crystallization. HWBi2394-3 and HWBi2394-4 showed no evidence of melt foaming during CCC (Figure 1). However, the relatively low SiO_2 and high B_2O_3 content in HWBi2394-3 resulted in a rather fluid melt (~ 16 poise at 1150°C , Table 7). The addition of 5 wt% SiO_2 at the expense of 5 wt% waste loading brought the viscosity into the normal range for processing in HWBi2394-4 (25 poise at 1150°C) (Table 7).

Crystalline phases in heat treated samples of the glasses were identified by SEM/EDS, and volume percents of crystals were determined by SEM in conjunction with image analysis. SEM images of heat treated samples of HLWBi2394-3 are given in Figures 2a-d. SEM images of the samples heat treated at 950°C and 900°C (Figures 2a and 2b) both show Fe-Cr-Ni spinels with Mn. HLWBi2394-3 samples heat treated at 850°C and 800°C (Figures 2c and 2d) show apatite in addition to the spinel crystals seen at the higher heat treatment temperatures. SEM images of heat treated samples of HLWBi2394-4 are given in Figures 3a-d. SEM images of the samples heat treated at 950°C and 900°C (Figures 3a and 3b) show only Fe-Cr-Ni spinels with Mn. Sample heat treated at 850°C (Figure 2c) show apatite in addition to the spinel crystals seen at the higher heat treatment temperatures. An HLWBi2394-4 sample heat treated at 800°C (Figure 2d) shows spinel, apatite and an Fe-Cr oxide phase. As shown in Figure 4, the total crystal contents are similar for HWBi2394-3 and HWBi2394-4 after heat treatment at temperatures from 950 to 800°C but considerably more phosphate phase formed at 800°C in HWBi2394-4 in spite of its lower waste loading.

HWBi2394-3 and HWBi2394-4 both show acceptable leaching results on the 7-day PCT and the TCLP. The normalized PCT releases (Table 8) are about an order of magnitude smaller than those for the DWPF-EA reference glass and the TCLP releases are well below the delisting limits (Table 9).

Overall, both HWBi2394-3 and HWBi2394-4 are recommended for further considerations for Waste Batch 2394 based on their processing and performance parameters. The viscosity of HWBi2394-3 is somewhat below the lower limit for WTP HLW glasses but has higher waste loading of 45 wt% and slightly lower total crystal content. HWBi2394-4 has a viscosity that is within the WTP HLW limits but has a 5 wt% lower waste loading.

5.2 Glass Formulations for Waste Batch 4098

Waste Batch 4098 has the highest concentrations of P_2O_5 and Al_2O_3 and the lowest concentration of Bi_2O_3 among the three HLW waste streams investigated in this work (Table 2). Formulation HWBi4098-1 for Waste Batch 4098 has 50 wt% loading and includes high boron and aluminum and added lithium (Table 5b). Although crystallization is limited with a minor presence of spinel and phosphate after isothermal heat treatment (Table 6b), gas vesicles are present in the CCC sample indicative of melt foaming during the cooling process (Figure 2). Two formulations at 45 wt% waste loading with 4 to 6 wt% CaO (HWBi4098-2 and HWBi4098-3) successfully suppressed foaming during CCC but produced substantially more crystallization of calcium phosphate (Table 6b, Figure 5). HWBi4098-4 was formulated with similar glass forming additives but at 5 wt% lower waste loading than HWBi4098-1. Crystallization in HWBi4098-4 after isothermal heat treatment was similar to that of HWBi4098-1 (Table 6b) and only one gas vesicle was observed near the bottom of the crucible in the CCC sample (Figure 5). However, the as-melted glass specimens of both HWBi4098-4 and HWBi4098-1 displayed traces of crystallization by visual inspection. HWBi4098-5 is a variation from HWBi4098-4 with the same 45 wt% waste loading but with 5 wt% SiO_2 in exchange for Al_2O_3 , which resulted in slightly more crystallization (Table 6b). HWBi4098-7 includes further additions of Al_2O_3 , B_2O_3 and Li_2O at constant 45 wt% waste loading to HWBi4098-4 and displayed very limited crystallization and no sign of foaming after CCC heat treatment.

Four glasses were formulated at waste loadings below 45 wt% for Waste batch 4098. HWBi4098-6, which is a lower waste loading version of HWBi4098-4 with more SiO_2 as a glass forming additive, showed similar crystal content to HWBi4098-7 and more phosphate formation at 900 and 850°C. One gas vesicle was evident near the bottom of the CCC sample (Figure 5). There were some signs of trace crystallization in the as-melted glasses of HWBi4098-9 and HWBi4098-8 with 40 wt% loading. HWBi4098-10 at 35 wt% waste loading shows little crystallization and is free of foaming during CCC heat treatment but at the expense of significantly lower waste loading.

SEM images of heat treated samples of HLWBi4098-6 are given in Figures 6a-d. SEM images of the sample heat treated at 950°C (Figure 6a) show only Fe-Cr-Ni-Mn spinels. The sample heat treated at 900°C (Figure 6b) shows apatite and La-phosphate in addition to the same type of spinel observed at 950°C. An HLWBi4098-6 sample heat treated at 850°C (Figures 6c) shows apatite in addition to the spinel crystals seen at the higher heat treatment temperatures. The sample heat treated at 800°C (Figure 6d) shows spinel, apatite and La-phosphate. The SEM image also shows some dark cavities that are probably voids formed by the dissolution of alkaline phosphates during sample polishing. SEM images of heat treated samples of

HLWBi4098-7 are given in Figures 7a-d. SEM images of the samples heat treated at 950°C and 900°C (Figures 7a and 3b) show only Fe-Cr-Ni-Mn spinels. The sample heat treated at 850°C (Figure 7c) shows apatite in addition to the Fe-Cr-Ni-Mn spinel crystals. AN HLWBi4098-7 sample heat treated at 800°C shows spinel (Figure 7d), apatite (Figure 7e) and dark cavities likely due to dissolution of alkaline phosphates during sample polishing (Figure 7d). The volume percent crystals are comparable for HLWBi4098-6 and HLWBi4098-7, as shown in Figure 8.

In summary, HWBi4098-7 (45 wt% waste loading) and HWBi4098-6 (40 wt% waste loading) represent the best compromises in terms of high waste loading, acceptable crystal contents, and absence or near-absence of foaming during CCC heat treatment. The normalized 7-day PCT releases of B and Na for HWBi4098-7 are nearly three times those of HWBi4098-6 (Table 8). Nevertheless, the normalized 7-day PCT releases for both glasses are almost an order of magnitude lower than those of the DWPF-EA reference glass. The TCLP releases for both glasses are well below the delisting limits (Table 9).

Overall, both HWBi4098-7 and HWBi4098-6 are acceptable formulations for Waste Batch 4098 with regard to their leaching resistance, crystal content, and foaming during CCC heat treatment. The viscosity and electrical conductivity of HWBi4098-7 are within the WTP HLW operational ranges (Table 7); although the viscosity and electrical conductivity for HWBi4098-6 were not measured, they are expected to also be within the WTP limits based on the results for HW4098-7 and the compositions of the two glasses.

5.3 Glass Formulations for Waste Batch 4006

Waste Batch 4006 with the highest concentrations of Na₂O, Cr₂O₃, MnO, and NiO among the three HLW streams investigated in this work (Table 2) proved to be the most challenging waste stream to incorporate at high waste loadings due to spinel crystallization.

Formulation for Waste Batch 4006 started at 50 wt% loading with relatively high boron and aluminum oxides (~15 wt% each). Lithium oxide was not used in HWBi4006-1 (Table 5c) due to the high sodium content in Waste Batch 4006. Although melt foaming in the CCC sample was negligible (Figure 9), nearly 3 vol% of crystalline phases (spinel plus phosphate) was present in the glass after 950°C heat treatment (Table 6c). An additional 5 wt% of B₂O₃ and SiO₂ at the expense of 5 wt% waste loading in HWBi4006-3 did not reduce the amount of crystallization. In HWBi4006-2, 2 wt% Li₂O was added in exchange for B₂O₃ and SiO₂ in HWBi4006-3 at the same 45 wt% waste loading, which reduced spinel crystallization to 1.1 vol%; however, the as-melted glass sample of HWBi4006-2 showed trace crystallization by visual inspection.

