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Spinel Dissolution Via Addition of Glass Forming Chemicals: Results of Preliminary Experiments

F. C. Johnson

K. M. Fox

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EXECUTIVE SUMMARY

Increased loading of high level waste in glass can lead to crystallization within the glass. Some crystalline species, such as spinel, have no practical impact on the chemical durability of the glass, and therefore may be acceptable from both a processing and a product performance standpoint. In order to operate a melter with a controlled amount of crystallization, options must be developed for remediating an unacceptable accumulation of crystals. This report describes preliminary experiments designed to evaluate the ability to dissolve spinel crystals in simulated waste glass melts via the addition of glass forming chemicals (GFCs).

The objective of this study was to determine whether the addition of GFCs could be tailored to modify the composition of the glass in the melter to simultaneously:

- Reduce the spinel liquidus temperature (T_L) of the glass,
- Dissolve an accumulated layer of spinel crystals,
- Maintain acceptable properties for processing the glass, such as glass viscosity, and
- Maintain acceptable glass product performance, as determined by the predicted Product Consistency Test response of the modified glass composition.

Glass compositions with a reduced spinel T_L were developed with the aid of a quasicrystalline freezing point depression model. These modified compositions were blended with a simulated waste glass containing spinel crystals and heat treated at 1150 °C. After heat treatment, select glasses were examined via X-ray diffraction and optical microscopy. The results demonstrated that tailored GFC additions can successfully reduce the concentration of spinel crystals in a glass, and that a settled layer of spinel crystals can be removed when thorough mixing occurs in combination with the GFC addition.

Further work on this concept may provide the Hanford Tank Waste Treatment and Immobilization Plant with the ability to recover from an unacceptable accumulation of spinel crystals in a melter using only a change in feed composition, without facility modifications or impact to quality of the glass product. The next series of experiments will investigate the efficacy of bubbling in providing the necessary mixing to achieve dissolution of settled spinel crystals.

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LIST OF ABBREVIATIONS

DOE-ORP	U.S. Department of Energy – Office of River Protection
DWPF	Defense Waste Processing Facility
GFCs	Glass Forming Chemicals
HLW	High Level Waste
ICP-AES	Inductively Coupled Plasma – Atomic Emission Spectroscopy
PCCS	Product Composition Control System
PCT	Product Consistency Test
PNNL	Pacific Northwest National Laboratory
RSM	Research-Scale Melter
SEM	Scanning Electron Microscopy
SRNL	Savannah River National Laboratory
T_L	Liquidus Temperature
WTP	Hanford Tank Waste Treatment and Immobilization Plant
XRD	X-ray Diffraction

1.0 Introduction

The U.S. Department of Energy – Office of River Protection (DOE-ORP) is building the Hanford Tank Waste Treatment and Immobilization Plant (WTP) to remediate 55 million gallons of radioactive waste that is being temporarily stored in 177 underground tanks. The low-activity waste fraction will be partitioned from the high-level waste (HLW) during the feed pretreatment step and then each waste stream will be separately vitrified into borosilicate glass using Joule-heated ceramic melters.[1]

Efforts are being made to increase the loading of Hanford tank wastes in glass. Higher waste loading must be balanced with meeting melter lifetime expectancies and ensuring that the glass meets facility requirements for processing. In addition, the glass product must remain compliant with disposal regulations, including product quality constraints.[2] Increased waste loading in HLW glasses can lead to crystallization within the glass. Some crystalline species, such as spinel, have no practical impact on the chemical durability of the glass,[3] and therefore may be acceptable from both a processing and a product performance standpoint. A more thorough understanding of processing of glasses containing a controlled volume of spinel crystals is being developed as part of the DOE-ORP advanced waste glass program,[4] as described in a recent road map document.[5]

This report describes preliminary experiments at the Savannah River National Laboratory (SRNL) designed to evaluate the ability to dissolve spinel crystals in simulated HLW glass melts via the addition of glass forming chemicals (GFCs). Operation of a HLW melter with a controlled volume of spinel crystals will require the development and implementation of process control models that can predict the growth and settling rate of spinel crystals as a function of glass composition and melter conditions.[5] This model will be expected to provide sufficient control such that spinel accumulation does not hinder melter operation during feeding, pouring, and idling conditions. However, should an off-normal event occur (e.g., unanticipated loss of melter power) resulting in an unacceptable accumulation of spinel crystals, a method will be needed for removing the accumulated crystals to restore full melter capability.

The objective of this study was to determine whether the addition of GFCs available at WTP could be tailored to modify the composition of the glass in the melter to simultaneously:

- Reduce the spinel liquidus temperature (T_L) of the glass,
- Dissolve a settled layer of spinel crystals,
- Maintain acceptable properties for processing the glass, such as glass viscosity, and
- Maintain acceptable glass product performance, as determined by the predicted Product Consistency Test[6] (PCT) response of the modified glass composition.

This method, if successful, may provide WTP with the ability to recover from an unacceptable accumulation of spinel crystals in a melter using only a change in feed composition, without impact to quality of the glass product. This report describes the results of preliminary experiments that were meant to prove viability of the concept at bench scale. The experiments and results are described chronologically in the following sections. Suggestions for a subsequent study are also provided.

1.1 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in Savannah River Site Manual E7, Procedure 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2. The experimental work described in this report was performed under an SRNL Task Technical and Quality Assurance Plan.[7]

2.0 PNNL-SP Glass

2.1 Selection of Experimental Glass Composition

An experimental glass composition used by the Pacific Northwest National Laboratory (PNNL) to study spinel settling, identified as Ni1.5/Fe17.5, was selected for this study because of its tendency to accumulate spinel crystals during relatively short heat treatment periods.[8,9] The composition of Ni1.5/Fe17.5 is given in Table 2-1. Fluorine and chlorine were removed from the targeted composition to simplify the procedure for fabrication at SRNL. The concentrations of the remaining components were normalized to a sum of 100 wt %, with the exception of RuO_2, which remained fixed at 0.01 wt % due to its potential to serve as a nucleating agent for spinel crystals. This modified composition was named PNNL-SP for the studies described in this report, and is listed in Table 2-1.

2.2 Glass Fabrication

Two batches of the PNNL-SP glass composition were fabricated using reagent-grade materials (instead of dry AZ-101 simulant[8,9]). These batches were identified as PNNL-SP2 and PNNL-SP4. The raw materials were hand mixed and placed into a 95%Pt-5%Au alloy crucible with a loose-fitting lid. The filled and covered crucibles were placed into a furnace at 1150 °C. The crucible was removed from the furnace after an isothermal hold at 1150 °C for 1 hour. The molten material was quenched in air by pouring the liquid onto a stainless steel plate. Photos of the quenched PNNL-SP glass and the glass remaining in the crucible after pouring are shown in Figure 2-1.

Table 2-1. Comparison of the Ni1.5/Fe17.5 and PNNL-SP Compositions

Oxide	Original Glass, Ni1.5/Fe17.5 (wt %)	PNNL-SP (wt %)		Oxide	Original Glass, Ni1.5/Fe17.5 (wt %)	PNNL-SP (wt %)
Al_2O_3	7.84	7.84		Li_2O	1.9	1.90
B_2O_3	7.63	7.63		MgO	0.12	0.12
BaO	0.09	0.09		MnO	0.33	0.33
CaO	0.54	0.54		Na_2O	17.81	17.82
CdO	0.62	0.62		Nd_2O_3	0.17	0.17
Ce_2O_3	0.19	0.19		NiO	1.5	1.50
Cl	0.02	0		P_2O_5	0.31	0.31
CoO	0.01	0.01		RuO_2	0	0.01
Cr_2O_3	0.16	0.16		SO_3	0.08	0.08
CuO	0.04	0.04		SiO_2	38.47	38.48
F	0.01	0		SnO_2	0.1	0.10
Fe_2O_3	17.51	17.51		TiO_2	0.03	0.03
K_2O	0.32	0.32		ZnO	0.02	0.02
La_2O_3	0.21	0.21		ZrO_2	3.97	3.97

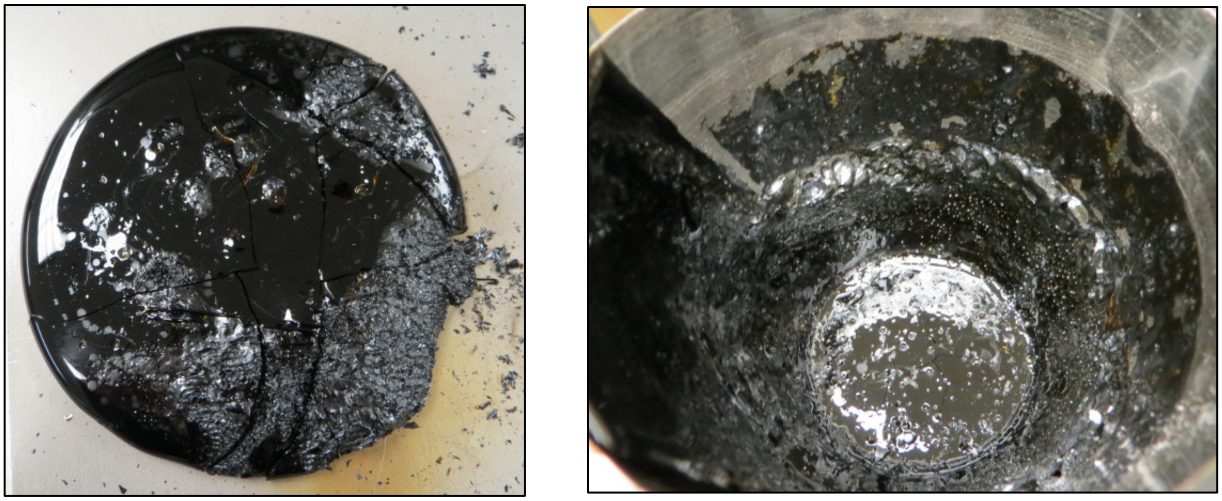

(a) (b)

Figure 2-1. Photos of the PNNL-SP glass after quenching (a) and the material remaining in the crucible after pouring (b)

For each batch of PNNL-SP glass, all of the quenched glass and the glass remaining in the crucible was collected and ground for approximately two minutes in a tungsten carbide ring pulverizer to support sampling and characterization.

2.3 Chemical Composition Measurements

Select samples of the ground PNNL-SP2 and PNNL-SP4 glasses were analyzed to verify that the targeted chemical composition was met. Each sample was prepared via sodium peroxide fusion and lithium metaborate fusion digestions methods.[10,11] The resulting solutions were analyzed twice by Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES), with the average elemental concentration values converted to oxides and reported in Table 2-2. The percent error is included in the table for those components with targeted concentrations of more than 0.5 wt %. These values are all within +/-10%, which was determined to indicate reasonable agreement with the targeted compositions for the purposes of this study.

Table 2-2. Targeted and Measured Compositions of PNNL-SP2 and PNNL-SP4

Oxide	PNNL-SP, Targeted (wt %)	PNNL-SP2, Measured (wt %)	PNNL-SP4, Measured (wt %)	PNNL-SP2, Percent Error	PNNL-SP4, Percent Error
Al_2O_3	7.84	7.73	7.83	-1.4%	-0.1%
B_2O_3	7.63	7.59	7.69	-0.6%	0.8%
BaO	0.09	0.09	0.09	-	-
CaO	0.54	0.57	0.58	5.6%	7.7%
CdO	0.62	0.60	0.61	-3.3%	-2.2%
CeO_2	0.19	0.19	0.20	-	-
CoO	0.01	<0.13	<0.13	-	-
Cr_2O_3	0.16	0.15	0.15	-	-
Cu_2O	0.04	0.06	0.04	-	-
Fe_2O_3	17.51	16.85	16.99	-3.7%	-3.0%
K_2O	0.32	0.34	0.34	-	-
La_2O_3	0.21	0.18	0.18	-	-
Li_2O	1.90	1.86	1.88	-2.1%	-0.8%
MgO	0.12	0.11	0.11	-	-
MnO	0.33	0.39	0.41	-	-
Na_2O	17.82	16.91	16.96	-5.1%	-4.8%
Nd_2O_3	0.17	0.18	0.18	-	-
NiO	1.50	1.46	1.46	-2.9%	-2.9%
P_2O_5	0.31	0.27	0.27	-	-
RuO_2	0.01	<0.13	<0.13	-	-
SO_3	0.08	<0.25	<0.25	-	-
SiO_2	38.48	39.37	39.68	2.3%	3.1%
SnO_2	0.10	0.12	0.12	-	-
TiO_2	0.03	0.04	0.04	-	-
ZnO	0.02	0.02	0.03	-	-
ZrO_2	3.97	3.76	3.79	-5.2%	-4.5%
Sum	100	98.83	99.62	-1.4%	-0.1%

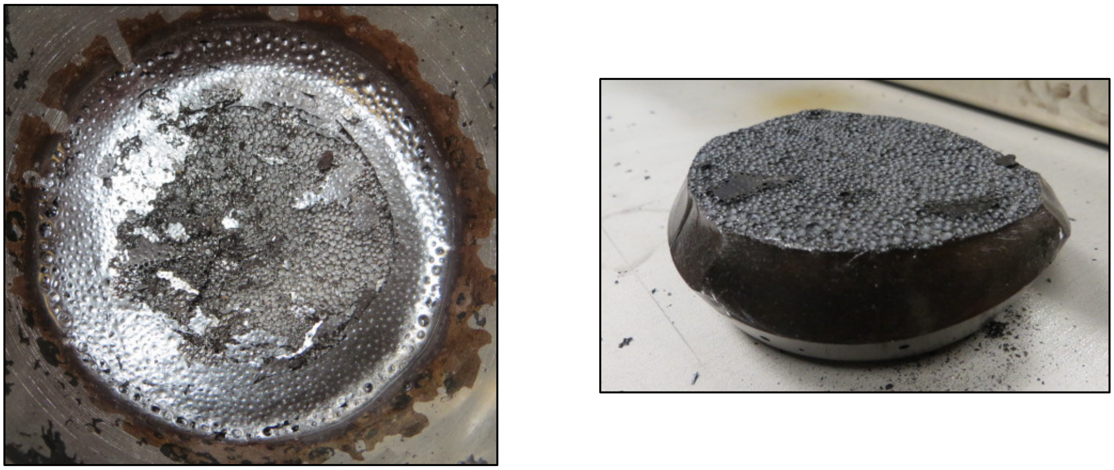
2.4 X-ray Diffraction Analysis

Samples of the quenched PNNL-SP2 and PNNL-SP4 glasses were characterized using X-ray diffraction (XRD) to identify crystallization. Prior to XRD analysis, the samples were further ground in an agate mortar and pestle to reduce the particle size and to homogenize the samples. The ground powder was placed on a glass slide. A few drops of a 10% Amyl Acetate/Collodion solution was added to the ground powder to fix the powder to the glass slide. The data were collected on a Bruker D8 X-ray Diffractometer with a CuKα source operated at 45 kV and 40 mA. A step scan was run over a 2θ range of 5-70° with a step size of 0.02° and a dwell time of 1 second. Search-match identification was performed with Jade software (Version 2010) from Materials Data Inc., combined with the PDF-4 database from the International Centre for Diffraction Data. The measurement conditions provided a 0.5 wt % detection limit. The results of the XRD analysis for glasses PNNL-SP2 and PNNL-SP4 are shown in Appendix A. Both glasses were found to contain trevorite ($NiFe_2O_4$).

2.5 Heat Treatment

Portions of the PNNL-SP2 and PNNL-SP4 glasses were heat treated to intentionally increase the concentration of spinel in the glass to support crystal dissolution experiments. The ground glass was placed into 95%Pt-5%Au alloy crucibles with lids and heat treated at approximately 850 °C for 48 hours. This temperature was selected based on heat treatment and crystallization data reported by PNNL.[8,9]

After the isothermal hold, the crucibles were removed from the furnace and allowed to cool in air. Photos of the glass after heat treatment are shown in Figure 2-2. Visual observation indicated that crystals were present throughout the glass.



