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Evaluation of Defense Waste Processing Facility (DWPF) Glass Samples After an Extended Melter Outage

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EXECUTIVE SUMMARY

The Savannah River Site Defense Waste Processing Facility (DWPF) melter was recently idled with glass remaining in the melt pool and riser for approximately three months. An outage of this duration presented a unique opportunity to collect and analyze glass pour stream samples. The objective of this study was to investigate the potential for precipitation of crystals in the glass during an extended idling period. The results obtained provide support for development of a crystal-tolerant glass approach for operation of the high level waste melter at the Hanford Tank Waste Treatment and Immobilization Plant (WTP).

Two glass pour stream samples were collected from DWPF when the melter was restarted after idling for three months. The samples did not contain crystallization that was detectable by X-ray diffraction. Electron microscopy identified occasional spinel and noble metal crystals of no practical significance. Occasional platinum particles were observed by microscopy as an artifact of the sample collection method. Reduction/oxidation measurements showed that the glass pour stream samples were fully oxidized, which was expected after the extended idling period.

Chemical analysis of the glass pour stream samples revealed slight differences in the concentrations of some oxides relative to analyses of the melter feed composition prior to the idling period. While these differences may be within the analytical error of the laboratories, the trends indicated that there may have been some amount of volatility associated with some of the glass components, and that there may have been interaction of the glass with the refractory components of the melter. These changes in composition, although small, can be attributed to the idling of the melter for an extended period. The changes in glass composition resulted in a 70-100 °C increase in the predicted spinel liquidus temperature (T_L) for the pour stream glass samples. This indicated that the potential for spinel crystallization increased as a result of idling for an extended period. However, the predicted T_L of the pour stream glasses remained 150-200 °C below the mean melt pool temperature of about 1125 °C during the idling period.

The U.S. Department of Energy is investigating an alternative approach to avoid the deleterious effects of crystallization in the WTP high level waste melter. WTP currently plans to control glass composition such that the temperature at which 1 vol % of spinel crystals is in equilibrium with the glass melt ($T_{1\%}$) remains below 950 °C. This constraint significantly influences waste loading and, therefore, the amount of glass to be produced. The possibility of controlling the glass composition such that the accumulation rate of spinel crystals in the melter does not exceed a melter life-related limit is being investigated to provide the technical basis for that limit as well as increase waste loading. The data in this report demonstrate that: 1) a glass with a predicted T_L below 1050 °C can still form some amount of spinel crystals in a melter, and, 2) the composition of the glass in a melter after an extended idling period can change, and this change can result in an increase in the predicted T_L . These findings are important for implementation of spinel crystallization control strategies for WTP. The current WTP crystal tolerant glass program is developing an improved understanding of spinel crystallization, settling, and accumulation in the WTP melter to allow for operation at maximum waste loading in glass composition systems limited by crystallinity constraints.

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LIST OF ABBREVIATIONS

ARP	Actinide Removal Process
BSE	Backscattered Electron
DOE	U.S. Department of Energy
DWPF	Defense Waste Processing Facility
EA	Environmental Assessment
EDS	Energy Dispersive Spectroscopy
HLW	High Level Waste
ICP-AES	Inductively Coupled Plasma – Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma – Mass Spectroscopy
JHCM	Joule-Heated Ceramic Melter
LAW	Low Activity Waste
MA	Mixed Acid
MCU	Modular Caustic Side Solvent Extraction Unit
MFT	Melter Feed Tank
PCCS	Product Composition Control System
PF	Peroxide Fusion
REDOX	REDuction/OXidation
SB8	Sludge Batch 8
SE	Secondary Electron
SEM	Scanning Electron Microscopy
SME	Slurry Mix Evaporator
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
UV-Vis	Ultraviolet-Visible
WTP	Hanford Tank Waste Treatment and Immobilization Plant
WVDP	West Valley Demonstration Project
XRD	X-ray Diffraction

1.0 Introduction

The U.S. Department of Energy (DOE) is building a Tank Waste Treatment and Immobilization Plant (WTP) at the Hanford Site in Washington to remediate 55 million gallons of radioactive waste that is being temporarily stored in underground tanks. It is planned that the WTP will vitrify the Hanford wastes into borosilicate glass with Joule-heated ceramic melter (JHCMS).¹ This melting technology was successfully used from 1996 to 2002 at the West Valley Demonstration Project (WVDP) in New York and has been in continuous use at the Defense Waste Processing Facility (DWPF) at the Savannah River Site (SRS) since 1996. Efforts are now being made to increase the targeted loading of Hanford tank wastes in glass while maintaining the ability to meet processing, regulatory compliance, and product quality requirements.

Recent glass formulation and melter testing data have suggested that significant increases in waste loading in high level waste (HLW) and low activity waste (LAW) glasses are possible over current WTP system planning estimates.² The data (although limited in some cases) were evaluated to determine a set of constraints and models that could be used to estimate the maximum loading of specific waste compositions in glass. It was recognized that some of the models are preliminary in nature and some do not currently address prediction uncertainties that would be needed before they could be used in plant operations. However, the assessments based on these enhanced models or advanced glass formulation show significant improvement in waste loading and thus continuing to assess their potential applicability is of utmost importance.

One of the most restricting constraints on the estimated Hanford HLW glass waste loadings is the limit of no more than one volume percent spinel crystals in the melt ($T_{1\%}$) at a temperature of 950 °C.³ Crystallization constraints are included in process control systems to prevent premature or catastrophic failure of the melter from bulk devitrification and to mitigate negative impacts from crystallization as glass is produced. The current WTP strategy is to process a glass with some fraction of crystallization through the HLW melter to meet waste loading expectations. A road map was developed to guide research and development efforts to support this strategy.⁴ One option that is being considered is the use of an empirical model predicting the crystal accumulation in the glass discharge riser of the WTP melter as a function of glass composition, time, and temperature. When coupled with an associated constraint, this model could then be integrated into the process control algorithms to formulate crystal tolerant HLW glasses targeting higher waste loadings while still meeting process related constraints and melter lifetime expectancies.

As part of the road map, historical information from the DWPF flowsheet development and operational experience has been documented to provide insight into operational issues associated with crystallization within the melter, riser, pour spout, and glass.⁵ However, additional information on the potential for crystal accumulation can be gained from glass samples collected from the DWPF melter pour stream after operation in off-normal conditions.

The DWPF melter was recently idled with Sludge Batch 8 (SB8) glass remaining in the melt pool and riser for approximately three months (October 2013 through December 2013). This situation presented a unique opportunity to collect and analyze glass pour stream samples for crystallinity, elemental composition, and iron REDuction/OXidation (REDOX). This information, coupled with the measured temperature profiles of the melter and riser during the idling period, can provide insight into crystallization, settling, and accumulation of spinel crystals in a full-scale and operational HLW melter.

The objective of this study was to investigate the potential for precipitation of crystals in the glass during an extended idling period. The results provide support for development of a crystal-tolerant glass approach for operation of the high level waste melter at WTP.

1.1 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in Savannah River Nuclear Solutions Manual E7, 2.60. The Savannah River National Laboratory (SRNL) documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2. This study was performed following Task Technical and Quality Assurance Plan SRNL-RP-2013-00853, Revision 1.⁶

2.0 Melter Glass Sampling

2.1 DWPF Melter Idling Period

The full scale DWPF melter is cylindrical, with a melt pool diameter of about 1.83 m and Monofrax[®] K-3 as the glass contact refractory (see Figure 2-1). All metallic components within the melter are Inconel[®] 690. The riser is lined with Inconel[®] 690 and surrounded by an electrical resistance heater, while the melt pool is surrounded by Monofrax[®] K-3 refractory and is Joule heated. The DWPF is currently operating with its second JHCM, referred to as Melter 2. Melter 2 entered service in March 2003 and has operated on a semi-continuous basis since then.

