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Crystallization Constraints for WTP LAW Operations: Assessment of CCC Impacts on VHT and PCT

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U.S. DEPARTMENT OF ENERGY

Prepared for the U.S. Department of Energy
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Summary

Much work has been done to expand the glass composition region available for operation of the Hanford Waste Treatment and Immobilization Plant. This includes the development of updated glass property-composition models as well as constraints. This report supports this effort by suggesting constraints for avoiding excessive, and likely detrimental, crystallization during slow cooling of the low-activity glass waste forms in their containers.

The constraints target crystals in the Na-Al-silicate and Na-Ca-silicate families. These types of crystals were found to be potentially detrimental to glass durability as they remove Al and Si from the glass matrix, resulting in poor performance of the residual glass during testing such as the Product Consistency Test and the Vapor Hydration Test. Using previously acquired results and results from testing during this effort, the following constraints (Table S.1) were determined, and are suggested as options to reduce the risk of forming crystals of the types and concentrations that are likely detrimental to glass durability.

Table S.1. Low-Activity Waste Glass Slow-Cooled Glass Crystallization Constraints

Constraint	Limit (wt%)
Na-Al silicate	$Al_2O_3 \leq 15.80 - 0.280*(Na_2O + 0.66* K_2O)$
Na-Al silicate alternative	$Al_2O_3 \leq 11.5$
Na-Ca silicate	$CaO \leq 14.36 - 0.272*(Na_2O + 0.66* K_2O)$
Na-Ca silicate alternative	$CaO \leq 20.84 - 0.528*(Na_2O + 0.66* K_2O)$

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The authors gratefully acknowledge the financial support provided by the U.S. Department of Energy Office of River Protection Waste Treatment Plant Project managed by Tom Fletcher, with technical oversight by Albert Kruger.

The authors thank Kevin Fox and Madison Hsieh of Savannah River National Laboratory for their help in the analysis and testing of the glasses. We also thank Tony Jin for the technical review, Matt Wilburn (PNNL) for his editorial review, as well as David MacPherson and Veronica Perez (PNNL) for programmatic support during the conduct of this work.

Acronyms and Abbreviations

CCC	container centerline cooling
DOE	U.S. Department of Energy
DWPF	Defense Waste Processing Facility
EA	Environmental Assessment
HLW	high-level waste
ICP-OES	inductively coupled plasma optical emission spectroscopy
LAW	low-activity waste
NQAP	Nuclear Quality Assurance Program
PCT	Product Consistency Test
PNNL	Pacific Northwest National Laboratory
VHT	Vapor Hydration Test
VSL	The Vitreous State Laboratory at the Catholic University of America
WTP	Hanford Waste Treatment and Immobilization Plant
XRD	X-ray diffraction

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1.0 Introduction

The Hanford Waste Treatment and Immobilization Plant (WTP) will operate to vitrify approximately 56 million gallons of tank waste currently stored on the Hanford Site near Richland, Washington. The waste will be separated into a high-level fraction, to be converted into high-level waste (HLW) glass, and a low-activity fraction, which will be converted into low-activity waste (LAW) glass. Vitrification operations through the WTP will be inextricably tied to process control models, which are the technical backbone of the integrated flowsheet. Key decisions in all unit operations rely on the ability to demonstrate that the waste feed can be safely and effectively processed through the melter and the resulting glass product will meet disposal criteria. The demonstration of safe and effective processing is derived from composition-property predictions and their relation to predefined acceptance criteria. In some instances, there is a lack of reasonable constraint criteria that reduce operational risks while allowing for increased waste loading, especially for crystallization constraints in processing of LAW. This work will contribute to the development of new crystallization constraints for the LAW glass.

The objective of this task is to identify at least one constraint, in the form of multi-component equations, that provides a basis for effectively avoiding glass compositions that are prone to detrimental crystal formation. The crystal formation of concern is that which is likely to occur during glass cooling in a LAW glass container. The crystal constraint suggested will reduce the risk of glass property degradation while allowing for a broad processing envelope and thus low processing risk. Accompanying the constraint will be the data that support the constraint development. This report presents the suggested crystallization constraints that were formed from data gathered from previous reports and from new testing described in this report.

1.1 Low-Activity Waste Glass Constraints

Existing models to constrain the composition and loading of the LAW glasses include properties such as sulfur tolerance, viscosity and electrical conductivity at 1150 °C, refractory corrosion, Product Consistency Test (PCT) response, Vapor Hydration Test (VHT) response, and others. A recent effort on enhanced glass models and constraints mentioned a combined limit for ZrO_2, SnO_2, Al_2O_3, and CaO with relation to alkali (Vienna et al. 2016). That constraint was described as originating from “lessons learned” based on previous efforts, particularly with VHT failure, and examples of limits that should be added in the future. The equation proposed by Vienna et al. is

$$g_{ZrO_2} + g_{SnO_2} + g_{Al_2O_3} \leq 0.17 \quad (1.1)$$

$$g_{Na_2O} + 0.66 g_{K_2O} + 2.07 g_{Li_2O} - g_{ZrO_2} - g_{SnO_2} - g_{CaO} \leq 0.15 \quad (1.2)$$

where g_x = mass fraction of component x.

An updated model report is ongoing, which will incorporate the work described in this report.

1.2 Quality Assurance

This work was performed in accordance with the Pacific Northwest National Laboratory (PNNL) Nuclear Quality Assurance Program (NQAP). The NQAP complies with DOE Order 414.1D, *Quality Assurance*, and 10 CFR 830 Subpart A, *Quality Assurance Requirements*. The NQAP uses NQA-1-2012, *Quality Assurance Requirements for Nuclear Facility Application*, as its consensus standard and NQA-1-2012, Subpart 4.2.1, as the basis for its graded approach to quality.

The NQAP works in conjunction with PNNL's laboratory-level Quality Management Program, which is based on the requirements as defined in DOE Order 414.1D and 10 CFR 830, *Nuclear Safety Management*, Subpart A, Quality Assurance Requirements.

The work of this report was performed to the QA level of applied research with a technology readiness level of 6. This work was performed to support technology development. Data obtained may be used to support design input.

2.0 Existing Literature Data

To evaluate the effect of slow cooling on glass performance, existing data on the glasses that were subjected to slow cooling according to the simulated container centerline cooling (CCC) schedule and tested for PCT and/or VHT were collected. These previously determined data were gathered into a database from various reports. The glass IDs and the corresponding data used for the constraints in this work are given in Appendix A with the associated references. Sources for the relevant slow-cooling and quenched glass data were taken from work completed by PNNL (Lonergan et al. 2020; Russell et al. 2017, 2021) as well as the Vitreous State Laboratory at the Catholic University of America (VSL) (Matlack et al. 2001, 2006a-b; Muller et al. 2001, 2005, 2006, 2008; Muller and Pegg 2003a-e; Rielley et al. 2004). After preliminary evaluation of existing literature data, some questionable results were identified and therefore repeat tests were performed for selected glasses. The experimental methods and test results are discussed in Sections 3.0 and 4.1, respectively.

Data gathered from previous reports as well as the repeat testing were used for the slow-cooling crystallization constraints discussed in Sections 4.3 and 4.4. The constraints for crystallinity of isothermal treated glasses are being developed in a separate study. Appendix A summarizes the CCC crystallinity and PCT and VHT responses of quenched and CCC-treated samples.

3.0 Experimental Description

This section describes how select glasses were re-tested to verify reproducibility of responses. All quenched glass materials used were from previous efforts. The following sections describe the approach for determining CCC data for (1) heat treatments and crystallinity analysis on 8 glasses (Section 3.1) and (2) PCT response on 10 glasses (Section 3.2).

3.1 CCC Heat Treatments and Crystal Characterization

A portion (~30 g) of each test glass was subjected to the simulated CCC temperature profile shown in Table 3.1 and Figure 3.1. This profile is a temperature schedule, with modification by PNNL, expected at the center of a container of poured Hanford LAW glass after being melted at the WTP.[1]

Crushed glass was placed in a Pt-10%Rh crucible and covered with a Pt-10%Rh lid. The glass samples were brought to the final melt temperature of the glass, typically the highest temperature used to melt the glass during preparation, and held for 30 min. Then they were quickly cooled to 1114 °C. The cooling profile was then started from 1114 °C to room temperature based on nine cooling segments, given in Table 3.1.

Table 3.1. Container Centerline Cooling Profile for LAW Glass

Segment	Time (min)	Start Temp. (°C)	Rate (°C/min)
1	-30	Melt temp.	0
2	0	1114	-7.125
3	0-16	1000	-1.754
4	16-73	900	-0.615
5	73-195	825	-0.312
6	195-355	775	-0.175
7	355-640	725	-0.130
8	640-1600	600	-0.095
9	1600-3710	Room temp.	NA

Source: Memorandum, “Container Centerline Cooling Data,” Rev. 1, CCN: 074181, RPP-WTP, October 29, 2003. Bechtel National, Inc., Richland, WA.

[1] Memorandum, “Container Centerline Cooling Data,” Rev. 1, CCN: 074181, RPP-WTP, October 29, 2003. Bechtel National, Inc., Richland, WA.

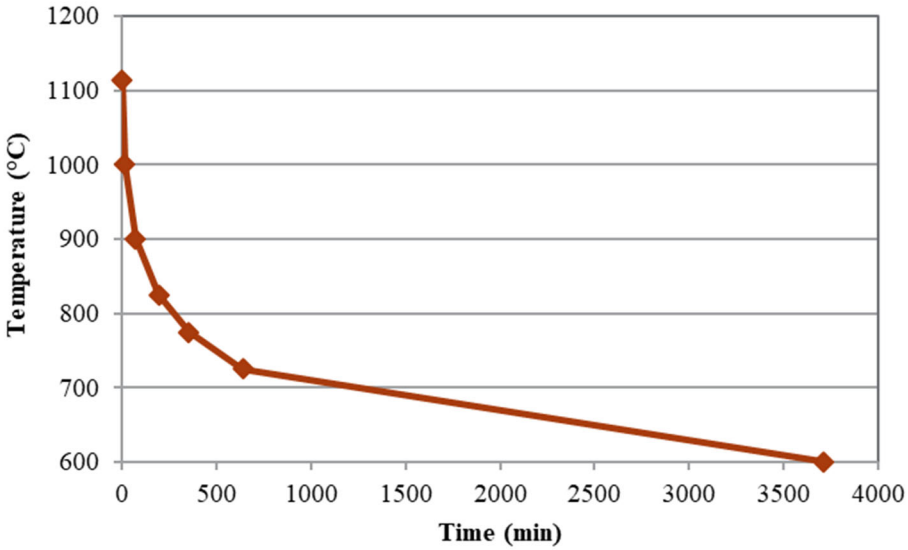

Figure 3.1. Plot of temperature schedule during CCC heat treatment of Hanford LAW glasses.