HWBi4006-6, which has a lower waste loading of 40 wt% but is otherwise similar to HWBi4006-2, showed similar crystal content (1.1 vol% at 950°C) (Table 6c) and good phase quality based on visual inspection of the as-melted glass. SEM images of heat treated samples of HLWBi4006-6 are given in Figures 10a-d. SEM images of the sample heat treated at 950°C (Figure 10a) show only Fe-Cr-Ni-Mn spinels. The samples heat treated at 900°C and 850°C

(Figures 10b and 10c) show La-phosphate in addition to Fe-Cr-Ni-Mn spinel. An HLWBi4006-6 sample heat treated at 800°C (Figure 10d) shows La-phosphate and a Ni-rich spinel with smaller amounts of Cr, Fe and Mn. Na-Ca phosphate phases were also seen in samples heat treated at 800°C and 850°C. The volume percent crystals in heat treated samples of HLWBi4006-6 varies from about 1.1 vol% at 950°C to 3.5 vol% at 800°C, as shown in Table 6c and Figure 11. HWBi4006-7, formulated by replacing some Al_2O_3 for SiO_2 in HWBi4006-03, showed somewhat less crystallization of a Na-Ca phosphate phase but more spinel crystallization after isothermal heat treatment. SEM/EDS analysis indicated that the spinel crystals present in the heat treated HWBi4007-7 accommodated considerable amounts of Al_2O_3 , which is apparently responsible for the increased spinel formation in HWBi4006-7. SEM images of HLWBi4006-7 samples heat treated at 950°C and 800°C are given in Figures 12a and 12b, respectively. The sample heat treated at 950°C (Figure 12a) shows La-phosphate and an Fe-Cr-Ni-Mn spinel with Al. SEM images of the sample heat treated at 800°C (Figure 12b) show La-phosphate, Fe-Cr-Ni-Mn spinel with considerable amount of Al, and dark cavities likely due to the dissolution of Na-Ca phosphates during sample polishing.

Based on these results, the Al_2O_3 from the glass forming additives was decreased for formulations HWBi4006-4 and HWBi4006-5, both of which have 45 wt% waste loading. HWBi4006-4 and HWBi4006-5, which differ in their B_2O_3 and SiO_2 contents (15 wt% and 42 wt%, 10 wt% and 47 wt%, respectively), do not show signs of foaming during CCC and show considerably less spinel crystallization and acceptable total crystal contents after heat treatment. SEM images of heat treated samples of HLWBi4006-4 are given in Figures 13a-d. All of the samples show spinels with varying amounts of Ni, Cr, Mn and Fe, and Na-Ca phosphate partially dissolved during sample polishing. The volume percent crystals in heat treated samples of HLWBi4006-4 varies from about 1.1 vol% at 950°C to 3.2 vol% at 800°C, as shown in Table 6c and Figure 11.

The formation of Al-bearing spinels also occurred in other high- and moderately high-Al glasses over a range of heat treatment temperatures: HWBi4006-8 with 40 wt% waste loading from 950 to 800°C; HWBi4006-9 with 35 wt% loading from 950 to 800°C and HWBi4006-10 with 35 wt% waste loading at 800°C. The total crystal content in HWBi4006-8 is high but the two other glasses are acceptable except for their relatively low waste loadings.

Three glasses for Waste Batch 4006 stand out: at 45 wt% waste loading, two low-Al formulations, HWBi4006-4 and HWBi4006-5, showed low crystal contents after heat treatment and no sign of foaming during CCC; at 40 wt% waste loading, HWBi4006-6 with moderately high Al and low Si shows similar characteristics.

The 7-day normalized PCT releases for HWBi4006-5 are lower than those for HWBi4006-4 and HWBi4006-6 by about an order of magnitude but the values for all three glasses are well below those for the DWPF-EA reference glass (Table 8). The better leaching resistance of HWBi4006-5 is likely due to its higher SiO_2 content, which also resulted in a higher melt viscosity in comparison to HWBi4006-4. At the normal operating temperature (1150°C), the viscosity of HWBi4006-5 (156 poise) is above the WTP upper limit whereas the viscosity of HWBi4006-4 (62 poise) falls within the WTP processing limits. The TCLP leachate

concentrations for all of the glass are well below the delisting limits and therefore this is not a distinguishing factor.

Overall, therefore, HWBi4006-4 with 45 wt% waste loading is considered the best candidate for Waste Batch 4006. At 40 wt% waste loading, HWBi4006-6, which has a higher Al content and lower Si content is a viable alternative in view of its likely faster melt rate as suggested by the results from small scale VGF tests for HLW-Bi-F9, which has a similar composition [3].

SECTION 6.0 CONCLUSIONS

In this work new glass formulations have been developed for several high Bi-P HLW compositions that are expected to be processed at the WTP, but have not been tested previously. WTP HLW feed compositions were reviewed to select waste batches that are high in Bi-P and that are reasonably distinct from the Bi-limited waste that has been tested previously [1, 3]. Three such high Bi-P HLW compositions were selected for this work. New high waste loading glass formulations were developed for each of the three representative Bi-P HLW wastes and characterized with respect to key processing and product quality properties and, in particular, those relating to crystallization and foaming tendency during CCC heat treatment. Based on the results from previous investigations of the mechanism of the observed foaming during CCC heat treatment, formulation modifications were made as necessary to mitigate such foaming. A total of 24 new glasses were designed, fabricated, and characterized in this work and the results were analyzed to select candidate formulations for each of the three new HLW streams. The results for each of the three HLW streams are summarized below.

Of the three new HLW streams, Waste Batch 2394 has the highest Fe_2O_3 content and the lowest P_2O_5 content. Glass formulation issues observed for this stream included a strong tendency for spinel formation in addition to melt foaming during CCC heat treatment. Since Al_2O_3 was originally proposed as an additive to compete with chromium for phosphorus [3], less alumina was used for Waste Batch 2394, which is relatively poor in P_2O_5 . HWBi2394-3, which has a moderate Al_2O_3 content, a high B_2O_3 content, and a waste loading of 45 wt%, exhibited acceptable properties except for a relatively low melt viscosity. HWBi2394-4, which has a slightly lower waste loading of 40 wt%, is an acceptable alternative formulation with improved melt viscosity that falls within the WTP operating range.

Waste Batch 4098 has the highest P_2O_5 content of the high Bi-P wastes studied to date. High-Al and high-B formulations were designed for this waste stream to manage the tendency for foaming during CCC heat treatment and crystallization. The crucible test results indicate that both HWBi4098-7 and HWBi4098-6 are acceptable formulations for Waste Batch 4098 with regard to their leaching resistance, crystal content and foaming during CCC heat treatment. HWBi4098-7 and HWBi4098-6 have waste loadings of 45 and 40 wt%, respectively. The viscosity and electrical conductivity of HWBi4098-7 are within the WTP HLW operational ranges; although the viscosity and electrical conductivity for HWBi4098-6 were not measured, they are expected to also be within the WTP limits based on the results for HW4098-7 and the compositions of the two glasses.

Waste Batch 4006 contains significant amounts of spinel-forming components (Cr, Mn and Ni) as well as more than double the Na_2O content of the original Bi-limited waste. Although previous studies [3] and the present work have shown that higher levels of aluminum are beneficial for controlling foaming during CCC heat treatment by virtue of competing with

phosphorus for chromium, it was found that aluminum was incorporated to a significant extent into the spinels that formed in glasses for this waste stream, which resulted in undesirably high crystal contents at 950°C. Therefore, the recommended formulation for this waste stream, HWBi4006-4 with a waste loading of 45 wt%, contains much lower Al_2O_3 than the formulations for the other two waste streams. In addition, Li_2O was not added to this formulation because of the high sodium content of Waste Batch 4006. This glass exhibits acceptable processing and product quality properties and although its 7-day PCT releases are relatively high, they are still well below those for the DWPF-EA reference glass.