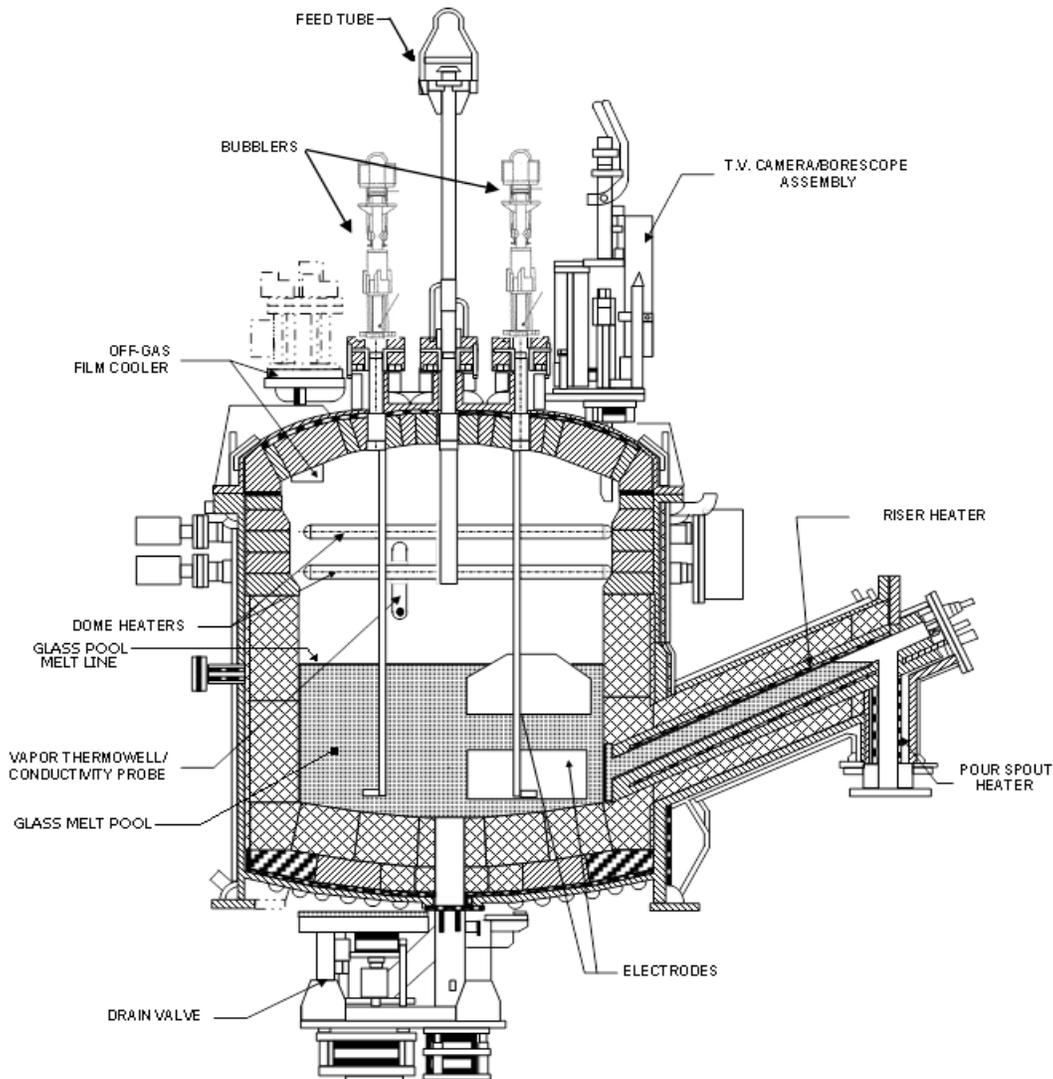


Figure 2-1. Cross-sectional Overview of the DWPF Melter

Melter idling periods, some examples of which are described in detail elsewhere,⁵ occur infrequently and are generally the result of maintenance activities or delays in melter feed preparation. Idling periods typically last for a few hours in the case of unplanned maintenance, a few days for feed delays, and up to about four weeks for planned maintenance outages. An unusually lengthy idling period occurred at the DWPF from early October 2013 to late December 2013. An outage of this duration presented a unique opportunity to collect and characterize glass pour stream samples for crystallinity, elemental composition, and iron REDOX.

2.2 Pour Stream Sample Collection

SRNL requested that DWPF engineering and operations collect two glass pour stream samples in support of this study when restarting melter operation.⁷ The first sample was intended to represent the material that had been within the riser during the three month idling period. The second sample was intended to be material that was in the melt pool during the idling period. Temperature conditions were expected to be somewhat different within the riser versus the melt pool during the idling period. As previously mentioned, the riser is lined with Inconel[®] 690 and surrounded by an electrical resistance heater, while the

melt pool is surrounded by Monofrax® K-3 refractory and is Joule heated. It was assumed that any convective currents were inconsequential in transferring glass between the riser and melt pool during the idling period.

For the purposes of this study, the DWPF melter outage began at 12am on October 3, 2013, and ended just after 12am on December 31, 2013.^a Glass pour stream samples are collected using a remotely operated sample collector that is placed on top of a DWPF canister prior to lowering the pour spout bellows onto the top of the canister. The sampler contains a platinum-alloy boat^b that can be moved into and out of the path of the glass pour stream using a remotely operated manipulator. Once the bellows is lowered, the sampler is not removed until the canister is filled. As a result of this method, only a single sample can be retrieved per canister and the sampled glass cools at an uncontrolled (but likely rapid) rate.

The first pour stream sample was collected between approximately 4:57am and 4:59am on December 31, 2013. DWPF operations collected the sample as soon as was practically possible upon initiating pouring. Figure 2-2 shows select data recorded from the DWPF instrumentation during this time period. Pour spout pressure is reduced in order to initiate glass pouring. The glass weight^c in the canister then begins to rise. A signal is manually triggered in the data acquisition system to indicate when the sampler has been moved into the path of the pour stream. The status of this signal is indicated by the black line in Figure 2-2. Feed was being supplied to the melter from the Melter Feed Tank (MFT) as pouring was started.

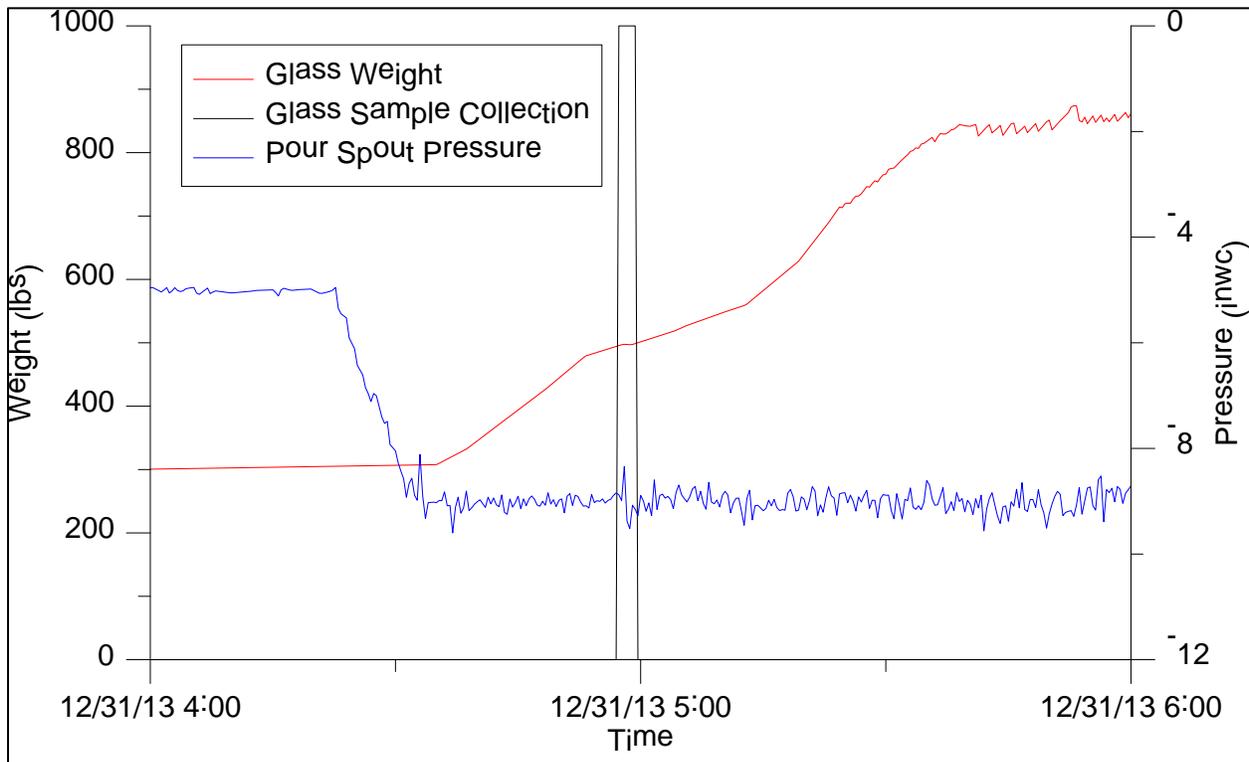


Figure 2-2. Detail of collection of first glass sample after three month outage

^a These times are approximate, but are of sufficient precision to support this study of crystallization in the glass during the idle period.

^b Approximate dimensions of platinum alloy boat were 40 mm long, 30 mm wide, and 15 mm deep.

^c Note that the canister weight indication is used at DWPF as a reference only. Actual glass height in the canister is monitored using an infra-red camera. Relative changes in canister weight were used to identify the beginning of pouring periods and the amount of glass poured for the purposes of this report.

Based on the data shown in Figure 2-2, approximately 192 lbs of glass were poured into the canister before the sampler was inserted into the pour stream. The DWPF riser contains approximately 70 lbs of glass.^a Therefore, the first pour stream sample may not be representative of glass that remained in the riser during the extended idling period as was intended. However, given that the melter contains roughly 13,500 lbs of glass, this sample remains representative of some of the earliest glass to be poured from the melter after the extended idling period.

The second pour stream sample was collected between approximately 5:47am and 5:50am on January 3, 2014. DWPF operations collected the sample as soon as was practically possible upon initiating pouring of the second canister after the extended idling period. Figure 2-3 shows select data recorded from the DWPF instrumentation during this time period. These data show that approximately 17 lbs of glass were poured into the canister before the sampler was inserted into the pour stream.^b Approximately 3773 lbs of glass were poured between the end of the idling period and collection of the second sample. Feed was being supplied to the melter from the MFT during the pouring of the first canister and as pouring of the second canister was started. No transfers were made from the Slurry Mix Evaporator (SME) to the MFT during this time period. That is, there were no changes to the composition of the melter feed during this time period.

^a The mass of glass in the riser was estimated using the riser dimensions provided in E. I. DuPont de Nemours drawing number W801372, with an assumed glass density of 2.65 g/ml at approximately 1050 °C.

^b The second pour stream sample was collected closer to the time when pouring was initiated, as compared to the first pour stream sample. This is likely a result of the need for DWPF operations personnel to monitor many aspects of the glass production operation when first exiting the outage, with collection of the pour stream sample being a secondary priority during the resumption of glass pouring. However, given the complexity of the operations, the timing of the sample collection is as good as or better than could be expected.