The amounts and types of crystalline phases that formed during CCC heat treatment were analyzed using X-ray diffraction (XRD) according to Section 12.4.4 of ASTM Standard C1720. Powdered glass samples were prepared using ~5 wt% CeO_2 as an internal standard phase with 1.5-2.5 g of powdered glass. Glass and CeO_2 were milled together for 2 min in a 10-cm^3 tungsten carbide milling chamber. The powdered glass samples were loaded into XRD sample holders and scanned at a 0.015° 2θ step size, 1.5-s dwell time, from 5° to 90° 2θ scan range. XRD spectra were analyzed with TOPAS® 4.2 Software (Bruker AXS Inc., Madison, Wisconsin) for phase identification and Rietveld refinement to semi-quantify the amounts of crystal phases in some samples with high crystalline content. These results are given in Appendix B.

3.2 Product Consistency Test

PCT responses were measured in triplicate for quenched and CCC samples of each glass using Method B (PCT-B) of ASTM Standard C1285. Also included in the PCT experimental test matrix and tested in triplicate were the Defense Waste Processing Facility Environmental Assessment (DWPF EA) glass and blanks. Glass samples were ground, sieved to -100 +200 mesh, washed, and prepared according to the ASTM C1285 procedure. The prepared glass was added to deionized water in a 1 g to 10 mL ratio, resulting in a surface area-to-solution volume ratio of approximately 2000 m^{-1}. The vessels used were desensitized Type 304L stainless steel. The vessels were closed, sealed, and placed into an oven at 90 ± 2 °C for varying times. Samples were taken at 6 days ± 3 h (PCT-B) and then the same vessels were left in the oven for 21 days ± 6 hours (PCT-B) and sampled.

For the 6-day sampling period, approximately 1 mL of solution was pulled from the vessels and the vessels were returned to the oven. Each test solution was then passed through a 0.45-µm filter and acidified at a ratio of 1 mL leachate to 5 mL of 2 vol% HNO_3 (prepared from concentrated, high-purity HNO_3) to ensure that the cations present remained in solution. For the termination of the tests at 21 days, the vessels were removed from the oven and allowed to cool to room temperature. The final mass of the vessel and the solution pH were measured. Each test solution was then passed through a 0.45-µm filter and acidified at a ratio of 1 mL leachate to 5 mL of 2 vol% HNO_3 (prepared from concentrated, high-purity HNO_3) to ensure that the cations present remained in solution. The resulting solutions were analyzed by Savannah River National Laboratory for Al, Cr, Si, Na, and B. Samples of a multi-element, standard solution were also analyzed as a check on the accuracy of the inductively coupled plasma-optical

emission spectroscopy (ICP-OES) instrument and procedure. Normalized releases (g/L) were calculated based on measured concentrations averaged by three ICP-OES measurements. Calculations were completed by using a density of 2.65 g/cm^3, the target mass fraction of the element in the unleached glass, and an assumed surface area over volume of 2000 m^{-1}. Results from the PCT work are published elsewhere (Hsieh and Fox 2020); a short summary of these results is included in Section 4.1.

4.0 Results and Discussion

This section describes two crystal constraints designed to avoid formation of excessive sodium aluminosilicate- and sodium calcium silicate-based crystals. A summary of the data used for constraint development can be found in Appendix A. Questions arose during the data mining that led to experimental work, the results of which are summarized in the appendices of this report. The experimental efforts consisted primarily of confirmatory testing of select glasses for PCT and crystal formation after CCC.

The results of interest were PCT and VHT response for quenched and post-CCC samples. During data analysis it was determined that every glass with quench and post-CCC values for VHT also had values for the PCT. Additionally, the glass compositions where PCT response was impacted by CCC treatment also affected the VHT response and, as there were more PCT responses available for analysis, only PCT was considered when designing the constraints.

4.1 Data Verification Efforts

Select data that were previously published were verified by repeat testing on existing glass samples during this effort. This included performing heat treatments and crystallinity analysis on 8 glasses as well as PCT response determination on 10 glasses. The data generated in this effort were similar to previously determined values with only two exceptions for crystallinity, which are discussed below.

In a previous report, crystallization quantification after CCC treatment for NEW-OL-108249Mod resulted in a crystallinity content of 107.6 wt% (Russell et al. 2017). As this is greater than 100%, it was decided to heat treat the quenched glass according to the LAW CCC profile and subsequently analyze it with XRD to determine an updated crystal content value. The post-CCC XRD data were extremely complex, hence the initial result of >100%. The re-test showed an actual crystalline concentration of ~83 wt% (Figure 4.1), with more than 10 crystals contributing to the diffractogram as summarized in Table 4.1.

Additionally, NEW-IL-87749 was melted and subjected to the LAW CCC heat treatment profile. XRD was completed but a standard was absent from the sample analyzed, so the amount of crystals present was identified as “some.” The crystallized glass was reanalyzed with CeO_2 as the standard and the crystal quantification resulted in 5.7 wt% nepheline. The diffractogram for NEW-IL-87749 can be seen in Figure 4.2.

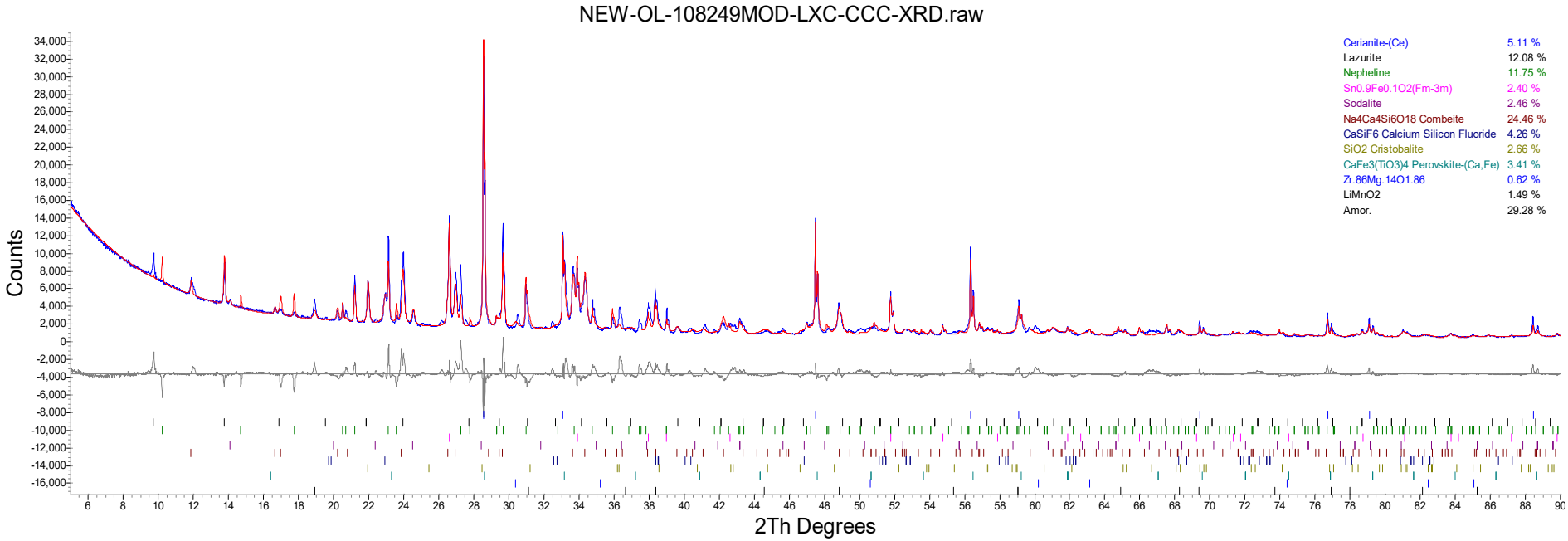

Figure 4.1. XRD data for NEW-OL-108249Mod retested for crystal concentration and phases. Note that cerianite is the internal standard in this figure.

Table 4.1. Summary of Crystals for NEW-OL-108249Mod after CCC Treatment

	Phase Name	Wt% of Spiked	Wt% in Spiked sample	Wt% in Original sample
1	Cerianite-(CeO_2)	5.11	5.11	0
2	Lazurite	0	12.077	12.728
3	Nepheline	0	11.753	12.386
4	$Sn_{0.9}Fe_{0.1}O_2$(Fm-3m)	0	2.404	2.534
5	Sodalite	0	2.464	2.596
6	$Li_2O_3(SiO_3)$	0	13.156	13.864
7	$Na_4Ca_4Si_6O_{18}$ combeite	0	24.464	25.781
8	$CaSiF_6$ calcium silicon fluoride	0	4.261	4.491
9	SiO_2 cristobalite	0	2.665	2.808
10	$CaFe_3(TiO_3)_4$ perovskite-(Ca,Fe)	0	3.409	3.592
11	$Zr_{.86}Mg_{.14}O_{1.86}$	0	0.623	0.656
12	$LiMnO_2$	0	1.495	1.575

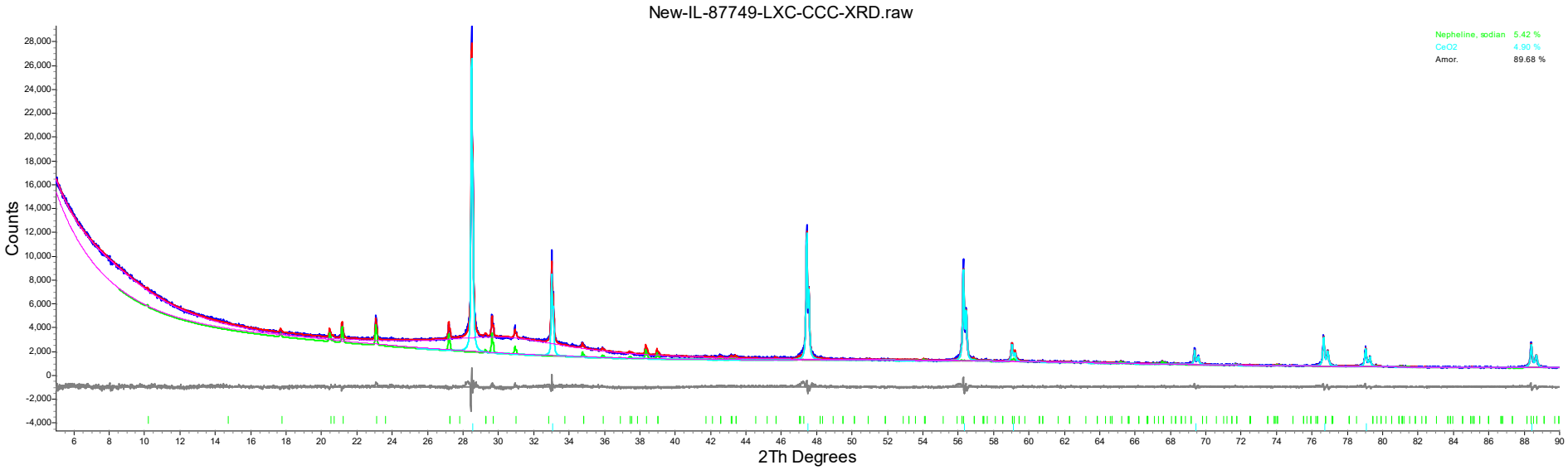

Figure 4.2. XRD data for NEW-IL-87749-LXC-CCC retested for crystal concentration and phases. Note that cerianite is the internal standard in this figure.