(a) (b)

Figure 2-2. Photos of the PNNL-SP glass composition after heat treatment at ~850°C for 48 hours, showing the top surface before removal from the crucible (a), and the side of the glass after removal from the crucible (b), where fracture surfaces allowed for observation of crystals within the glass

3.0 Reducing the T_L of the PNNL-SP Composition via GFC Additions

3.1 Selection of Modified Glass Compositions

GFCs that will be available at WTP[12] were explored as potential additives to the PNNL-SP glass composition to reduce the spinel T_L while maintaining acceptable processing properties and performance. The intent was to demonstrate that accumulated spinel crystals can be dissolved by reducing the spinel T_L of the glass melt. Specifically, additions of Na_2O and SiO_2 (which would occur via additions of the GFCs Na_2CO_3 and SiO_2 at WTP) were selected for modifying the glass composition. A quasicrystalline freezing point depression model[13,14] was used to predict the spinel T_L resulting from varying GFC additions. The pseudobinary acmite-nepheline phase diagram that accompanies this model is shown in Figure 3-1. As an example, consider the potential glass composition with spinel crystals present denoted by point A in Figure 3-1. GFC additions can be selected, with the assistance of the quasicrystalline freezing point depression model, to shift the composition of the glass to point B on the diagram where it is anticipated that spinel crystals will then dissolve into the melt. PNNL-SP glass compositions modified in this manner were further evaluated using the Defense Waste Processing Facility (DWPF) Product Composition Control System (PCCS) models[15] to determine whether the processing properties and product performance constraints would be met.[a]

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[a] The DWPF models were used rather than WTP models due to ease of accessibility and implementation for this preliminary study. It is acknowledged that constraints for the two facilities may not overlap.

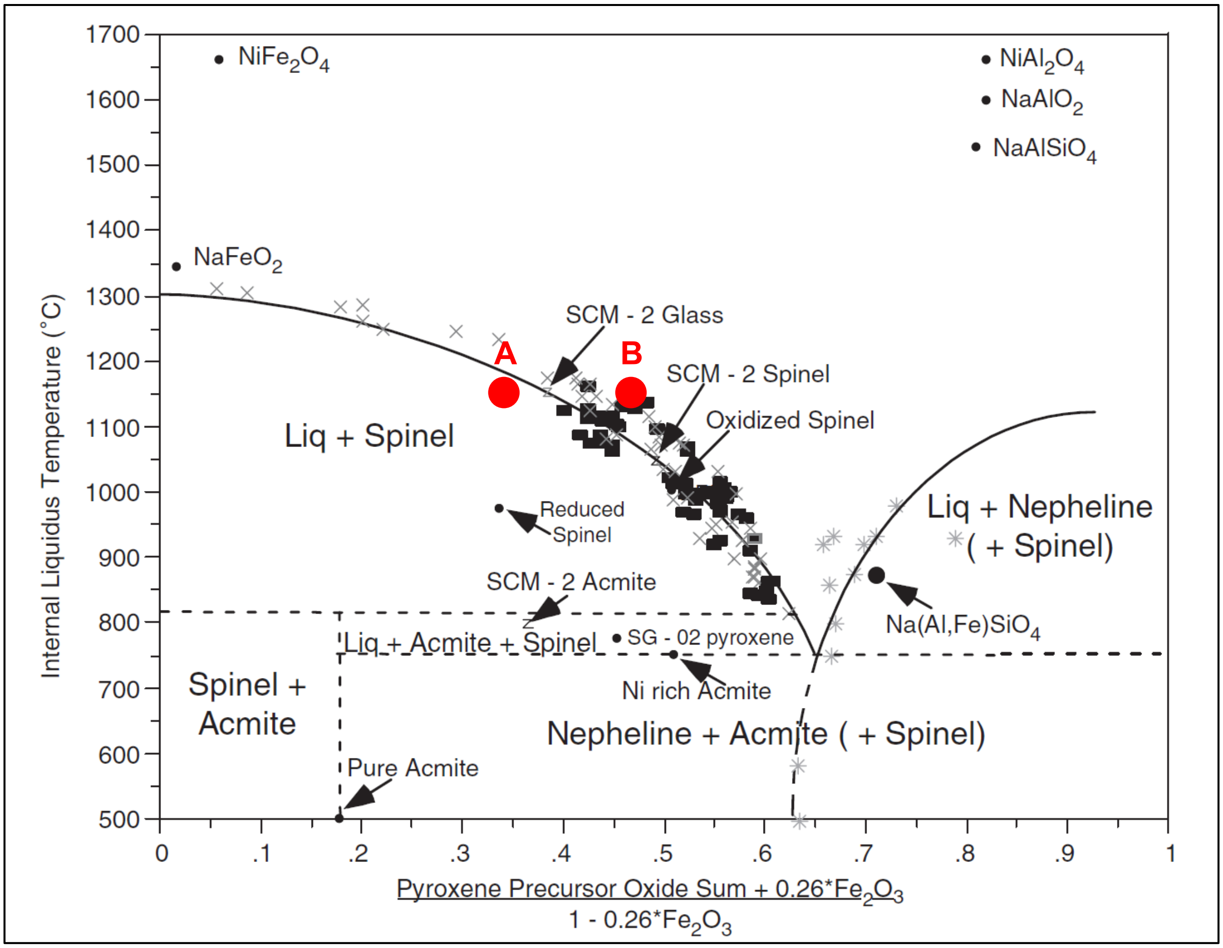

Figure 3-1. Pseudobinary acmite-nepheline phase diagram from Jantzen and Brown[14]

The model outputs indicated that increasing the Na_2O concentration reduced the predicted spinel T_L, and that increasing the SiO_2 concentration was required to maintain a predicted PCT response that met the durability constraints in PCCS. Eight modified versions of the PNNL-SP glass composition were identified for further testing, based on the component additions and model predictions summarized in Table 3-1. The compositions of the eight modified glasses are listed in Table 3-2.

Table 3-1. Summary of GFC Additions and T_L Predictions

Sample ID	Na_2O Addition, g/100 g of PNNL-SP glass	SiO_2 Addition, g/100 g of PNNL-SP glass	Mass Ratio of Additives to PNNL-SP Glass	Predicted Spinel T_L (°C)	Predicted Viscosity (Poise)	Predicted Normalized Leachate for Boron (g/L)
PNNL-SP	0	0	-	1089	10	1.13
PNNL-SP2-HT-1	15	45	0.60	835	49	2.81
PNNL-SP2-HT-2	20	60	0.80	779	60	3.29
PNNL-SP2-HT-3	24	75	0.99	739	74	3.20
PNNL-SP2-HT-4	13	40	0.53	859	46	2.47
PNNL-SP2-HT-5	11	35	0.46	886	44	2.15
PNNL-SP4-HT-6	9	30	0.39	916	41	1.84
PNNL-SP4-HT-7	7	25	0.32	945	38	1.55
PNNL-SP4-HT-8	5	20	0.25	979	35	1.28

Table 3-2. Targeted Compositions for Baseline and Modified Glasses After GFC Additions (wt %)

Oxide	PNNL-SP (Baseline)	PNNL-SP2-HT-1	PNNL-SP2-HT-2	PNNL-SP2-HT-3	PNNL-SP2-HT-4	PNNL-SP2-HT-5	PNNL-SP4-HT-6	PNNL-SP4-HT-7	PNNL-SP4-HT-8
Al_2O_3	7.84	4.90	4.36	3.94	5.13	5.37	5.64	5.94	6.27
B_2O_3	7.63	4.77	4.24	3.84	4.99	5.23	5.49	5.78	6.11
BaO	0.09	0.06	0.05	0.05	0.06	0.06	0.06	0.07	0.07
CaO	0.54	0.34	0.30	0.27	0.35	0.37	0.39	0.41	0.43
CdO	0.62	0.39	0.34	0.31	0.41	0.42	0.45	0.47	0.50
Ce_2O_3	0.19	0.12	0.11	0.10	0.12	0.13	0.14	0.14	0.15
CoO	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Cr_2O_3	0.16	0.10	0.09	0.08	0.10	0.11	0.12	0.12	0.13
CuO	0.04	0.03	0.02	0.02	0.03	0.03	0.03	0.03	0.03
Fe_2O_3	17.51	10.94	9.73	8.80	11.44	11.99	12.59	13.26	14.00
K_2O	0.32	0.20	0.18	0.16	0.21	0.22	0.23	0.24	0.26
La_2O_3	0.21	0.13	0.12	0.11	0.14	0.14	0.15	0.16	0.17
Li_2O	1.90	1.19	1.06	0.96	1.24	1.30	1.37	1.44	1.52
MgO	0.12	0.08	0.07	0.06	0.08	0.08	0.09	0.09	0.10
MnO	0.33	0.21	0.18	0.17	0.22	0.23	0.24	0.25	0.26
Na_2O	17.82	20.51	21.01	21.01	20.14	19.74	19.29	18.80	18.25
Nd_2O_3	0.17	0.11	0.09	0.09	0.11	0.12	0.12	0.13	0.14
NiO	1.50	0.94	0.83	0.75	0.98	1.03	1.08	1.14	1.20
P_2O_5	0.31	0.19	0.17	0.16	0.20	0.21	0.22	0.23	0.25
RuO_2	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
SO_3	0.08	0.05	0.04	0.04	0.05	0.05	0.06	0.06	0.06
SiO_2	38.48	52.18	54.71	57.03	51.30	50.33	49.27	48.09	46.79
SnO_2	0.10	0.06	0.06	0.05	0.07	0.07	0.07	0.08	0.08
TiO_2	0.03	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
ZnO	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.02
ZrO_2	3.97	2.48	2.21	2.00	2.60	2.72	2.86	3.01	3.18

3.2 Glass Fabrication

Using the proportions listed in Table 3-1, reagent grade Na_2CO_3 and SiO_2 were mixed with 50 grams of the ground PNNL-SP2 and PNNL-SP4 glass that had been heat treated at 850 °C for 48 hours as discussed in Section 2.5. These new batches were further heat treated at 850 °C for 24 hours. After the isothermal hold for 24 hours, the crucibles were removed and allowed to cool in air.

Each of the glasses was removed from the crucible and ground for approximately two minutes in a tungsten carbide ring pulverizer. Samples were submitted for chemical composition measurements as well as both qualitative and semi-quantitative XRD analysis.

3.3 Chemical Composition Measurements

Chemical composition measurements were performed using the method described in Section 2.3. The results are listed in Table B-1 of Appendix B. The percent error is included in the table for those components with targeted concentrations of more than 0.5 wt %. These values are all within +/-10%, which was determined to indicate reasonable agreement with the targeted compositions for the purposes of this study.

3.4 XRD Analysis

Qualitative XRD characterization was performed as described in Section 2.4. The qualitative XRD results are shown as Figure B-1 through Figure B-8 in Appendix B. Trevorite was detected in glasses PNNL-SP-HT-4 through -8. Additional samples of the PNNL-SP-HT-series glasses, along with samples of the heat treated PNNL-SP2 and PNNL-SP4 glasses, were prepared for quantitative XRD analysis. The glass samples were ground in an agate mortar and pestle to reduce the particle size and to homogenize the samples. The ground glass powder was weighed and an internal standard, CaF_2, was added at 5 wt %. The ground glass powder and internal standard were reground in an agate mortar and pestle. The ground glass powder and standard mixtures were packed into a 1 in. diameter, 1/16 in. deep well in a circular quartz low background slide cut along the c-axis from Gem Dugout. The excess material on the surface was shaved off with a razor blade to reduce preferred orientation effects.

3.5 Discussion of Results

The measured amounts of trevorite detected in each sample (on a wt % basis) are shown in Table 3-3. As expected, the additions of Na_2O and SiO_2 to the baseline glass reduced the amount of trevorite present. Two factors may have contributed to the reduction in the concentration of trevorite: the increased volume of glass resulting from the addition of Na_2O and SiO_2 to the baseline glass relative to the amount of existing spinel crystals (referred to here as dilution of the baseline glass spinel concentration), and dissolution of the spinel crystals into the melt due to the reduced spinel T_L of the modified glass composition.

In order to determine whether the measured weight fractions of trevorite corresponded only to dilution (i.e., whether the change in spinel concentration was only due to the volume increase resulting from the additions of Na_2O and SiO_2), the projected trevorite content that would result solely from dilution is provided in Table 3-3. The measured trevorite amounts, also reported in Table 3-3, are all below the values projected from the dilution effect alone. This is also shown graphically in Figure 3-2. This result indicates that the additions of Na_2O and SiO_2 resulted in the dissolution of some or all of the spinel crystals in the baseline glass. As a specific example, consider the results for glass PNNL-SP2-HT-3. As shown in Table 3-3, 49.5 g of additives were combined with 50 g of the original glass. Since the original glass contained 10.2 wt % spinel, the addition of the additives should reduce this number by half if dilution alone is considered. Thus, the expected spinel concentration in the modified glass would be 5.1 wt %. However, the measured spinel concentration for this glass was below the detection limit.

Therefore, it appears that dissolution of spinel crystals occurred in the modified glass, in addition to dilution of the spinel concentration.

Table 3-3. Projected and Measured Trevorite Content (wt %)

Sample ID	Mass of Original Glass, PNNL-SP (g)	Mass of Additives (g)	Dilution Factor	Projected Spinel Concentration (wt %)	Measured Spinel Concentration (wt %)
PNNL-SP2	-	-	-	-	10.2
PNNL-SP4	-	-	-	-	9.4
PNNL-SP2-HT-1	50	30	0.38	6.4	0
PNNL-SP2-HT-2	50	40	0.44	5.7	0
PNNL-SP2-HT-3	50	49.5	0.50	5.1	0
PNNL-SP2-HT-4	50	26.5	0.35	6.7	1.5
PNNL-SP2-HT-5	50	23	0.32	7.0	1.8
PNNL-SP4-HT-6	50	19.5	0.28	6.8	2.8
PNNL-SP4-HT-7	50	16	0.24	7.1	3.6
PNNL-SP4-HT-8	50	12.5	0.20	7.5	4.1

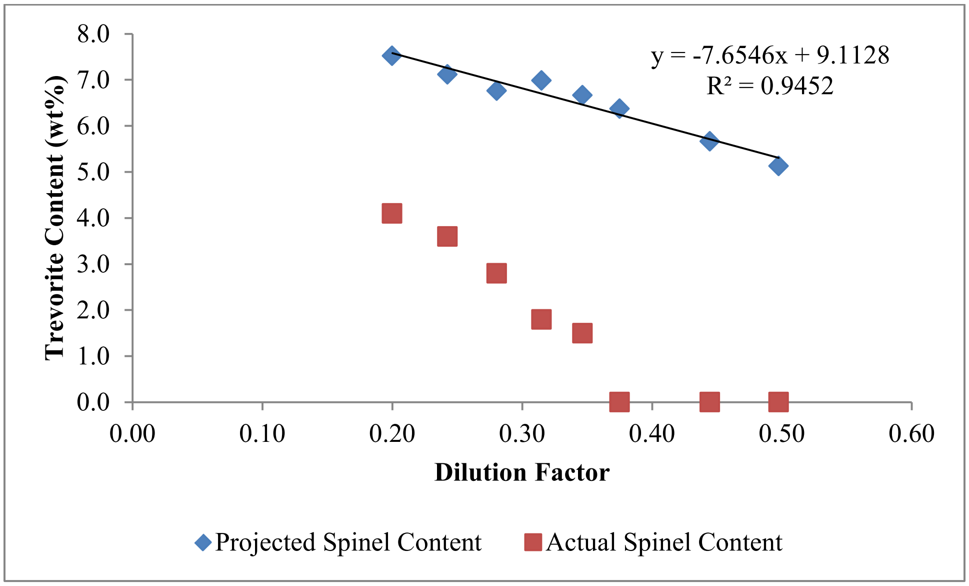

Figure 3-2. Comparison of projected and measured trevorite contents

4.0 Development of a Modified Glass Composition with a Higher Spinel T_L

4.1 Selection of Modified Glass Compositions

While the previous experiments demonstrated the ability to dissolve spinel crystals dispersed in a glass via the tailored addition of GFCs, spinel crystals are anticipated to grow and settle in a melter. The ability to dissolve a settled layer of spinel crystals is therefore of importance for facility operation. Thus, spinel settling in the experimental glass at the nominal melting temperature of 1150 °C was desirable in order to develop a laboratory experiment that is more representative of anticipated melter conditions. The baseline PNNL-SP glass composition did not exhibit appreciable spinel settling after heat treatment at 1150 °C for 24 hours, as shown in Figure 4-1. In order to increase the amount of spinel formed in the glass at 1150 °C, the quasicrystalline freezing point depression model[14] was used to determine appropriate additions of Fe_2O_3 and NiO to increase the predicted spinel T_L over that of the baseline PNNL-SP glass.