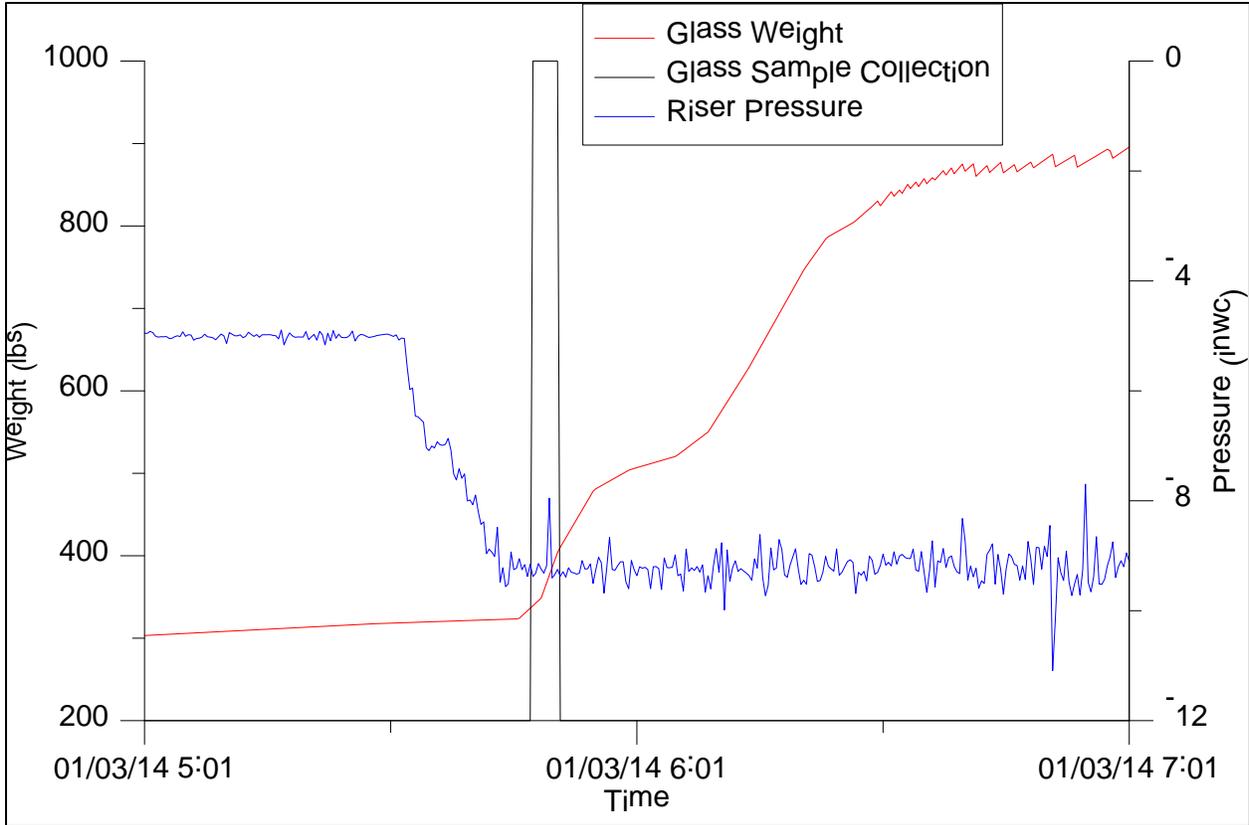


Figure 2-3. Detail of collection of second glass sample after three month outage

The two glass pour stream samples in the platinum-alloy boats were packaged and shipped from DWPF to SRNL for analysis. The first sample was labeled PC0125. The second sample was labeled PC0126.

3.0 Melter Conditions During Idling

The thermal history of the glass within the melter and riser during the extended idling period is important in evaluating the potential for precipitation, settling, and accumulation of crystals in the melter.

Figure 3-1 provides an overview of the melt pool, riser, and vapor space temperatures during the three month idling period. There are multiple thermocouples in the upper and lower regions of the DWPF melt pool. The means of the values recorded from these thermocouples are plotted in Figure 3-1 for simplicity. Similarly, the vapor space contains three thermocouples, with the mean of their values plotted in the figure. Four thermocouples monitor the temperature of the riser. These thermocouples are located on the outside of the 1.5 in. thick Inconel® 690 riser tube through which the glass flows, and therefore are indirect measurements of the temperature of the glass within the riser. One of these four thermocouples is selected by the DWPF control system as the control for the riser temperature. The values from this selected thermocouple are plotted in Figure 3-1.

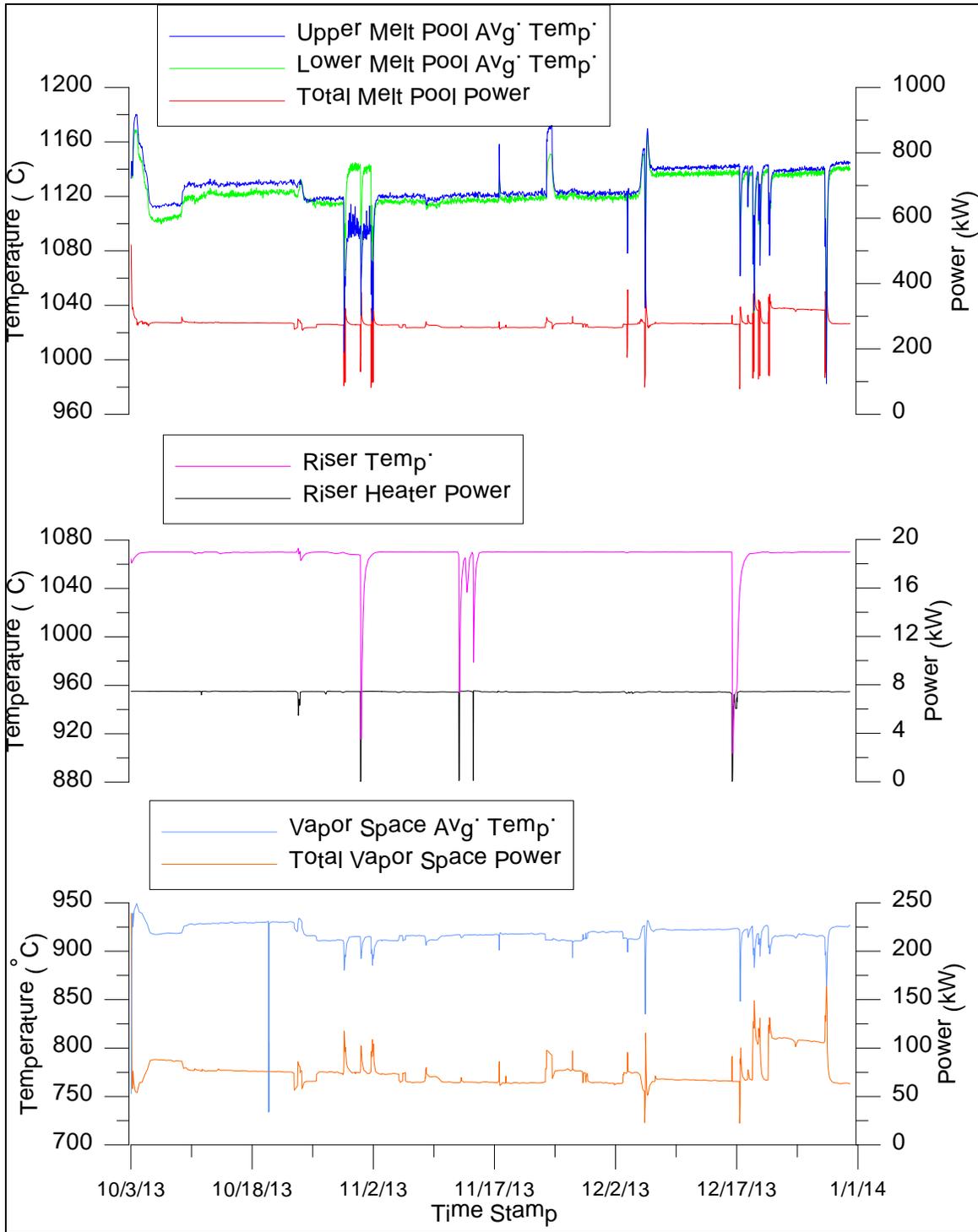


Figure 3-1. Overview of melter, riser, and vapor space temperatures and heater power during three month outage

The melt pool temperature was intentionally reduced below the nominal operating temperature of 1150 °C during the outage to reduce impacts to the components in contact with the glass. A review of Figure 3-1 shows that there were several transient drops in melt pool, vapor space, and riser temperatures

over the three month period. Data for the total melt pool power and the riser heater power are included in the plot to demonstrate that these variations are due to short duration reductions in power associated with planned maintenance activities during the extended idling period. The largest drop in riser temperature occurred over a period from December 16 to December 18, 2013. Data for the riser temperature and riser heater power during this period are plotted in Figure 3-2.