The rest of the data associated with retested materials can be found in Appendix B of this report.

Three glasses had repeat PCT results that match the overall trend of existing data better: New-IL-87749, LAWPH3-06, and LAWPH3-20. Therefore, the repeat results were used instead of the original data. All the PCT results generated in this testing effort are given in Table 4.2.

Table 4.2. Normalized Release for Glasses Tested in this Effort (relative to target compositions)

	Normalized Release				
	Al	B	Cr	Na	Si
Glass	g/L	g/L	g/L	g/L	g/L
New-OL-108249 MOD-LXC-Q	0.128	0.158	0.103	0.429	0.110
New-OL-108249 MOD-LXC-CCC	0.076	10.431	1.260	2.686	0.114
New-OL-116208 MOD-LXC-Q	0.202	4.882	2.947	4.116	0.678
New-OL-116208 MOD-LXC-CCC	0.286	3.090	2.618	2.524	0.620
LAWPH3-06-LXC-CCC	1.108	0.971	1.504	3.247	0.566
LAWPH3-06-LXC-CCC-21d	1.583	1.464	1.715	5.731	0.835
LAWPH3-06-LXC-Q	0.339	0.684	1.504	1.887	0.344
LAWPH3-10-LXC-CCC	0.423	15.219	7.856	8.304	0.758
LAWPH3-10-LXC-CCC-21d	0.491	15.959	8.273	9.446	0.914
LAWPH3-10-LXC-Q	0.451	2.048	2.429	2.874	0.611
LAWPH3-14-LXC-CCC	0.458	1.529	2.757	2.190	0.643
LAWPH3-14-LXC-CCC-21d	0.518	1.909	2.757	2.747	0.764
LAWPH3-14-LXC-Q	0.354	1.706	2.757	2.303	0.717
LAWPH3-17-LXC-CCC	1.580	5.359	3.068	6.955	0.865
LAWPH3-17-LXC-CCC-21d	1.683	5.622	3.343	7.959	1.001
LAWPH3-17-LXC-Q	0.486	1.679	2.237	3.664	0.764
LAWPH3-20-LXC-CCC	0.264	1.073	2.145	1.475	0.456
LAWPH3-20-LXC-CCC-21d	0.283	1.338	2.145	1.877	0.537
LAWPH3-20-LXC-Q	0.272	1.061	2.145	1.493	0.453
NEW-IL-166731-LXC-CCC	0.192	2.235	4.164	1.584	0.547
NEW-IL-166731-LXC-CCC-21d	0.113	16.554	4.164	9.969	1.918
NEW-IL-166731-LXC-A (quenched)	0.360	1.130	4.164	1.196	0.403
NEW-IL-87749-LXC-CCC	0.251	1.131	10.962	1.535	0.384
NEW-IL-87749-LXC-CCC-21d	0.328	1.337	10.962	2.014	0.472
NEW-IL-87749-LXC-Q	0.261	0.416	10.962	1.133	0.250
NEW-OL-62909MOD-LXC-CCC	0.120	0.691	2.827	0.625	0.112
NEW-OL-62909MOD-LXC-CCC-21d	0.154	0.772	2.827	0.744	0.120
NEW-OL-62909MOD-LXC-Q	0.170	0.677	2.827	0.906	0.150
DWPF-EA	0.306	18.349	NA	14.969	3.573
DWPF-EA-21d	0.306	21.456	NA	19.016	4.148
DWPF-EA-LXC	0.306	17.952	NA	14.556	3.521

Glasses were tested for either 6 days or 21 days. All 21-day samples are indicated with “21d” in the glass ID.

4.2 Effect of CCC Crystallinity on PCT and VHT Responses

Figure 4.3 and Figure 4.4 show the effects of CCC heat treatment on the PCT normalized releases and VHT alteration thickness, respectively. For a general trend, all glasses were split into two groups: (1) glasses with total crystal content greater than or equal to 10 wt% and (2) glasses with total crystal content less than 10 wt%. Figure 4.3 shows that for the PCT response, most glasses with less than 10 wt% total crystals tend to lie close to the 45-degree line, while a larger fraction of glasses with greater than or equal to 10 wt% total crystals tend to exhibit a significant increase of normalized release after CCC relative to the quenched glass response. However, for VHT there is no noticeable difference between the two groups (Figure 4.4), which is likely due to large experimental uncertainty involved in VHT measurements.

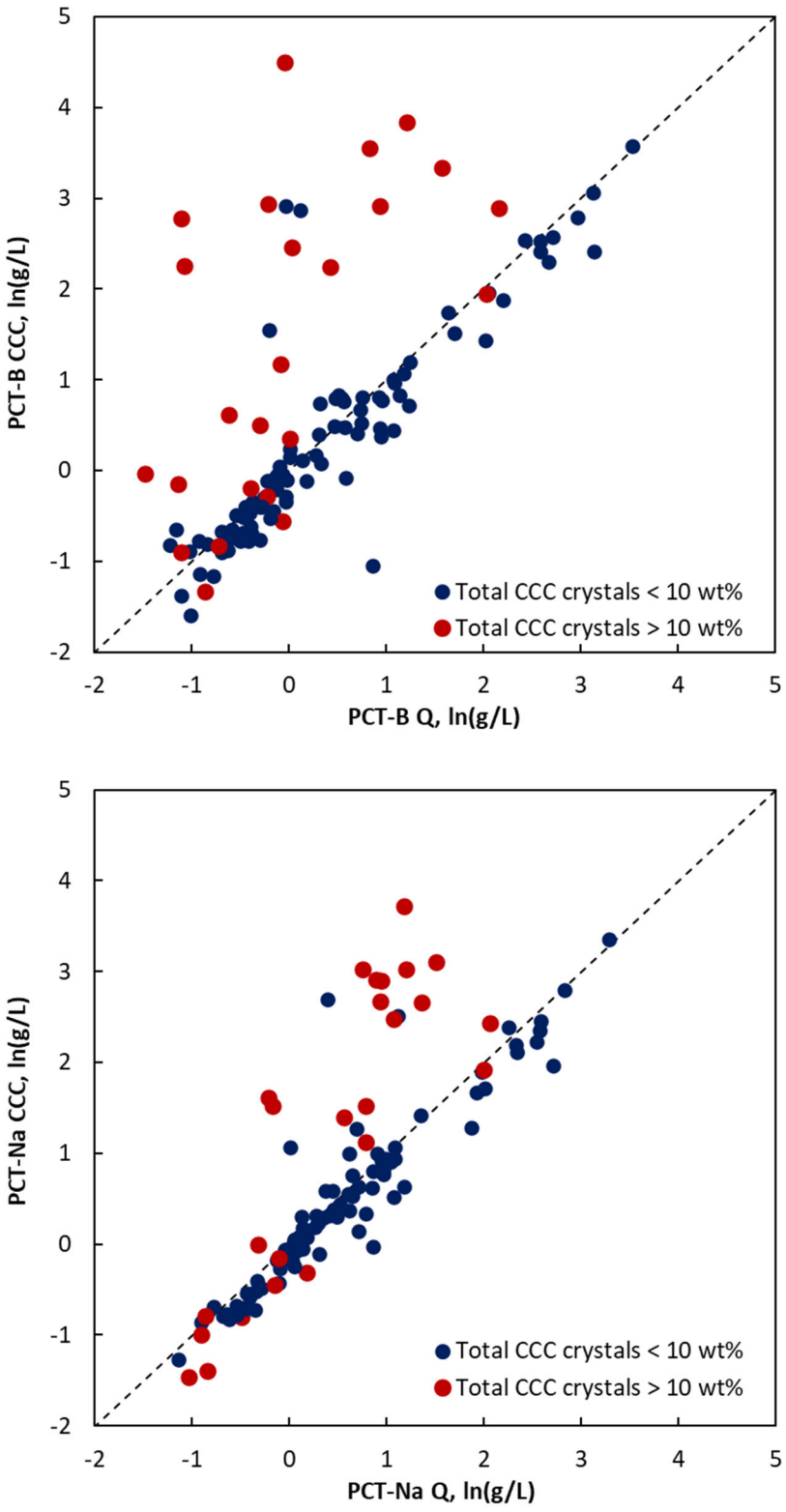

Figure 4.3. Comparison of PCT normalized releases between CCC-treated and quenched glasses for PCT-B (top) and PCT-Na (bottom).

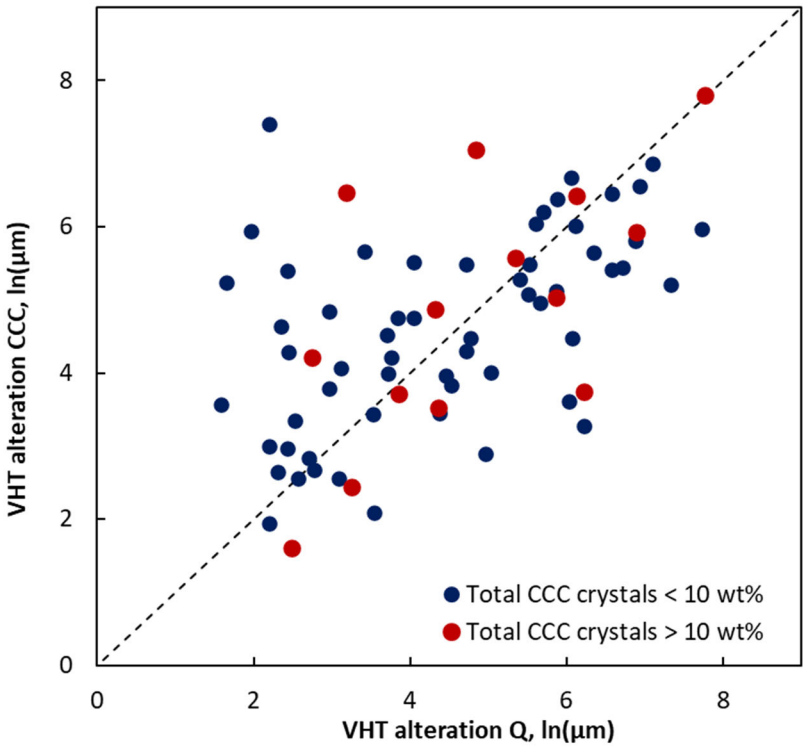

Figure 4.4. Comparison of VHT alteration thickness between CCC-treated and quenched glasses.