In summary, the results from this work indicate that the foaming during CCC heat treatment that was observed for the original bismuth-limited waste stream [1, 3] is also observed to a greater or lesser extent in the three new high Bi-P waste streams that were studied. The mitigation approach through glass formulation that was developed previously [3] was found to be effective in controlling such foaming for the new waste streams. As with the original waste stream, control of spinel formation on heat treatment was also a significant factor in achieving high waste loadings for these waste streams.

The focus of the present work was to determine whether the same type of issues as seen in previous work with high-Bi HLW [1, 3], such as foaming during CCC heat treatment, would be seen in HLW streams with different concentrations of Bi, P and Cr and also whether similar glass formulation development approaches would be successful in mitigating these issues. The work was not intended to provide final optimized formulations for subsequent melter testing. Thus, the candidate glass compositions from the current tests were characterized to ensure compliance with processing and product quality requirements applicable to the WTP. However, they were not subjected to vertical gradient furnace (VGF) tests to assess processing rates. We would recommend that such VGF tests be performed, followed by any indicated formulation adjustments, before any of the candidate compositions are selected for melter tests to support high-Bi HLW processing at the WTP.

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Table 1. Compositional Summary (wt% Oxide Basis) of the Bi-Limited Waste and the Candidate Wastes Selected.

Oxide	Bi-Limited Waste [1]	WTP HLW Glass Batch 2394 Waste ⁽¹⁾	WTP HLW Glass Batch 4006 Waste ⁽¹⁾	WTP HLW Glass Batch 4098 Waste ⁽¹⁾
Al ₂ O ₃	22.45%	23.51%	14.45%	26.05%
B ₂ O ₃	0.58%	0.30%	0.50%	—
BaO	0.02%	0.12%	—	—
Bi ₂ O ₃	12.91%	11.52%	6.15%	2.31%
CaO	1.61%	4.21%	1.71%	2.60%
Cr ₂ O ₃	1.00%	1.09%	1.46%	0.97%
F	1.58%	0.95%	0.81%	0.57%
Fe ₂ O ₃	13.40%	20.93%	6.27%	7.51%
K ₂ O	0.89%	0.15%	5.22%	0.58%
La ₂ O ₃	— ⁽²⁾	—	1.75%	0.55%
Li ₂ O	0.31%	—	—	—
MgO	0.82%	0.14%	0.75%	0.22%
MnO	—	1.58%	6.82%	1.74%
Na ₂ O	12.97%	10.96%	29.80%	19.52%
NiO	3.71%	0.86%	4.29%	1.41%
P ₂ O ₅	9.60%	4.51%	8.83%	12.04%
PbO	0.48%	0.81%	0.49%	1.43%
SO ₃	0.91%	0.83%	1.58%	0.81%
SiO ₂	12.04%	9.20%	4.35%	9.56%
SrO	—	0.63%	0.29%	0.65%
ThO ₂	0.25%	0.18%	—	—
TiO ₂	0.30%	—	—	—
Tl ₂ O	—	—	0.12%	—
UO ₃	3.48% ⁽³⁾	6.75%	3.23%	10.82%
ZnO	0.31%	—	—	—
ZrO ₂	0.40%	0.35%	0.27%	0.32%
TOTAL	100.0%	99.56%	99.16%	99.66%

⁽¹⁾ Minor oxides (i.e., < 0.1 wt%) omitted.

⁽²⁾ — indicates empty data field.

⁽³⁾ U₃O₈ for Bi-limited waste.

Table 2. Compositional Summary (wt% Oxide Basis) of the HLW Simulants.

Oxide	Bi-Limited Waste [1]	WTP HLW Glass Batch 2394 Waste	WTP HLW Glass Batch 4006 Waste	WTP HLW Glass Batch 4098 Waste
Al ₂ O ₃	23.31%	25.38%	15.06%	29.33%
B ₂ O ₃	0.60%	0.32%	0.52%	—
BaO	0.02%	0.13%	—	—
Bi ₂ O ₃	13.41%	12.44%	6.41%	2.61%
CaO	1.67%	4.55%	1.78%	2.93%
Cr ₂ O ₃	1.04%	1.18%	1.52%	1.09%
F	1.64%	1.03%	0.85%	0.64%
Fe ₂ O ₃	13.92%	22.59%	6.54%	8.45%
K ₂ O	0.92%	0.16%	5.44%	0.66%
La ₂ O ₃	—	—	1.83%	0.62%
Li ₂ O	0.32%	—	—	—
MgO	0.85%	0.16%	0.79%	0.25%
MnO	—	1.70%	7.11%	1.96%
Na ₂ O	13.47%	11.83%	31.06%	21.98%
NiO	3.85%	0.92%	4.47%	1.59%
P ₂ O ₅	9.97%	4.87%	9.21%	13.55%
PbO	0.50%	0.88%	0.51%	1.61%
SO ₃	0.95%	0.89%	1.65%	0.91%
SiO ₂	12.51%	9.93%	4.53%	10.76%
SrO	—	0.68%	0.30%	0.73%
TiO ₂	0.31%	—	—	—
Tl ₂ O	—	—	0.13%	—
ZnO	0.32%	—	—	—
ZrO ₂	0.42%	0.38%	0.28%	0.36%
TOTAL	100.0%	100.0%	100.0%	100.0%
Bi ₂ O ₃ /WTP Contract Limit	6.71	6.22	3.21	1.30
P ₂ O ₅ /WTP Contract Limit	3.32	1.62	3.07	4.52
Bi ₂ O ₃ /P ₂ O ₅	1.35	2.56	0.70	0.19

— Empty data field.

Table 3. HLW Canister Centerline Cooling Temperature Profile [13].

Segment	Time (min)	Start Temperature (°C)	Rate (°C/min)
1	0-45	1050	-1.556
2	45-107	980	-0.806
3	107-200	930	-0.591
4	200-329	875	-0.388
5	329-527	825	-0.253
6	527-707	775	-0.278
7	707-1776	725	-0.304

Table 4. Target Compositions of HLW Glasses Previously Developed for Bi-Limited Waste [1, 3].

Glass ID	HLW-E-Bi6	HLW-Bi-F3	HLW-Bi-F9
Waste Loading (wt%)	50 wt%	50 wt%	50 wt%
Data Type	Target (wt%)	Target (wt%)	Target (wt%)
Al ₂ O ₃	11.66	11.66	16.66
B ₂ O ₃	11.30	10.30	16.30
BaO	0.01	0.01	0.01
Bi ₂ O ₃	6.71	6.71	6.71
CaO	0.84	0.84	0.84
Cr ₂ O ₃	0.52	0.52	0.52
F	0.82	0.82	0.82
Fe ₂ O ₃	6.96	6.96	6.96
K ₂ O	0.46	0.46	0.46
La ₂ O ₃	0.00	0.00	0.00
Li ₂ O	0.16	0.16	5.16
MgO	0.43	0.43	0.43
MnO	0.00	0.00	0.00
Na ₂ O	15.74	18.74	7.74
Nd ₂ O ₃	0.00	0.00	0.00
NiO	1.93	1.93	1.93
P ₂ O ₅	4.99	4.99	4.99
PbO	0.25	0.25	0.25
SiO ₂	36.26	34.26	29.26
SrO	0.00	0.00	0.00
TiO ₂	0.16	0.16	0.16
SO ₃	0.48	0.48	0.48
ZnO	0.16	0.16	0.16
ZrO ₂	0.21	0.21	0.21
Sum	100.00	100.00	100.00

**Table 5a. Target and XRF Analysis of Glass Compositions for Waste Batch 2394 (wt%).
B₂O₃, Li₂O and F in XRF column are target values unless otherwise noted.**