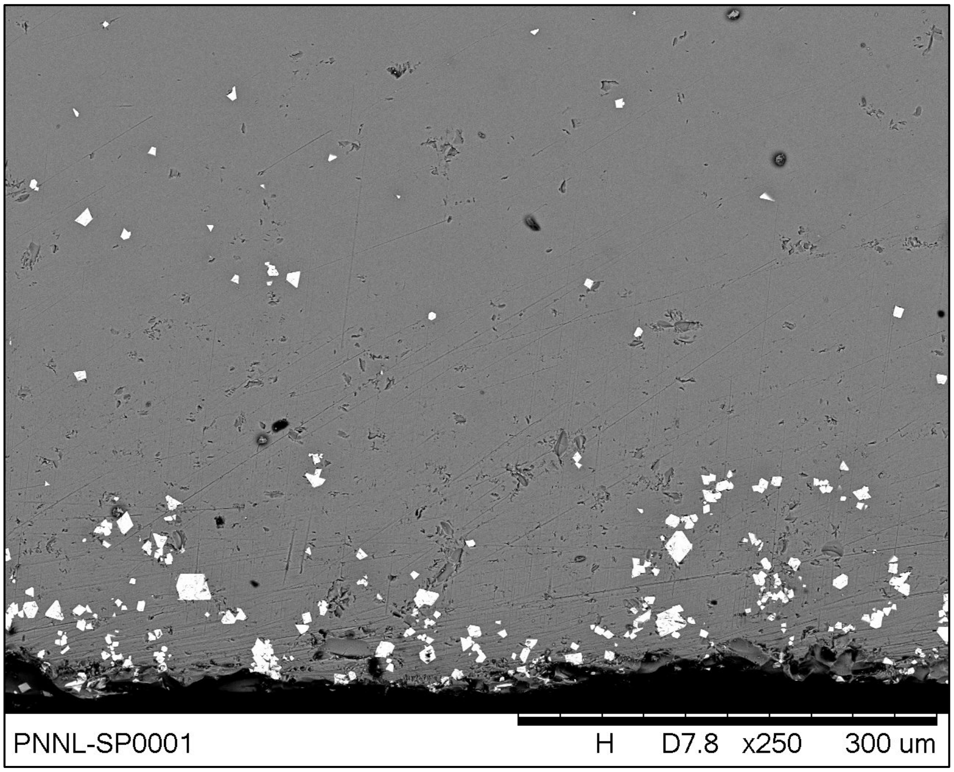

Figure 4-1. SEM image of cross section of PNNL-SP glass from the bottom of a crucible after heat treatment at 1150 °C for 24 hours

Based on the spinel T_L predictions, two compositions labeled SPGL-0.75 and SPGL-1.5 were selected for further study and are described in Table 4-1. The composition of the PNNL-SP glass was normalized to incorporate the increased concentrations of Fe_2O_3 and NiO. RuO_2 was removed from the compositions based on a report that Ru can slow the settling of spinel crystals.[a] The resulting targeted compositions for the two glasses are listed in Table 4-2. Both of these glasses have predicted viscosity values and PCT responses that meet the PCCS constraints.[15] These properties are also listed in Table 4-2.

Table 4-1. Fe_2O_3 and NiO Additions to Increase the Predicted Spinel T_L

Sample ID	Fe_2O_3 Addition (wt %)	NiO Addition (total wt %)	Predicted Spinel T_L (°C)
PNNL-SP	-	-	1089
SPGL-0.75	0.75	0.75	1148
SPGL-1.5	1.50	1.50	1205

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[a] J. Matyáš, A. R. Huckleberry, C. P. Rodriguez, J. B. Lang, A. T. Owen, and A. A. Kruger, "Crystal-Tolerant Glass Approach for Mitigation of Crystal Accumulation in Continuous Melters Processing Radioactive Waste," Pacific Northwest National Laboratory (in draft)

Table 4-2. Glass Compositions Modified for Higher Spinel T_L Values and Their Predicted Properties

Oxide	PNNL-SP (Baseline)	SPGL-0.75	SPGL-1.5
Al_2O_3	7.84	7.70	7.55
B_2O_3	7.63	7.49	7.35
BaO	0.09	0.09	0.09
CaO	0.54	0.53	0.52
CdO	0.62	0.61	0.60
Ce_2O_3	0.19	0.19	0.18
CoO	0.01	0.01	0.01
Cr_2O_3	0.16	0.16	0.15
CuO	0.04	0.04	0.04
Fe_2O_3	17.51	18.26	19.01
K_2O	0.32	0.31	0.31
La_2O_3	0.21	0.21	0.20
Li_2O	1.90	1.87	1.83
MgO	0.12	0.12	0.12
MnO	0.33	0.32	0.32
Na_2O	17.82	17.49	17.16
Nd_2O_3	0.17	0.17	0.16
NiO	1.50	2.25	3.00
P_2O_5	0.31	0.30	0.30
RuO_2	0.01	0.00	0.00
SiO_2	38.48	37.77	37.06
SnO_2	0.10	0.10	0.10
SO_3	0.08	0.08	0.08
TiO_2	0.03	0.03	0.03
ZnO	0.02	0.02	0.02
ZrO_2	3.97	3.90	3.82
Predicted Spinel T_L (°C)	1089	1148	1205
Predicted Viscosity (Poise)	10	10	9
Predicted Normalized Leachate for Boron (g/L)	1.13	1.06	0.93

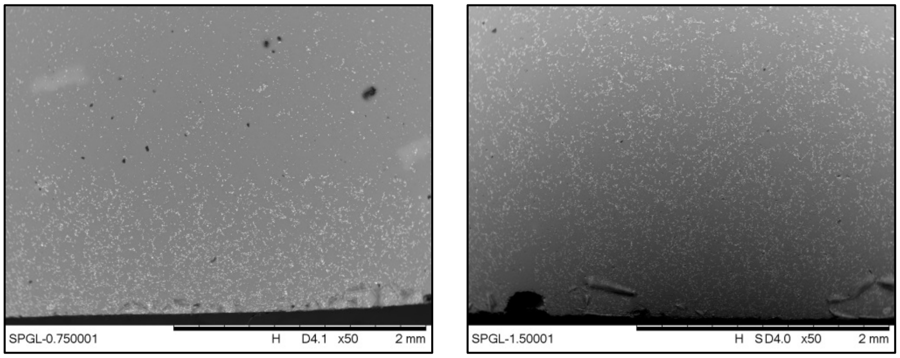
4.2 Glass Fabrication

Batches of the SPGL-0.75 and SPGL-1.5 glasses were prepared with reagent-grade materials. The raw materials were thoroughly blended with a shaker-mixer for five minutes with zirconia grinding media and placed into a 95%Pt-5%Au alloy crucible that was covered with a loose-fitting lid. The filled crucibles were placed into a furnace at the targeted melting temperature of 1150 °C. The crucibles were removed from the furnace after an isothermal hold at 1150 °C for 1 hour and allowed to cool in air. Each glass was removed from the crucible and ground for approximately 2 minutes in a tungsten carbide ring pulverizer.

The ground glasses were then heat treated at approximately1150 °C for 24 hours in 95%Pt-5%Au alloy crucibles. The crucibles were removed from the furnace after the isothermal hold and allowed to cool in air. In order to facilitate sectioning for microscopy, the samples were annealed at approximately 475 °C for 1 hour.

4.3 Microscopy Analysis

Each glass sample was sectioned with a low speed diamond saw, polished with a series of SiC grinding papers, and coated with carbon in preparation for observation via Scanning Electron Microscopy (SEM). A comparison of the samples viewed with SEM is shown in Figure 4-2.



(a) **(b)**

Figure 4-2. SEM micrographs of settled spinel crystals in samples of glasses SPGL-0.75 (a) and SPGL-1.5 (b) after heat treatment at 1150 °C

4.4 Discussion of Results

There was a relatively small accumulated later of spinel crystals at the bottom of the SPGL-0.75 glass. The SPGL-1.5 glass had a larger accumulated layer of spinel crystals that was visible by eye (also see Figure C-1 in Appendix C). While this degree of spinel settling is unrealistic for WTP operation, the SPGL-1.5 glass composition was selected to provide an exaggerated example of spinel accumulation to support further experiments.

5.0 Layering Studies with SPGL-1.5 and Lower T_L Glass Compositions

5.1 Selection of Modified Glass Compositions

In actual melter operation, an addition of GFCs to dissolve spinel crystals would result in the melt pool composition changing over a period of time as the new feed material is incorporated. As the GFCs are incorporated into the melt, the spinel T_L of the glass would be reduced and ideally dissolution of the accumulated spinel crystals would begin to occur when this lower T_L glass reaches the spinel layer. This series of experiments was intended to evaluate the ability to reduce the thickness of the accumulated layer of spinel crystals during further heat treatment at 1150 °C by “layering” a glass with a lower predicted spinel T_L on top of the SPGL-1.5 glass. In this testing, there was no agitation of the melt other than thermal convective currents. Based on the results discussed in Section 3.0, PNNL-SP-HT-3 (predicted spinel T_L of 737 °C) and PNNL-SP-HT-8 (predicted spinel T_L of 987 °C) were selected as the lower T_L glasses for these experiments.

5.2 Glass Fabrication

Batches of PNNL-SP-HT-3 and PNNL-SP-HT-8 were prepared with reagent-grade materials. The raw materials were thoroughly blended for 5 minutes with a shaker-mixer using zirconia grinding media and then placed into a 95%Pt-5%Au alloy crucibles covered with loose-fitting lids. The filled crucibles were placed into a furnace at the target melting temperature of 1150 °C. The crucibles were removed from the furnace after an isothermal hold at 1150 °C for 1 hour and allowed to cool in air. The glasses were removed from the crucibles and sized to +40/-5 mesh followed by ultrasonic cleaning in water (repeated four times) to remove fines. This provided uniformly sized glass particles for the layering experiments.

Fifty grams of the ground SPGL-1.5 glass (as described in Section 4.2) was placed into 95%Pt-5%Au alloy crucibles with lids and heat treated at 1150 °C for 24 hours to allow the spinel crystals to settle. After the isothermal thermal hold was completed, the crucibles were removed and allowed to cool in air.

The sized PNNL-SP-HT-3 and PNNL-SP-HT-8 glasses were placed on top of the heat treated SPGL-1.5 glass in two different ratios by weight as listed in Table 5-1. A lid was placed on each of the crucibles for the heat treatment. Each of these combinations, including a sample of SPGL-1.5 with no additives, was heat treated at 1150 °C for 24 hours. After the isothermal hold, the crucibles were removed and allowed to cool in air. In order to facilitate sectioning for microscopy, the samples were annealed at approximately 475 °C for 1 hour.

Table 5-1. Amounts of Lower Spinel T_L Glasses Layered Over the SPGL-1.5 Glass

Sample ID	Additive Glass	Amount (g) added to 50 g of SPGL-1.5 Glass	Mass Ratio of Additive Glass to SPGL-1.5
SPGL-1.5-HTL-0.25	PNNL-SP-HT-8	12.5	0.25
SPGL-1.5-HTL-1	PNNL-SP-HT-8	50.0	1.00
SPGL-1.5-LTL-0.25	PNNL-SP-HT-3	12.5	0.25
SPGL-1.5-LTL-1	PNNL-SP-HT-3	50.0	1.00

5.3 Microscopy Analysis

Each glass sample was sectioned with a low speed diamond saw and polished on one side with a series of SiC grinding papers, except for SPGL-1.5-HTL-1, which fractured during cutting and could not be prepared for analysis. Optical micrographs of the glasses and the settled layers of spinel crystals are provided for reference in Figure C-1 through Figure C-4 of Appendix C. The approximate, measured spinel layer thickness in each glass was determined using calibrated image analysis software and the results are presented in Table 5-2.

Table 5-2. Measured Spinel Layer Thickness for Layered Glasses

Sample ID	Approximate Spinel Layer Thickness (mm)
SPGL-1.5 (Baseline)	2.41
SPGL-1.5-HTL-0.25	2.93
SPGL-1.5-HTL-1	*
SPGL-1.5-LTL-0.25	2.42
SPGL-1.5-LTL-1	2.45

*Sample fractured and could not be measured

5.4 Discussion of Results

A review of the data in Table 5-2 shows that there were no obvious differences in the thickness of the settled spinel layers in the glasses. This indicates that the lower spinel T_L glasses were not sufficiently incorporated into the baseline SPGL-1.5 glass, which led to the next series of experiments where the glasses were mixed to simulate forced agitation of the melt pool.

6.0 Mixing Studies with SPGL-1.5 and a Low T_L Glass Composition

6.1 Selection of Modified Glass Compositions

The WTP HLW melter will utilize bubblers to force agitation and improve heat transfer between the melt pool and unincorporated melter feed material, improving melter throughput. It was hypothesized that bubbling can also provide the agitation needed to generate contact between a lower T_L glass and a settled layer of spinel crystals to accelerate dissolution. Prior to conducting studies under bubbled conditions, there was a desire to confirm the feasibility of using lower T_L glass compositions to reduce or eliminate the presence of spinel in the SPGL-1.5 glass at 1150 °C. In these experiments, the additive glass composition with the lowest predicted spinel T_L (PNNL-SP-HT-3 as described in Section 3.0) was ground for approximately 2 minutes with a tungsten carbide ring pulverizer and mixed with the SPGL-1.5 glass. PNNL-SP-HT-3 was selected as it was anticipated to have the greatest impact on the amount of spinel crystals present in the SPGL-1.5 glass.

6.2 Glass Fabrication

All of the original SPGL-1.5 glass was consumed in the previous experiments, so another batch of the same composition, identified as SPGL-1.5A, was prepared with reagent grade materials. The raw materials were thoroughly blended with a shaker-mixer for 5 minutes with zirconia grinding media and placed into a 95%Pt-5%Au alloy crucible that was covered with a loose-fitting lid. The filled crucible was placed into a furnace at the targeted melting temperature of 1150 °C. The crucible was removed from the furnace after an isothermal hold at 1150 °C for 1 hour and allowed to cool in air. The glass was removed from the crucible and ground for approximately 2 minutes in a tungsten carbide ring pulverizer.

Fifty grams of the ground SPGL-1.5A glass was placed into 95%Pt-5%Au alloy crucibles with lids and heat treated at 1150 °C for 24 hours to allow for additional formation of spinel crystals. After the isothermal hold was completed, the crucible was removed and allowed to cool in air. The glass was then removed from the crucible and ground for approximately two minutes in a tungsten carbide ring pulverizer.

The original PNNL-SP-HT-3 glass was also consumed during the previous experiments, so another batch of the same composition, identified as PNNL-SP-HT-3a, was prepared with reagent grade materials. The raw materials were thoroughly blended with a shaker-mixer for 5 minutes with zirconia grinding media and placed into a 95%Pt-5%Au alloy crucible that was covered with a loose-fitting lid. The filled crucible was placed into a high-temperature furnace at the targeted melting temperature of 1150 °C. The crucible was removed from the furnace after an isothermal hold at 1150 °C for 1 hour and allowed to cool in air. The glass was removed from the crucible and ground for approximately two minutes in a tungsten carbide ring pulverizer.

The ground PNNL-SP-HT-3a glass was added to the ground and heat treated SPGL-1.5A glass in various ratios by mass as listed in Table 6-1. The four glasses were thoroughly blended with a shaker-mixer for five minutes with zirconia grinding media and placed into a 95%Pt-5%Au alloy crucible that was covered with a loose-fitting lid. The glasses were heat treated at 1150 °C for 24 hours, along with a previously heat treated sample of SPGL-1.5A containing no PNNL-SP-HT-3a glass, which served as a baseline. After the isothermal hold was completed, the crucibles were removed from the furnace and allowed to cool in air. In order to facilitate sectioning for microscopy, the samples were annealed at approximately 475 °C for 1 hour.

Table 6-1. Amounts of PNNL-SP-HT-3a Glass Mixed with the SPGL-1.5A Glass

Sample ID	Amount (g) Added to 50 g of SPGL-1.5A Glass	Ratio of Additive Glass to SPGL-1.5A
SPGL-1.5A-LTL-0.25M	12.5	0.25
SPGL-1.5A-LTL-0.5M	25.0	0.50
SPGL-1.5A-LTL-0.75M	37.5	0.75
SPGL-1.5A-LTL-0.1M	50.0	1.00

6.3 Microscopy Analysis

Each glass sample was sectioned with a low speed diamond saw and polished on one side with a series of SiC grinding papers. Optical micrographs are provided as Figure D-1 through Figure D-5 of Appendix D. The approximate, measured spinel layer thickness in each glass was determined using calibrated image analysis software and the results are presented in Table 6-2.

Table 6-2. Measured Spinel Layer Thickness for Mixed Glasses

Sample ID	Approximate Spinel Layer Thickness (mm)
SPGL-1.5A-LTL-0M	2.08
SPGL-1.5A-LTL-0.25M	0.86
SPGL-1.5A-LTL-0.5M	0.30
SPGL-1.5A-LTL-0.75M	No spinel layer identified
SPGL-1.5A-LTL-1M	No spinel layer identified

6.4 Discussion of Results

A review of the data in Table 6-2 shows that for the mixed glasses, an additive ratio of 0.25 is sufficient to reduce the spinel layer thickness by approximately 60%. As the additive ratio increases, the thickness of the spinel layer is further reduced to the point where a layer could no longer be identified when the additive ratio was 0.75. These results suggest that the addition of a glass with a reduced spinel T_L could be effective at dissolving spinel crystals and potentially reducing the impact of a settled layer on melter operations if sufficient mixing is available.