Table 4.3 lists the crystals that were identified to have negative impact on PCT and/or VHT responses when present at greater than 10 wt%. Some crystals such as augite-aegirine show no effect on PCT or VHT response even when present in large concentrations up to 32 wt%. The constraints that can be used to avoid forming these crystals are discussed in the following two subsections.

Table 4.3. Crystals Identified To Have Negative Impact on PCT or VHT Crystal Group

	Nominal Chemical Formulas[(a)]
Na-Al silicate	Nepheline, $NaAlSiO_4$
	Nosean, $Na_8Al_6Si_6O_{24}(SO_4)$
Na-Ca silicate (includes Na-Ca-Al silicate)	Combeite, $Na_2Ca_2Si_3O_9$
	Hauyne, $Na_3CaAl_3Si_3O_{12}(SO_4)$
	Lazurite, $Na_3CaAl_3Si_3O_{12}(SO_4,S,S_2,S_3,Cl,OH)$

(a) Actual chemical composition can be different from these nominal formulas.

There were only two glasses (LP2-OL-04-1 and LP2-OL-24) where there was a clear relationship between the increase of VHT response after CCC treatment and the formation of crystals given in Table 4.3. However, these two glasses exhibited a similar negative impact on PCT responses after CCC; therefore, the CCC crystallinity constraints developed based on their PCT results treated in the following two subsections (4.3 and 4.4) will also cover the effect on VHT data in the present study. There were some glasses that formed no or a relatively low concentration of the crystals listed in Table 4.3 but showed a strong negative effect on PCT responses after CCC. A separate research study is needed to identify and investigate the source(s) of the unexpected results.

4.3 Sodium Aluminosilicate Constraint

One of the crystalline phases known to impact durability performance is nepheline ($NaAlSiO_4$) and similar crystals such as nosean ($Na_8Al_6Si_6O_{24}(SO_4)$) based on sodium aluminosilicate chemistries. These are especially important because of the lowered residual glass performance after crystallization. When the nepheline crystallizes, it removes Al and Si from the glass network. This influences glass behavior, particularly in relation to the PCT.

Figure 4.5 shows the Al_2O_3 concentration versus $Na_2O + 0.66K_2O$ (in wt%) plot used to develop the sodium aluminum silicate constraint. All the glasses were separated into three categories:

(i) glasses with Na-Al silicate > 10 wt% ("Na-Al silicate group"), two glasses with less than 10 wt% crystal were included in this category, instead of category iii, because of a strong negative effect on PCT (New-IL-166731 and New-IL-87749),

(ii) glasses with Na-Al silicate > 10 wt% but with no negative effect on PCT ("No effect on PCT"), and

(iii) glasses with no crystals or with Na-Al silicate < 10 wt% ("No crystals or Na-Al silicate < 10 wt%").

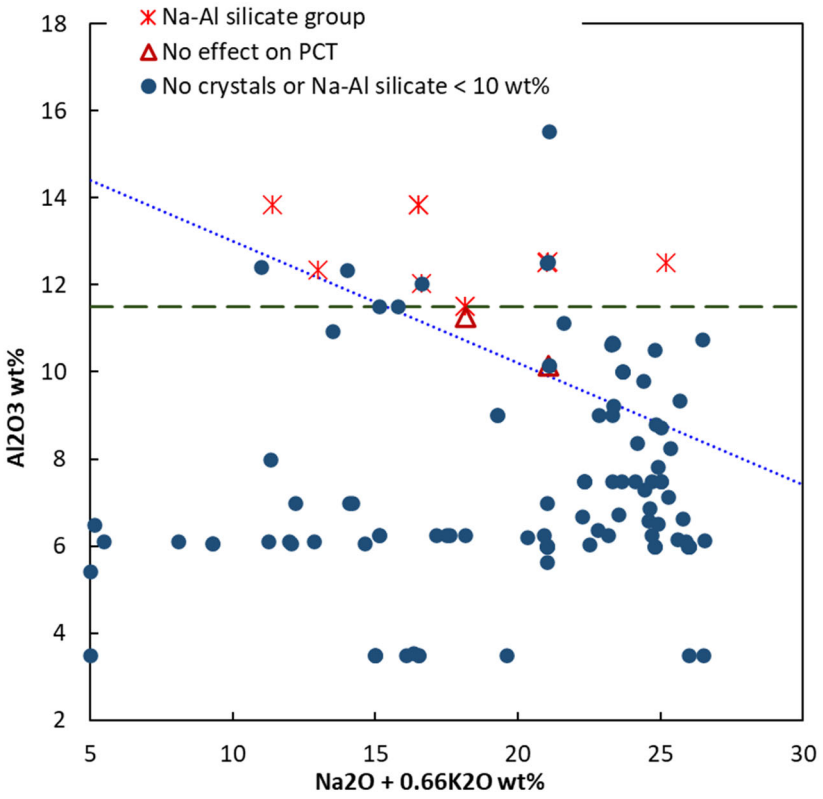

Figure 4.5. Plot of $Na_2O + 0.66K_2O$ versus Al_2O_3 to assess sodium aluminosilicate crystal formation. The blue dotted line shows the suggested constraint limit and the green dashed line shows a simpler alternative constraint.

As nepheline is a sodium aluminosilicate, it is expected that Na_2O and K_2O would also influence the tendency to crystallize; this can be seen with a decreasing slope of the constraint line. One of the suggested constraints is

$$g_{Al_2O_3} \leq 15.80 - 0.280 * (g_{Na_2O} + 0.66 g_{K_2O}) \quad 4.1$$

where g_x is the mass fraction (in wt%) of component x in glass. This constraint is shown by a blue dotted line in Figure 4.5.

Alternatively, a simpler constraint can be considered:

$$g_{Al_2O_3} \leq 11.5 \quad 4.2$$

which excludes two "No effect on PCT" category glasses. This constraint is shown by a green dashed line in Figure 4.5.

4.4 Sodium Calcium Silicate Constraint

Another of the crystalline phases known to impact durability performance is combeite ($Na_2Ca_2Si_3O_9$) and similar crystals based on sodium calcium-silicate chemistries. These crystals, similar to the sodium aluminosilicate crystals, are especially important because of the lowered residual glass performance after crystallization. When combeite, or similar phases, crystallizes, it removes Ca and Si from the glass network, which has been directly tied to increased PCT and VHT responses.

Figure 4.6 shows the CaO concentration versus $Na_2O + 0.66K_2O$ (in wt%) plot used to develop the sodium calcium silicate constraint. All the glasses were separated into three categories: (i) glasses with Na-Ca silicate > 10 wt% ("Na-Ca silicate group"), one glass was included in this category although Na-Ca silicate < 10 wt% because of strong negative effect on PCT (LAWPH3-17); (ii) glasses with Na-Ca silicate > 10 wt% but with no negative effect on PCT ("No effect on PCT"); and (iii) glasses with no crystals or with Na-Ca silicate < 10 wt% ("No crystals or Na-Ca silicate < 10 wt%").

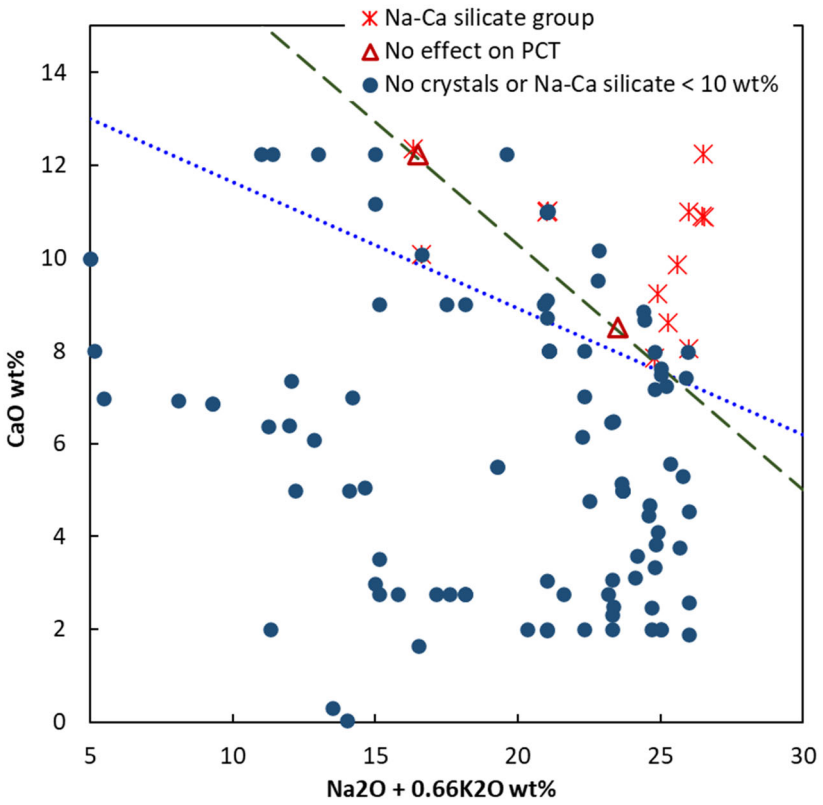

Figure 4.6. Plot of $Na_2O + 0.66K_2O$ versus CaO to assess sodium calcium-silicate crystal formation. The blue dotted line shows the suggested constraint limit and the green dashed line shows an alternative constraint.

This constraint is determined by the CaO concentration as well as the normalized alkali, not including Li_2O, of a given glass. One of the suggested constraints is

$$\mathrm{CaO} \leq 14.36 - 0.272 * (g_{Na_2O} + 0.66 g_{K_2O}) \quad 4.3$$

This constraint is shown by a blue dotted line in Figure 4.5.

An alternative constraint:

$$\mathrm{CaO} \leq 20.84 - 0.528 * (g_{Na_2O} + 0.66 g_{K_2O}) \quad 4.4$$

can be considered, which excludes one “Na-Ca silicate group” glass. This constraint is shown by a green dashed line in Figure 4.6.

5.0 Conclusions

An extensive data compilation effort, with some confirmatory testing, was conducted to provide suggested crystallization constraints for crystals anticipated to form during slow cooling of the LAW glasses in containers. Two crystal families were identified as the most impactful during heat treatments and subsequent crystal analysis: Na-Al-silicates and Na-Ca-silicates. The crystals that formed were found to impact PCT and VHT responses typically at concentrations of 10 wt% or more in a given glass. The primary constraints suggested would restrict the amount of Al_2O_3 and CaO, for the Na-Al-Silicates and Na-Ca-Silicates, respectively, with relation to Na_2O and K_2O concentrations in the glasses. These suggested constraints are presented as options to reduce the risk of forming crystals in two main families, in concentrations that are likely to be detrimental to durability responses of the final glass waste form.

