

Fluorine Limits and Impacts in High-Level Waste Glass Compositions

July 2020

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Prepared for
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Summary

The impact of elevated fluorine (F) content on Hanford high-level waste (HLW) glasses has not previously been studied in detail. The effort documented in this report represents the first systematic study to determine what F concentration limits should be used for the design of alkali-borosilicate-based Hanford Waste Treatment and Immobilization Plant (WTP) HLW glasses, and to document the technical basis for that limit. If alkali borosilicate glass made from Hanford HLW can accommodate a large amount of F, the large capital costs for complex sludge washing facilities may be avoided, as would much of the operational costs and negative schedule impacts associated with handling the large volumes of water required to dissolve these salts.

In order to determine a limit for F in likely HLW glass compositions, an evaluation was conducted on glasses with $F \geq 0.90$ mass% from previous nuclear waste glass studies. The collected dataset contains 239 glasses (232 HLW glasses and 7 low-activity waste [LAW] glasses) including 109 glasses with $0.9 \leq F \text{ mass\%} \leq 2.5$, 116 with $2.5 < F \text{ mass\%} \leq 8.0$, and 14 with $F \text{ mass\%} \geq 8$ (max. $F \text{ mass\%} = 17.42$).

The collected composition and property data were analyzed to determine the basis for the F tolerance, i.e., the maximum F concentration that can be processed without potential glass quality or melter operation issues. Fluorine volatility, Product Consistency Test (PCT) response, liquidus temperature (T_L), glass melt viscosity, and crystallinity have been investigated. No limits for F concentration can be established based on F volatility, T_L , or glass melt viscosity, because the data show that high F in glasses does not indicate, with high probability, being restricted by those property constraints. However, crystallinity and PCT response were used to estimate the F tolerance. The results show that glasses with high F (≥ 0.90 mass%) are more likely to form large fractions of F-containing crystal phases which may increase PCT responses, i.e., decrease the glass durability. Based on the results of crystallinity and PCT data, the F tolerance of 4.5 mass% is estimated. There is no evidence that other glass components, such as calcium oxides and alkali metal oxides, have combined impacts with F on the glass properties.

Overall, the available high-F glass data are limited, especially in the designed HLW glass composition regions. Future work on formulation and testing of HLW glasses with $F \geq 0.9$ mass% will close the data gaps and expand operational flexibility with respect to the F tolerances. Volatility of F from melters and corrosion of materials in contact with glass melts are important for processing of high-F wastes; yet no test data are currently available. It is recommended that tests be conducted to address these two potential issues.

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Acronyms and Abbreviations

CCC	canister centerline cooled
CUA	The Catholic University of America
DF	decontamination factor
DFHLW	Direct Feed High-Level Waste
HEME	high-efficiency mist eliminator
HEPA	high-efficiency particulate air filter
HLW	high-level waste
INEEL	Idaho National Engineering and Environmental Laboratory (now Idaho National Laboratory)
LAW	low-activity waste
PCT	Product Consistency Test
PFP	Plutonium Finishing Plant
PNNL	Pacific Northwest National Laboratory
QA	quality assurance
R&D	research and development
SBS	submerged bed scrubber
SCO	selective catalytic oxidizer
SCR	selective catalytic reducer
TWINS	Tank Waste Information Network System
WESP	wet electrostatic precipitator
WRPS	Washington River Protection Solutions
WTP	Waste Treatment and Immobilization Plant
WWFTP	WRPS Waste Form Testing Program

Contents

Summary	ii
Acknowledgments.....	iii
Acronyms and Abbreviations	iv
Contents	v
1.0 Introduction.....	1
2.0 Quality Assurance.....	3
3.0 Data Used in Analyses	4
4.0 Rule Development	5
4.1 Fluorine Volatility.....	5
4.2 PCT Response of Quenched and Canister Centerline Cooled Samples.....	6
4.3 Liquidus Temperature.....	9
4.4 Glass Melt Viscosity	9
4.5 Crystallinity and Fluorine Tolerance	10
5.0 Conclusions and Recommendations	13
6.0 References.....	14
Appendix A – Fu et al. 1993 Report “Vitrification Development Studies for OU1 Wastes”	A.1