Sample ID	HWBi2394-1		HWBi2394-2		HWBi2394-3	
Waste loading	50		50		45	
Data Type	Target	XRF	Target	XRF	Target	XRF
Al ₂ O ₃	12.69	12.59	12.69	12.37	11.42	11.24
B ₂ O ₃	15.16	15.16	18.16	18.16	18.14	18.87*
BaO	0.07	0.00 ^{\$\$}	0.07	0.00 ^{\$\$}	0.06	0.00 ^{\$\$}
Bi ₂ O ₃	6.22	6.50	6.22	6.88	5.60	6.00
Cl	0.00	0.01	0.00	0.02	0.00	0.02
CaO	2.27	2.25	2.27	2.37	2.05	2.08
Cr ₂ O ₃	0.59	0.55	0.59	0.59	0.53	0.50
F	0.51	NA	0.51	NA	0.46	0.46
Fe ₂ O ₃	11.29	11.49	11.29	11.37	10.16	10.13
K ₂ O	0.08	0.12	0.08	0.12	0.07	0.09
La ₂ O ₃	0.00	0.00	0.00	0.00	0.00	0.00
Li ₂ O	4.00	4.00	6.00	6.00	6.00	5.99*
MgO	0.08	0.12	0.08	0.10	0.07	0.07
MnO	0.85	0.85	0.85	0.84	0.77	0.77
Na ₂ O	10.91	11.62	5.91	5.86	5.32	5.41
NiO	0.46	0.49	0.46	0.50	0.42	0.46
P ₂ O ₅	2.43	3.01	2.43	3.07	2.19	2.25
PbO	0.44	0.49	0.44	0.53	0.40	0.46
SiO ₂	30.97	29.96	30.97	30.33	35.47	34.32
SrO	0.34	0.32	0.34	0.35	0.30	0.31
TiO ₂	0.00	0.03	0.00	0.00	0.00	0.02
Tl ₂ O ^{\$}	0.00	0.00	0.00	0.01	0.00	0.00
SO ₃	0.45	0.26	0.45	0.33	0.40	0.38
ZrO ₂	0.19	0.19	0.19	0.22	0.17	0.17
Sum	100.00	100.00	100.00	99.99	100.00	99.99

*: B₂O₃ and Li₂O from DCP analysis

^{\$}: Reported as Tl₂O₃ by XRF and converted

^{\$\$}: BaO was inadvertently omitted

NA: Not analyzed

**Table 5a. Target and XRF Analysis of Glass Compositions for Waste Batch 2394 (wt%).
 B₂O₃, Li₂O and F in XRF column are target values unless otherwise noted (continued).**

Sample ID	HWBi2394-3r		HWBi2394-4	
Waste loading	45		40	
Data Type	Target	XRF	Target	XRF
Al ₂ O ₃	11.42	11.04	10.15	10.21
B ₂ O ₃	18.14	18.14	18.13	18.13
BaO	0.06	0.07	0.05	0.00 ^{ss}
Bi ₂ O ₃	5.60	6.55	4.98	5.60
Cl	0.00	0.02	0.00	0.02
CaO	2.05	2.15	1.82	1.86
Cr ₂ O ₃	0.53	0.55	0.47	0.49
F	0.46	NA	0.41	NA
Fe ₂ O ₃	10.16	10.67	9.04	9.13
K ₂ O	0.07	0.08	0.06	0.10
La ₂ O ₃	0.00	0.00	0.00	0.00
Li ₂ O	6.00	6.00	6.00	6.00
MgO	0.07	0.08	0.06	0.07
MnO	0.77	0.76	0.68	0.72
Na ₂ O	5.32	5.14	4.73	4.78
NiO	0.42	0.48	0.37	0.44
P ₂ O ₅	2.19	2.45	1.95	2.22
PbO	0.40	0.49	0.35	0.43
SiO ₂	35.47	34.50	39.97	39.01
SrO	0.30	0.30	0.27	0.27
TiO ₂	0.00	0.02	0.00	0.02
Tl ₂ O ^s	0.00	0.00	0.00	0.00
SO ₃	0.40	0.30	0.36	0.34
ZrO ₂	0.17	0.21	0.15	0.17
Sum	100.00	99.99	100.00	100.00

^s: Reported as Tl₂O₃ by XRF and converted

^{ss}: BaO was inadvertently omitted

NA: Not analyzed

Table 5b. Target and XRF Analysis of Glass Compositions for Waste Batch 4098 (wt%).
B₂O₃, Li₂O and F in XRF column are target values unless otherwise noted.

Sample ID	HWBi4098-1		HWBi4098-2		HWBi4098-3	
Waste loading	50		45		45	
Data Type	Target	XRF	Target	XRF	Target	XRF
Al ₂ O ₃	18.66	18.06	20.20	19.27	19.20	18.94
B ₂ O ₃	17.00	17.00	19.00	19.00	18.00	18.00
BaO	0.00	0.00	0.00	0.00	0.00	0.00
Bi ₂ O ₃	1.30	1.35	1.17	1.26	1.17	1.26
Cl	0.00	0.03	0.00	0.04	0.00	0.02
CaO	1.47	1.43	4.32	4.36	6.32	6.40
Cr ₂ O ₃	0.54	0.49	0.49	0.48	0.49	0.45
F	0.32	NA	0.29	NA	0.29	NA
Fe ₂ O ₃	4.23	4.09	3.80	3.84	3.80	3.94
K ₂ O	0.33	0.40	0.30	0.36	0.30	0.32
La ₂ O ₃	0.31	0.39	0.28	0.40	0.28	0.34
Li ₂ O	3.00	3.00	4.00	4.00	4.00	4.00
MgO	0.13	0.15	0.11	0.09	0.11	0.13
MnO	0.98	0.95	0.88	0.86	0.88	0.90
Na ₂ O	10.99	12.07	9.89	10.34	9.89	10.06
NiO	0.79	0.81	0.72	0.81	0.72	0.82
P ₂ O ₅	6.77	8.32	6.10	7.58	6.10	6.45
PbO	0.80	0.74	0.72	0.74	0.72	0.72
SiO ₂	31.38	29.73	26.84	25.70	26.84	26.38
SrO	0.36	0.34	0.33	0.33	0.33	0.32
TiO ₂	0.00	0.02	0.00	0.00	0.00	0.02
Tl ₂ O [§]	0.00	0.00	0.00	0.00	0.00	0.00
SO ₃	0.45	0.43	0.41	0.37	0.41	0.34
ZrO ₂	0.18	0.20	0.16	0.19	0.16	0.19
Sum	100.00	100.00	100.00	100.00	100.00	100.00

[§]: Reported as Tl₂O₃ by XRF and converted

NA: Not analyzed

Table 5b. Target and XRF Analysis of Glass Compositions for Waste Batch 4098 (wt%).
B₂O₃, Li₂O and F in XRF column are target values unless otherwise noted (continued).

Sample ID	HWBi4098-4		HWBi4098-5		HWBi4098-6	
Waste loading	45		45		40	
Data Type	Target	XRF	Target	XRF	Target	XRF
Al ₂ O ₃	17.20	17.19	13.20	13.31	17.73	17.39
B ₂ O ₃	17.00	17.00	17.00	17.00	17.00	17.15*
BaO	0.00	0.00	0.00	0.00	0.00	0.00
Bi ₂ O ₃	1.17	1.36	1.17	1.26	1.04	1.17
Cl	0.00	0.03	0.00	0.03	0.00	0.03
CaO	1.32	1.42	1.32	1.32	1.17	1.18
Cr ₂ O ₃	0.49	0.47	0.49	0.43	0.44	0.39
F	0.29	NA	0.29	NA	0.26	0.26
Fe ₂ O ₃	3.80	3.97	3.80	3.95	3.38	3.43
K ₂ O	0.30	0.31	0.30	0.31	0.26	0.29
La ₂ O ₃	0.28	0.35	0.28	0.30	0.25	0.26
Li ₂ O	3.00	3.00	3.00	3.00	4.00	4.01*
MgO	0.11	0.12	0.11	0.13	0.10	0.13
MnO	0.88	0.92	0.88	0.86	0.78	0.78
Na ₂ O	9.89	9.56	9.89	9.86	8.79	8.73
NiO	0.72	0.82	0.72	0.77	0.64	0.70
P ₂ O ₅	6.10	6.47	6.10	6.39	5.42	5.94
PbO	0.72	0.79	0.72	0.73	0.64	0.66
SiO ₂	35.84	35.33	39.84	39.38	37.30	36.66
SrO	0.33	0.34	0.33	0.32	0.29	0.29
TiO ₂	0.00	0.00	0.00	0.02	0.00	0.02
Tl ₂ O [§]	0.00	0.00	0.00	0.00	0.00	0.00
SO ₃	0.41	0.35	0.41	0.41	0.36	0.35
ZrO ₂	0.16	0.20	0.16	0.20	0.14	0.18
Sum	100.00	100.00	100.00	100.00	100.00	100.00

*: B₂O₃ and Li₂O from DCP analysis

§: Reported as Tl₂O₃ by XRF and converted

NA: Not analyzed

Table 5b. Target and XRF Analysis of Glass Compositions for Waste Batch 4098 (wt%).
B₂O₃, Li₂O and F in XRF column are target values unless otherwise noted (continued).