6.0 References

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Appendix A – Summary of Compiled Data for Constraints

This appendix provides the data analyzed to generate the constraints presented in the main report (Sections 4.3 and 4.4). Included along with the Product Consistency Test (PCT) and Vapor Hydration Test (VHT) responses for each of the glasses (as indicated by glass IDs) are the crystals formed after container centerline cooling (CCC) and the references for the data sources. Three glasses had repeat PCT results, as presented in this report, that match the overall trend of existing data better: New-IL-87749, LAWPH3-06, and LAWPH3-20. Therefore the updated values are referenced below. The same is true for crystallinity information for NEW-OL-108249Mod and NEW-IL-87749 and the crystal information reflected in Table A.1 below.

Table A.1. Summary of glasses prepared at Pacific Northwest National Laboratory and used for constraint design and the associated CCC crystal phases and amounts, PCT normalized release before and after CCC for boron and sodium, as well as the VHT alteration thickness for quench and post-CCC samples. NV = no values due to none measured or samples being fully corroded after testing.

Glass ID	Reference	Total CCC Crystallinity (wt%)	Summary of Crystals Post-CCC Heat Treatment and Crystal Amounts (wt% in parenthesis)	PCT normalized release (ln(g/L))				VHT Alteration Thickness (ln(μm))	
				PCT-B Q	PCT-B CCC	PCT-Na Q	PCT-Na CCC	VHT Q	VHT CCC
EWG-LAW-Centroid-1	PNNL-26630, Rev. 0	0	NONE	-0.218	-0.119	0.047	0.041	NV	NV
EWG-LAW-Centroid-2	PNNL-26630, Rev. 0	0	NONE	-0.228	-0.114	0.053	0.051	NV	NV
LAW-ORP-LD1(1)	PNNL-26630, Rev. 0	14.9	Nosean (11.2), Hauyne (2.5)	-0.068	-0.562	0.176	-0.307	NV	NV
LAW-ORP-LD1(2)	PNNL-26630, Rev. 0	7.8	Nosean (6.5), Hauyne (1.3)	-0.165	-0.440	0.033	-0.189	NV	NV
LAW-ORP-LD1(M)	PNNL-26630, Rev. 0	0	NONE	-0.501	-0.772	-0.345	-0.514	NV	NV
New-IL-103151	PNNL-26630, Rev. 0	0	NONE	0.747	0.524	0.706	0.636	NV	NV
New-IL-151542	PNNL-26630, Rev. 0	0	NONE	-0.456	-0.397	-0.051	-0.064	NV	NV
New-IL-166697	PNNL-26630, Rev. 0	13.4	Nosean (9.1), Hauyne (2.6)	-0.223	-0.282	-0.110	-0.151	NV	NV
New-IL-166731	PNNL-26630, Rev. 0	4.0	Hauyne (1.2), Nosean (1.8), Silicon Oxide (1)	-0.208	1.548	0.004	1.070	NV	NV
New-IL-1721	PNNL-26630, Rev. 0	0	NONE	0.937	0.470	0.780	0.338	NV	NV
New-IL-42295	PNNL-26630, Rev. 0	0	NONE	2.968	2.791	2.580	2.454	NV	NV
New-IL-456	PNNL-26630, Rev. 0	0	NONE	-0.693	-0.677	-0.103	-0.269	NV	NV
New-IL-5253	PNNL-26630, Rev. 0	0	NONE	0.470	0.793	0.372	0.592	NV	NV
New-IL-5255	PNNL-26630, Rev. 0	0	NONE	2.580	2.531	2.326	2.198	NV	NV
New-IL-70316	PNNL-26630, Rev. 0	0.4	Baddeleyite	-0.468	-0.507	0.299	0.236	NV	NV
New-IL-87749	PNNL-26630, Rev. 0, This work	5.7	Nepheline	-0.877	0.123	0.125	0.429	NV	NV
New-IL-93907	PNNL-26630, Rev. 0	0	NONE	-0.849	-0.807	-0.654	-0.764	NV	NV
New-IL-94020	PNNL-26630, Rev. 0	1.3	Cassiterite	-0.697	-0.896	-0.403	-0.573	NV	NV
New-OL-100210	PNNL-26630, Rev. 0	0	NONE	0.726	0.673	1.037	0.902	NV	NV
New-OL-108249Mod	PNNL-26630, Rev. 0, This work	83.0	lazurite (12.728), nepheline (12.386), $Li_2O_3(SiO_3)$	-1.115	2.779	-0.174	1.517	NV	NV

Glass ID	Reference	Total CCC Crystallinity (wt%)	Summary of Crystals Post-CCC Heat Treatment and Crystal Amounts (wt% in parenthesis)	PCT normalized release (ln(g/L))				VHT Alteration Thickness (ln(μm))	
				PCT-B Q	PCT-B CCC	PCT-Na Q	PCT-Na CCC	VHT Q	VHT CCC
			(13.156), Combeite (24.464) + 7 other crystals						
New-OL-116208Mod	PNNL-26630, Rev. 0	50.6	Combeite (15.5), Nepheline type (6.3), nosean (4.6), Zirsinalite (5.3), and 8 more phases	2.152	2.894	2.063	2.437	NV	NV
New-OL-122817	PNNL-26630, Rev. 0	0	NONE	-1.224	-0.821	0.073	-0.070	NV	NV
New-OL-127708Mod	PNNL-26630, Rev. 0	0	NONE	-0.594	-0.654	-0.620	-0.826	NV	NV
New-OL-14844	PNNL-26630, Rev. 0	47.5	Combeite (13.5), Akermanite (12.8), Lithium Magnesium Silicate (13.7), and 9 more phases	2.029	1.946	1.998	1.915	NV	NV
New-OL-15493	PNNL-26630, Rev. 0	77.0	Combeite (50.2), nepheline (24.9), and others	-0.049	4.495	1.174	3.722	NV	NV
New-OL-17130	PNNL-26630, Rev. 0	0	NONE	3.125	3.065	2.829	2.794	NV	NV
New-OL-45748	PNNL-26630, Rev. 0	49.2	Nepheline (36.7)	-1.487	-0.039	-0.911	-1.000	NV	NV
New-OL-54017	PNNL-26630, Rev. 0	0	NONE	-1.016	-1.599	-0.662	-0.794	NV	NV
New-OL-57284	PNNL-26630, Rev. 0	2.8	Fluorapatite	0.535	0.800	0.442	0.592	NV	NV
New-OL-62380	PNNL-26630, Rev. 0	0	NONE	-1.109	-1.378	-0.689	-0.790	NV	NV
New-OL-62909Mod	PNNL-26630, Rev. 0	36.1	Nepheline (34)	-0.863	-1.332	-0.494	-0.803	NV	NV
New-OL-65959Mod	PNNL-26630, Rev. 0	44.8	Nepheline (31.6), Lithium Magnesium Silicate (11.2)	1.206	3.839	0.890	2.911	NV	NV
New-OL-80309	PNNL-26630, Rev. 0	1.0	Spinel	3.137	2.414	2.716	1.963	NV	NV
New-OL-8445	PNNL-26630, Rev. 0	0	NONE	-0.635	-0.877	-0.449	-0.701	NV	NV
New-OL-8788Mod	PNNL-26630, Rev. 0	1.2	Iron Lithium Oxide	-1.165	-0.650	-0.906	-0.863	NV	NV
New-OL-90780	PNNL-26630, Rev. 0	16.4	Nosean (15)	1.577	3.337	1.075	2.484	NV	NV
LP2-IL-01	PNNL-28838, Rev. 2	3.7	Combeite (2.48), Lazurite (1.22)	0.318	0.737	0.617	1.002	6.111	6.017
LP2-IL-02	PNNL-28838, Rev. 2	0	NONE	0.130	0.117	0.277	0.312	1.960	5.934
LP2-IL-03	PNNL-28838, Rev. 2	0	NONE	-0.264	-0.293	0.105	0.087	7.335823	5.209486
LP2-IL-04	PNNL-28838, Rev. 2	0	NONE	0.307	0.395	0.646	0.758	2.197	7.402
LP2-IL-05	PNNL-28838, Rev. 2	0	NONE	0.003	0.153	0.129	0.306	3.843744	4.757891
LP2-IL-06	PNNL-28838, Rev. 2	9.9	Lazurite (8.83) and others	0.925	0.810	0.625	0.548	7.093	6.865
LP2-IL-07	PNNL-28838, Rev. 2	0	NONE	1.081	0.970	0.940	0.930	6.932584	6.550264
LP2-IL-08	PNNL-28838, Rev. 2	0	NONE	0.275	0.172	0.452	0.388	4.70953	5.480639
LP2-IL-09	PNNL-28838, Rev. 2	0	NONE	1.244	1.191	0.991	0.936	5.657739	4.959342
LP2-IL-10	PNNL-28838, Rev. 2	0	NONE	-0.127	-0.057	0.136	0.183	6.872273	5.802118
LP2-IL-11	PNNL-28838, Rev. 2	0	NONE	-0.543	-0.485	-0.041	-0.058	5.505332	5.075174
LP2-IL-12	PNNL-28838, Rev. 2	0	NONE	0.325	0.079	0.403	0.309	6.030685	3.618993
LP2-IL-13	PNNL-28838, Rev. 2	0	NONE	0.704	0.413	0.490	0.306	2.962692	3.788725