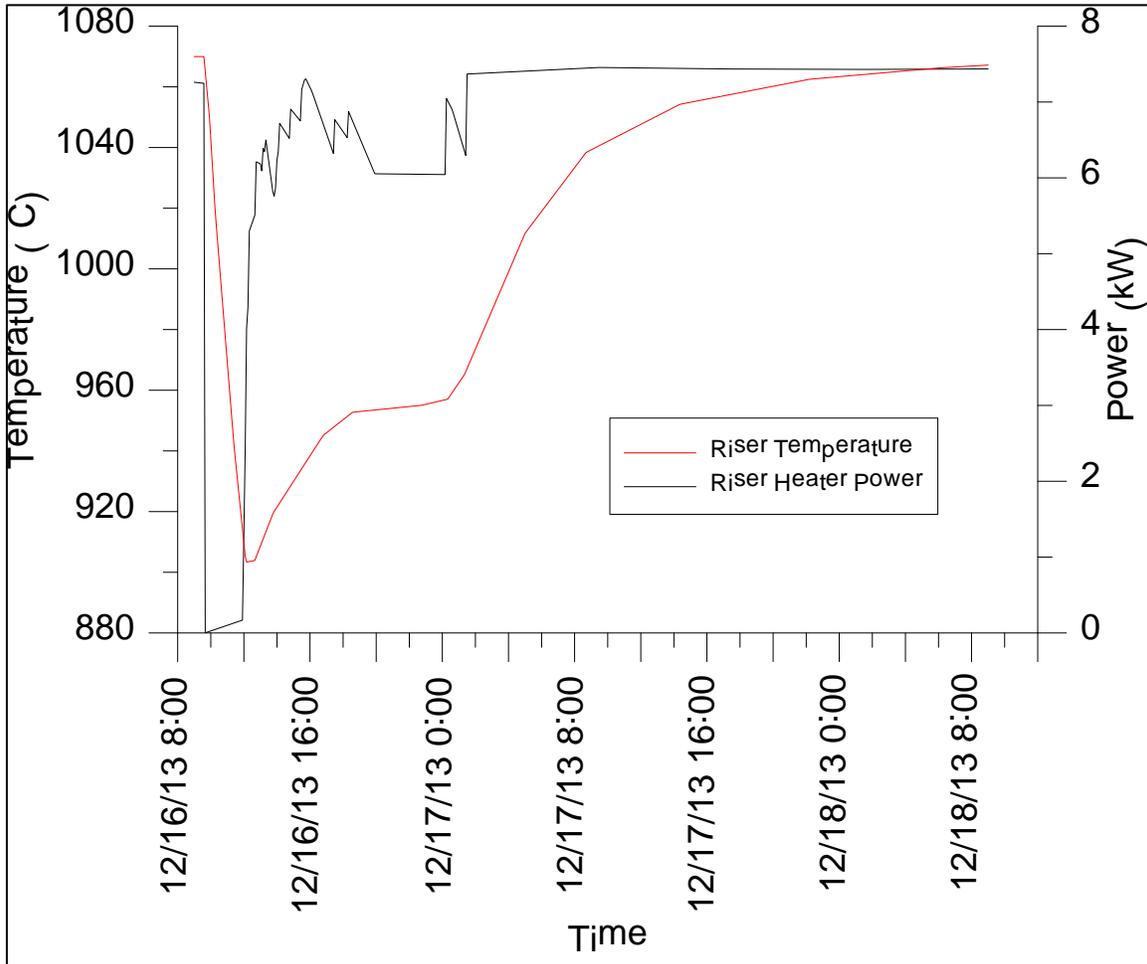


Figure 3-2. Detail of transient drop in riser temperature due to approximately two hour outage of riser heater

Lower temperatures such as those shown in Figure 3-2 present more favorable conditions for precipitation of spinel crystals in the glass. However, as will be shown through the analysis of the pour stream glass samples in the following sections, these occasional low temperature periods were likely of insufficient duration for crystals to form. In general, the temperature data demonstrate that melter and riser temperatures were relatively constant, although they also demonstrate the possibility for temperature fluctuations to occur during an extended idling period.

4.0 Melter Glass Characterization

The two DWPF melter pour stream glass samples were received by SRNL in its shielded cells facility. The masses of PC0125 and PC0126 upon receipt, including their platinum-alloy boats, were 57.067 g and 51.885 g, respectively. Photographs of the two glass samples appear in Figure 4-1 and Figure 4-2. There was no crystallization visible on the surfaces of the two samples. Both appeared shiny with black,

homogeneous coloring. There were no signs of dull patches on the surface of the samples that may have indicated the presence of surface crystallization. This is consistent with observations of previous DWPF pour stream samples.⁸⁻¹⁷



Figure 4-1. Photograph of first pour stream glass sample, PC0125, as received in platinum boat



Figure 4-2. Photograph of second pour stream glass sample, PC0126, as received in platinum boat

The samples were removed from the Pt boats by placing them in plastic bags and striking them with a hammer configured for use with a remotely operated manipulator. A single shard of each glass was collected for analysis via Scanning Electron Microscopy (SEM) with Energy Dispersive Spectroscopy (EDS). The rest of the glass was ground to less than 200 mesh using a SPEX Mixer/Mill 5300 with a clean agate canister and two agate balls. A separate canister and balls were used for each pour stream

glass to avoid potential cross-contamination. Subsamples of the ground glass were collected to support X-ray diffraction (XRD), REDOX, and chemical composition analyses.

4.1 XRD

The ground glass powder prepared in the shielded cells (approximately 0.2 g for each pour stream sample) was transferred to a glove box and attached to a plate glass slide using ethanol. The XRD data were collected on a Bruker D8 X-ray Diffractometer. The instrument parameters and run conditions are listed in Table 4-1.

Table 4-1. XRD Parameters and Run Conditions

Radiation Source	Cu K α
Source Power	45 kV, 40 mA
Divergence Soller Slit	None
Divergence Antiscatter (fixed)	2 mm
Specimen Rotation	No
Diffracted Beam Antiscatter (fixed)	Open
Diffracted Beam Soller Slit	2°
Receiving Slit	0.6 mm
Secondary Monochromator	Curved pyrolytic graphite
Detector Scatter Slit	2 mm
Detector	NaI Scintillation
2 θ Range	5° - 70°
Step Interval	0.02° (2 θ)
Fixed Counting Time	2 seconds per step

The XRD data from glasses PC0125 and PC0126 are shown in Figure 4-3 and Figure 4-4, respectively. The results show that the samples were X-ray amorphous (i.e., there are no signs of crystallization, only an amorphous hump). It should be noted that based on the XRD run conditions, the estimated detection limit is approximately 0.5 wt % crystallization. That is, any crystallization present at less than 0.5 wt % would not be detected.

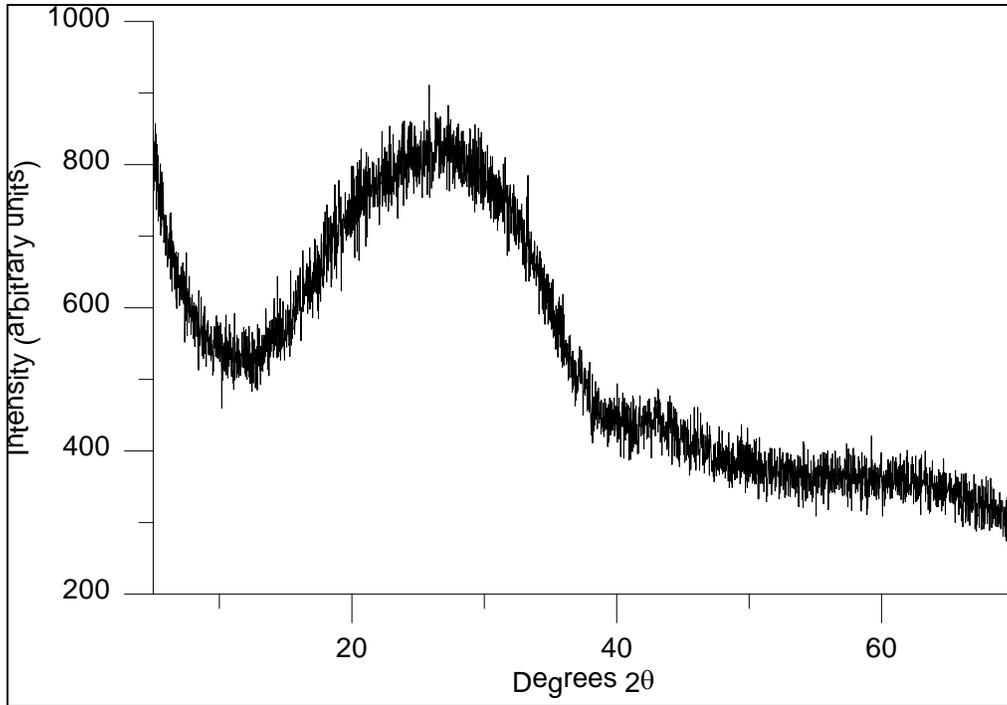


Figure 4-3. XRD Data from the First DWPF Pour Stream Sample (PC0125)

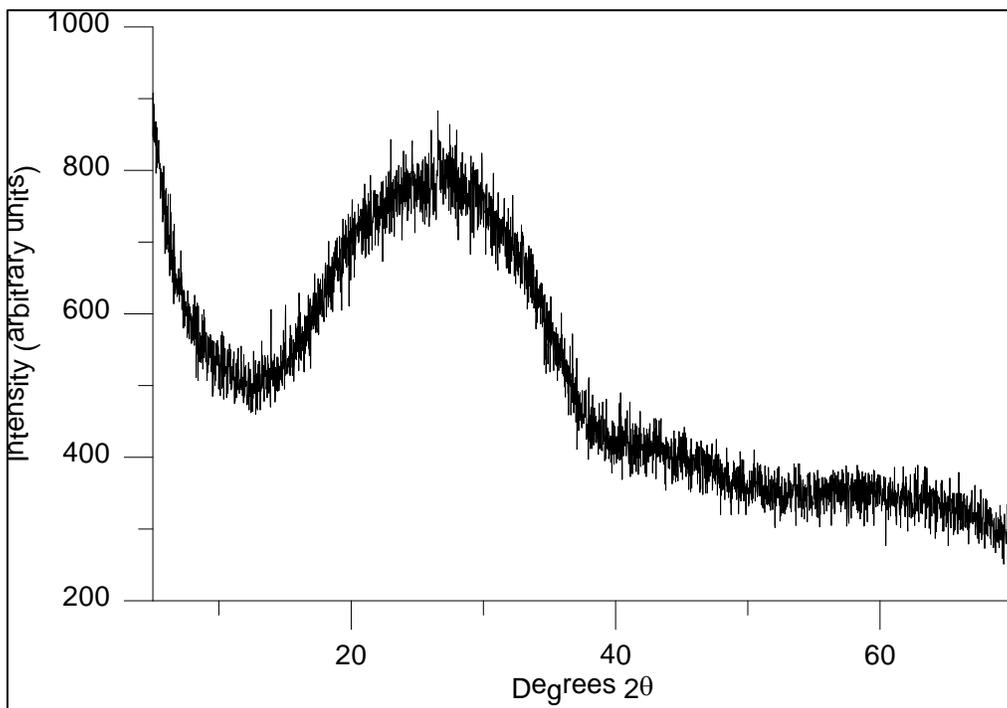


Figure 4-4. XRD Data from the Second DWPF Pour Stream Sample (PC0126)

4.2 SEM/EDS

The shards of the two pour stream glasses, collected as described earlier, were attached to separate SEM specimen stubs using carbon tape and were then transferred out of the shielded cells to a glove box containing sample preparation equipment and the SEM. Each sample was coated with a heavy layer of evaporated carbon to reduce charging by the electron beam. The specimens were observed in the SEM using both secondary electron (SE) and backscattered electron (BSE) detectors to identify surface features and any variation in average atomic number. EDS was used to provide qualitative composition information for any observed heterogeneity.