Figures

Figure 1. Fluorine Retention of INEEL, Fernald, and Hanford-LAW Glasses. Retention % is estimated by linear fitting of target and measured F mass%.	5
Figure 2. Comparison of the Natural Log of Normalized PCT Release for B between Quenched and CCC Samples. Orange dashed lines mark the WTP contract limit of PCT release, 8.35 g/m ² (Vienna et al. 2016).....	8
Figure 3. Comparison of the Natural Log of Normalized PCT Release Na between Quenched and CCC Samples. Orange dashed lines mark the WTP contract limit of PCT release, 6.675 g/m ² (Vienna et al. 2016)	8
Figure 4. Comparison of the Natural Log of Normalized PCT Release for Li between Quenched and CCC Samples. Orange dashed lines mark the WTP contract limit of PCT release, 4.785 g/m ² (Vienna et al. 2016).....	9
Figure 5. Viscosity at 1150 °C, $\eta(1150)$, Measured and Model (Vienna et al. 2016) Estimated.....	10
Figure 6. F Tolerance Grouping Plot. Pass/Fail/Unknown Categories Plotted with Concentration (mass%) of CaO vs. F.	11
Figure 7. F Tolerance Grouping Plot. Pass/Fail/Unknown Categories Plotted with Concentration (mass%) of NaLiK (Na ₂ O + 2.07 Li ₂ O + 0.66 K ₂ O) vs. F.....	12
Figure 8. F Tolerance Grouping Plot. Pass/Fail/Unknown Categories Plotted with Concentration (mass%) of AlZr (Al ₂ O ₃ + ZrO ₂) vs. F.	12

Tables

Table 1. Summary of Effects of F on HLW Glass Properties from Previous Studies	2
Table 2. Summary of High-F Glass Data.....	4
Table 3. Crystallinity Data Categories for PCT Response Comparison between Quenched and CCC Samples.....	7
Table 4. Crystallinity Data Categories for the Quenched Glasses	11

1.0 Introduction

The impact of elevated fluorine (F) content on Hanford high-level waste (HLW) glasses has not previously been studied in detail. The effort documented in this report represents the first systematic study to determine what F concentration limits should be used for the design of alkali-borosilicate-based Hanford Waste Treatment and Immobilization Plant (WTP) HLW glasses, and to document the technical basis for that limit. Literature data for high-F glasses (≥ 0.90 mass%) were gathered. The glass properties of the high-F glasses from literature were evaluated and, based on the data currently available, a F concentration limit is recommended in this report, and the qualitative influence of F concentrations on HLW glass properties is summarized. If alkali borosilicate glass made from Hanford HLW can accommodate a large amount of F, the large capital costs for complex sludge washing facilities may be avoided, as would much of the operational cost and negative schedule impact associated with handling the large volumes of water required to dissolve these salts.

Significant quantities of F were used in fuel and target processing at Hanford and were discharged to the waste storage tanks. Roughly 1200 tonnes of F inventory¹ are stored in the Hanford tanks. The largest sources of F were zirconium cladding removal, hydrofluoric acid additions in the Plutonium Finishing Plant (PFP), and reagent chemical impurities. Therefore, F is found in large concentrations in neutralized cladding removal waste and many PFP wastes. Given the large concentration of fluoride in the waste, fluoride salts have precipitated from the waste. These salts include villiaumite (NaF), kogarkoite (Na_3FSO_4), and natrophosphate ($\text{Na}_7\text{F}(\text{PO}_4)_2 \cdot 19\text{H}_2\text{O}$) (Herting et al. 2002; 2015; Mahoney et al. 2020). However, there has been limited evaluation of fluoride solubility in HLW glass, presumably because it was assumed that these salts would be dissolved from the waste in a water washing process (Lumetta et al. 1998; Geeting and Hallen 2005). Fluoride salts, however, are sparingly soluble. NaF solubility is only about 0.98 moles/kg of water at ambient temperatures and a recent study has determined that it requires approximately 6.1 million liters of water to dissolve NaF from one single tank (Reynolds and Belsher 2017). Thus, the fluoride salts may be difficult to dissolve in a washing step, potentially requiring long mixing times and elevated temperatures. So, although much of the F is predicted to be soluble and assumed to be processed through the WTP Low-Activity Waste (LAW) Facility in fully washed sludge liquids, some tanks will still contain a relatively large fraction of less-soluble F. Also, if HLW processing begins before the WTP Pretreatment Facility is operational, significant underwashing may result in higher-F HLW batches.

High F concentrations tend to cause crystallization in silicate-based waste glass melts (Fu and Pegg 1998; Langowski 1996; Staples et al. 2000; Scholes et al. 2000). Crystallization effects on HLW glass properties and processing in the melter can be important if they degrade the durability of glass or disrupt the melter process. One measure of glass durability, a Product Consistency Test (PCT), has been used to measure the chemical durability of glasses (ASTM 2014), and the PCT response is a critical property constraint for waste glass formulation (Vienna et al. 2016).

Among the previous high-F HLW glass studies, between 3 and 5 mass% F can be incorporated in the glass without forming secondary phase(s) if glasses are properly formulated. Comparable F limits have not been demonstrated for WTP HLW glasses; glass property data are mostly from compositions with low F (< 0.90 mass%) (Vienna et al. 2009; Muller et al. 2012). Glass compositions with >2.5 mass% F in other non-Hanford waste glasses are mostly reported in glass composition studies from the Idaho National Engineering and Environmental Laboratory (INEEL, now Idaho National Laboratory) (Edwards et al.