Glass ID	Reference	Total CCC Crystallinity (wt%)	Summary of Crystals Post-CCC Heat Treatment and Crystal Amounts (wt% in parenthesis)	PCT normalized release (ln(g/L))				VHT Alteration Thickness (ln(μm))	
				PCT-B Q	PCT-B CCC	PCT-Na Q	PCT-Na CCC	VHT Q	VHT CCC
LP2-IL-14	PNNL-28838, Rev. 2	0	NONE	1.068	0.998	0.857	0.802	5.873525	6.382541
LP2-IL-15	PNNL-28838, Rev. 2	0	NONE	0.577	-0.081	0.308	-0.104	4.043051	4.749271
LP2-IL-16	PNNL-28838, Rev. 2	0	NONE	-0.029	-0.099	0.180	0.134	6.066108	4.471639
LP2-IL-17	PNNL-28838, Rev. 2	0.58	Lazurite (0.58)	0.575	0.478	0.345	0.292	6.341	5.647
LP2-OL-01-3	PNNL-28838, Rev. 2	0	NONE	-0.408	-0.470	0.131	-0.046	1.579	3.564
LP2-OL-02-1	PNNL-28838, Rev. 2	0	NONE	-0.065	-0.042	0.044	-0.017	2.425	5.391
LP2-OL-03 MOD2	PNNL-28838, Rev. 2	67.3	Combeite (40.78), Sodium Aluminum Silicate (18.87), Nepheline (6.72)	-0.300	0.496	0.937	2.675	5.347	5.580
LP2-OL-04-1	PNNL-28838, Rev. 2	69.4	Combeite (37.52), Nepheline (18.16), Sodium Peroxide (5.17)	0.426	2.246	0.749	3.024	3.186	6.464
LP2-OL-05	PNNL-28838, Rev. 2	23.4	Hauyne (11.91), Nosean (8.51), Combeite (3)	-1.143	-0.149	-0.322	-0.010	3.855	3.716
LP2-OL-07-1	PNNL-28838, Rev. 2	4.1	Hauyne	-0.135	-0.207	0.001	-0.168	4.963	2.899
LP2-OL-08 MOD	PNNL-28838, Rev. 2	69.7	Combeite (49.56), nepheline (6.36), Sodium Iron Aluminum Oxide (7.12), Nasicon $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ (6.68)	0.930	2.919	1.509	3.108	6.899	5.920
LP2-OL-09-1	PNNL-28838, Rev. 2	0	NONE	1.137	0.837	0.611	0.374	4.527209	3.838376
LP2-OL-10 MOD	PNNL-28838, Rev. 2	28.3	Nepheline (11.45), Combeite (10.25)	-1.082	2.260	-0.212	1.611	4.363	3.523
LP2-OL-11	PNNL-28838, Rev. 2	0	NONE	2.046	1.964	1.975	1.898	6.217604	3.275256
LP2-OL-12	PNNL-28838, Rev. 2	0	NONE	3.533	3.576	3.289	3.353	7.734183	5.968342
LP2-OL-13	PNNL-28838, Rev. 2	45.2	Combeite (42.36), nepheline (2.84)	0.031	2.455	1.357	2.655	6.131	6.418
LP2-OL-14	PNNL-28838, Rev. 2	0	NONE	2.672	2.295	2.546	2.229	NV	NV
LP2-OL-15	PNNL-28838, Rev. 2	0	NONE	-0.594	-0.740	-0.134	-0.174	2.424803	2.962692
LP2-OL-16 MOD	PNNL-28838, Rev. 2	0	NONE	0.959	0.779	0.960	0.767	3.545298	2.091864
LP2-OL-17	PNNL-28838, Rev. 2	0	NONE	2.419	2.536	2.250	2.382	NV	NV
LP2-OL-18	PNNL-28838, Rev. 2	3.8	Lazurite	0.861	-1.050	0.863	-0.033	4.454	3.970
LP2-OL-19	PNNL-28838, Rev. 2	0	NONE	-0.252	-0.302	0.602	0.556	NV	NV
LP2-OL-20	PNNL-28838, Rev. 2	16.7	Combeite (14.46)	-0.616	0.614	0.780	1.517	7.768	7.804
LP2-OL-21	PNNL-28838, Rev. 2	0	NONE	-0.104	-0.015	0.040	0.003	5.404927	5.285739
LP2-OL-22	PNNL-28838, Rev. 2	0	NONE	-0.929	-0.779	0.075	0.050	2.529721	3.342862
LP2-OL-23	PNNL-28838, Rev. 2	0	NONE	-0.040	-0.284	0.177	0.074	2.965	4.840
LP2-OL-24	PNNL-28838, Rev. 2	66.6	Nepheline	-0.090	1.176	0.557	1.394	**4.836**	**7.058**
LP2-OL-25	PNNL-28838, Rev. 2	0	NONE	1.639	1.740	1.352	1.420	5.525453	5.48272
LAWPH3-01	PNNL-29847, Rev. 0	0	NONE	2.198	1.884	2.010	1.713	NV	NV

Glass ID	Reference	Total CCC Crystallinity (wt%)	Summary of Crystals Post-CCC Heat Treatment and Crystal Amounts (wt% in parenthesis)	PCT normalized release (ln(g/L))				VHT Alteration Thickness (ln(μm))	
				PCT-B Q	PCT-B CCC	PCT-Na Q	PCT-Na CCC	VHT Q	VHT CCC
LAWPH3-02	PNNL-29847, Rev. 0	0	NONE	2.712	2.573	2.574	2.355	NV	NV
LAWPH3-03	PNNL-29847, Rev. 0	0	NONE	2.015	1.434	1.874	1.285	NV	NV
LAWPH3-04	PNNL-29847, Rev. 0	0	NONE	0.942	0.378	1.180	0.631	5.605802	6.042633
LAWPH3-05 mod6	PNNL-29847, Rev. 0	0	NONE	2.586	2.409	2.340	2.110	NV	NV
LAWPH3-06	PNNL-29847, Rev. 0, This work	0	NONE	-0.380	-0.029	0.635	1.178	4.045	5.513
LAWPH3-07	PNNL-29847, Rev. 0	0	NONE	0.002	0.239	0.848	0.618	NV	NV
LAWPH3-08	PNNL-29847, Rev. 0	0	NONE	-0.375	-0.345	0.268	0.194	1.656	5.236
LAWPH3-09	PNNL-29847, Rev. 0	25.2	Nepheline (10.03), sodium phosphate (8.79), sodium calcium silicate (6.29)	0.822	3.552	1.195	3.029	6.217	3.742
LAWPH3-10	PNNL-29847, Rev. 0	0	NONE	0.512	0.827	0.903	0.995	6.054	6.670
LAWPH3-11	PNNL-29847, Rev. 0	0	NONE	1.177	1.066	1.079	0.937	NV	NV
LAWPH3-12	PNNL-29847, Rev. 0	0	NONE	1.071	0.445	0.710	0.140	6.584002	6.45789
LAWPH3-13	PNNL-29847, Rev. 0	46.5	Combeite (45.38)	-0.212	2.939	0.945	2.897	NV	NV
LAWPH3-14	PNNL-29847, Rev. 0	0	NONE	0.466	0.490	0.970	0.816	NV	NV
LAWPH3-15	PNNL-29847, Rev. 0	0	NONE	0.557	0.760	1.082	1.066	5.69575	6.208877
LAWPH3-16	PNNL-29847, Rev. 0	0	NONE	1.703	1.511	1.919	1.670	NV	NV
LAWPH3-17	PNNL-29847, Rev. 0	4.7	Hauyne (3.38), potassium chromium oxide fluoride (0.45), aluminum phosphate (0.8)	0.116	2.874	1.111	2.516	5.867	5.114
LAWPH3-18	PNNL-29847, Rev. 0	0	NONE	-0.103	0.041	0.519	0.443	3.421	5.656
LAWPH3-19 mod1	PNNL-29847, Rev. 0	11.8	Combeite	0.003	0.358	0.784	1.118	5.867	5.037
LAWPH3-20	PNNL-29847, Rev. 0, This work	0	NONE	0.059	0.070	0.401	0.389	4.372	3.454

Table A.2. Summary of glasses prepared at the Vitreous State Laboratory (VSL) and used for constraint design and the associated CCC crystal phases and amounts, PCT normalized release before and after CCC for boron and sodium, as well as the VHT alteration thickness for quench and post-CCC samples. NV = no values due to none measured or samples being fully corroded after testing. * For VSL glasses, the vol% given in the source reports was converted to wt% based on assumed density of 2.65 g/cm^3 for glass, 5.2 g/cm^3 for spinel, and 3.4 g/cm^3 for augite-aegirine.

				PCT Normalized Release (ln(g/L))				VHT Alteration Thickness (ln(μm))	
Glass ID	Reference	Total CCC Crystallinity (wt%*)	Summary of Crystals Post-CCC Heat Treatment	PCT-B Q	PCT-B CCC	PCT-Na Q	PCT-Na CCC	VHT Q	VHT CCC
LAWM2	VSL-04R4480-1, Rev. 0	47.1	Augite-aegirine	-0.400	-0.190	-0.151	-0.454	4.317	4.871
LAWCrP7	VSL-06R6480-2, Rev. 0	19.5	Augite-aegirine	-0.726	-0.835	-1.036	-1.461	2.485	1.609
LAWM7	VSL-04R4480-1, Rev. 0	18.5	Augite-aegirine	-1.386	-2.096	-0.844	-1.390	3.258	2.442
LAWE9HCr1	VSL-08R1410-1, Rev. 0	16.1	Augite-aegirine	-1.112	-0.901	-0.865	-0.785	2.741	4.220
LAWCrP6	VSL-06R6480-2, Rev. 0	7.1	Augite-aegirine	-0.400	-0.620	-0.552	-0.774	2.565	2.565
LAWM43	VSL-04R4480-1, Rev. 0	4.1	Augite-aegirine	-0.416	-0.770	-0.431	-0.681	2.197	2.996
LAWE9HCr2	VSL-08R1410-1, Rev. 0	3.1	Augite-aegirine	-0.476	-0.683	-0.451	-0.715	3.701	4.522
LAWM41	VSL-04R4480-1, Rev. 0	1.9	Augite-aegirine	-1.022	-0.884	-0.528	-0.738	3.761	4.212
LAWM25	VSL-04R4480-1, Rev. 0	0.9	Augite-aegirine	-0.198	-0.528	-0.545	-0.679	3.714	3.998
LAWCrP11	VSL-08R1410-1, Rev. 0	1.2	Cr-rich spinel with Fe and Zn	-0.383	-0.408	-0.439	-0.536	2.442	4.284
LAWCrP12	VSL-08R1410-1, Rev. 0	0.6	Cr-rich spinel with Fe and Zn	-0.280	-0.403	-0.322	-0.480	2.351	4.635
12U-G-86A	VSL-05R5460-1, Rev. 0	0	NONE	NV	NV	NV	NV	2.708	2.833
A100-G-115A	VSL-01R3501-2, Rev. 0	0	NONE	-0.030	-0.342	-0.105	-0.431	4.766	4.477
AZ-102 Actual	VSL-05R5460-1, Rev. 0	0	NONE	-0.916	-1.139	-1.139	-1.273	NV	NV
C100-G-136B	VSL-01R3501-2, Rev. 0	0	NONE	-0.307	-0.768	-0.360	-0.724	3.118	4.067
C2-AN102C35	VSL-03R3460-2, Rev. 0	0	NONE	-0.386	-0.693	-0.288	-0.478	5.037	4.007
EWV-G-89B	VSL-06R6900-1, Rev. 0	0	NONE	0.751	0.811	0.642	0.531	6.711	5.438
EWV-G-93B	VSL-06R6900-1, Rev. 0	0	NONE	NV	NV	NV	NV	6.578	5.407
GTSD-1126	VSL-05R5460-1, Rev. 0	0	NONE	NV	NV	NV	NV	2.303	2.639
LAWA126	VSL-05R5460-1, Rev. 0	0	NONE	0.179	-0.110	0.047	-0.242	3.091	2.565
LAWA187	VSL-03R3470-2, Rev. 0	0	NONE	1.230	0.723	1.072	0.519	NV	NV
LAWA44	VSL-01R3560-2, Rev. 0	0	NONE	-0.301	-0.400	-0.329	-0.400	2.197	1.946
LAWB83	VSL-03R3460-1, Rev. 0	0	NONE	NV	NV	NV	NV	2.773	2.674
LAWB88	VSL-03R3470-1, Rev. 0	0	NONE	NV	NV	NV	NV	3.526	3.434
LAWM39	VSL-04R4480-1, Rev. 0	0	NONE	-0.616	-0.711	-0.777	-0.685	4.718	4.304

Appendix B – X-ray Diffraction Results for Glasses Post-CCC

The data provided in this appendix are the result of heat treating existing quenched glasses according to the low-activity waste (LAW) container centerline cooling (CCC) profile and subsequently analyzing the glasses with X-ray diffraction (XRD). "LXC" indicates glasses that were taken as quenched and subjected to the CCC profile as part of this testing. Glass IDs without "LXC" indicate previous heat treatment data that were re-analyzed without re-performing the heat treatment.