Sample ID	HWBi4098-7		HWBi4098-8		HWBi4098-9	
Waste loading	45		40		40	
Data Type	Target	XRF	Target	XRF	Target	XRF
Al ₂ O ₃	20.20	19.85	20.73	20.03	11.73	11.56
B ₂ O ₃	19.00	18.95*	20.00	20.00	18.00	18.00
BaO	0.00	0.00	0.00	0.00	0.00	0.00
Bi ₂ O ₃	1.17	1.30	1.04	1.26	1.04	1.22
Cl	0.00	0.02	0.00	0.04	0.00	0.02
CaO	1.32	1.34	1.17	1.28	1.17	1.27
Cr ₂ O ₃	0.49	0.45	0.44	0.46	0.44	0.46
F	0.29	0.29	0.26	NA	0.26	NA
Fe ₂ O ₃	3.80	3.96	3.38	3.61	3.38	3.51
K ₂ O	0.30	0.34	0.26	0.26	0.26	0.27
La ₂ O ₃	0.28	0.28	0.25	0.37	0.25	0.33
Li ₂ O	5.00	5.09*	5.00	5.00	4.00	4.00
MgO	0.11	0.13	0.10	0.13	0.10	0.10
MnO	0.88	0.90	0.78	0.84	0.78	0.85
Na ₂ O	9.89	10.09	8.79	8.21	8.79	8.16
NiO	0.72	0.76	0.64	0.76	0.64	0.76
P ₂ O ₅	6.10	6.43	5.42	6.23	5.42	6.34
PbO	0.72	0.75	0.64	0.75	0.64	0.71
SiO ₂	28.84	28.19	30.30	29.88	42.30	41.56
SrO	0.33	0.34	0.29	0.32	0.29	0.32
TiO ₂	0.00	0.00	0.00	0.02	0.00	0.03
Tl ₂ O [§]	0.00	0.00	0.00	0.00	0.00	0.00
SO ₃	0.41	0.35	0.36	0.40	0.36	0.35
ZrO ₂	0.16	0.20	0.14	0.19	0.14	0.18
Sum	100.00	100.00	100.00	99.99	100.00	99.99

*: B₂O₃ and Li₂O from DCP analysis

§: Reported as Tl₂O₃ by XRF and converted

NA: Not analyzed

**Table 5b. Target and XRF Analysis of Glass Compositions for Waste Batch 4098 (wt%).
B₂O₃, Li₂O and F in XRF column are target values unless otherwise noted (continued).**

Sample ID	HWBi4098-10	
Waste loading	35	
Data Type	Target	XRF
Al ₂ O ₃	20.27	19.91
B ₂ O ₃	19.00	19.00
BaO	0.00	0.00
Bi ₂ O ₃	0.91	1.12
Cl	0.00	0.04
CaO	1.03	1.14
Cr ₂ O ₃	0.38	0.36
F	0.22	NA
Fe ₂ O ₃	2.96	3.04
K ₂ O	0.23	0.22
La ₂ O ₃	0.22	0.33
Li ₂ O	5.00	5.00
MgO	0.09	0.12
MnO	0.69	0.70
Na ₂ O	7.69	7.36
NiO	0.56	0.63
P ₂ O ₅	4.74	5.48
PbO	0.56	0.62
SiO ₂	34.77	34.16
SrO	0.25	0.28
TiO ₂	0.00	0.01
Tl ₂ O [§]	0.00	0.00
SO ₃	0.32	0.33
ZrO ₂	0.12	0.17
Sum	100.00	99.99

[§]: Reported as Tl₂O₃ by XRF and converted
NA: Not analyzed

Table 5c. Target and XRF Analysis of Glass Compositions for Waste Batch 4006 (wt%).
B₂O₃, Li₂O and F in XRF column are target values unless otherwise noted.

Sample ID	HWBi4006-1		HWBi4006-2		HWBi4006-3	
Waste loading	50		45		45	
Data Type	Target	XRF	Target	XRF	Target	XRF
Al ₂ O ₃	15.53	15.10	14.78	14.39	14.78	14.47
B ₂ O ₃	15.26	15.26	17.23	17.23	18.23	18.23
BaO	0.00	0.00	0.00	0.00	0.00	0.00
Bi ₂ O ₃	3.21	3.45	2.89	3.22	2.89	3.15
Cl	0.00	0.03	0.00	0.03	0.00	0.03
CaO	0.89	0.90	0.80	0.85	0.80	0.83
Cr ₂ O ₃	0.76	0.71	0.69	0.70	0.69	0.66
F	0.42	NA	0.38	NA	0.38	NA
Fe ₂ O ₃	3.27	3.46	2.94	3.06	2.94	3.02
K ₂ O	2.72	2.67	2.45	2.56	2.45	2.52
La ₂ O ₃	0.91	1.06	0.82	1.09	0.82	0.98
Li ₂ O	0.00	0.00	2.00	2.00	0.00	0.00
MgO	0.39	0.32	0.35	0.27	0.35	0.30
MnO	3.56	3.46	3.20	3.24	3.20	3.25
Na ₂ O	15.53	16.18	13.98	13.91	13.98	14.29
NiO	2.24	2.39	2.01	2.26	2.01	2.20
P ₂ O ₅	4.60	5.74	4.14	5.14	4.14	4.36
PbO	0.26	0.26	0.23	0.27	0.23	0.27
SiO ₂	29.27	28.08	30.04	28.92	31.04	30.54
SrO	0.15	0.15	0.14	0.14	0.14	0.14
TiO ₂	0.00	0.02	0.00	0.01	0.00	0.01
Tl ₂ O ^s	0.06	0.05	0.06	0.04	0.06	0.04
SO ₃	0.82	0.57	0.74	0.51	0.74	0.56
ZrO ₂	0.14	0.16	0.13	0.14	0.13	0.14
Sum	100.00	100.00	100.00	99.99	100.00	100.00

^s: Reported as Tl₂O₃ by XRF and converted
 NA: Not analyzed

**Table 5c. Target and XRF Analysis of Glass Compositions for Waste Batch 4006 (wt%).
 B_2O_3 , Li_2O and F in XRF column are target values unless otherwise noted (continued).**

Sample ID	HWBi4006-4		HWBi4006-5		HWBi4006-6	
Waste loading	45		45		40	
Data Type	Target	XRF	Target	XRF	Target	XRF
Al_2O_3	6.78	6.75	6.78	6.94	14.02	13.79
B_2O_3	15.23	15.86*	10.23	10.69*	18.21	18.21
BaO	0.00	0.00	0.00	0.00	0.00	0.00
Bi_2O_3	2.89	3.12	2.89	3.10	2.57	2.87
Cl	0.00	0.02	0.00	0.02	0.00	0.03
CaO	0.80	0.84	0.80	0.81	0.71	0.75
Cr_2O_3	0.69	0.67	0.69	0.68	0.61	0.61
F	0.38	0.38	0.38	0.38	0.34	NA
Fe_2O_3	2.94	3.05	2.94	2.92	2.62	2.78
K_2O	2.45	2.46	2.45	2.44	2.17	2.30
La_2O_3	0.82	1.12	0.82	0.73	0.73	0.90
Li_2O	0.00	0.00*	0.00	0.00*	2.00	2.00
MgO	0.35	0.27	0.35	0.29	0.31	0.25
MnO	3.20	3.17	3.20	3.14	2.85	2.87
Na_2O	13.98	13.87	13.98	14.36	12.43	12.53
NiO	2.01	2.19	2.01	2.24	1.79	2.04
P_2O_5	4.14	4.15	4.14	4.35	3.68	3.93
PbO	0.23	0.26	0.23	0.26	0.21	0.26
SiO_2	42.04	40.93	47.04	45.69	33.81	33.06
SrO	0.14	0.14	0.14	0.14	0.12	0.13
TiO_2	0.00	0.02	0.00	0.02	0.00	0.02
Tl_2O^s	0.06	0.05	0.06	0.05	0.05	0.04
SO_3	0.74	0.57	0.74	0.66	0.66	0.50
ZrO_2	0.13	0.14	0.13	0.11	0.11	0.13
Sum	100.00	100.00	100.00	100.00	100.00	100.00

*: B_2O_3 and Li_2O from DCP analysis

s : Reported as Tl_2O_3 by XRF and converted

NA: Not analyzed

Table 5c. Target and XRF Analysis of Glass Compositions for Waste Batch 4006 (wt%).
B₂O₃, Li₂O and F in XRF column are target values unless otherwise noted (continued).