¹ Tank Waste Information Network System (TWINS) database inventory (<https://twins.labworks.org/twinsdata/Forms/About.aspx?subject=TWINS>) obtained 6/19/2020 by selecting “Best-Basis Inventory”, selecting “Best-Basis Summary”, selecting “F”, decay to 7/1/2015, and pressing “Submit Query.”

1999; Staples et al. 2000; Scholes et al. 2000; Musick et al. 2000; Pittman et al. 2000; Riley et al. 2001) and Fernald waste glasses (Fu et al. 1994).

The impacts of F on waste glass properties are not well established. Table 1 summarizes relevant studies on HLW glasses, in which F effects on properties (increase or decrease) were presented based on coefficients of F in empirical models (positive, negative, or undetermined), except one in the Fu et al. 1994 report. The most recent PNNL models for HLW glasses (Vienna et al. 2016), i.e., the 2016 models, do not show a measurable impact of F on the PCT response; however, an earlier model showed that F slightly increases PCT response (Vienna et al. 2013). The 2016 viscosity model shows that viscosity tends to decrease with increasing F levels (Vienna et al. 2016), which is consistent with literature on simple glass systems (Baasner et al. 2013). However, a set of HLW glass models from 2008 (Piepel et al. 2008), fit using 305 WTP HLW glasses (with maximum F of 0.44 mass%), does not show any impact of F on glass properties, including viscosity.

Table 1. Summary of Effects of F on HLW Glass Properties from Previous Studies

Reference	Number of Glasses ^(a)	Number of Glasses with ≥ 0.90 Mass% F	F Mass% Range	F Effect on HLW Glass Properties		
				Viscosity	PCT Responses	Liquidus Temperature (T _L)
Fu et al. 1994 ^(b)	27	27	1.39-17.42	Decrease	Decrease	Decrease 1-10 mass% F; Increase > 10 mass% F
Piepel et al. 2008	305	0	0.05-0.44	Undetermined ^(c)	Undetermined ^(c)	NA ^(c)
Vienna et al. 2009	> 3000	47	0-2.5	Decrease	Undetermined ^(c)	Undetermined ^(c)
Vienna et al. 2013	> 2000	50	0-2.5	Decrease	Increase	Undetermined ^(c)
Vienna et al. 2016	> 2000	50	0-2.5	Decrease	Undetermined ^(c)	Undetermined ^(c)

(a) Total number of glasses in the collected dataset; models of each property were developed based on a sub-dataset with fewer glasses.

(b) F effects were obtained by observation, while other references used empirical model methods.

(c) Undetermined means F counted as “others”; NA “not applicable” means no model available.

Another potential issue is that high F in the glass may influence the corrosion of metallic and ceramic materials in contact with glass in the melter. WTP baseline models were not developed for refractory corrosion; however, understanding the correlation between glass melt composition and refractory corrosion rate is important to prevent risk of refractory failure in designed life of WTP melter(s). For the candidate high-Cr Monofrax K-3 refractory material, a preliminary corrosion rate model was developed based on data of ~ 350 glasses (Muller et al. 2018). However, the model did not support a conclusion in either direction (increasing or decreasing corrosion rate), thus leaving the fluorine impact as undetermined, possibly because the model was based on low-F glasses (≤ 0.49 mass%).

Furthermore, crystallization caused by high F concentrations makes assessment of F impact more complicated. A constraint may be needed to avoid phase separation and formation of F-bearing crystal phases.

This report analyses a large dataset of glasses containing greater than 0.90 mass% F (Section 3.0) and assesses the development of F tolerance rules (Section 4.0) based on F volatility, PCT response, liquidus temperature, glass melt viscosity, and crystallinity. Section 5.0 discusses conclusions that can be drawn, gaps in the available information with recommendations to close these identified technical gaps, and provides an effective F-concentration limit to be used for Hanford HLW glass formulation.

2.0 Quality Assurance

This work was conducted with funding from Washington River Protection Solutions (WRPS) under Pacific Northwest National Laboratory (PNNL) Project 75807, contract 36437-301, with the title “Flowsheet Maturation Studies.”

All research and development (R&D) work at PNNL is performed in accordance with PNNL’s Laboratory-level Quality Management Program, which is based on a graded application of NQA-1-2000, *Quality Assurance Requirements for Nuclear Facility Applications*, to R&D activities. To ensure that all client quality assurance (QA) expectations were addressed, the QA controls of the WRPS Waste Form Testing Program (WWFTP) QA program were also implemented for this work. The WWFTP QA program implements the requirements of NQA-1-2008, *Quality Assurance Requirements for Nuclear Facility Applications*, and NQA-1a-2009, *Addenda to ASME NQA-1-2008*, and consists of the WWFTP Quality Assurance Plan (QA-WWFTP-001) and associated procedures that provide detailed instructions for implementing NQA-1 requirements for R&D work.