Figure 4-5 is a low magnification, BSE micrograph of the first pour stream sample (PC0125). Figure 4-6 is a low magnification, BSE micrograph of the second pour stream sample (PC0126). The shards collected were intentionally small in order to keep radiation levels low enough for handling in a glove box. As both of the samples were observed, it became apparent that there were no differences between the two glasses discernable via SEM/EDS analysis. Therefore, the two samples will be described interchangeably in this section.

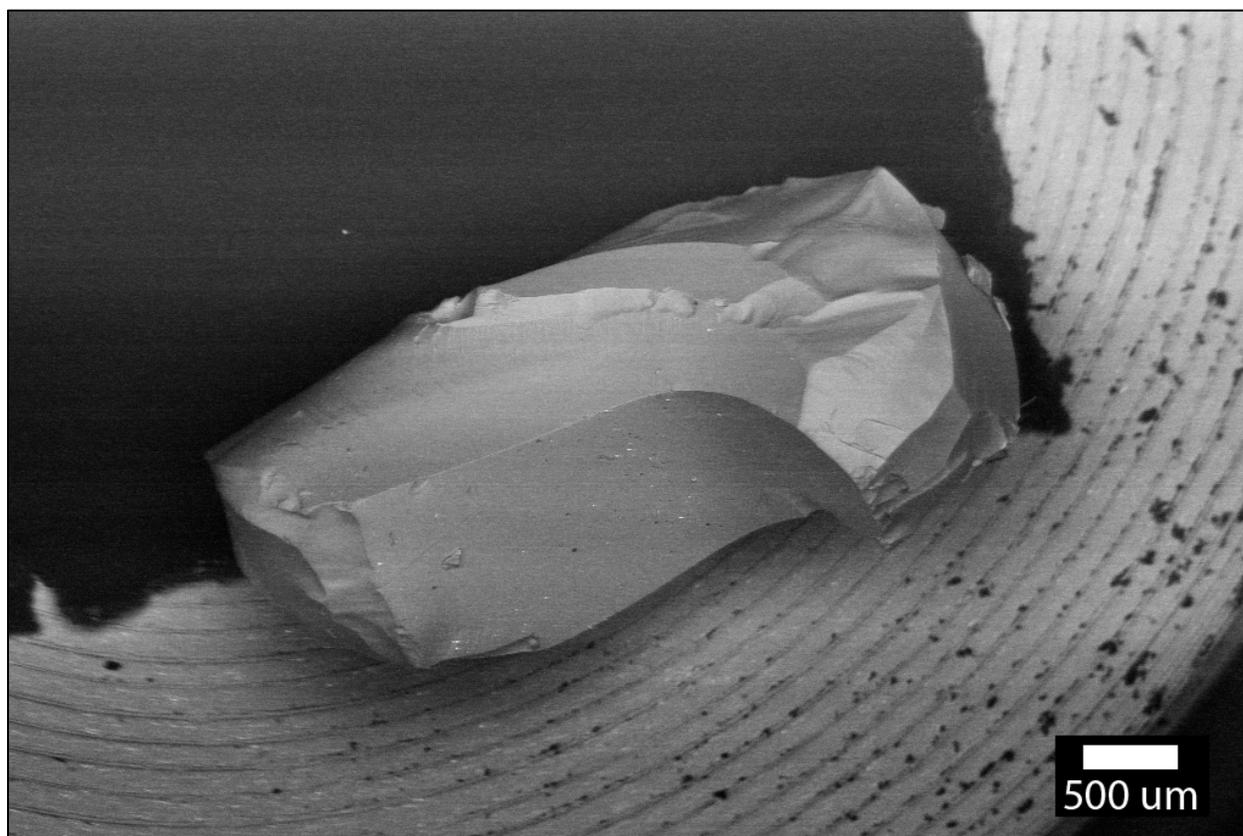


Figure 4-5. Low Magnification BSE Micrograph of the First Pour Stream Sample (PC0125)

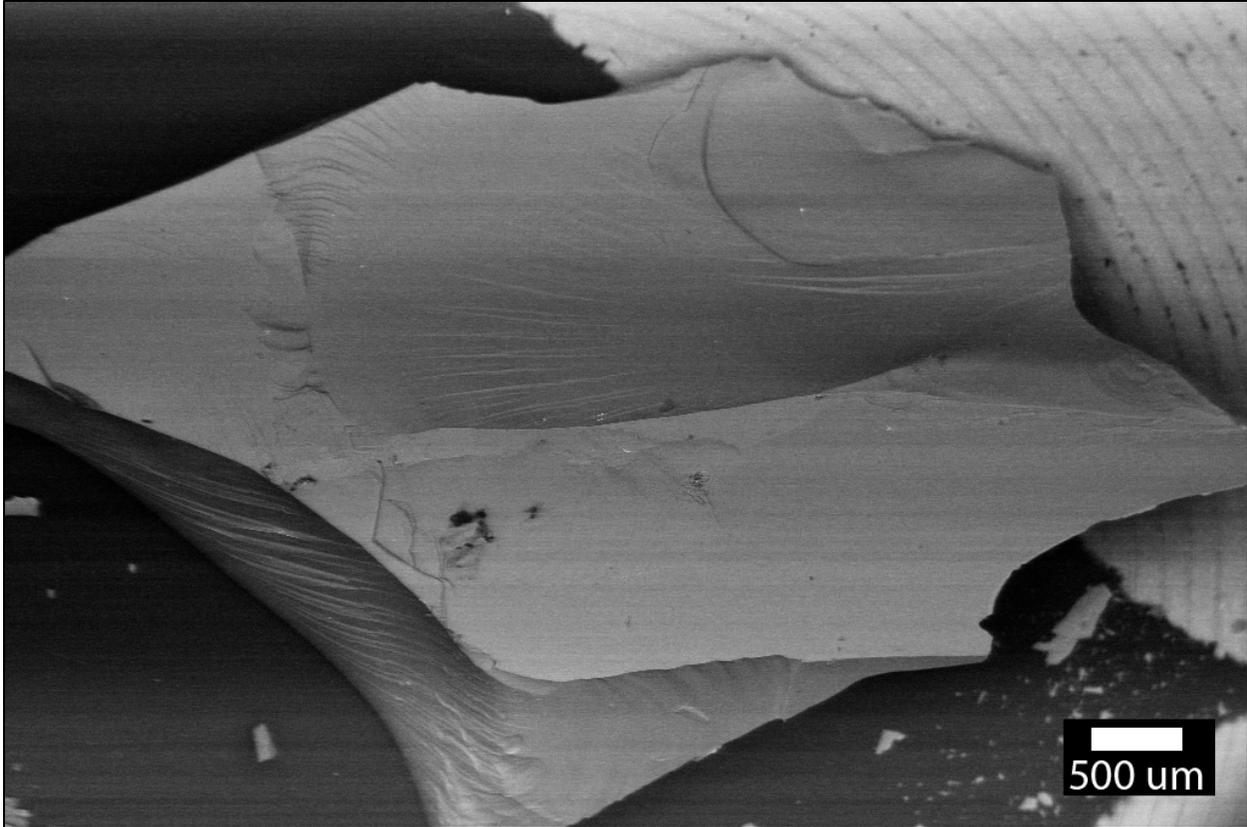


Figure 4-6. Low Magnification BSE Micrograph of the Second Pour Stream Sample (PC0126)

A higher magnification SE image of the surface of sample PC0125 is shown in Figure 4-7. The particulates visible on the surfaces of the glasses are likely remnants of the crushing that was done in the shielded cells. Thorough cleaning of the samples prior to observation was not practical in the glove box. Other than the particulates on the surface, the glasses appeared generally homogeneous.