Sample ID	HWBi4006-7		HWBi4006-8		HWBi4006-9	
Waste loading	45		40		35	
Data Type	Target	XRF	Target	XRF	Target	XRF
Al ₂ O ₃	19.78	19.33	21.02	20.20	13.77	13.36
B ₂ O ₃	18.23	18.23	19.21	19.23*	18.18	18.18
BaO	0.00	0.00	0.00	0.00	0.00	0.00
Bi ₂ O ₃	2.89	3.26	2.57	3.04	2.24	2.78
Cl	0.00	0.02	0.00	0.04	0.00	0.03
CaO	0.80	0.85	0.71	0.74	0.62	0.69
Cr ₂ O ₃	0.69	0.60	0.61	0.55	0.53	0.55
F	0.38	NA	0.34	0.34	0.30	NA
Fe ₂ O ₃	2.94	3.01	2.62	2.75	2.29	2.50
K ₂ O	2.45	2.50	2.17	2.18	1.90	1.79
La ₂ O ₃	0.82	1.10	0.73	1.07	0.64	0.84
Li ₂ O	0.00	0.00	0.00	0.00*	3.50	3.50
MgO	0.35	0.27	0.31	0.23	0.27	0.21
MnO	3.20	3.25	2.85	2.91	2.49	2.63
Na ₂ O	13.98	14.21	12.43	12.10	10.87	10.21
NiO	2.01	2.16	1.79	1.92	1.57	1.89
P ₂ O ₅	4.14	4.44	3.68	4.01	3.22	3.75
PbO	0.23	0.27	0.21	0.24	0.18	0.23
SiO ₂	26.04	25.66	27.81	27.56	36.59	36.01
SrO	0.14	0.14	0.12	0.13	0.11	0.12
TiO ₂	0.00	0.00	0.00	0.00	0.00	0.02
Tl ₂ O ^{\$}	0.06	0.04	0.05	0.05	0.04	0.04
SO ₃	0.74	0.52	0.66	0.58	0.58	0.53
ZrO ₂	0.13	0.14	0.11	0.14	0.10	0.13
Sum	100.00	100.00	100.00	100.00	100.00	100.00

*: B₂O₃ and Li₂O from DCP analysis

^{\$}: Reported as Tl₂O₃ by XRF and converted

NA: Not analyzed

Table 5c. Target and XRF Analysis of Glass Compositions for Waste Batch 4006 (wt%).
B₂O₃, Li₂O and F in XRF column are target values unless otherwise noted (continued).

Sample ID	HWBi4006-10	
Waste loading	35	
Data Type	Target	XRF
Al ₂ O ₃	20.27	19.65
B ₂ O ₃	19.18	19.18
BaO	0.00	0.00
Bi ₂ O ₃	2.24	2.75
Cl	0.00	0.04
CaO	0.62	0.67
Cr ₂ O ₃	0.53	0.56
F	0.30	NA
Fe ₂ O ₃	2.29	2.53
K ₂ O	1.90	2.06
La ₂ O ₃	0.64	0.96
Li ₂ O	2.00	2.00
MgO	0.27	0.21
MnO	2.49	2.55
Na ₂ O	10.87	10.55
NiO	1.57	1.77
P ₂ O ₅	3.22	3.64
PbO	0.18	0.23
SiO ₂	30.59	29.85
SrO	0.11	0.12
TiO ₂	0.00	0.02
Tl ₂ O ^{\$}	0.04	0.04
SO ₃	0.58	0.50
ZrO ₂	0.10	0.12
Sum	100.00	99.99

^{\$}: Reported as Tl₂O₃ by XRF and converted
 NA: Not analyzed

Table 6a. Characterization of Glass Samples for Waste Batch 2394 (Sp=Spinel; Apt=Apatite).

Glass ID	HWBi2394-1	HWBi2394-2	HWBi2394-3	HWBi2394-4
Waste loading (wt%)	50	50	45	40
Visual Inspection of Poured Glass Specimen	Trace Crystallization	Vitreous	Vitreous	Vitreous
Foaming During CCC	Large vesicles near bottom	None	None	None
Vol% of Crystalline Phase at 950°C	1.1% Sp	1.81% Sp	0.77% Sp	1.22% Sp
Vol% of Crystalline Phase at 900°C	1.8%, Sp + trace Apt	1.97% Sp	1.16% Sp	1.33% Sp
Vol% of Crystalline Phase at 850°C	2.3% Sp + trace Apt	2.6% Sp + trace Apt	1.98% Sp + trace Apt	1.85% Sp + trace Apt
Vol% of Crystalline Phase at 800°C	2.7% Sp + 0.3% Apt	3.5% Sp + 0.5% Apt + trace phosphate (?)	2.32% Sp + 0.5% phosphate (?) + 0.2% Apt	2.5% Sp + 1.1% Apt + 1.3% phosphate (?)
Viscosity (Poise) at 1150°C	-	-	15.6 Poise	25 Poise
Electrical Conductivity (S/cm) at 1150°C	-	-	0.38 S/cm	0.35 S/cm
7 Day PCT-B (g/L)	-	-	0.849	0.941
TCLP	-	-	PASS	PASS

— Empty data field.

Table 6b. Characterization of Glass Samples for Waste Batch 4098 (Sp=Spinel; Apt=Apatite).

Glass ID	HWBi4098-1	HWBi4098-2	HWBi4098-3	HWBi4098-4	HWBi4098-5	HWBi4098-6
Waste loading (wt%)	50	45	45	45	45	40
Visual Inspection of Poured Glass Specimen	Trace Crystallization	Trace Crystallization	Trace Crystallization	Trace Crystallization	Trace Crystallization	Vitreous
Foaming During CCC	Large vesicles near bottom/side	Few vesicles on bottom/side	None	One vesicle on bottom	Few vesicles on bottom	One large vesicle on bottom
Vol% of Crystalline Phase at 950°C	0.8 % Sp	2.33% Apt + 0.66% Sp	3.95% Apt + 0.85 Sp	0.76% Sp + 0.08% Apt	0.48% Apt + 0.44% Sp + 0.35% Na-Ca phosphate	0.73% Sp with Al
Vol% of Crystalline Phase at 900°C	1.3% Apt + 0.9% Sp	3.97% Apt + 0.94% Sp	6.2% Apt + 1.2% Sp	0.98% Apt + 0.66% Sp + trace La-phosphate	1.5% Na-Ca phosphate + 1% Apt + 0.5% Sp	0.62% Sp with Al + 0.41% Apt + trace La-phosphate
Vol% of Crystalline Phase at 850°C	1.5% Apt + 1.1% Sp	4.9% Apt + 1% Sp	7.2% Apt + 1.4 Sp	1.2% Sp + 0.8% Apt + 0.2% Na-Ca phosphate	1.61% Apt + 1.6% Na-Ca phosphate + 0.58% Sp	1.1% Apt + 0.78% Sp with Al + trace La-phosphate + trace Na-Ca Phosphate
Vol% of Crystalline Phase at 800°C	0.6 % Sp + 0.4% Apt + 0.1% Na-Ca Phosphate	6% Apt + 1.2% Sp	8.8% Apt + 1% Sp	2.1% Apt + 0.9% Sp + 0.5% Na-Ca phosphate	2.26% Apt + 2% Na-Ca phosphate + 0.66% Sp	2.1% Apt + 1% Sp with Al + 0.8% phosphate
Viscosity (Poise) at 1150°C	-	-	-	-	-	-
Electrical Conductivity (S/cm) at 1150°C	-	-	-	-	-	-
7 Day PCT-B (g/L)	-	-	-	-	-	0.657
TCLP	-	-	-	-	-	PASS

— Empty data field.