7.0 Summary

The objective of this study was to demonstrate the potential for dissolution of accumulated spinel crystals in a molten glass via the addition of GFCs while maintaining a glass composition that is acceptable for processing and disposal. Process control models were used to develop a matrix of test compositions with acceptable processing and performance properties. Bench scale experiments showed that tailored GFC additions can be used to reduce spinel concentrations in glasses during processing. This was demonstrated via the addition of a glass composition with a reduced spinel T_L, which may be a more bounding condition than direct addition of GFCs. Accumulated spinel crystals at the bottom of the melt were removed via the combination of thorough mixing and the addition of a lower spinel T_L glass.

8.0 Path Forward

The next series of experiments will be designed to demonstrate the ability to dissolve spinel crystals under conditions that are more similar to those expected in the WTP HLW melter. A furnace with bubbling capability has been assembled for this purpose. Bubbled crucible melts will be characterized to determine whether the amount of agitation is sufficient to dissolve a settled layer of spinel crystals. Crucibles made of Monofrax K-3 could be used to determine whether spinel crystals adhere to the refractory material, and whether bubbling is sufficient to dislodge them. Direct addition of GFCs, rather than addition of a pre-melted glass with a lower spinel T_L, will be added to bubbled melts to more closely simulate melter operation. Minimum mixing ratios will be determined so as to minimize impact to melter processing and waste loading.

The results of this next series of experiments will then be used to suggest parameters for test runs using the Research-Scale Melter (RSM) at PNNL.[9] The RSM will be operated to first build up a settled layer of spinel crystals, based on results from previous experiments with the Ni1.5/Fe17.5 glass. Tailored GFC additions will then be made to the melter feed and their impact on reducing the thickness of the accumulated layer of crystals will be determined by sectioning the melter after the test.

9.0 References

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Appendix A. XRD Spectra for Glasses PNNL-SP2 and PNNL-SP4

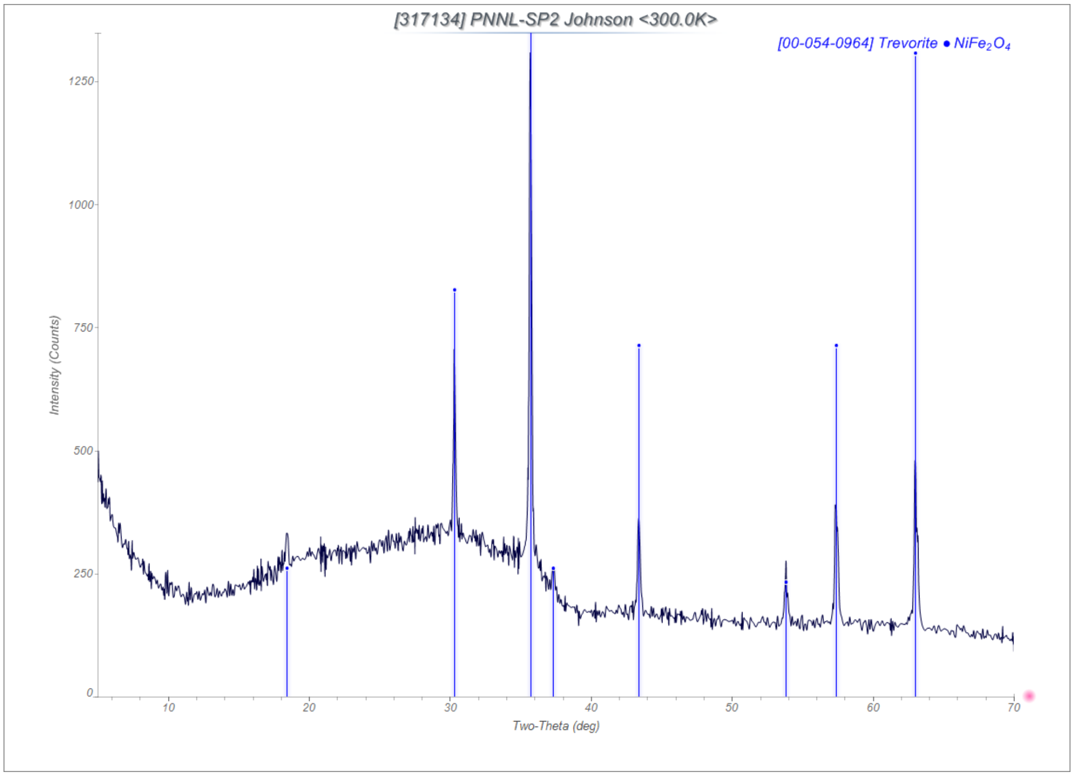


Figure A-1. XRD spectrum of quenched sample of PNNL-SP2

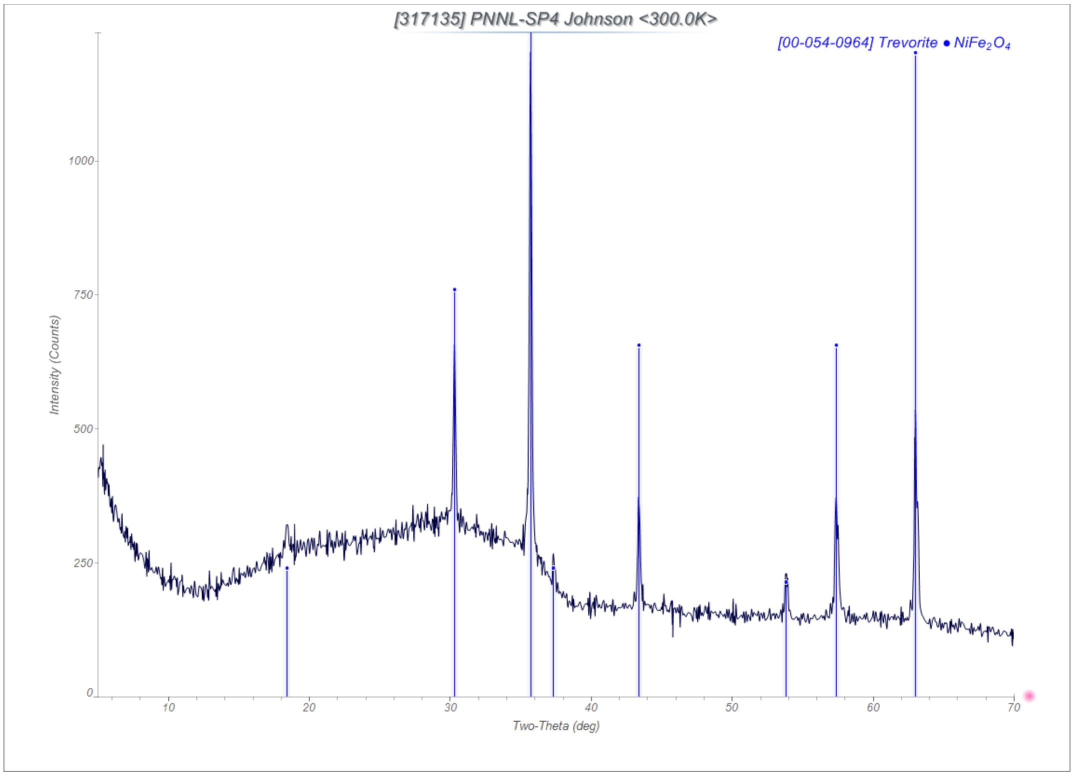


Figure A-2. XRD spectrum of quenched sample of PNNL-SP4

Appendix B. Characterization Data for the PNNL-SP-HT Series Glasses

Table B-1. Comparison of Targeted and Measured Compositions for the PNNL-SP-HT Series Glasses

Glass ID	Oxide	Targeted Concentration (wt %)	Measured Concentration (wt %)	Percent Error
PNNL-SP2-HT-1	Al_2O_3	4.90	4.86	-0.91
PNNL-SP2-HT-1	B_2O_3	4.77	4.77	-0.07
PNNL-SP2-HT-1	BaO	0.06	0.05	-
PNNL-SP2-HT-1	CaO	0.34	0.37	-
PNNL-SP2-HT-1	CdO	0.39	0.38	-
PNNL-SP2-HT-1	Ce_2O_3	0.12	0.12	-
PNNL-SP2-HT-1	CoO	0.01	<0.01	-
PNNL-SP2-HT-1	Cr_2O_3	0.10	0.10	-
PNNL-SP2-HT-1	CuO	0.03	0.05	-
PNNL-SP2-HT-1	Fe_2O_3	10.94	10.51	-3.91
PNNL-SP2-HT-1	K_2O	0.20	0.20	-
PNNL-SP2-HT-1	La_2O_3	0.13	0.11	-
PNNL-SP2-HT-1	Li_2O	1.19	1.20	1.14
PNNL-SP2-HT-1	MgO	0.08	0.07	-
PNNL-SP2-HT-1	MnO	0.21	0.20	-
PNNL-SP2-HT-1	Na_2O	20.51	19.46	-5.13
PNNL-SP2-HT-1	Nd_2O_3	0.11	0.12	-
PNNL-SP2-HT-1	NiO	0.94	0.93	-1.42
PNNL-SP2-HT-1	P_2O_5	0.19	0.17	-
PNNL-SP2-HT-1	RuO_2	0.01	<0.01	-
PNNL-SP2-HT-1	SO_3	0.05	<0.25	-
PNNL-SP2-HT-1	SiO_2	52.18	52.44	0.49
PNNL-SP2-HT-1	SnO_2	0.06	0.08	-
PNNL-SP2-HT-1	TiO_2	0.02	0.03	-
PNNL-SP2-HT-1	ZnO	0.01	0.02	-
PNNL-SP2-HT-1	ZrO_2	2.48	2.34	-5.64
PNNL-SP2-HT-2	Al_2O_3	4.36	4.40	0.86
PNNL-SP2-HT-2	B_2O_3	4.24	4.29	1.23
PNNL-SP2-HT-2	BaO	0.05	0.05	-
PNNL-SP2-HT-2	CaO	0.30	0.37	-
PNNL-SP2-HT-2	CdO	0.34	0.34	-
PNNL-SP2-HT-2	Ce_2O_3	0.11	0.10	-
PNNL-SP2-HT-2	CoO	0.01	<0.01	-
PNNL-SP2-HT-2	Cr_2O_3	0.09	0.09	-
PNNL-SP2-HT-2	CuO	0.02	0.05	-
PNNL-SP2-HT-2	Fe_2O_3	9.73	9.36	-3.79
PNNL-SP2-HT-2	K_2O	0.18	0.19	-
PNNL-SP2-HT-2	La_2O_3	0.12	0.10	-
PNNL-SP2-HT-2	Li_2O	1.06	1.09	3.14
PNNL-SP2-HT-2	MgO	0.07	0.07	-
PNNL-SP2-HT-2	MnO	0.18	0.18	-
PNNL-SP2-HT-2	Na_2O	21.01	20.33	-3.22
PNNL-SP2-HT-2	Nd_2O_3	0.09	0.10	-
PNNL-SP2-HT-2	NiO	0.83	0.83	0.24

Table B-1. Comparison of Targeted and Measured Compositions for the PNNL-SP-HT Series Glasses (continued)

Glass ID	Oxide	Targeted Concentration (wt %)	Measured Concentration (wt %)	Percent Error
PNNL-SP2-HT-2	P_2O_5	0.17	0.14	-
PNNL-SP2-HT-2	RuO_2	0.01	<0.01	-
PNNL-SP2-HT-2	SO_3	0.04	<0.25	-
PNNL-SP2-HT-2	SiO_2	54.71	54.77	0.1
PNNL-SP2-HT-2	SnO_2	0.06	0.07	-
PNNL-SP2-HT-2	TiO_2	0.02	0.03	-
PNNL-SP2-HT-2	ZnO	0.01	0.03	-
PNNL-SP2-HT-2	ZrO_2	2.21	2.05	-7.09
PNNL-SP2-HT-3	Al_2O_3	3.94	3.94	0.07
PNNL-SP2-HT-3	B_2O_3	3.84	3.81	-0.67
PNNL-SP2-HT-3	BaO	0.05	0.04	-
PNNL-SP2-HT-3	CaO	0.27	0.31	-
PNNL-SP2-HT-3	CdO	0.31	0.31	-
PNNL-SP2-HT-3	Ce_2O_3	0.10	0.09	-
PNNL-SP2-HT-3	CoO	0.01	<0.01	-
PNNL-SP2-HT-3	Cr_2O_3	0.08	0.08	-
PNNL-SP2-HT-3	CuO	0.02	0.03	-
PNNL-SP2-HT-3	Fe_2O_3	8.80	8.45	-3.98
PNNL-SP2-HT-3	K_2O	0.16	0.17	-
PNNL-SP2-HT-3	La_2O_3	0.11	0.09	-
PNNL-SP2-HT-3	Li_2O	0.96	0.98	2.35
PNNL-SP2-HT-3	MgO	0.06	0.05	-
PNNL-SP2-HT-3	MnO	0.17	0.16	-
PNNL-SP2-HT-3	Na_2O	21.01	20.42	-2.79
PNNL-SP2-HT-3	Nd_2O_3	0.09	0.10	-
PNNL-SP2-HT-3	NiO	0.75	0.75	-0.29
PNNL-SP2-HT-3	P_2O_5	0.16	0.13	-
PNNL-SP2-HT-3	RuO_2	0.01	<0.01	-
PNNL-SP2-HT-3	SO_3	0.04	<0.25	-
PNNL-SP2-HT-3	SiO_2	57.03	57.48	0.78
PNNL-SP2-HT-3	SnO_2	0.05	0.07	-
PNNL-SP2-HT-3	TiO_2	0.02	0.03	-
PNNL-SP2-HT-3	ZnO	0.01	0.02	-
PNNL-SP2-HT-3	ZrO_2	2.00	1.88	-5.93
PNNL-SP2-HT-4	Al_2O_3	5.13	5.09	-0.71
PNNL-SP2-HT-4	B_2O_3	4.99	4.94	-0.94
PNNL-SP2-HT-4	BaO	0.06	0.06	-
PNNL-SP2-HT-4	CaO	0.35	0.39	-
PNNL-SP2-HT-4	CdO	0.41	0.40	-
PNNL-SP2-HT-4	Ce_2O_3	0.12	0.12	-
PNNL-SP2-HT-4	CoO	0.01	<0.01	-
PNNL-SP2-HT-4	Cr_2O_3	0.10	0.10	-
PNNL-SP2-HT-4	CuO	0.03	0.03	-
PNNL-SP2-HT-4	Fe_2O_3	11.44	11.07	-3.21
PNNL-SP2-HT-4	K_2O	0.21	0.23	-

Table B-1. Comparison of Targeted and Measured Compositions for the PNNL-SP-HT Series Glasses (continued)

Glass ID	Oxide	Targeted Concentration (wt %)	Measured Concentration (wt %)	Percent Error
PNNL-SP2-HT-4	La_2O_3	0.14	0.12	-
PNNL-SP2-HT-4	Li_2O	1.24	1.25	0.85
PNNL-SP2-HT-4	MgO	0.08	0.07	-
PNNL-SP2-HT-4	MnO	0.22	0.21	-
PNNL-SP2-HT-4	Na_2O	20.14	19.72	-2.1
PNNL-SP2-HT-4	Nd_2O_3	0.11	0.12	-
PNNL-SP2-HT-4	NiO	0.98	0.98	0
PNNL-SP2-HT-4	P_2O_5	0.20	0.18	-
PNNL-SP2-HT-4	RuO_2	0.01	<0.01	-
PNNL-SP2-HT-4	SO_3	0.05	<0.25	-
PNNL-SP2-HT-4	SiO_2	51.30	52.39	2.13
PNNL-SP2-HT-4	SnO_2	0.07	0.08	-
PNNL-SP2-HT-4	TiO_2	0.02	0.03	-
PNNL-SP2-HT-4	ZnO	0.01	0.02	-
PNNL-SP2-HT-4	ZrO_2	2.60	2.47	-5.1
PNNL-SP2-HT-5	Al_2O_3	5.37	5.42	0.99
PNNL-SP2-HT-5	B_2O_3	5.23	5.32	1.79
PNNL-SP2-HT-5	BaO	0.06	0.06	-
PNNL-SP2-HT-5	CaO	0.37	0.41	-
PNNL-SP2-HT-5	CdO	0.42	0.41	-
PNNL-SP2-HT-5	Ce_2O_3	0.13	0.13	-
PNNL-SP2-HT-5	CoO	0.01	<0.01	-
PNNL-SP2-HT-5	Cr_2O_3	0.11	0.11	-
PNNL-SP2-HT-5	CuO	0.03	0.03	-
PNNL-SP2-HT-5	Fe_2O_3	11.99	11.38	-5.05
PNNL-SP2-HT-5	K_2O	0.22	0.22	-
PNNL-SP2-HT-5	La_2O_3	0.14	0.12	-
PNNL-SP2-HT-5	Li_2O	1.30	1.36	4.54
PNNL-SP2-HT-5	MgO	0.08	0.11	-
PNNL-SP2-HT-5	MnO	0.23	0.21	-
PNNL-SP2-HT-5	Na_2O	19.74	18.81	-4.7
PNNL-SP2-HT-5	Nd_2O_3	0.12	0.13	-
PNNL-SP2-HT-5	NiO	1.03	1.00	-3.02
PNNL-SP2-HT-5	P_2O_5	0.21	0.18	-
PNNL-SP2-HT-5	RuO_2	0.01	<0.01	-
PNNL-SP2-HT-5	SO_3	0.05	<0.25	-
PNNL-SP2-HT-5	SiO_2	50.33	51.16	1.65
PNNL-SP2-HT-5	SnO_2	0.07	0.14	-
PNNL-SP2-HT-5	TiO_2	0.02	0.05	-
PNNL-SP2-HT-5	ZnO	0.01	0.08	-
PNNL-SP2-HT-5	ZrO_2	2.72	2.55	-6.28
PNNL-SP4-HT-6	Al_2O_3	5.64	5.59	-0.97
PNNL-SP4-HT-6	B_2O_3	5.49	5.41	-1.53
PNNL-SP4-HT-6	BaO	0.06	0.07	-
PNNL-SP4-HT-6	CaO	0.39	0.46	-