The work described in this report was assigned the technology level “Applied Research” and was planned, performed, documented, and reported in accordance with procedure QA-NSLW-1102, *Scientific Investigation for Applied Research*. All staff members contributing to the work received appropriate technical and QA training prior to performing quality-affecting work.

3.0 Data Used in Analyses

A dataset of 239 glasses (232 HLW glasses and 7 LAW glasses) with F concentrations equal to, or greater than, 0.90 mass% was gathered. As shown in Table 2, this dataset includes 116 glasses containing 2.5-8.0 mass% F and 14 glasses containing over 8.0 mass% F (max. 17.42 mass%). The glasses with 2.5-8.0 mass% F are mostly from INEEL reports (Edwards et al. 1999; Staples et al. 2000; Scholes et al. 2000; Musick et al. 2000; Pittman et al. 2000; Riley et al. 2001; Vienna et al. 2002) and Fernald glass reports (Fu et al. 1994); and the glasses with over 8.0 mass% F are exclusively from the Fernald glass report.² Previous Hanford glass formulation had not focused on high F compositional region; data of high-F glasses are very limited. Only 56 Hanford HLW and 7 Hanford LAW glasses with F concentrations between 0.90 and 3.01 mass% were reported (Fu and Pegg 1998; Kot and Pegg 2001; Muller et al. 2001, 2012; Matlack et al. 2006, 2007; Gan et al. 2015).

Table 2. Summary of High-F Glass Data

Study	Number of Glasses	F Range (mass%)	Number of Glasses with F mass% Range		
			$0.9 \leq F \leq 2.5$	$2.5 < F \leq 8.0$	$F > 8.0$
INEEL	149	0.90 – 7.41	49	100	0
Fernald (Fu et al. 1994)	27	1.39 – 17.42	2	11	14
<i>Fernald (Fu et al. 1993)^(a)</i>	35	<i>6.28 – 15.44</i>	<i>0</i>	<i>4</i>	<i>31</i>
Hanford-HLW	56	0.90 – 2.80	52	4	0
Hanford-LAW	7	0.93 – 3.01	6	1	0
Total	239	0.90 – 17.42	109	116	14

(a) Complete data from Fu et al. 1993 were not available, so values for these glasses are not included in the totals.

² GTS Duratek Inc. and Vitreous State Laboratory, The Catholic University of America (CUA), developed and tested glasses for wastes stored at the Fernald Environmental Management Project site. Two reports were published by Fu et al., one each in 1993 and 1994. However, PNNL currently only has access to the Fu et al. 1994 report. Part of the data in the Fu et al. 1993 report (glass IDs and compositions of 18 glass, while there were ~35 glasses tested in the report) was provided via personal communication by Ian Pegg (CUA) in April 2020. However, since PNNL was not able to review the data for these glasses in the context of the complete report, these glasses were omitted from the current study. Scanned images of the pages containing glass IDs and compositions of the 18 glasses from Fu et al. 1993 are shown in Appendix A of this report.

4.0 Rule Development

4.1 Fluorine Volatility

The 118 crucible melts with measured concentrations had an average F loss due to volatilization of 12%, 13%, and 25% from Fernald, INEEL, and Hanford LAW glasses, respectively (Volatility % = 100% – Retention %, Figure 1). These losses are important when considering models for impact of F on glass properties if target glass compositions are used. Of equal or more importance is the volatility from melter processes.