Table 6b. Characterization of Glass Samples for Waste Batch 4098 (Sp=Spinel; Apt=Apatite) (continued).

Glass ID	HWBi4098-7	HWBi4098-8	HWBi4098-9	HWBi4098-10
Waste loading (wt%)	45	40	40	35
Visual Inspection of Poured Glass Specimen	Vitreous	Trace Crystallization	Trace Crystallization	Vitreous
Foaming During CCC	None	One large vesicle on bottom	None	None
Vol% of Crystalline Phase at 950°C	0.78% Sp with Al	0.66% Sp with Al	1.76% Sp with Al + 0.14% La-phosphate	0.64% Sp with Al
Vol% of Crystalline Phase at 900°C	0.68% Sp with Al	1.02% Sp with Al	2.31% Sp with Al + 0.37% La-phosphate	0.81% Sp with Al
Vol% of Crystalline Phase at 850°C	1.08% Sp with Al + 0.27% Apt	1.05% Sp with Al + trace Apt + trace La-phosphate	2.4% Sp with Al + 0.3% La-phosphate	1% Sp with Al + trace Apt + trace La-phosphate
Vol% of Crystalline Phase at 800°C	1.53% Apt + 1.46% phosphate (?) + 1.36% Sp with Al + trace La-phosphate	1.4% phosphate (?) + 1.16% Apt + 1.14% Sp + trace La-phosphate	1.02% Sp + 0.96% Apt + 0.26% La-phosphate + 0.16% phosphate (?)	1.6% Na-Ca phosphate + 1.3% Apt + 1% Sp + trace La-phosphate
Viscosity (Poise) at 1150°C	25.6 Poise	-	-	-
Electrical Conductivity (S/cm) at 1150°C	0.43S/cm	-	-	-
7 Day PCT-B (g/L)	1.801	-	-	-
TCLP	PASS	-	-	-

— Empty data field.

Table 6c. Characterization of Glass Samples for Waste Batch 4006 (Sp=Spinel; Apt=Apatite).

Glass ID	HWBi4006-1	HWBi4006-2	HWBi4006-3	HWBi4006-4	HWBi4006-5	HWBi4006-6	HWBi4006-7
Waste loading (wt%)	50	45	45	45	45	40	45
Visual Inspection of Poured Glass Specimen	Trace Crystallization	Trace Crystallization	Trace Crystallization	Vitreous	Vitreous	Vitreous	Trace Crystallization
Foaming During CCC	Few vesicles near bottom	One vesicle near bottom	None	None	None	None	None
Vol% of Crystalline Phase at 950°C	2.6% Sp + 0.3% Ca-Na phosphate	1.11% Sp	2.2% Sp + 0.9% Na-Ca phosphate	0.69% Sp + 0.4% Na-Ca phosphate	0.29% Sp + 0.3% Na-Ca phosphate	1.10% Sp	2.93% Sp with Al + 0.32% La-phosphate
Vol% of Crystalline Phase at 900°C	3% Ca-Na phosphate + 2.1% Sp	1.81% Sp	2.2% Sp + 1% Na-Ca phosphate + trace La-phosphate	1% Sp + 0.8% Na-Ca phosphate	1.2% Na-Ca phosphate + 0.5% Sp	1.44% Sp + trace La-phosphate	2.9% Sp with Al + 0.4% La-phosphate + 0.26% Na-Ca phosphate
Vol% of Crystalline Phase at 850°C	4.4% Ca-Na phosphate + 2.2% Sp	2.2% Sp + 1.1 Na-Ca Phosphate	2.4% Na-Ca Phosphate + 2.4% Sp	3.1% phosphate + 1% Sp	1.5% Na-Ca phosphate + 0.49% Sp	1.9% Sp + 0.3% Na-Ca Phosphate + trace La-Phosphate	2.6% Sp with Al + 0.93% Na-Ca phosphate + 0.06% La-P
Vol% of Crystalline Phase at 800°C	2% Sp + 1% Na-Ca phosphate	3.3% Na-Ca phosphate + 1.7% Sp	2.3% Na-Ca phosphate + 2.1% Sp	2.2% phosphate + 1% Sp	3.5% Na-Ca phosphate + 0.1% Sp	2.3% Sp + 1.2 Na-Ca phosphate + trace La-phosphate	3% Sp with Al + 1.3% Na-Ca phosphate + 0.1% La-phosphate
Viscosity (Poise) at 1150°C	-	-	-	62.5 Poise	155.8 Poise	-	-
Electrical Conductivity (S/cm) at 1150°C	-	-	-	0.27 S/cm	0.26 S/cm	-	-
7 Day PCT-B (g/L)	-	-	-	3.789	0.374	4.487	-
TCLP	-	-	-	PASS	PASS	PASS	-

— Empty data field.

Table 6c. Characterization of Glass Samples for Waste Batch 4006 (Sp=Spinel; Apt=Apatite) (continued).

Glass ID	HWBi4006-8	HWBi4006-9	HWBi4006-10
Waste loading (wt%)	40	35	35
Visual Inspection of Poured Glass Specimen	Trace Crystallization	Vitreous	Vitreous
Foaming During CCC	None	None	None
Vol% of Crystalline Phase at 950°C	2.41% Sp with Al + 0.35% La-phosphate	0.73% Sp with Al	0.3% Na-Ca Phosphate + 0.1% Sp
Vol% of Crystalline Phase at 900°C	2.7% Sp with Al + 0.5% La-phosphate + 0.3% Apt	1.21% Sp with Al	0.5% Na-Ca phosphate + 0.23% Sp
Vol% of Crystalline Phase at 850°C	3% Sp with Al + 0.3 La-phosphate + 0.3% Apt	1.25% Sp with Al + trace La-Phosphate	1.82% Na-Ca phosphate + 0.88% Apt + 0.47% Sp
Vol% of Crystalline Phase at 800°C	2.73% Sp with Al + 0.33% Apt + 0.18% La-phosphate	1.89% Sp with Al + 1.1% phosphate (?) + trace La-P	3.4% Na-Ca phosphate + 2.27% Apt + 0.46% Sp with Al + trace La-phosphate
Viscosity (Poise) at 1150°C	-	-	-
Electrical Conductivity (S/cm) at 1150°C	-	-	-
7 Day PCT-B (g/L)	3.327	-	-
TCLP	PASS	-	-

— Empty data field.

Table 7. Viscosity and Electrical Conductivity of Selected Bi-P Glass Melts.

Temperature (°C)	HWBi4006-4		HWBi4006-5		HWBi4098-7		HWBi2394-3		HWBi2394-4	
	Viscosity (Poise)	Conductivity (S/cm)	Viscosity (Poise)	Conductivity (S/cm)	Viscosity (Poise)	Conductivity (S/cm)	Viscosity (Poise)	Conductivity (S/cm)	Viscosity (Poise)	Conductivity (S/cm)
1250	28.24	0.35	64.62	0.36	12.63	0.58	7.86	0.50	12.80	0.45
1150	62.49	0.27	155.82	0.26	25.64	0.43	15.57	0.38	25.00	0.35
1050	174.81	0.19	473.62	0.18	62.50	0.31	36.77	0.27	59.47	0.25
950	698.55	0.11	2016.28	0.12	198.38	0.21	111.80	0.17	190.68*	0.15

*: Extrapolated from three data points above due to non-Newtonian behavior at 956°C in actual measurement.