Table B-1. Comparison of Targeted and Measured Compositions for the PNNL-SP-HT Series Glasses (continued)

Glass ID	Oxide	Targeted Concentration (wt %)	Measured Concentration (wt %)	Percent Error
PNNL-SP4-HT-6	CdO	0.45	0.43	-
PNNL-SP4-HT-6	Ce_2O_3	0.14	0.14	-
PNNL-SP4-HT-6	CoO	0.01	<0.01	-
PNNL-SP4-HT-6	Cr_2O_3	0.12	0.11	-
PNNL-SP4-HT-6	CuO	0.03	0.04	-
PNNL-SP4-HT-6	Fe_2O_3	12.59	12.07	-4.09
PNNL-SP4-HT-6	K_2O	0.23	0.24	-
PNNL-SP4-HT-6	La_2O_3	0.15	0.13	-
PNNL-SP4-HT-6	Li_2O	1.37	1.37	-0.22
PNNL-SP4-HT-6	MgO	0.09	0.08	-
PNNL-SP4-HT-6	MnO	0.24	0.24	-
PNNL-SP4-HT-6	Na_2O	19.29	18.50	-4.09
PNNL-SP4-HT-6	Nd_2O_3	0.12	0.13	-
PNNL-SP4-HT-6	NiO	1.08	1.05	-2.41
PNNL-SP4-HT-6	P_2O_5	0.22	0.19	-
PNNL-SP4-HT-6	RuO_2	0.01	<0.01	-
PNNL-SP4-HT-6	SO_3	0.06	<0.25	-
PNNL-SP4-HT-6	SiO_2	49.27	50.04	1.56
PNNL-SP4-HT-6	SnO_2	0.07	0.09	-
PNNL-SP4-HT-6	TiO_2	0.02	0.08	-
PNNL-SP4-HT-6	ZnO	0.01	0.03	-
PNNL-SP4-HT-6	ZrO_2	2.86	2.71	-5.31
PNNL-SP4-HT-7	Al_2O_3	5.94	5.89	-0.76
PNNL-SP4-HT-7	B_2O_3	5.78	6.07	5.08
PNNL-SP4-HT-7	BaO	0.07	0.07	-
PNNL-SP4-HT-7	CaO	0.41	0.47	-
PNNL-SP4-HT-7	CdO	0.47	0.46	-
PNNL-SP4-HT-7	Ce_2O_3	0.14	0.14	-
PNNL-SP4-HT-7	CoO	0.01	<0.01	-
PNNL-SP4-HT-7	Cr_2O_3	0.12	0.11	-
PNNL-SP4-HT-7	CuO	0.03	0.04	-
PNNL-SP4-HT-7	Fe_2O_3	13.26	12.80	-3.5
PNNL-SP4-HT-7	K_2O	0.24	0.25	-
PNNL-SP4-HT-7	La_2O_3	0.16	0.14	-
PNNL-SP4-HT-7	Li_2O	1.44	1.48	2.71
PNNL-SP4-HT-7	MgO	0.09	0.08	-
PNNL-SP4-HT-7	MnO	0.25	0.25	-
PNNL-SP4-HT-7	Na_2O	18.80	18.25	-2.92
PNNL-SP4-HT-7	Nd_2O_3	0.13	0.14	-
PNNL-SP4-HT-7	NiO	1.14	1.11	-2.29
PNNL-SP4-HT-7	P_2O_5	0.23	0.20	-
PNNL-SP4-HT-7	RuO_2	0.01	<0.01	-
PNNL-SP4-HT-7	SO_3	0.06	<0.25	-
PNNL-SP4-HT-7	SiO_2	48.09	49.70	3.35
PNNL-SP4-HT-7	SnO_2	0.08	0.10	-

Table B-1. Comparison of Targeted and Measured Compositions for the PNNL-SP-HT Series Glasses (continued)

Glass ID	Oxide	Targeted Concentration (wt %)	Measured Concentration (wt %)	Percent Error
PNNL-SP4-HT-7	TiO_2	0.02	0.03	-
PNNL-SP4-HT-7	ZnO	0.02	0.02	-
PNNL-SP4-HT-7	ZrO_2	3.01	2.88	-4.25
PNNL-SP4-HT-8	Al_2O_3	6.27	6.18	-1.36
PNNL-SP4-HT-8	B_2O_3	6.11	5.91	-3.2
PNNL-SP4-HT-8	BaO	0.07	0.07	-
PNNL-SP4-HT-8	CaO	0.43	0.49	-
PNNL-SP4-HT-8	CdO	0.50	0.48	-
PNNL-SP4-HT-8	Ce_2O_3	0.15	0.15	-
PNNL-SP4-HT-8	CoO	0.01	<0.01	-
PNNL-SP4-HT-8	Cr_2O_3	0.13	0.12	-
PNNL-SP4-HT-8	CuO	0.03	0.04	-
PNNL-SP4-HT-8	Fe_2O_3	14.00	13.44	-4.01
PNNL-SP4-HT-8	K_2O	0.26	0.28	-
PNNL-SP4-HT-8	La_2O_3	0.17	0.14	-
PNNL-SP4-HT-8	Li_2O	1.52	1.49	-1.72
PNNL-SP4-HT-8	MgO	0.10	0.09	-
PNNL-SP4-HT-8	MnO	0.26	0.26	-
PNNL-SP4-HT-8	Na_2O	18.25	17.55	-3.81
PNNL-SP4-HT-8	Nd_2O_3	0.14	0.14	-
PNNL-SP4-HT-8	NiO	1.20	1.16	-3.26
PNNL-SP4-HT-8	P_2O_5	0.25	0.21	-
PNNL-SP4-HT-8	RuO_2	0.01	<0.01	-
PNNL-SP4-HT-8	SO_3	0.06	<0.25	-
PNNL-SP4-HT-8	SiO_2	46.79	48.09	2.78
PNNL-SP4-HT-8	SnO_2	0.08	0.10	-
PNNL-SP4-HT-8	TiO_2	0.02	0.04	-
PNNL-SP4-HT-8	ZnO	0.02	0.03	-
PNNL-SP4-HT-8	ZrO_2	3.18	3.02	-5.07