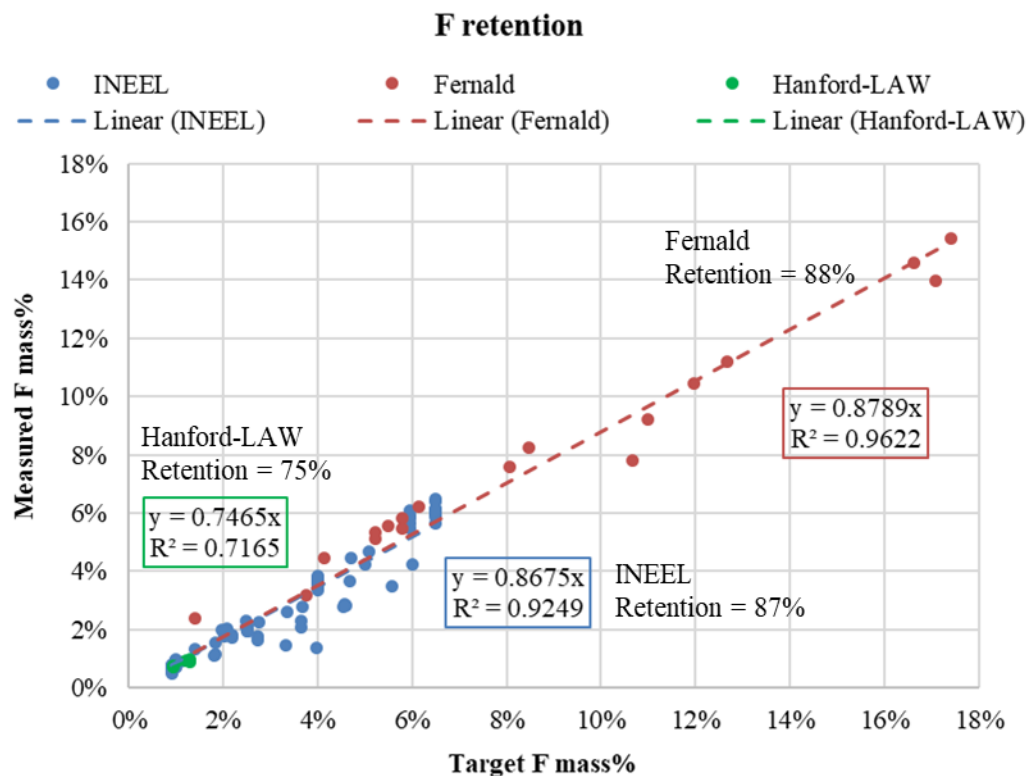


Figure 1. Fluorine Retention of INEEL, Fernald, and Hanford-LAW Glasses. Retention % is estimated by linear fitting of target and measured F mass%.

WTP melter volatility values were reported by Petkus and Vienna (2012) for LAW glasses and Nelson (2013) for HLW glasses. Both documents reported a log-normal distribution of F decontamination factors (DFs)³. They were unable to resolve a quantitative relationship between melter DF and melt composition or melter operating parameters. The median ln[DF]s are 1.3 for HLW and 1.5 for LAW. These translate roughly to retentions of 73% (for HLW) and 77% (for LAW) under normal melter operating conditions. By comparison, Deng (2018) reports constant retentions of 19% and 47% for HLW and LAW melters, respectively. Evaluating the discrepancies is beyond the scope of this study. The remaining fraction of F (100% – Retention % in melter operation) will report to the off-gas stream, primarily as a particulate salt. Most of this remaining fraction would be captured in 1) the combined transfer line between the melter and the submerged bed scrubber (SBS) (DF not modeled by Deng 2018), 2) the SBS (98% retention; Deng 2018), 3) the wet electrostatic precipitator (WESP) (50% retention; Deng 2018), 4) the high-efficiency

³ Decontamination factor (DF) is the ratio of one component's input to output in melter operation, $DF = 1/(1-100\%/Retention\%)$.

mist eliminator (HEME) (87% retention; Deng 2018), and 5) the high-efficiency particulate air filter (HEPA) (99.99994 % retention; Deng 2018). Assuming Deng (2018) split factors from melter through HEME, one part in 1077 of melter feed will pass through to the HEPA and secondary off-gas treatment system. The wet fractions (SBS, WESP, and HEME) will capture most of the F for recycle back to melter feed. There is a potential that the transfer line would be flushed back to the melter to return the largest (although not modeled by Deng 2018) fraction of the volatile F back to the melter. The small fraction (modeled to be less than 1:1000) of F will report to the secondary off-gas system, which will further treat the stream and remove F.

Carroll and Shafazand (2019) evaluated the impacts of waste feed delivery on HLW operations under a Direct Feed High-Level Waste (DFHLW) flowsheet scenario. This assessment included, among other issues, the potential for elevated F concentrations. They concluded that the increased flowrate of F in DFHLW feeds compared to baseline feeds may shorten the lives of the guard-bed for the carbon bed (current 1-year life), the silver mordenite (AgZ) column (current 19-year life), and potentially the catalyst for the selective catalytic oxidizer (SCO) and selective catalytic reducer (SCR) (current 3-year life). However, the correlation between F concentration and bed lives is based on many preliminary assumptions; most significant among them is the secondary off-gas system F mass flowrate. A more detailed evaluation of the flowrates and bed life estimates should be performed to draw more definitive estimates of F effects on the service lives of the secondary off-gas system components. Once those estimates are available, a cost-benefit analysis can be applied to determine the relative impacts of 1) reducing off-gas component service life, 2) implementing more-stringent HLW washing capabilities and the associated water handling, and/or 3) reducing HLW loading in glass for high-F waste streams.

4.2 PCT Response of Quenched and Canister Centerline Cooled Samples

As stated earlier, PCT response is a critical property constraint. Crystallization can adversely affect PCT response of glasses (Kim et al. 1995). When the glass melt is poured from the melter into stainless steel canisters, a portion of the glass cast into canisters is quenched on the canister walls, and another portion of glass, near the canister centerline, cools slowly. The temperature history of the canister centerline cooled (CCC) glasses is most favorable for crystalline phases to form. CCC heat treatment is a procedure of slowly cooling a glass melt in a crucible with a controlled cooling profile to simulate the temperature history of the glasses cooled at the canister centerline. The resultant CCC heat treatment samples are the CCC glasses that have been used for durability tests.