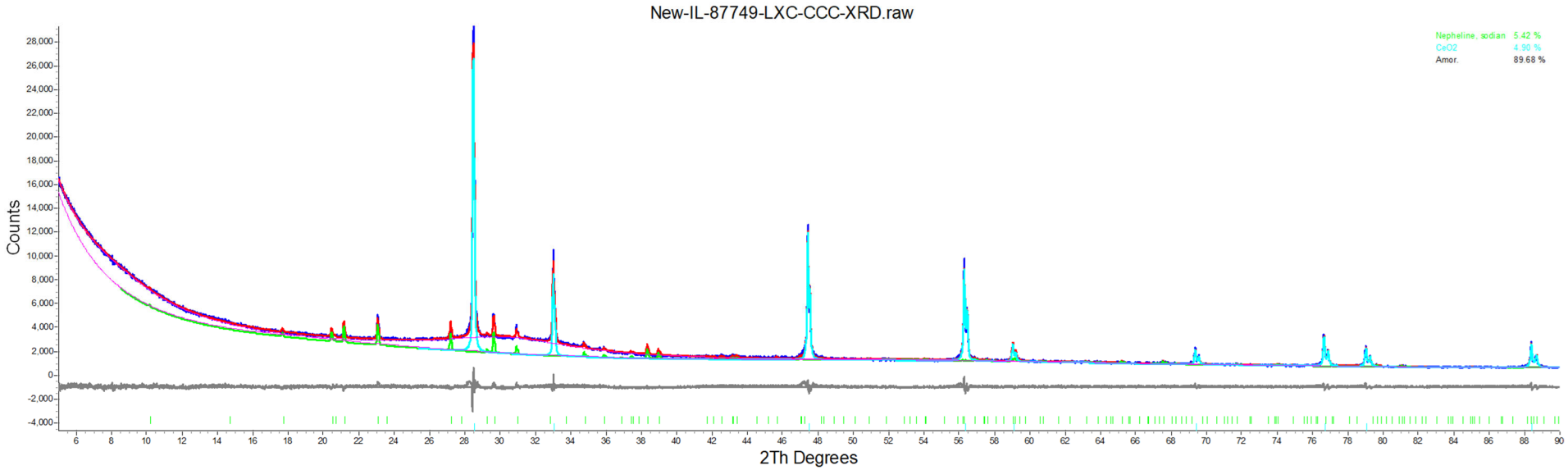

Figure B.1. XRD data for New-IL-87749-LXC-CCC

Table B.1. XRD data for New-IL-87749-LXC-CCC

Phase Name	Wt% of Spiked	Wt% in Spiked Sample	Wt% in Original Sample
Nepheline, sodian	0	5.42	5.699
CeO_2	4.9	4.9	0

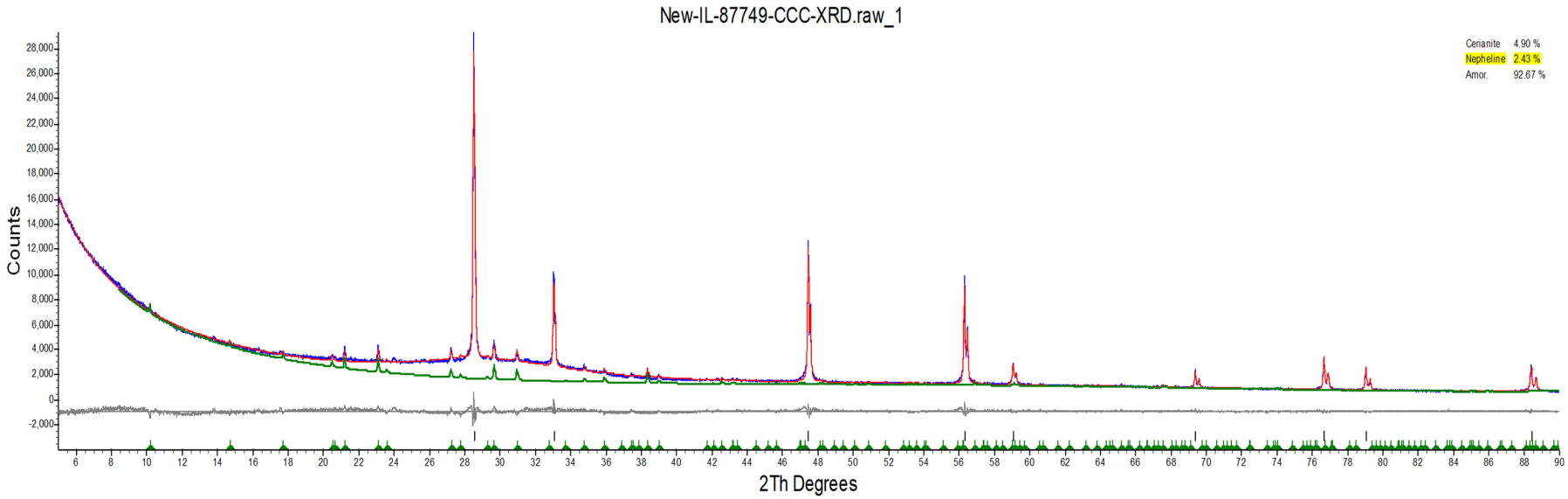

Figure B.2. XRD data for New-IL-87749- CCC

Table B.2. XRD data for New-IL-87749- CCC

Phase Name	Wt% of Spiked	Wt% in Spiked Sample	Wt% in Original Sample
Cerianite	4.9	4.9	0
Nepheline	0	2.432	2.557

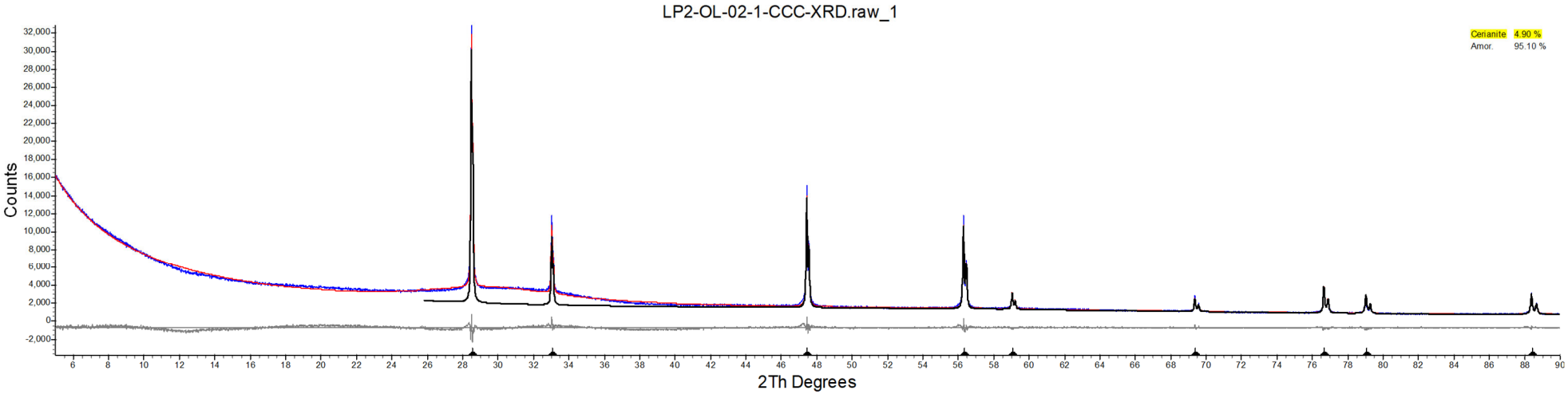

Figure B.3. XRD data for LP2-OL-02-1-CCC

Table B.3. XRD data for LP2-OL-02-1-CCC

Phase Name	Wt% of Spiked	Wt% in Spiked Sample	Wt% in Original Sample
Cerianite	4.9	4.9	0
Nepheline	0	0.006	0.006

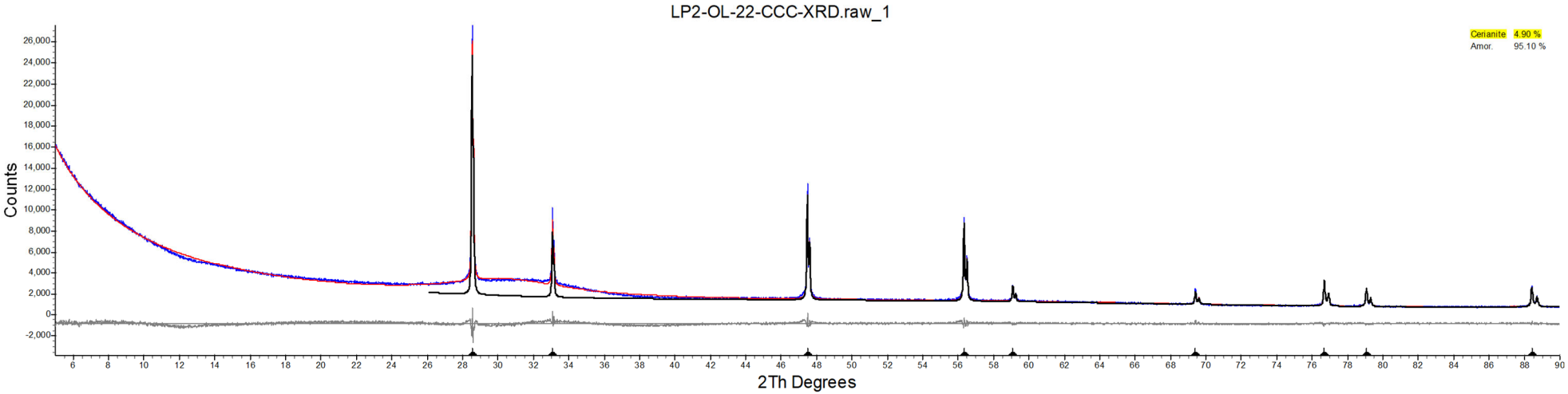

Figure B.4. XRD data for LP2-OL-22-CCC

Table B.4. XRD data for LP2-OL-22-CCC

Phase Name	Wt% of Spiked	Wt% in Spiked Sample	Wt% in Original Sample
Cerianite	4.9	4.9	0