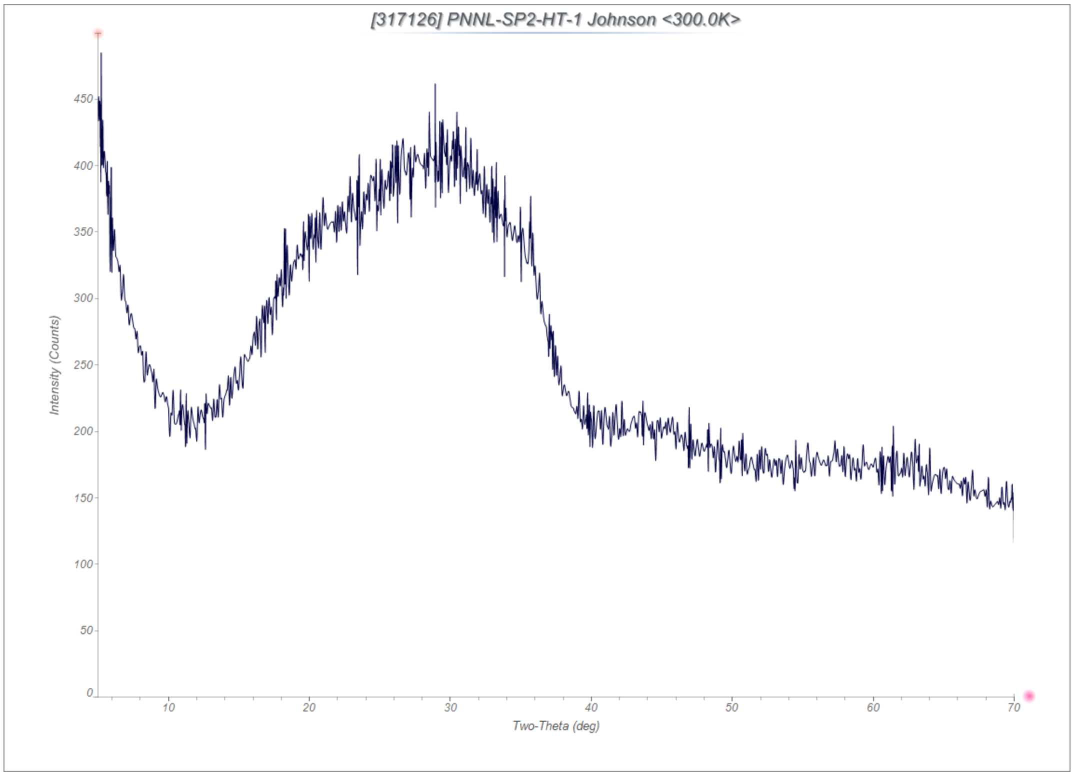


Figure B-1. XRD spectrum of heat treated sample of PNNL-SP2-HT-1

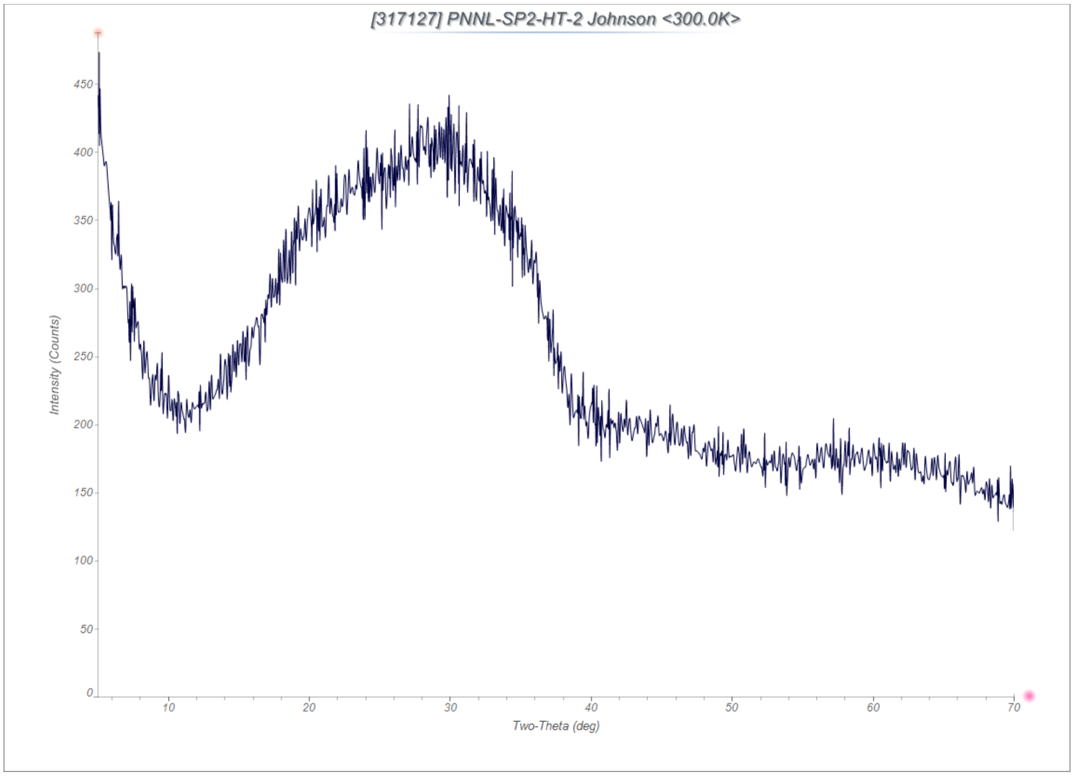


Figure B-2. XRD spectrum of heat treated sample of PNNL-SP2-HT-2

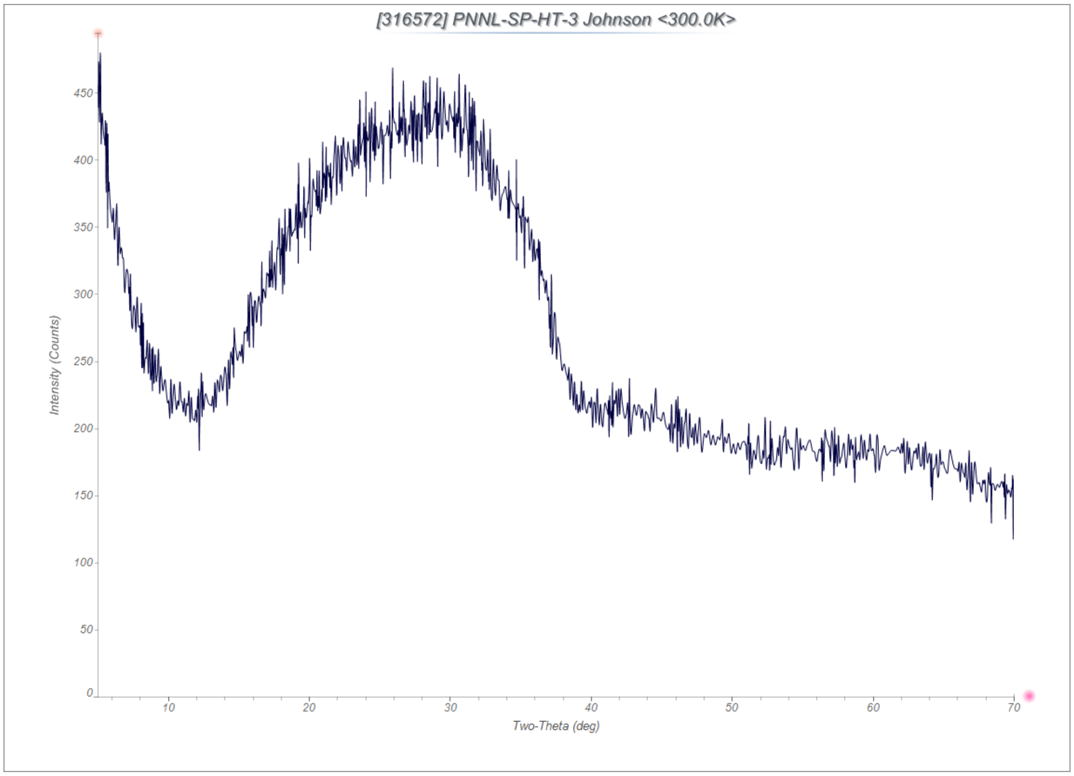


Figure B-3. XRD spectrum of heat treated sample of PNNL-SP2-HT-3

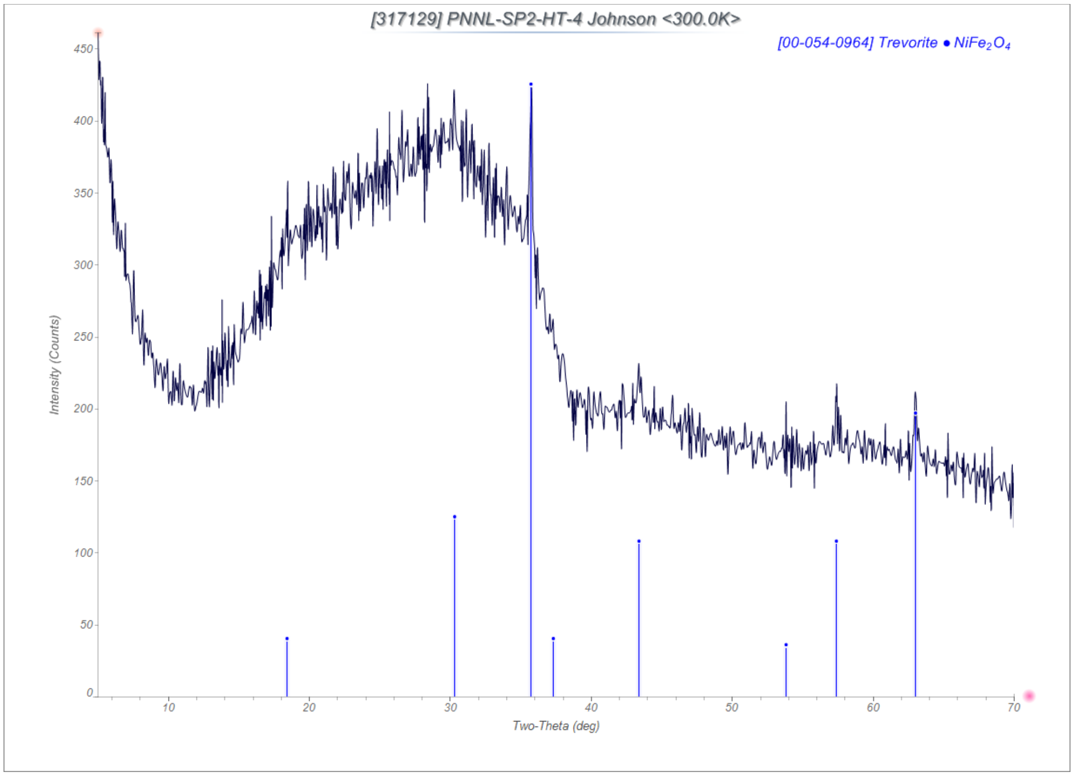


Figure B-4. XRD spectrum of heat treated sample of PNNL-SP2-HT-4

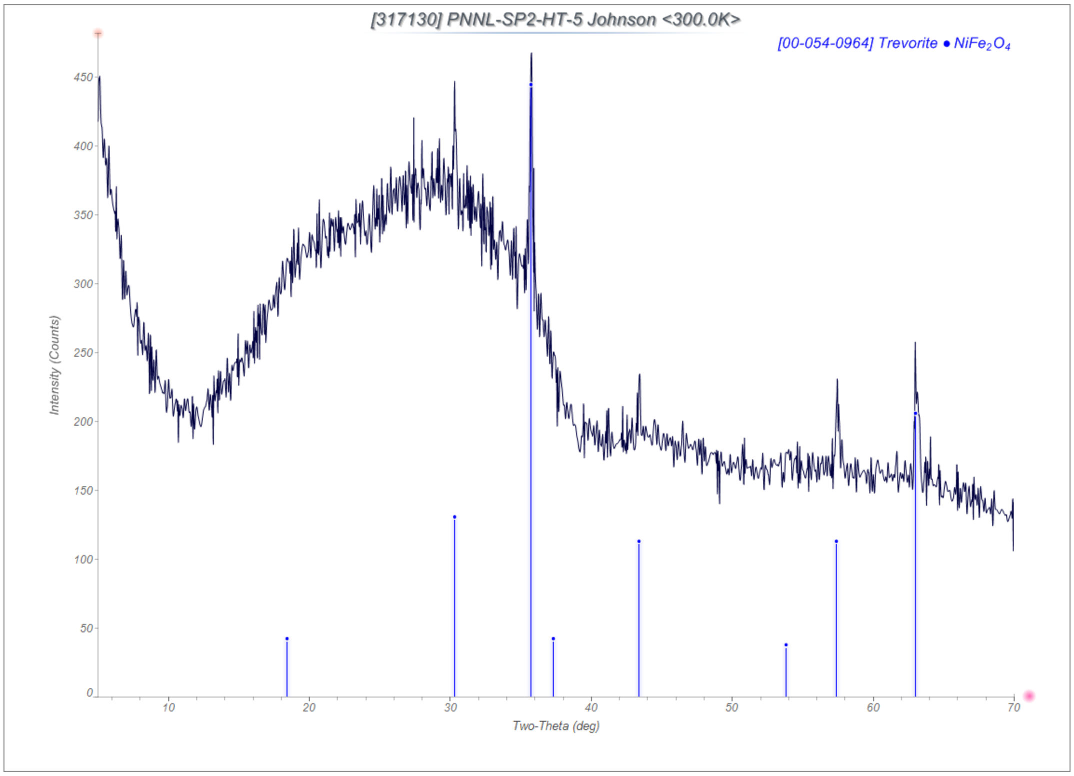


Figure B-5. XRD spectrum of heat treated sample of PNNL-SP2-HT-5

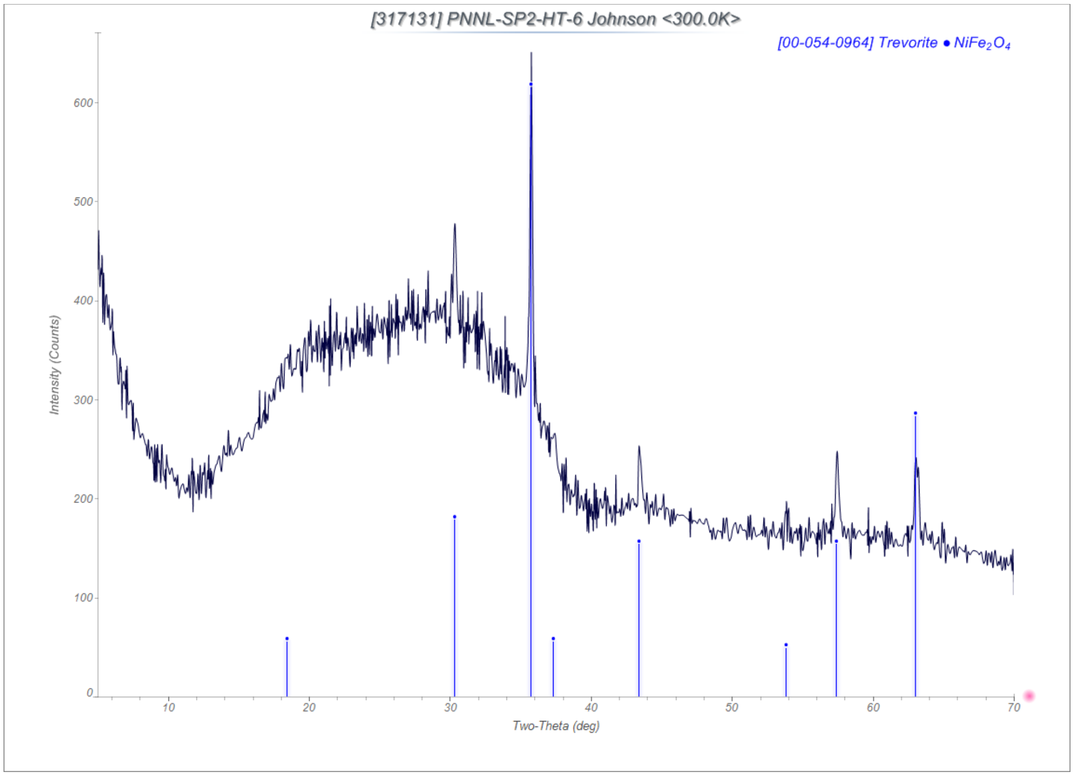


Figure B-6. XRD spectrum of heat treated sample of PNNL-SP4-HT-6

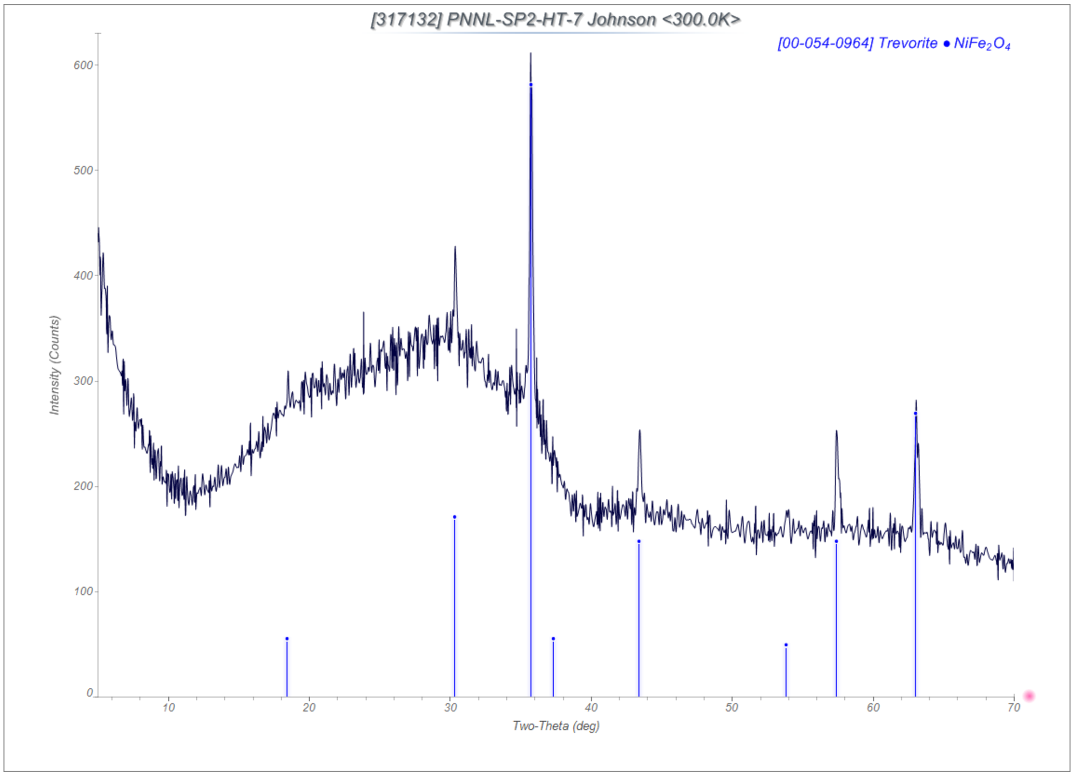


Figure B-7. XRD spectrum of heat treated sample of PNNL-SP4-HT-7

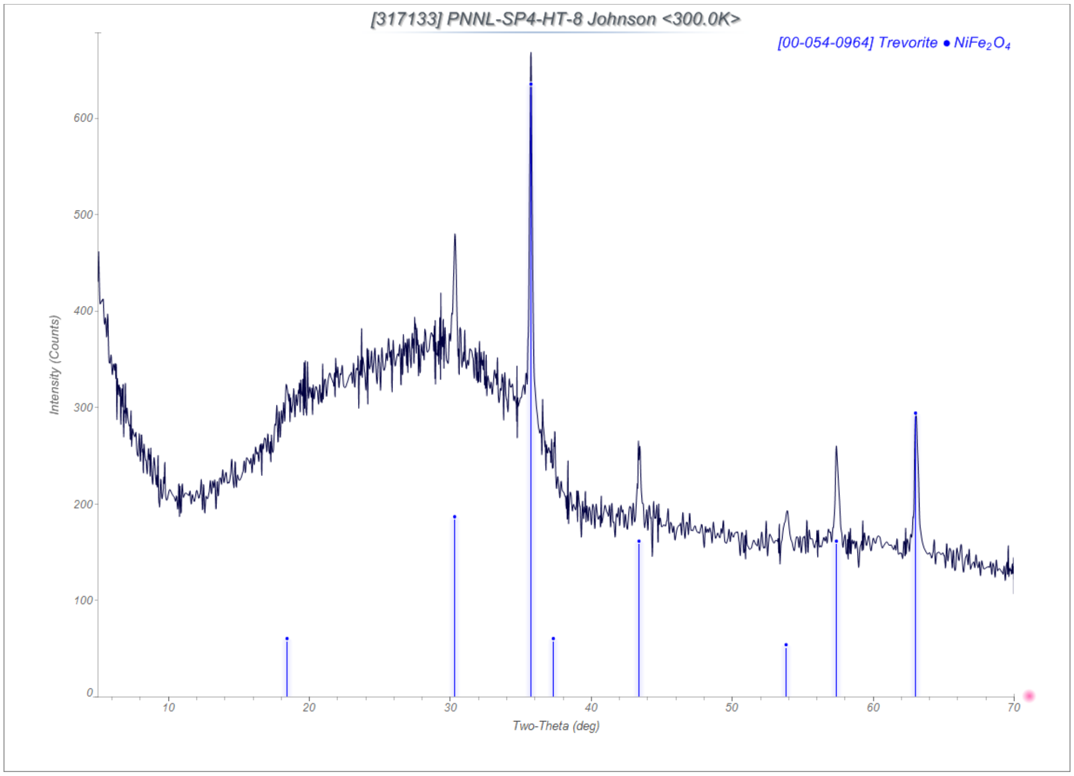


Figure B-8. XRD spectrum of heat treated sample of PNNL-SP4-HT-8

Appendix C. Optical Micrographs Supporting the SPGL-1.5 Layering Experiments

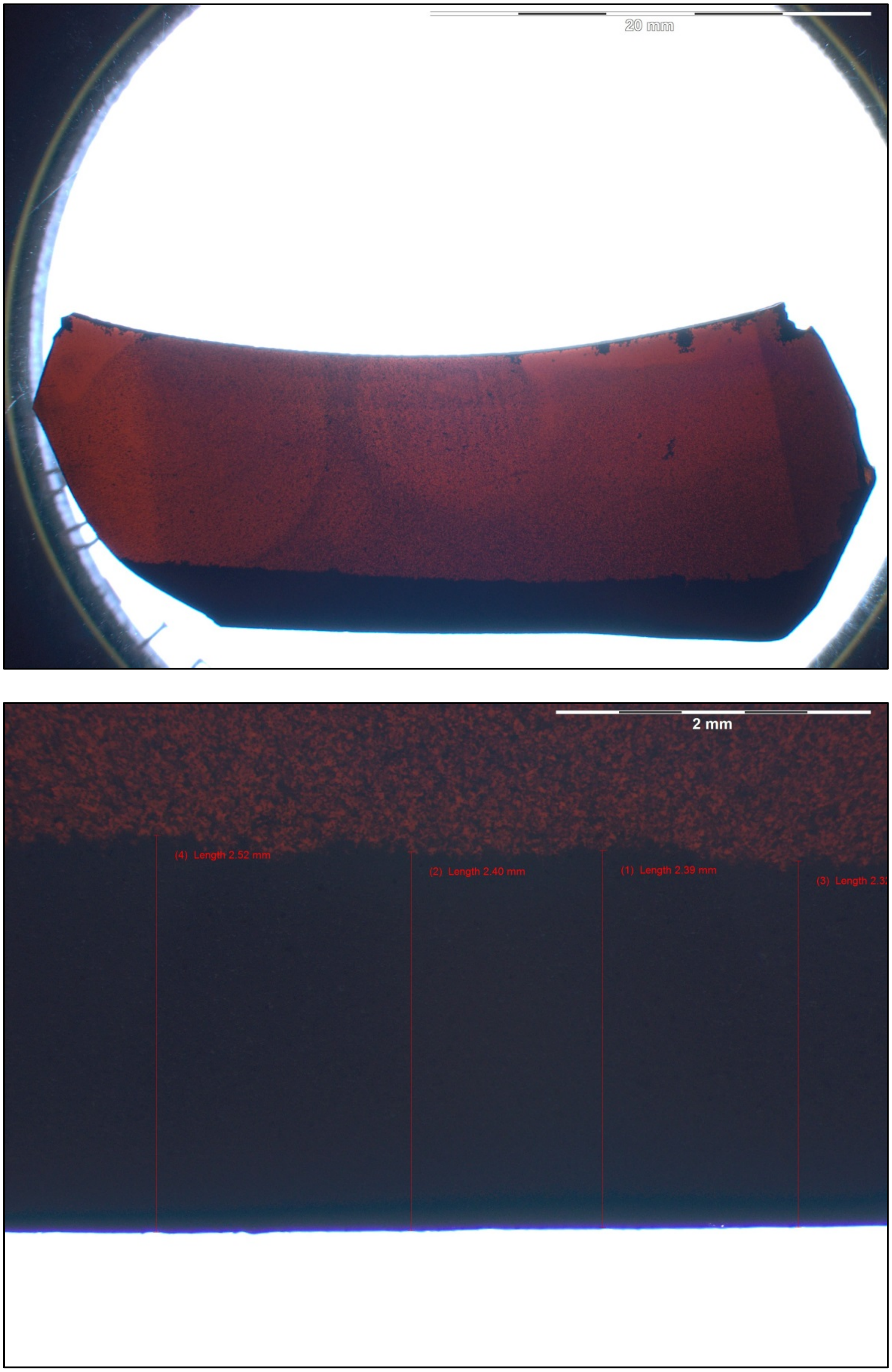


Figure C-1. Optical micrographs of SPGL-1.5 (baseline glass for layering experiments) after heat treatment at 1150 °C for 24 hours