PCT responses were reported on 208 quenched glasses, and both quenched and CCC sample PCT responses for 51 glasses from Pittman et al. (2000) and Riley et al. (2001). No clear correlation between normalized PCT releases (g/m^2) of B, Na, or Li and F mass% in glasses was identified. The PCT responses for the sub-dataset of 50 CCC glasses were categorized into three groups after removing one glass (DP-12) with abnormal behavior after CCC, as shown in Table 3. The excluded sample, DP-12, had crystals in the quenched sample and no crystal phases after CCC, which is potentially an error. It should be noted that most glasses in this sub-dataset also contained relatively high ZrO_2 concentrations of 4 to 8 mass% (as will be the case for most high-F Hanford HLW glasses, e.g., neutralized cladding removal waste; Reynolds et al. 2014).

Among the 50 glasses, 27 were amorphous for the quenched samples; of the other 23 glasses, ZrO_2 -containing crystal phases were found in most of them and F-containing crystals were in several samples. After the CCC heat treatment, only 10 glasses remained amorphous. Most of the samples that crystallized after CCC (i.e., Groups B and C), formed F-containing phases; only four CCC samples had non-F crystal phases.

A high amount of crystallization has the potential to impact PCT performance. Figure 2, Figure 3, and Figure 4, respectively, show comparison plots of normalized PCT releases of B, Na, and Li between quenched and CCC glass samples. As shown in the figures, most glasses did not show much difference between quenched and CCC samples; however, there were two glasses with a significant B release decrease after CCC heat treatment (bottom right in Figure 2). The cause of this unusual behavior is not known, but it is possibly an experiment error. As expected, Group A showed little difference between quenched and CCC glasses; on the other hand, some Group B and Group C glasses showed significant increases in PCT responses after CCC heat treatment. The increase in PCT response after CCC heat treatment can be attributed to nepheline formation for most cases, which is known to increase PCT releases (Kim et al. 1995). However, there were two glasses with increased PCT response that cannot be attributed to nepheline phase formation after CCC heat treatment (red dashed circles in Figure 2), which was possibly caused by F-containing crystal phases. These glasses were 1) DZr-CV-2 with 20.4 mass% hiortdahlite, $(Ca,Na,Y)_3(Zr,Ti)Si_2O_7(F,O,OH)_2$, 3.5 mass% nepheline, and 13.1 mass% sodium aluminum silicate sulfide after CCC; and 2) DZr-CV-5 with 1.7 mass% fluorapatite $Ca_5(PO_4)_3F$ after CCC heat treatment.

In summary, comparison between quenched and CCC samples shows that formation of crystal phases may increase PCT responses. Some such cases are related to nepheline formation, which removes more glass formers (SiO_2 and Al_2O_3) than modifiers (Na_2O) from the amorphous phase. In general, formation of high- SiO_2 , Al_2O_3 , or ZrO_2 crystal phases during CCC heat treatment could have a similar effect of increasing PCT responses. Many glasses containing small amounts of F-containing crystals do not show changes of PCT response after CCC heat treatment. More importantly, the correlation between the F-containing crystal phases and the F concentration in the initial glasses is undetermined.

Table 3. Crystallinity Data Categories for PCT Response Comparison between Quenched and CCC Samples

Group	Description	Number of Glasses
A	Crystal-free in both quenched and CCC samples	10
B	Crystal phases in both quenched and CCC samples	23
C	Crystal-free in quenched samples and crystal phases found in CCC samples	17
Total		50