Table 8. Normalized 7-Day PCT Element Releases for Selected Bi-P HLW Glasses.

Glass ID	B (g/L)	Li (g/L)	Na (g/L)
DWPF-EA	16.7	9.6	13.3
HWBi4006-4	3.789	-	2.363
HWBi4006-5	0.374	-	0.461
HWBi4006-6	4.487	2.931	2.420
HWBi4006-8	3.327	-	1.974
HWBi4098-6	0.657	0.800	0.286
HWBi4098-7	1.801	1.340	0.974
HWBi2394-3	0.849	0.806	0.463
HWBi2394-4	0.941	0.904	0.394

Table 9. TCLP Element Releases from Selected Bi-P HLW Glasses.

Glass ID	Ba (ppm)	Cr (ppm)	Ni (ppm)	Pb (ppm)
Delisting Limit	100	4.95	22.6	5
HWBi4006-4	-	0.09	0.66	<0.1
HWBi4006-5	-	0.09	0.34	<0.1
HWBi4006-6	-	0.04	0.23	<0.1
HWBi4006-8	-	<0.01	0.17	<0.1
HWBi4098-6	-	0.02	0.10	<0.1
HWBi4098-7	-	0.03	0.13	0.13
HWBi2394-3	-	0.03	0.08	<0.1
HWBi2394-3r	0.02	0.03	0.07	<0.1
HWBi2394-4	-	0.02	0.05	<0.1

— Empty data field.

Figure 1. Cross sections of glass CCC samples of Waste Batch 2394.

Figure 2a. SEM image of HLWBi2394-3 heat treated at 950°C (Fe-Cr-Ni spinel with Mn).

Figure 2b. SEM image of HLWBi2394-3 heat treated at 900°C (Fe-Cr-Ni spinel with Mn).

Figure 2c. SEM image of HLWBi2394-3 heat treated at 850°C (bright phase: Fe-Cr-Ni spinel with Mn; grey phase: Apatite).

Figure 2d. SEM image of HLWBi2394-3 heat treated at 800°C (bright phase: Fe-Cr-Ni spinel with Mn; grey phase: Apatite).

Figure 3a. SEM image of HLWBi2394-4 heat treated at 950°C (Fe-Cr-Ni spinel with Mn).

Figure 3b. SEM image of HLWBi2394-4 heat treated at 900°C (Fe-Cr-Ni spinel with Mn).

Figure 3c. SEM image of HLWBI2394-4 heat treated at 850 °C (bright phase: Cr-Fe spinel with Ni and Mn; grey phase: Apatite).

Figure 3d. SEM image of HLWBI2394-4 heat treated at 800 °C (bright diamond shaped phase: Fe-Cr-Ni spinel with Mn; bright acicular shaped phase: Fe-Cr oxide; grey phase: Apatite).

Figure 4. Total amount of crystalline phases (vol%) after isothermal heat treatment of HWBi2394-3 (45 wt% waste loading, blue open circles) and HWBi2394-4 (40 wt% waste loading, red open squares).

HWBi-4098-1CCC

HWBi-4098-2CCC

HWBi-4098-3CCC

HWBi-4098-4CCC

Figure 5. Cross sections of glass CCC samples of Waste Batch 4098.

HWBi4098-5CCC

HWBi4098-6CCC

HWBi4098-7CCC

HWBi4098-8CCC

Figure 5. Cross sections of glass CCC samples of Waste Batch 4098 (continued).

Figure 5. Cross sections of glass CCC samples of Waste Batch 4098 (continued).

50μm

Figure 6a. SEM image of HLWBi4098-6 heat treated at 950°C (Cr-Fe-Mn-Ni spinel).

60μm

Figure 6b. SEM image of HLWBi4098-6 heat treated at 900°C (bright diamond shaped phase: Cr-Fe-Mn-Ni spinel; grey phase: Apatite; very bright platelet: La-phosphate).

Figure 6c. SEM image of HLWBi4098-6 heat treated at 850° C (bright phase: Cr-Fe-Mn-Ni spinel; grey phase: Apatite).

Figure 6d. SEM image of HLWBi4098-6 heat treated at 800° C (light grey diamond shaped clusters : Cr-Fe-Mn-Ni spinel; grey phase near top center: Apatite; very bright phase near center: La-phosphate; black segmented cavity: probably voids created by dissolution of alkaline phosphate during sample polishing).

Figure 7a. SEM image of HLWBi4098-7 heat treated at 950° C (Cr-Fe-Mn-Ni spinel).

Figure 7b. SEM image of HLWBi4098-7 heat treated at 900° C (Cr-Fe-Mn-Ni spinel).

Figure 7c. SEM image of HLWBi4098-7 heat treated at 850°C (bright phase: Cr-Fe-Mn-Ni spinel; grey phase: Apatite).

Figure 7d. SEM image of HLWBi4098-7 heat treated at 800°C (bright phase: Cr-Fe-Mn-Ni spinel; black segmented cavity: Probably voids from alkaline phosphate dissolved during sample polishing).

Figure 7e. SEM image of HLWBi4098-7 heat treated at 800°C (grey phase: Apatite).

Figure 8. Total amount of crystalline phases (vol%) after isothermal heat treatment of HWBi4098-7 (45 wt% waste loading, blue open circles) and HWBi4098-6 (40 wt% waste loading, red open squares).

HWBi-4006-1CCC

HWBi-4006-2CCC

HWBi-4006-3CCC

HWBi-4006-4CCC

Figure 9. Cross sections of glass CCC samples of Waste Batch 4006.

Figure 9. Cross sections of glass CCC samples of Waste Batch 4006 (continued).

Figure 9. Cross sections of glass CCC samples of Waste Batch 4006 (continued).

Figure 10a. SEM image of HLWBi4006-6 heat treated at 950° C (Cr-Fe-Mn-Ni Spinel).

Figure 10b. SEM image of HLWBi4006-6 heat treated at 900° C (grey phase: Cr-Fe-Mn-Ni spinel; bright phase on the left side: La-phosphate).

Figure 10c. SEM image of HLWBi4006-6 heat treated at 850° C (bright phase: La-phosphate; grey phase: Cr-Fe-Mn-Ni spinel).

Figure 10d. SEM image of HLWBi4006-6 heat treated at 800° C (bright angular phase near center: La-phosphate; grey platelets: Ni-rich spinel with Cr, Fe and Mn).

Figure 11. Total amount of crystalline phases (vol%) after isothermal heat treatment of HWBi4006-4 (45 wt% waste loading, blue open circles) and HWBi4006-6 (40 wt% waste loading, red open squares).

Figure 12a. SEM image of HLWBi4006-7 heat treated at 950° C (bright phase near bottom and top: La-phosphate; grey phase: Cr-Fe-Mn-Ni spinel with Al).

Figure 12b. SEM image of HLWBi4006-7 heat treated at 800° C (bright platelet near bottom right corner: La-phosphate; Grey phase: Cr-Fe-Mn-Ni spinel with considerable amount of Al; black globular shapes: Voids probably due to dissolution of Na-Ca phosphate during sample polishing).

Figure 13a. SEM image of HLWBi4006-4 heat treated at 950 °C (bright tabular phase: Ni-Cr spinel with Mn and Fe; globular regions along the boundary between dark grey (glass) and black (epoxy) area: Voids and remnants of Na-Ca phosphate partially dissolved during sample polishing).

Figure 13b. SEM image of HLWBi4006-4 heat treated at 900 °C (bright phase: Ni-Cr spinel with Mn and Fe; dark grey globular shapes: Voids and remnants of Na-Ca phosphate with La, partially dissolved during sample polishing).

Figure 13c. SEM image of HLWBi4006-4 heat treated at 850°C (bright phase near center: Ni-Cr spinel with Mn and Fe; black globular regions: Probably voids due to dissolution of Na-Ca phosphate during sample polishing).

Figure 13d. SEM image of HLWBi4006-4 heat treated at 800°C (bright platelet: Ni-Mn spinel with Cr and Fe; black globular regions near center: Voids and remnants of Na-Ca phosphate partially dissolved during sample polishing).