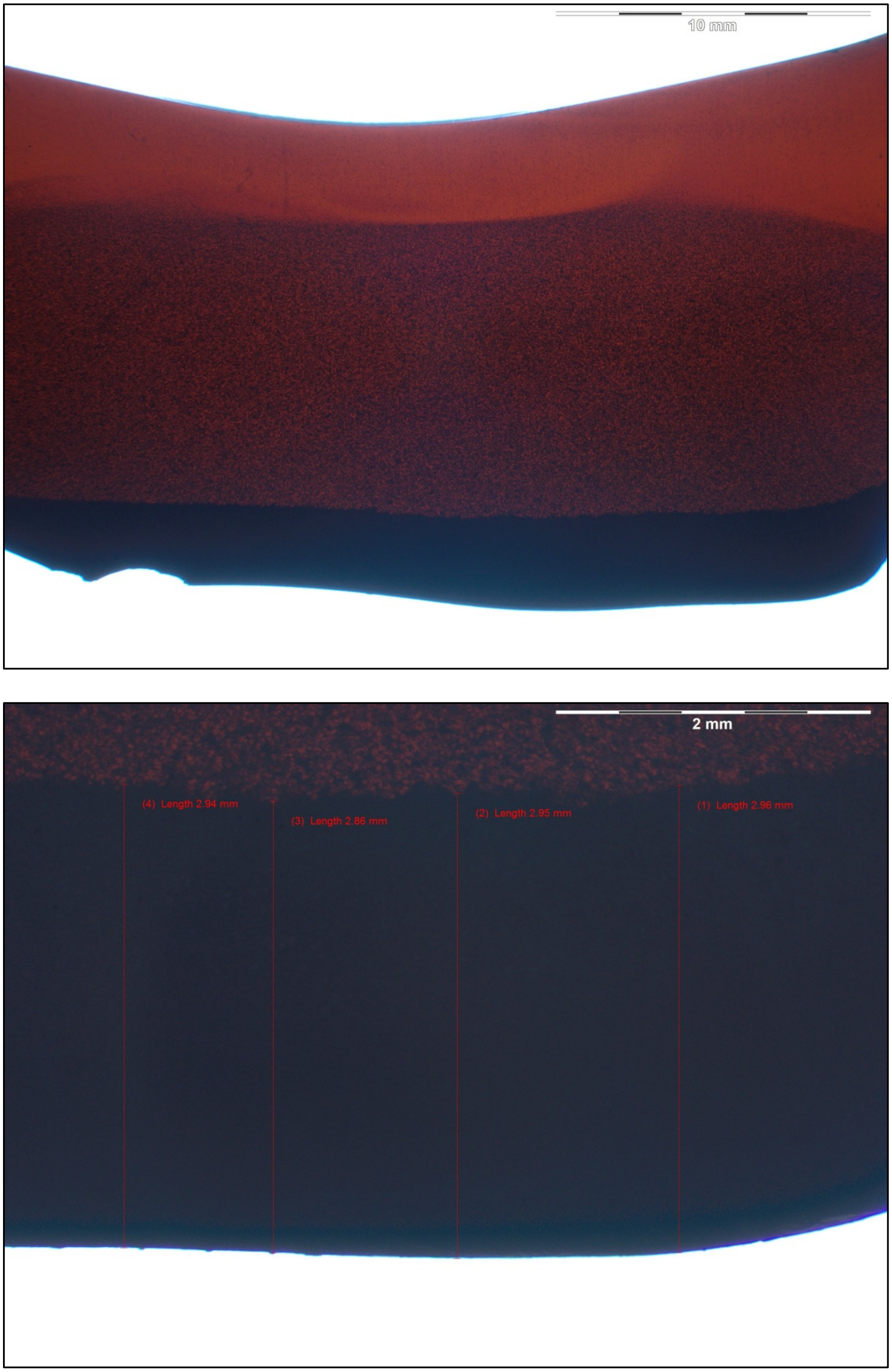


Figure C-2. Optical micrographs of SPGL-1.5-HTL-0.25 glass (additive glass PNNL-SP-HT-8) after heat treatment at 1150 °C for 24 hours

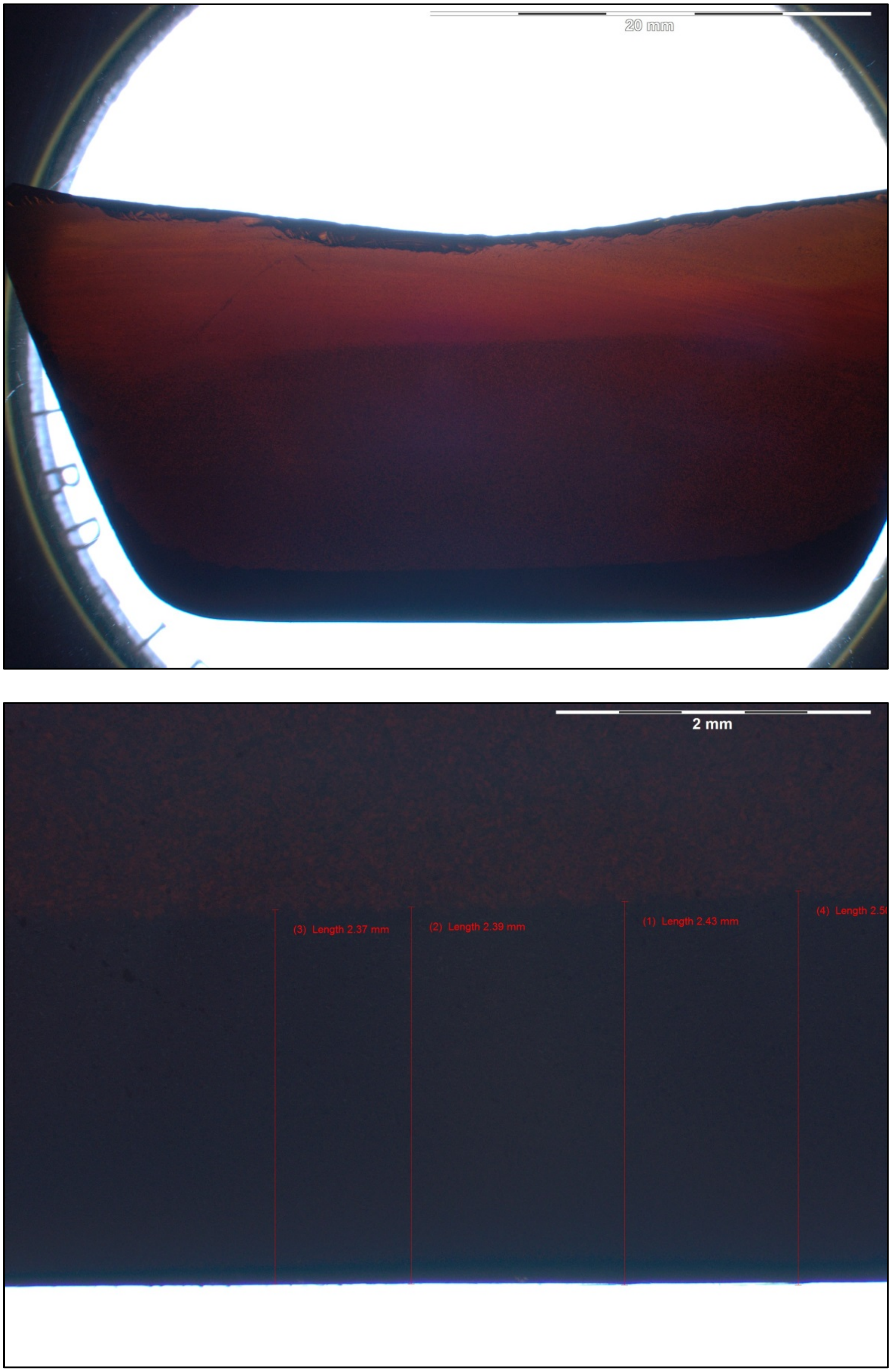


Figure C-3. Optical micrographs of SPGL-1.5-LTL-0.25 (additive glass PNNL-SP-HT-3) after heat treatment at 1150 °C for 24 hours

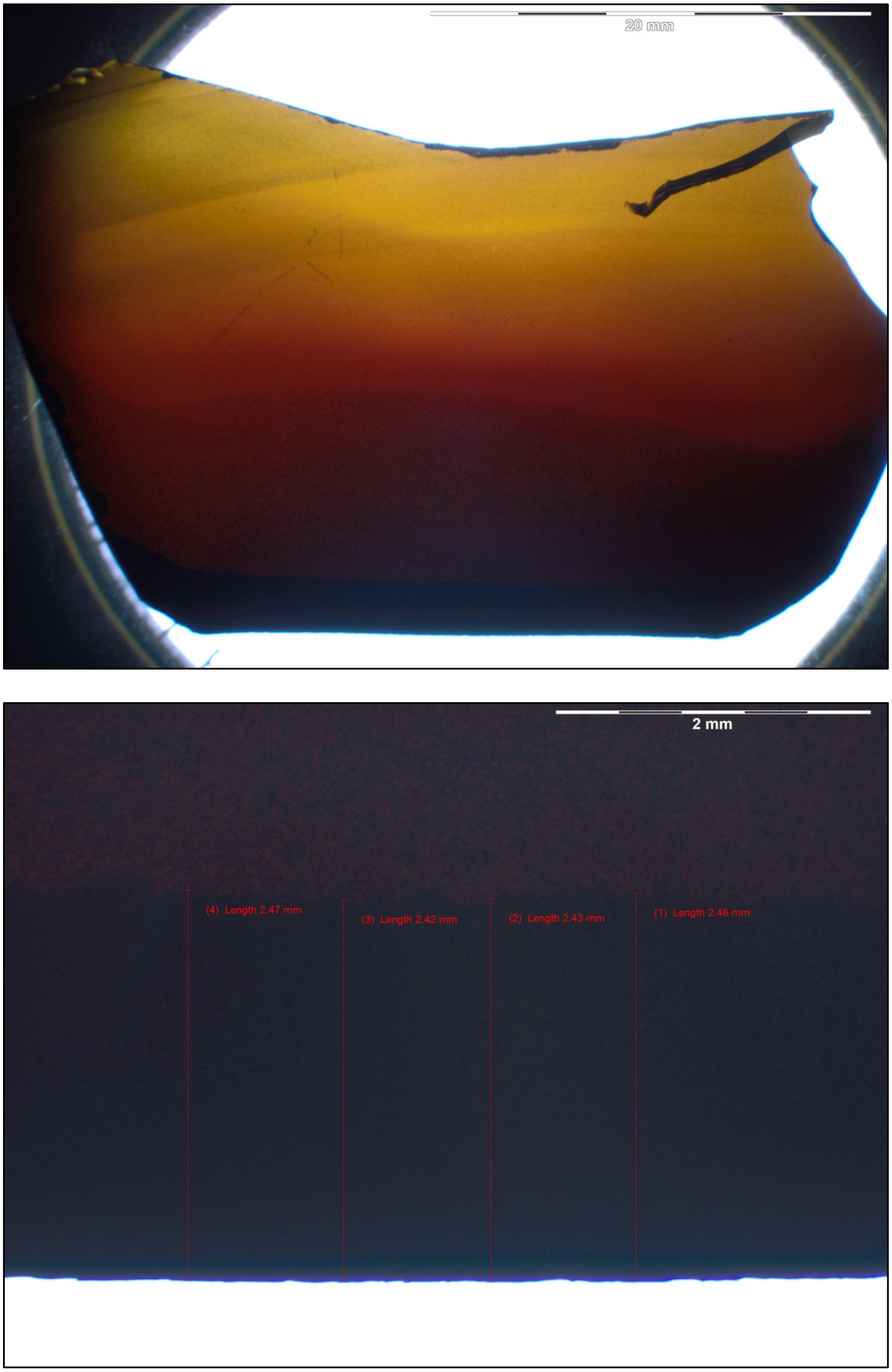


Figure C-4. Optical micrographs of SPGL-1.5-LTL-1 (additive glass PNNL-SP-HT-3) after heat treatment at 1150 °C for 24 hours

Appendix D. Optical Micrographs Supporting the SPGL-1.5A Mixing Experiments

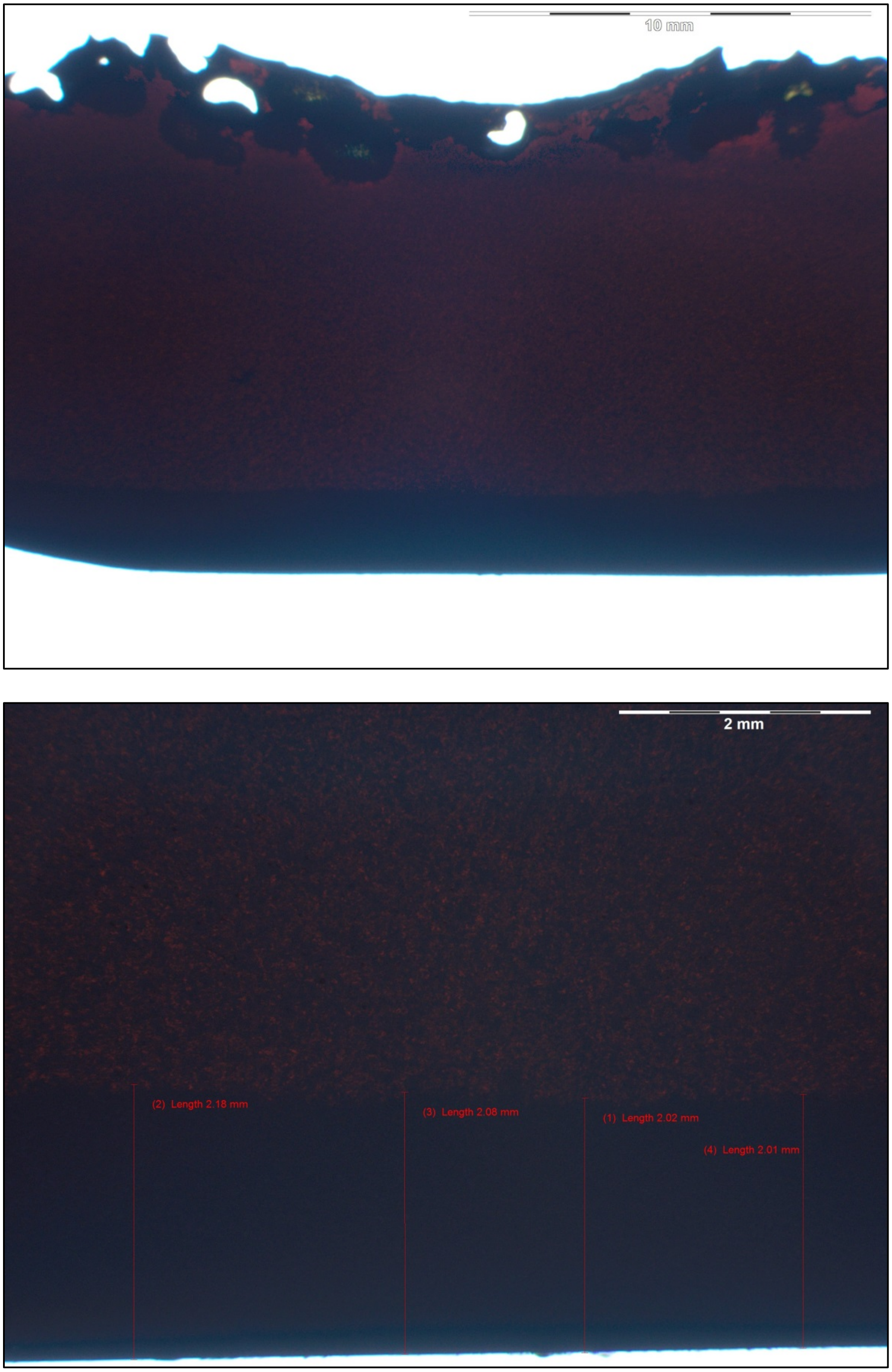


Figure D-1. Optical micrographs of glass SPGL-1.5A-LTL-0M (baseline with no additive) after heat treatment at 1150 °C for 24 hours