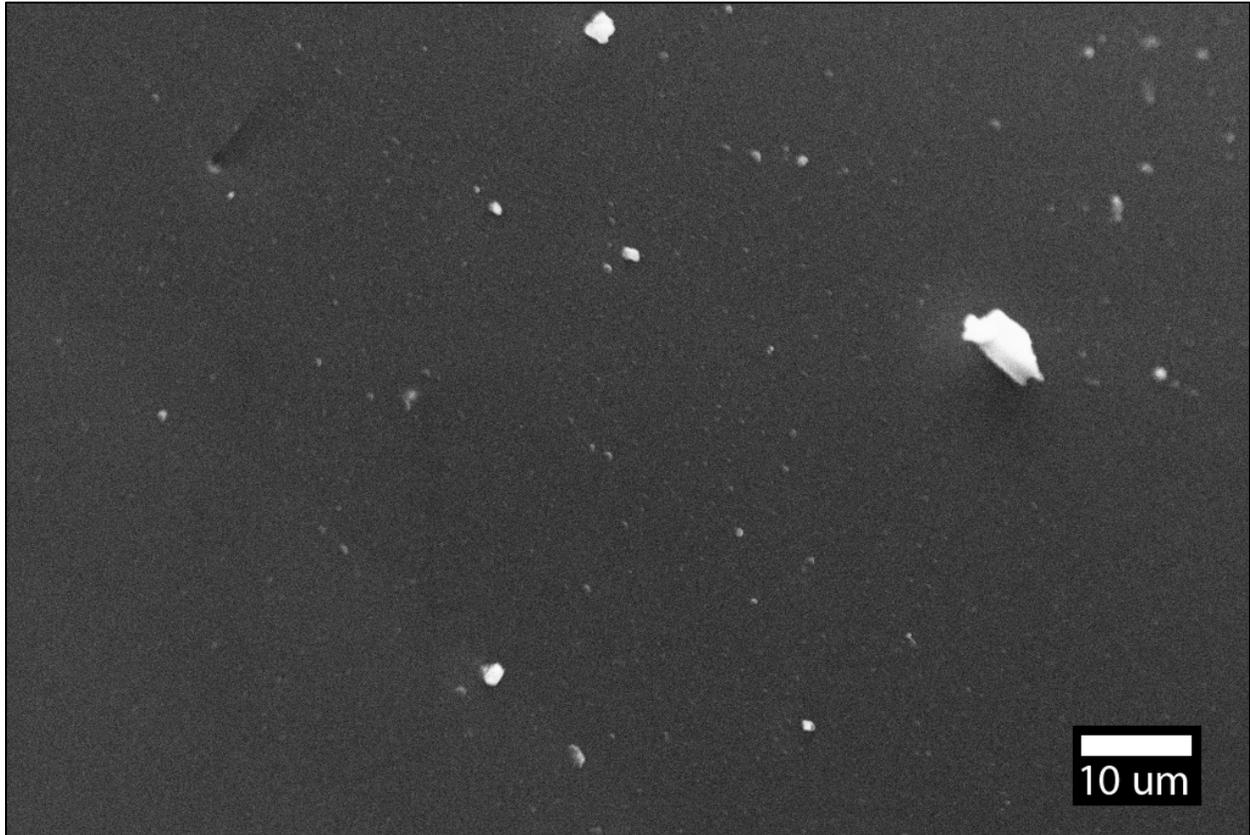


Figure 4-7. Higher Magnification SE Micrograph of the Surface of Sample PC0125

Occasional spinel crystals could be observed on the surface of the glasses, as shown in Figure 4-8. The EDS spectra, included in Figure 4-8, show that the crystal is enriched in Cr, Fe, and Mn relative to the surrounding glass.

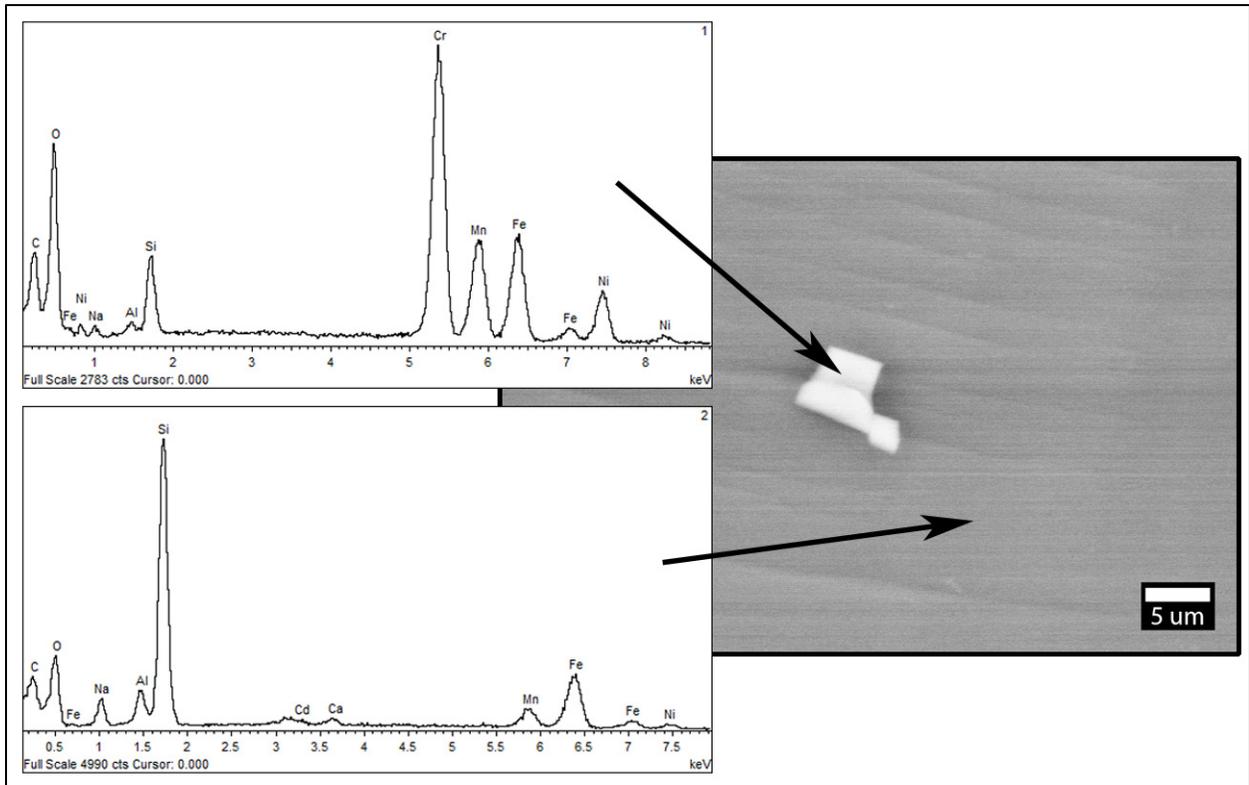


Figure 4-8. BSE Micrograph and EDS Spectra of a Spinel Crystal Observed in Glass PC0126

Occasional crystals containing noble metals were observed on the surface of the glasses, as shown in Figure 4-9. EDS identified this crystal as enriched in rhodium. A small volume of noble metal crystals is typical of DWPF HLW glasses.⁵

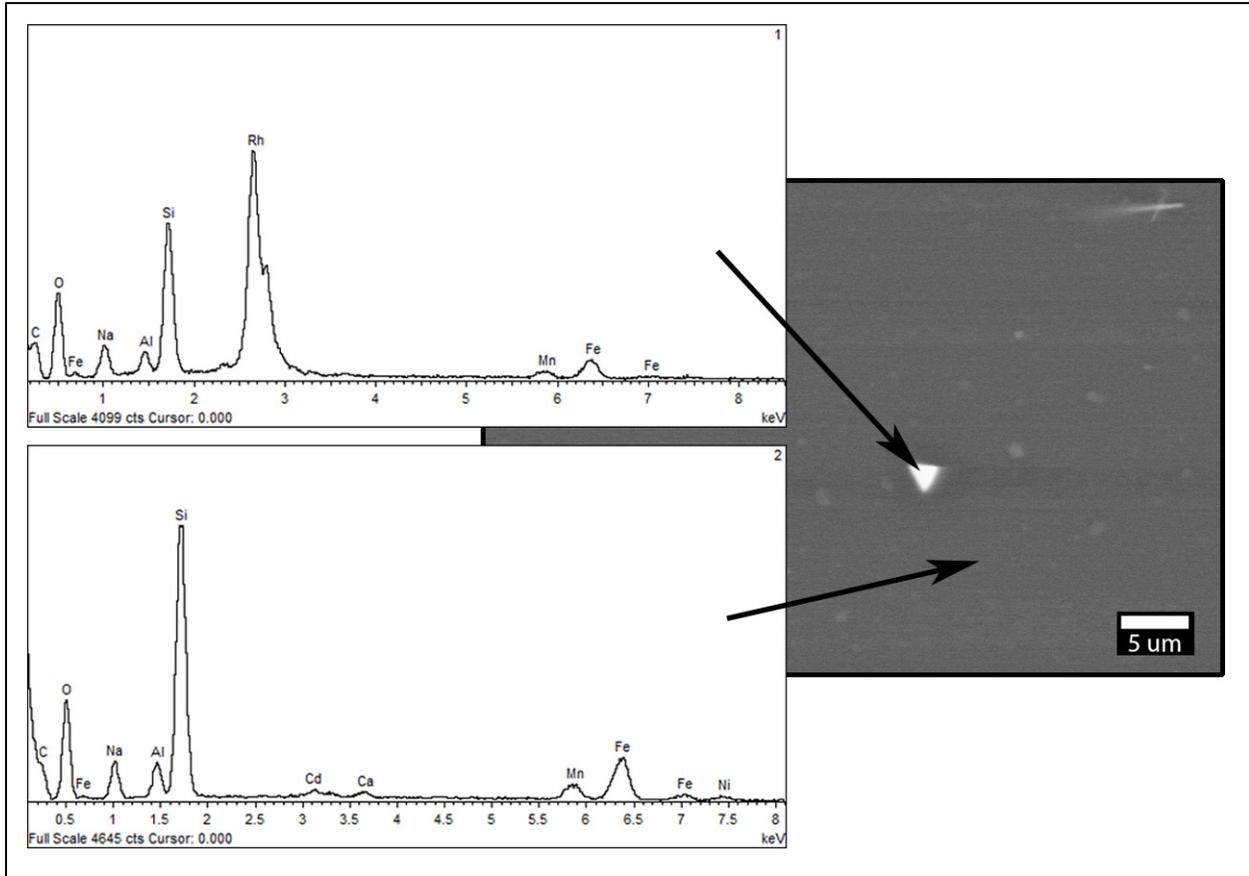


Figure 4-9. BSE Micrograph and EDS Spectrum of a Noble Metal Crystal Observed in Glass PC0126

A small number of platinum particles were also observed on the surface of the glass, as shown in Figure 4-10. These particles are likely residuals from the platinum boat used to catch the pour stream glass. The glass is difficult to remove from the platinum boats in a remote environment without minor contamination. Overall, there was very little observable crystallization in the specimens from the first (PC0125) and second (PC0126) pour stream samples, which is in agreement with the XRD data.