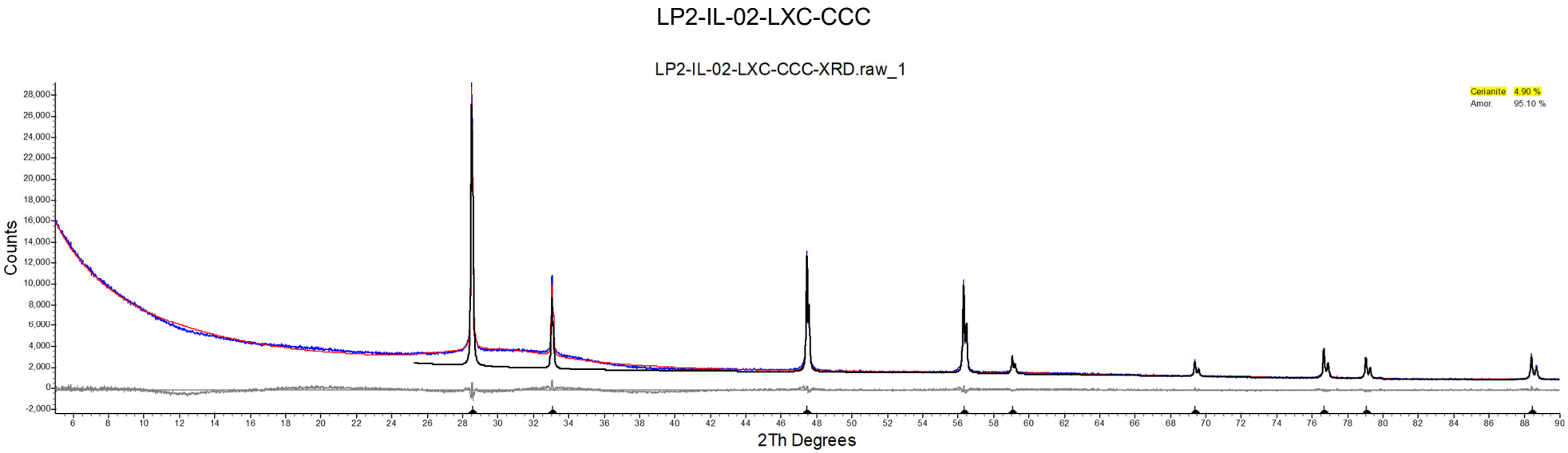

Figure B.5. XRD data for LP2-IL-02-LXC-CCC

Table B.5. XRD data for LP2-IL-02-LXC-CCC

Phase Name	Wt% of Spiked	Wt% in Spiked Sample	Wt% in Original Sample
Cerianite	4.9	4.9	0

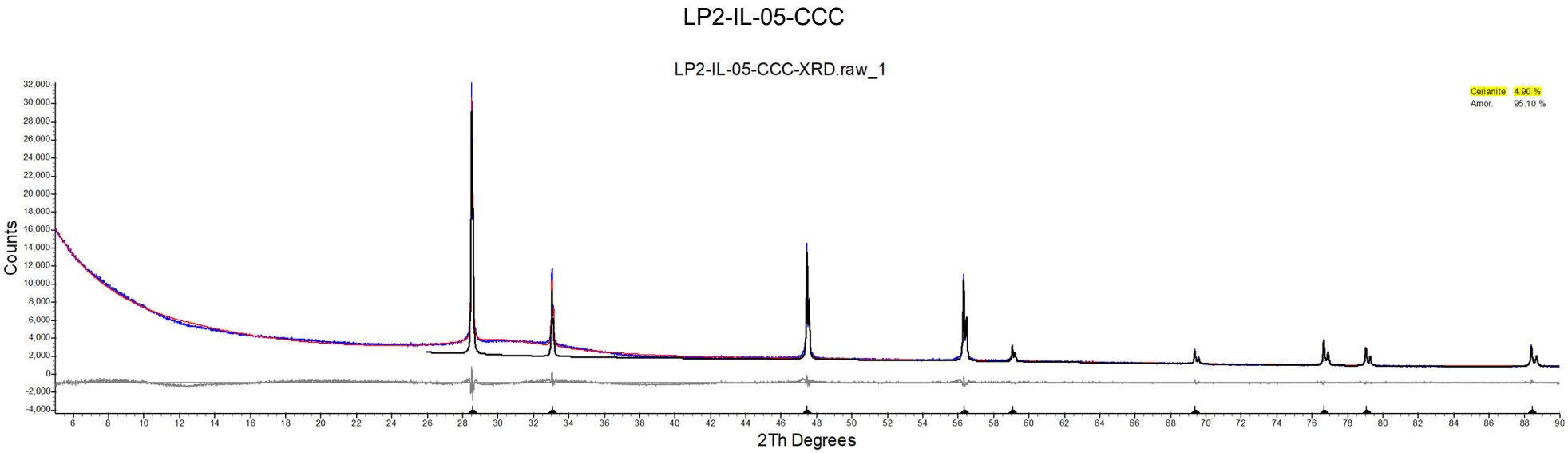

Figure B.6. XRD data for LP2-IL-02-LXC-CCC

Table B.6. XRD data for LP2-IL-02-LXC-CCC

Phase Name	Wt% of Spiked	Wt% in Spiked Sample	Wt% in Original Sample
Cerianite	4.9	4.9	0

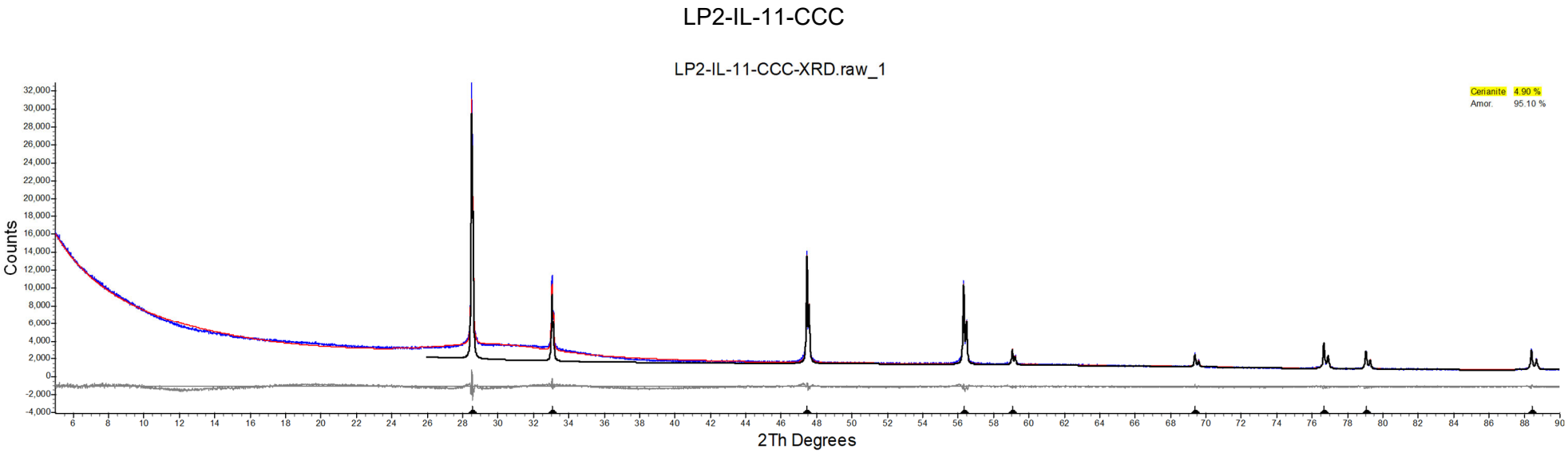

Figure B.7. XRD data for LP2-IL-11-CCC

Table B.7. XRD data for LP2-IL-11-CCC

Phase Name	Wt% of Spiked	Wt% in Spiked Sample	Wt% in Original Sample
Cerianite	4.9	4.9	0

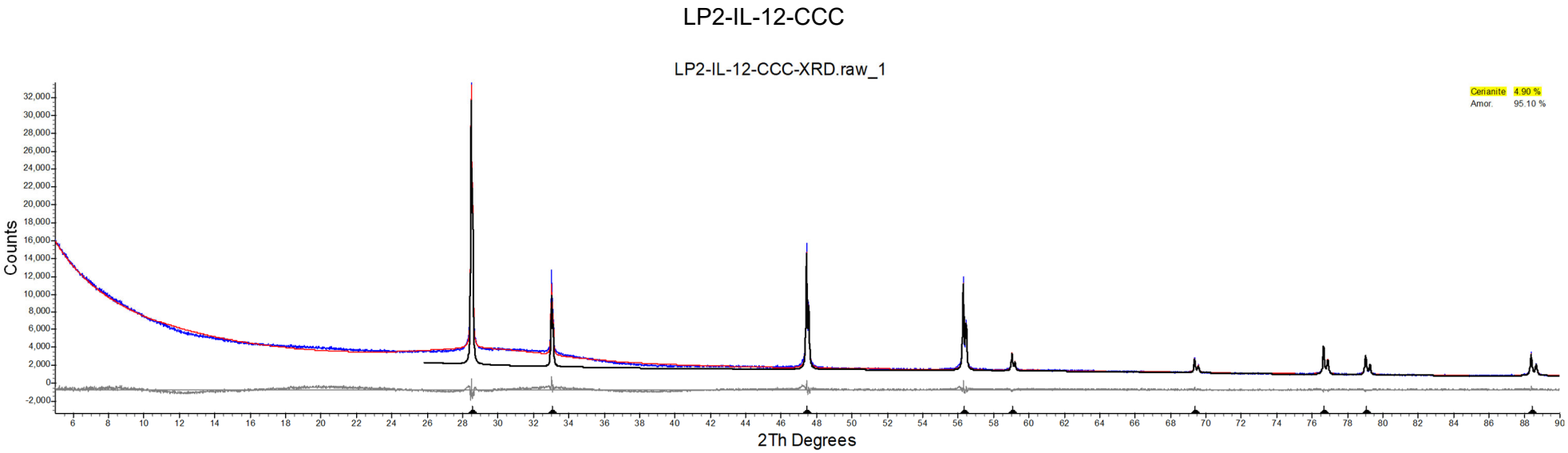

Figure B.8. XRD data for LP2-IL-12-CCC

Table B.8. XRD data for LP2-IL-12-CCC

Phase Name	Wt% of Spiked	Wt% in Spiked Sample	Wt% in Original Sample
Cerianite	4.9	4.9	0

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