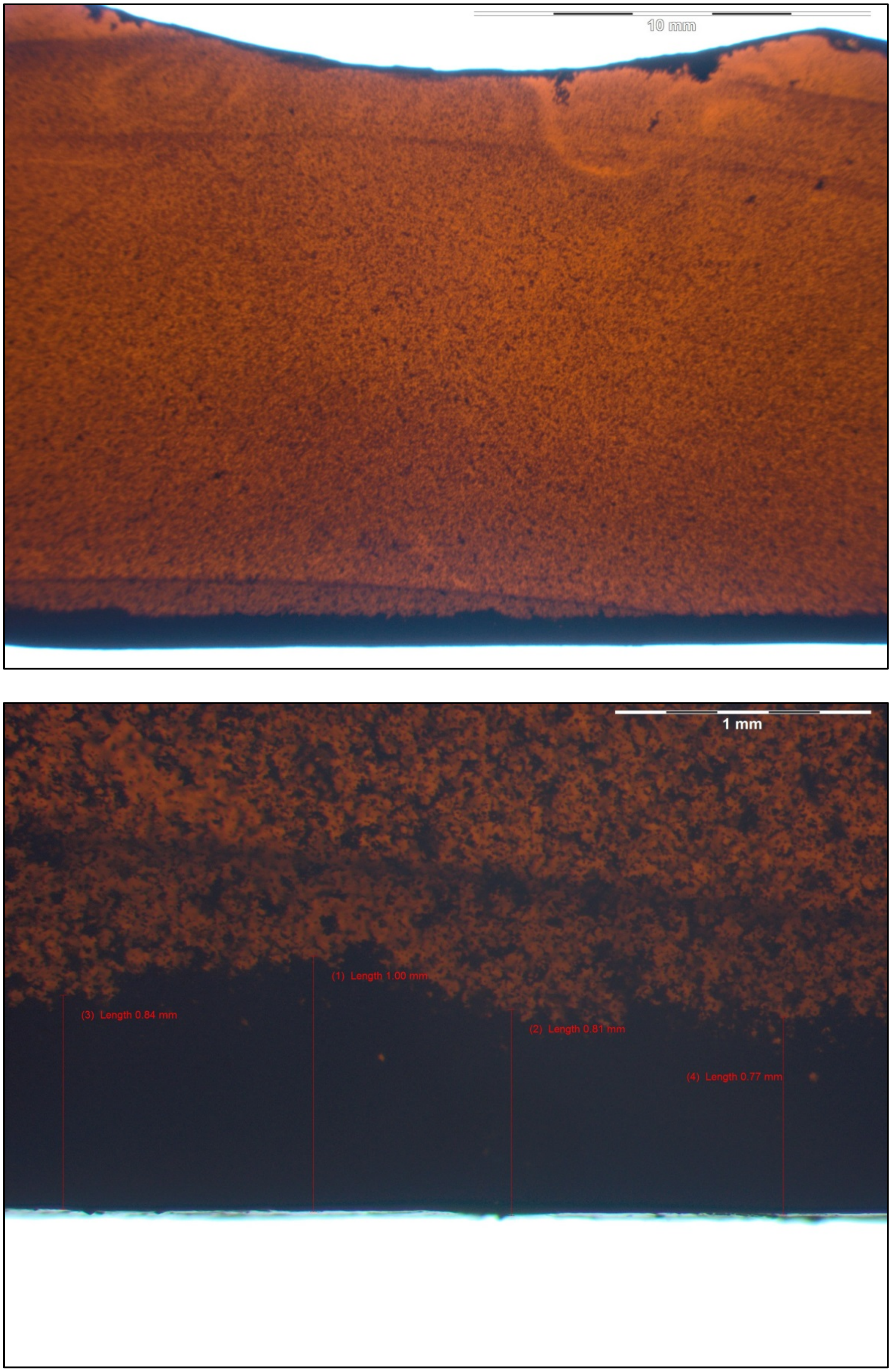


Figure D-2. Optical micrographs of glass SPGL-1.5A-LTL-0.25M after heat treatment at 1150 °C for 24 hours

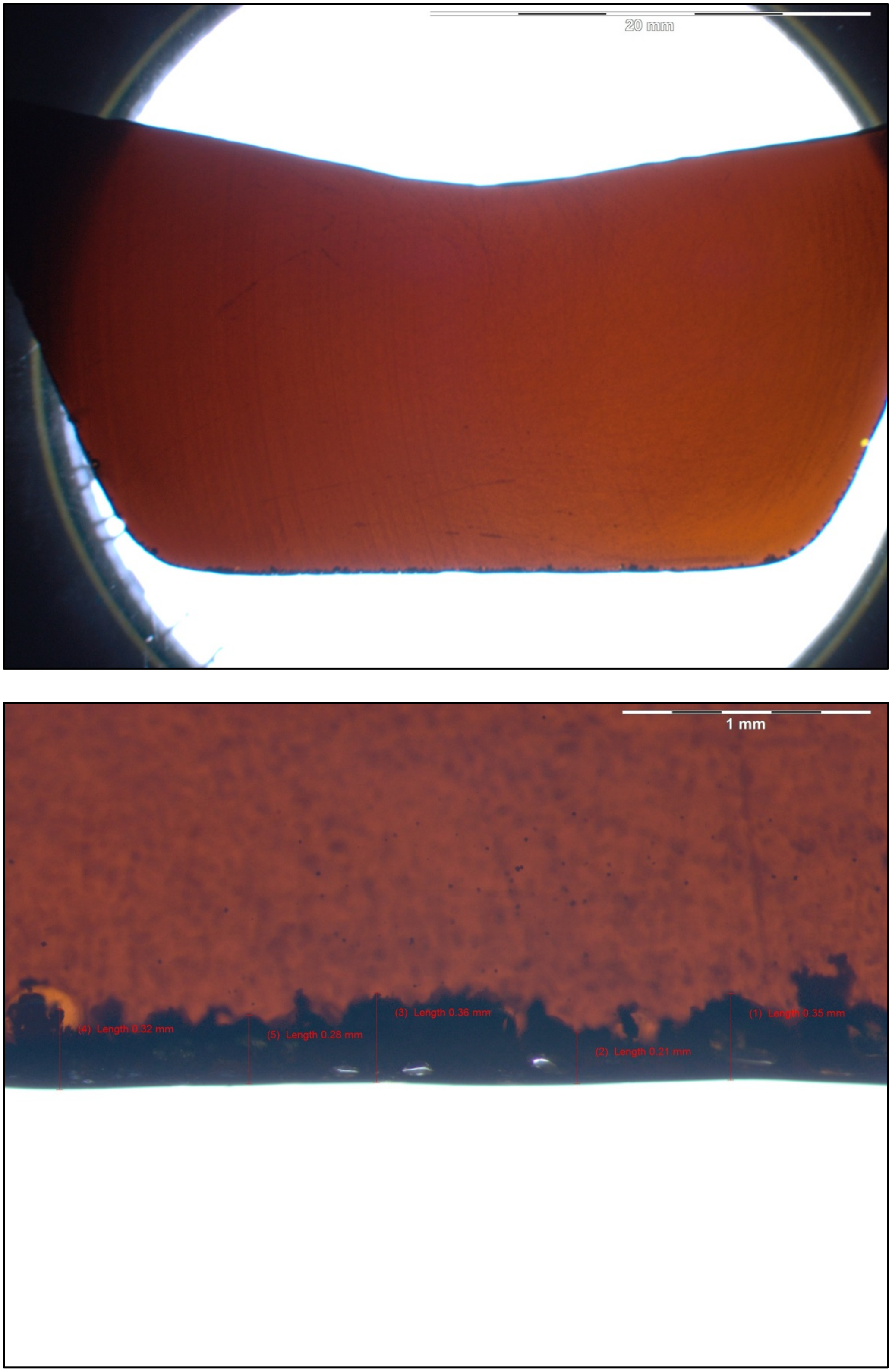


Figure D-3. Optical micrographs of glass SPGL-1.5A-LTL-0.5M after heat treatment at 1150 °C for 24 hours

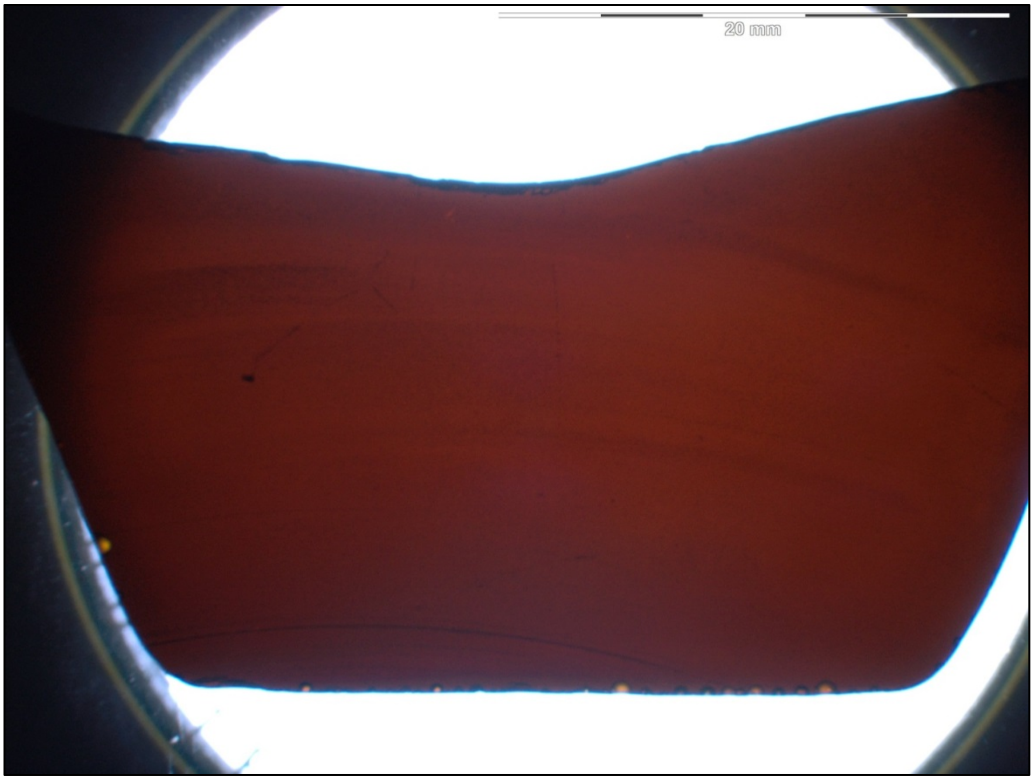
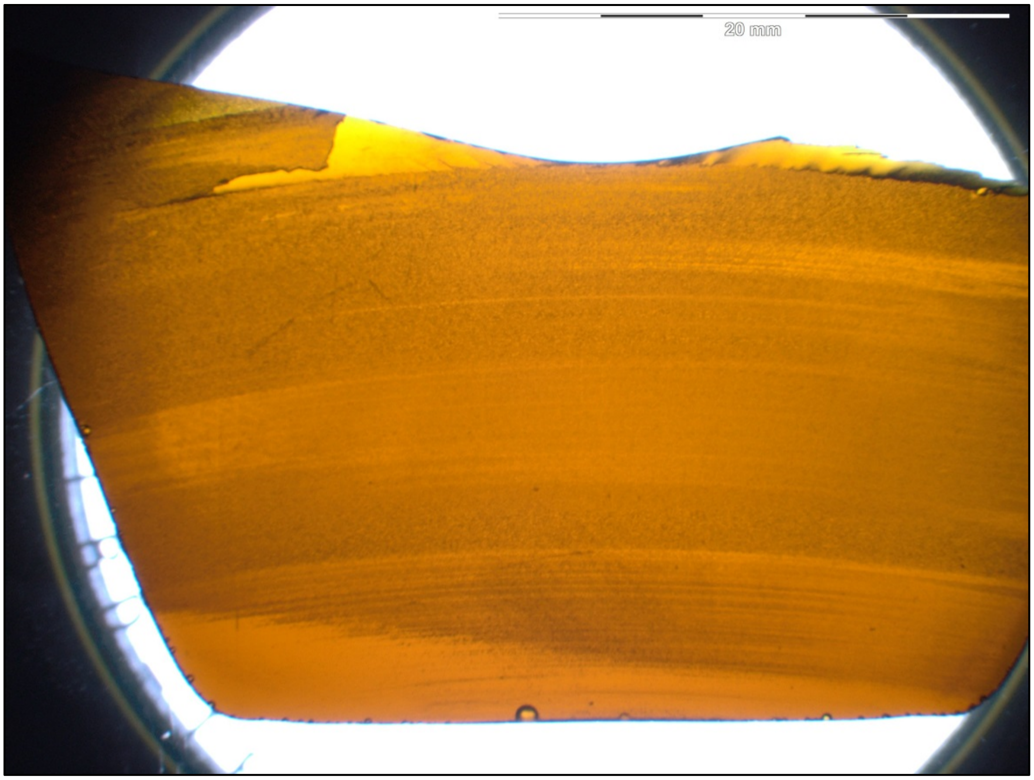


Figure D-4. Optical micrograph of glass SPGL-1.5A-LTL-0.75M after heat treatment at 1150 °C for 24 hours



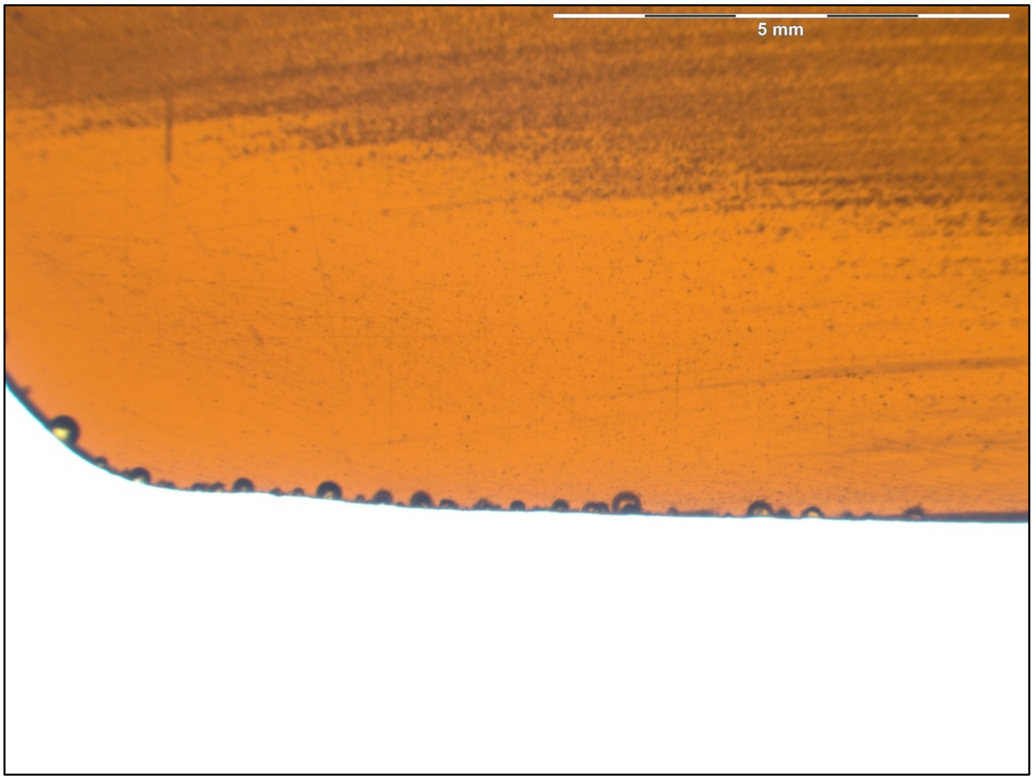


Figure D-5. Optical micrographs of glass SPGL-1.5A-LTL-1M after heat treatment at 1150 °C for 24 hours

Distribution:

J. W. Amoroso, 999-W
T. B. Brown, 773-A
H. H. Burns, 773-41A
A. S. Choi, 999-W
A. D. Cozzi, 999-W
C. L. Crawford, 773-42A
J. V. Crum, PNNL
D. E. Dooley, 999-W
A. P. Fellinger. 773-42A
S. D. Fink, 773-A
K. M. Fox, 999-W
E. K. Hansen, 999-W
C. C. Herman, 773-A
E. N. Hoffman, 999-W
J. E. Hyatt, 773-A
C. M. Jantzen, 773-A
F. C. Johnson, 999-W
D. S. Kim, PNNL
A. A. Kruger, DOE-ORP
J. C. Marra, 999-2W
J. Matyáš, PNNL
D. J. McCabe, 773-42A
D. L. McClane, 999-W
D. H. McGuire, 999-W
D. H. Miller, 999-W
D. K. Peeler, PNNL
F. M. Pennebaker, 773-42A
M. R. Poirier, 773-42A
M. J. Schweiger, PNNL
M. E. Stone, 999-W
J. D. Vienna, PNNL
A. L. Washington, 773-42A
W. R. Wilmarth, 773-A
Records Administration (EDWS)