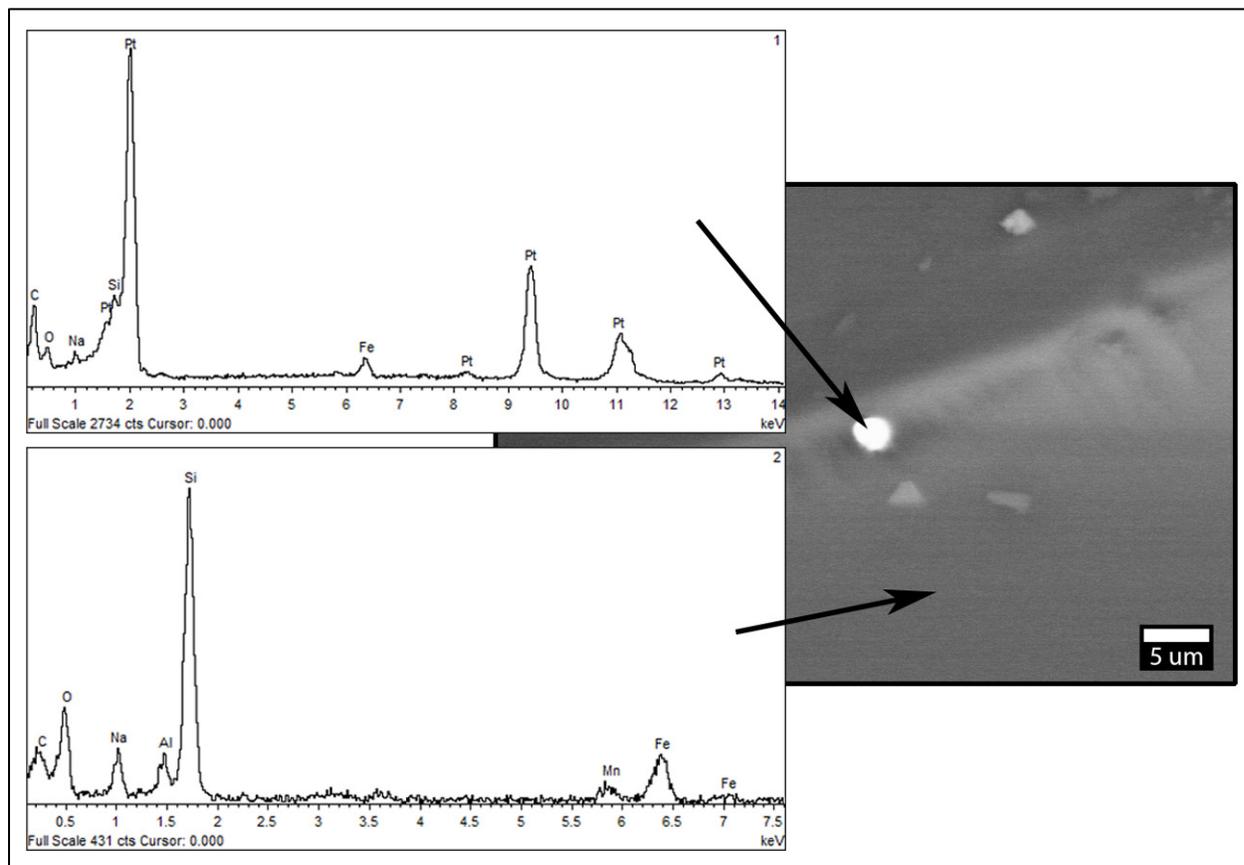


Figure 4-10. BSE Micrograph and EDS Spectrum of a Platinum Particle Observed in Glass PC0126

4.3 REDOX

Duplicate samples were taken from each ground pour stream glass for measurements of REDOX. The Environmental Assessment (EA) glass was included in duplicate as a REDOX standard¹⁸ to provide an internal check of the measured REDOX values. Details of the sample preparation and REDOX measurements using an ultraviolet-visible (UV-Vis) spectrometer are available in the SRNL procedure.¹⁹ In general, the procedure consisted of the following steps:

- The ground glass was dissolved in a sulfuric-hydrofluoric acid mixture containing ammonium vanadate, which preserves the Fe^{2+} content. In this step all Fe^{2+} is oxidized to Fe^{3+} and V^{5+} is reduced to V^{4+} .
- Boric acid was added to destroy iron-fluoride complexes.
- A pH 5 buffer and ferrozine reagent were added to form the magenta-colored ferrous-ferrozine complex, followed by UV-Vis measurement of the absorbance for the determination of Fe^{2+} content. In this step, the original Fe^{2+} is reduced from Fe^{3+} to Fe^{2+} and the V^{4+} is oxidized to V^{5+} .

- Ascorbic acid was added to reduce Fe³⁺ to Fe²⁺, followed by a second UV-Vis absorbance measurement that determined total Fe content.

The measured REDOX data for the EA reference glasses are given in Table 4-2. The EA glass results are consistent with the accepted value (0.22-0.23±0.01 for Fe²⁺/Fe³⁺), indicating that the measurements were in control.¹⁸ The Fe²⁺ values for the pour stream glasses were all essentially at detection limits.^a Therefore, both the PC0125 and PC0126 glass samples were fully oxidized. It should be noted that DWPF generally targets a predicted Fe²⁺/ΣFe ratio of 0.15 through the use of nitric acid and formic acid additions to the melter feed. In addition, during the outage, DWPF maintained a minimal bubbling rate of Ar through the melt to prevent blockage of the bubbler tubes. Although Ar is expected to slightly reduce the melt pool,²⁰ the REDOX results suggest that the amount of air that the glass was exposed to was sufficient to drive the REDOX state of the glass samples to fully oxidized.

Table 4-2. Measured REDOX Data for the Reference Glasses

Sample ID	Fe ²⁺	Fe ³⁺	ΣFe	Fe ²⁺ /Fe ³⁺	Fe ²⁺ /ΣFe
EA-1	0.17	0.77	0.95	0.23	0.18
EA-2	0.13	0.60	0.72	0.21	0.17

4.4 Glass Composition

Triplicate samples of each of the two ground pour stream glasses were digested by two methods – mixed acid (MA)²¹ and sodium peroxide fusion (PF)²² – in preparation for chemical composition analysis. A sample of the Analytical Reference Glass (ARG-1)²³ was digested by each method and submitted for analysis with the pour stream samples. A multi-element standard and a blank were included with the samples to assess the performance of the instruments over the course of the analyses. All of the prepared samples were analyzed for elemental composition by Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES) and Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS). A separate axial ICP-AES method was used for sulfur analysis to improve the detection limit for this element.^b

The data were reviewed to determine the appropriate preparation method and analysis method for reporting the concentration of each component of the glasses on an oxide basis. The results of this review are given in Table 4-3. ICP-AES analysis of the PF prepared samples was used to report the concentrations of the majority of the glass components. ICP-AES analysis of the MA prepared samples was used to report the concentrations of CaO, K₂O, Na₂O^c and ZrO₂, since the PF digestion method contains a minor amount of calcium impurity, introduces sodium, and is performed in zirconium crucibles. The detection limit for K₂O was lower for the MA prepared samples. ICP-MS analysis of the PF prepared samples was used to report the concentrations of PbO, PdO, Rh₂O₃, and RuO₂. ICP-MS analysis was found to be more reliable than ICP-AES for PbO (as well as U₃O₈ and ThO₂) for these samples due to spectral interferences. The concentrations of PdO, Rh₂O₃, and RuO₂ were determined from the ICP-MS data following a method that accounts for the isotopes of these elements present in Savannah River Site

^a Further calculations with the Fe²⁺ values of the pour stream glasses were considered unreliable since the measurements were at detection limits.

^b Axial methods generally have a reduced dynamic range when compared to radial (routine) analysis methods used for the majority of the elements in these glasses. Therefore, this method was used only for sulfur, since sulfur was expected to have a low concentration in the glasses and was not suitable for measurement by ICP-MS.

^c Sodium concentrations were determined using only the 588.995 nm emission line, which provided data that were in better agreement with the ARG-1 reference glass for this element.

waste sludges.²⁴ ICP-MS analysis of both the PF and MA prepared samples was used to report the concentrations of ThO₂ and U₃O₈, since both preparation methods yielded similar results for these components. As mentioned above, a separate ICP-AES method was used to measure and report the SO₄²⁻ concentration using the MA prepared samples.

Table 4-3. Digestion and Measurement Methods Selected for Each Glass Component

Oxide	Digestion Method	Measurement Method
Ag ₂ O	PF	ICP-AES
Al ₂ O ₃	PF	ICP-AES
B ₂ O ₃	PF	ICP-AES
BaO	PF	ICP-AES
CaO	MA	ICP-AES
CdO	PF	ICP-AES
Ce ₂ O ₃	PF	ICP-AES
Cr ₂ O ₃	PF	ICP-AES
CuO	PF	ICP-AES
Fe ₂ O ₃	PF	ICP-AES
K ₂ O	MA	ICP-AES
La ₂ O ₃	PF	ICP-AES
Li ₂ O	PF	ICP-AES
MgO	PF	ICP-AES
MnO	PF	ICP-AES
Na ₂ O	MA	ICP-AES
NiO	PF	ICP-AES
PbO	PF	ICP-MS
PdO	PF	ICP-MS
Rh ₂ O ₃	PF	ICP-MS
RuO ₂	PF	ICP-MS
SO ₄ ²⁻	MA	ICP-AES (Sulfur Method)
SiO ₂	PF	ICP-AES
SrO	PF	ICP-AES
ThO ₂	MA & PF	ICP-MS
TiO ₂	PF	ICP-AES
U ₃ O ₈	MA & PF	ICP-MS
ZnO	PF	ICP-AES
ZrO ₂	MA	ICP-AES

The mean of the three measured concentration values for each element was multiplied by the appropriate gravimetric factor to arrive at the reported concentration for each oxide. In the case of ThO₂ and U₃O₈, the six measured concentrations were included when calculating the mean. During this review of the data, it was discovered that a dilution error occurred during the preparation of one of the triplicate PF digestions for glass PC0126. The values reported from these samples were omitted from the calculations. Therefore, the mean values for the oxides of glass PC0126 measured from the PF prepared samples are the result of duplicate rather than triplicate analyses. There were no issues with the measurements of the other analytes in the blanks.

Table 4-4 provides the published²³ and measured compositions of the ARG-1 glass and the percent error between the two values for each oxide. The percent error is better than ±10% for all of the oxides present at more than 0.2 wt %, indicating that the measurements were in control.