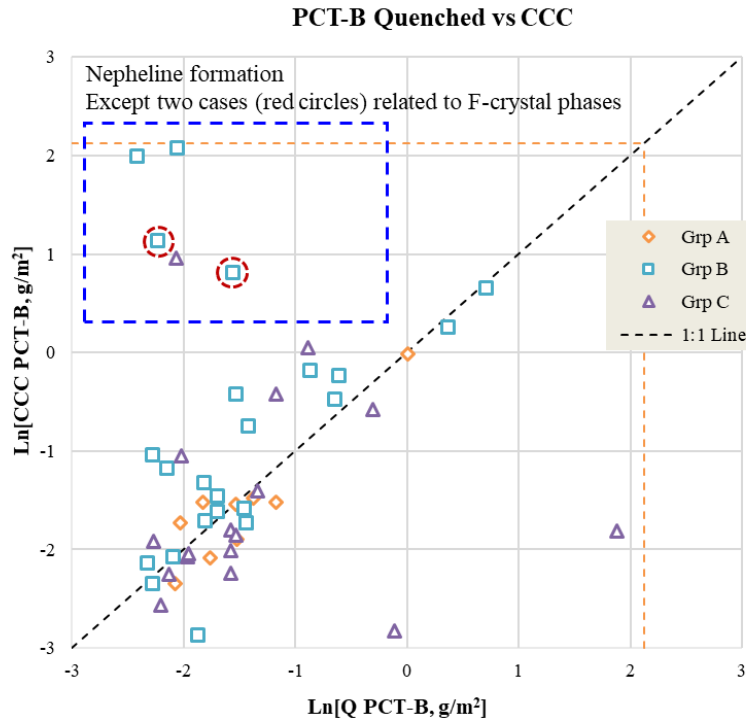


Figure 2. Comparison of the Natural Log of Normalized PCT Release for B between Quenched and CCC Samples. Orange dashed lines mark the WTP contract limit of PCT release, 8.35 g/m^2 (Vienna et al. 2016)

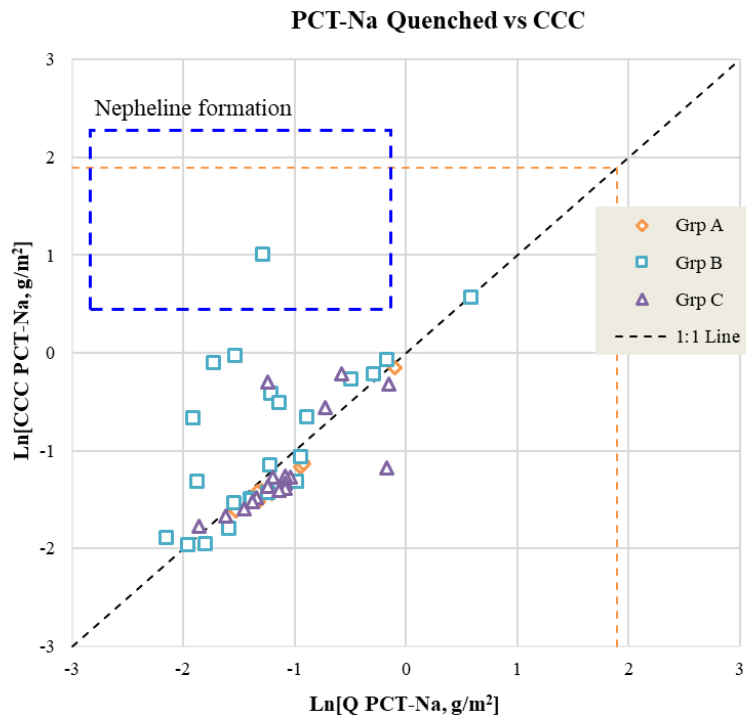


Figure 3. Comparison of the Natural Log of Normalized PCT Release Na between Quenched and CCC Samples. Orange dashed lines mark the WTP contract limit of PCT release, 6.675 g/m^2 (Vienna et al. 2016)

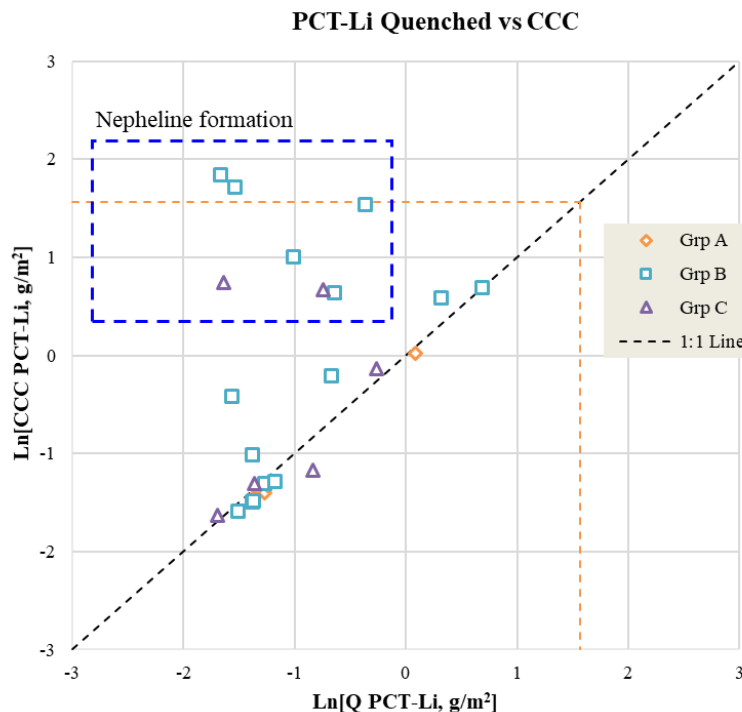


Figure 4. Comparison of the Natural Log of Normalized PCT Release for Li between Quenched and CCC Samples. Orange dashed lines mark the WTP contract limit of PCT release, 4.785 g/m^2 (Vienna et al. 2016)

4.3 Liquidus Temperature

Liquidus temperature (T_L) was measured on 65 glasses in this dataset of 239 glasses (Table 2), and 14 of them were over $1000 \text{ }^\circ\text{C}$, which has traditionally been used as a melter processability constraint (Perez et al. 2001; Kim and Vienna 2002). However, the primary crystal phases in these glasses with a liquidus temperature above $1000 \text{ }^\circ\text{C}$ were all Zr-containing phases; that is, all glasses with a F-containing phase as a primary phase had a liquidus temperature below $1000 \text{ }^\circ\text{C}$. The results suggest no basis for a T_L -related limit for F.