Table 4-4. Published and Measured Composition of ARG-1 Reference Glass

Oxide	Published ²³ (wt %)	Measured (This Study) (wt %)	Percent Error
Al ₂ O ₃	4.73	5.04	7
B ₂ O ₃	8.67	8.34	-4
BaO	0.088	0.09	2
CaO	1.43	1.46	2
Cr ₂ O ₃	0.093	0.11	18
CuO	0.004	<0.06	-
Fe ₂ O ₃	14.0	14.13	1
K ₂ O	2.71	2.67	-1
Li ₂ O	3.21	3.21	0
MgO	0.86	0.87	1
MnO	1.88	1.83	-3
Na ₂ O	11.5	10.92	-5
NiO	1.05	1.07	2
P ₂ O ₅	0.22	NM	-
SiO ₂	47.9	48.78	2
SrO	0.0037	0.0047	27
TiO ₂	1.15	1.04	-10
ZnO	0.02	0.03	50
ZrO ₂	0.13	0.16	23

NM = Not Measured

The measured compositions of the two pour stream glass samples are given in Table 4-5.

Table 4-5. Measured Composition (wt %) of Pour Stream Glasses

Oxide	PC0125	PC0126
Ag ₂ O	<0.03	<0.03
Al ₂ O ₃	6.46	6.56
B ₂ O ₃	4.33	4.46
BaO	0.04	0.04
CaO	0.62	0.62
CdO	<0.03	<0.03
Ce ₂ O ₃	<0.27	<0.27
Cr ₂ O ₃	0.20	0.18
CuO	0.18	<0.07
Fe ₂ O ₃	10.13	10.59
K ₂ O	<1.22	<1.23
La ₂ O ₃	0.03	0.03
Li ₂ O	3.55	3.66
MgO	<0.32	<0.32
MnO	2.78	2.92
Na ₂ O	14.41	14.70
NiO	1.13	1.05
PbO	0.02	0.02
PdO	0.001	0.001
Rh ₂ O ₃	0.006	0.007
RuO ₂	0.008	0.013
SO ₄ ²⁻	<0.30	0.32
SiO ₂	48.56	50.49
SrO	0.02	0.02
ThO ₂	0.37	0.38
TiO ₂	0.24	0.27
U ₃ O ₈	1.83	1.84
ZnO	0.05	0.03
ZrO ₂	<0.58	<0.58

The DWPF melter is fed via a recirculating loop from the MFT. The contents of the MFT (and therefore the contents of the melter) are composed of several batches from the SME. The SME is sampled and analyzed at DWPF to verify feed acceptability²⁵ before its contents are transferred to the MFT. DWPF Engineering advised that the contents of the melter and MFT during the outage and at the time that the pour stream samples were collected came from SME batches 685 through 689. The data from the composition analyses of these SME batches were retrieved from DWPF electronic records by SRNL and are shown in Table 4-6. The corresponding measured composition values for the pour stream glasses are included in Table 4-6 for comparison.

Table 4-6. Comparison of DWPF SME Batch Compositions and Pour Stream Glass Compositions, with Predicted T_L Values

Oxide (wt %)	DWPF SME Batch Analyses						Pour Stream Glass Analyses	
	685	686	687	688	689	Average	PC0125	PC0126
Al ₂ O ₃	6.05	5.60	6.04	5.75	5.64	5.82	6.46	6.56
B ₂ O ₃	4.82	5.24	4.79	5.03	4.91	4.96	4.33	4.46
CaO	0.56	0.51	0.60	0.60	0.58	0.57	0.62	0.62
Cr ₂ O ₃	0.05	0.04	0.05	0.08	0.05	0.05	0.20	0.18
CuO	0.02	0.02	0.03	0.03	0.02	0.02	0.18	<0.07
Fe ₂ O ₃	10.89	10.53	10.72	10.88	10.59	10.72	10.13	10.59
K ₂ O	<0.01	0.05	<0.01	0.08	0.09	0.06	<1.22	<1.23
Li ₂ O	3.78	3.89	3.69	3.70	3.68	3.75	3.55	3.66
MgO	0.19	0.17	0.19	0.17	0.17	0.18	<0.32	<0.32
MnO	3.02	3.05	3.00	3.05	3.02	3.03	2.78	2.92
Na ₂ O	15.06	14.36	15.30	15.35	15.32	15.08	14.41	14.70
NiO	0.92	0.95	0.93	0.90	0.97	0.93	1.13	1.05
SiO ₂	50.96	54.13	50.23	51.42	52.16	51.78	48.56	50.49
ThO ₂	0.53	0.53	0.49	0.54	0.50	0.52	0.37	0.38
TiO ₂	0.22	0.24	0.29	0.25	0.21	0.24	0.24	0.27
U ₃ O ₈	1.76	1.41	1.61	1.64	1.61	1.61	1.83	1.84
ZrO ₂	0.11	0.11	0.10	0.11	0.10	0.11	<0.58	<0.58
PCCS Predictions								
T_L (°C)	863	850	858	860	845	-	946	934

A review of the data in Table 4-6 led to several observations. The compositions of the two pour stream samples are similar considering the measurement uncertainty associated with the analysis. The concentrations of some of the oxides in the pour stream glasses vary slightly from the concentrations of those oxides measured in the SME batches. These differences are small and may be within the analytical error of the DWPF and SRNL laboratories; however, some trends are observed in the data. The concentrations of B₂O₃ and Na₂O in the pour stream glasses are slightly lower than those in the SME batches. This may be due to volatilization during the extended idling period,²⁶ particularly given the lack of a cold cap and the elevated vapor space temperature during the outage (refer to Figure 3-1). The concentrations of Al₂O₃, Cr₂O₃, and NiO are slightly higher than those in the SME batches. This may be due to interaction of the glass with the refractory components of the melter (Al₂O₃ and Cr₂O₃ from Monofrax[®] K-3 and NiO from Inconel[®] 690) during the extended idling period.

Each of the SME batches shown in Table 4-6 and both of the pour stream glass samples were verified as being acceptable for processing using the DWPF Product Composition Control System (PCCS).²⁵ PCCS is a series of glass property model algorithms that uses the composition of a glass to predict its properties and performance for comparison with melter processing and waste form acceptability requirements. One of these models predicts the spinel liquidus temperature (T_L) of the glass.²⁷ The predicted T_L values from the PCCS model for each of the SME analyses and for the two pour stream glass compositions are provided at the bottom of Table 4-6. There is a notable increase in the predicted T_L values for the pour stream glasses as compared to those for the SME batches. This increase is driven by the (relatively small) differences in B₂O₃, Cr₂O₃, Na₂O, and NiO concentrations. The T_L model predicts spinel formation, thus it is particularly sensitive to the increased concentrations of Cr₂O₃ and NiO in the pour stream glasses. The reductions in B₂O₃ and Na₂O concentrations also contribute to the higher predicted T_L values.

5.0 Discussion and Conclusions

Characterization of the glass pour stream samples collected after the outage revealed a small number of spinel crystals and noble metal particles. The crystals were present in an amount considered to be insignificant in disrupting melter operation. The first glass pour stream sample was collected after 192 lbs of glass had been poured from the melter following the extended idling period. The DWPF riser contains approximately 70 lbs of glass. Therefore, the first pour stream sample may not be representative of glass that remained in the riser during the extended idling period as was intended. It is possible that if spinel crystals had accumulated in the riser, they could have been swept into the canister prior to collection of the first pour stream sample.

Comparisons of the chemical composition measurements of the pour stream glass samples with the corresponding SME batch analyses showed slight differences in the concentrations of some oxides. While these differences may be within the analytical error of the laboratories, the trends indicated a small amount of volatility for some of the glass components, and that there may have been interaction of the glass with the refractory components of the melter. The changes in glass composition, although small, can be attributed to the idling of the melter for an extended period. These changes resulted in a 70-100 °C increase in the predicted T_L for the glass pour stream samples, which indicates that the potential for spinel crystallization increased as a result of idling for an extended period. However, the predicted T_L of the pour stream glasses remained 150-200 °C below the mean melt pool temperature during the idling period.

The DWPF melter is operated with a model that predicts the spinel T_L of the glass as a function of its composition. A T_L constraint is used to minimize the risk of bulk devitrification in the melt pool. The predicted T_L value must be at least 100 °C below the nominal melter operating temperature of 1150 °C in order for the feed to be acceptable for transfer to the DWPF melter.²⁵ This approach sets the liquidus temperature constraint at the point where no spinel crystals are detected, and the 100 °C offset provides additional margin to account for composition and processing uncertainty (in addition to the uncertainties already accounted for in the model).

The U.S. Department of Energy is investigating an alternative approach to T_L to avoid the deleterious effects of crystallization in the WTP high level waste melter. WTP currently plans to control glass composition such that the temperature at which 1 vol % of spinel crystals is in equilibrium with the glass melt ($T_{1\%}$) remains below 950 °C. This constraint significantly influences waste loading and, therefore, the amount of glass to be produced. The possibility of controlling the glass composition such that the accumulation rate of spinel crystals in the melter does not exceed a melter life-related limit is being investigated to provide the technical basis for that limit and allow for increased waste loading. The data in this report demonstrate that: 1) a glass with a predicted T_L below 1050 °C can still form some amount of spinel crystals in a melter, and, 2) the composition of the glass in a melter after an extended idling period can change, and this change can result in an increase in the predicted T_L . These findings are important for implementation of spinel crystallization control strategies for WTP.

The WTP crystal tolerant glass program is developing an improved understanding of crystallization, settling, and accumulation of spinel crystals in the WTP melter to allow for operation at maximum waste loading in glass composition systems limited by crystallinity constraints. The program aims to develop an empirical model to predict the thicknesses of accumulated layers of crystals as a function of time, temperature, and composition that can be used to control and mitigate crystal deposition in the melter. Further detail of the crystal tolerant glass program is provided in a recent road map document.⁴

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