4.4 Glass Melt Viscosity

Previous studies on various glass systems have mostly demonstrated that glass melt viscosity decreases with increasing F concentration (Fu et al. 1994; Vienna et al. 2009, 2013, 2016). Figure 5 plots the measured and model-estimated viscosity at $1150 \text{ }^\circ\text{C}$ (fitted by Arrhenius equation from a measured temperature-viscosity curve) for 100 glasses from the collected dataset of 239 glasses (Table 2). The model used for this plot is from Vienna et al. (2016) and was developed from glasses with a F range of 0 to 2.5 mass%; within the range, most glasses contained $< 0.90 \text{ mass\% F}$. The measured viscosity values were from glasses with $\geq 0.90 \text{ mass\% F}$. Figure 5 shows a reasonable predictability of viscosity for the glasses with higher F concentration. Even for the Fernald glasses, with more than half of the glasses containing $> 8.0 \text{ mass\% F}$, which is far beyond the F range of the model, the model estimations match the trend of the experimental data with a modest offset. The impact of F on viscosity, as indicated by several models (Table 1), is assumed to be the same in a much wider concentration range of F although the HLW glass models were developed for glasses containing 0 – 2.5 mass% F. Therefore, the effect of F on viscosity obtained from glasses with low-F concentrations (i.e., $< 2.5 \text{ mass\%}$; Vienna et al. 2016) can

reasonably be extrapolated to high-F glasses, although before processing high-F glasses, the glass melt viscosity models will be updated to be inclusive of such F concentrations.

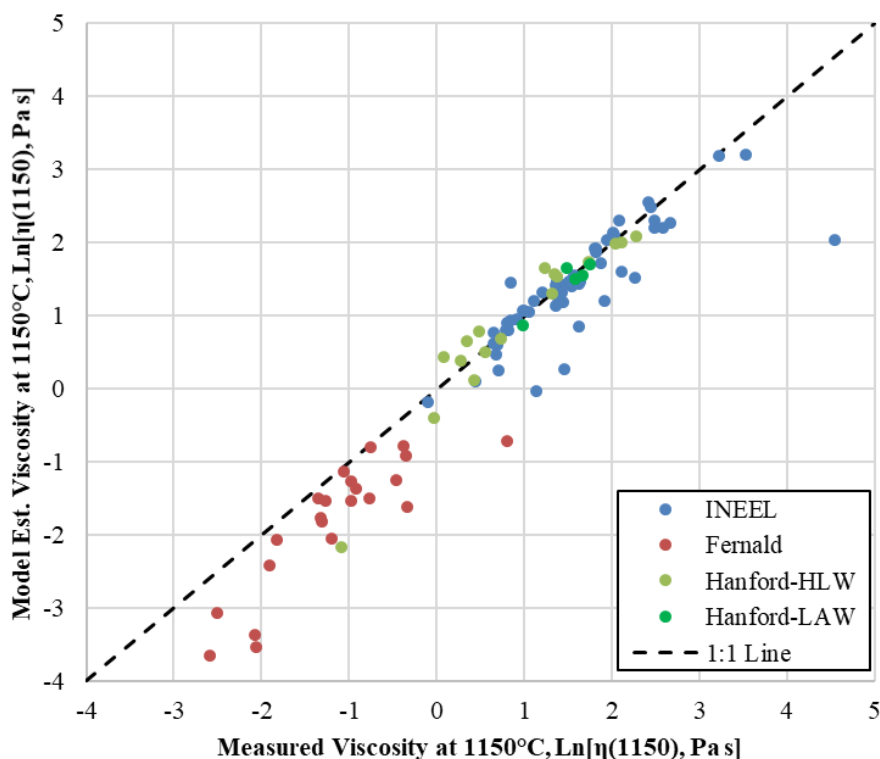


Figure 5. Viscosity at 1150 °C, $\eta(1150)$, Measured and Model (Vienna et al. 2016) Estimated.

4.5 Crystallinity and Fluorine Tolerance

The solubility of F in glasses, i.e., the maximum F mass% in the glasses without forming F-containing crystal phases, strongly depends on glass composition. Although there are some glasses with F solubility over 8 to 10 mass% according to Carroll and Webster (1994) and Langowski (1996), the probability of forming F-containing crystal phases, sometimes in the form of “undissolved chunks” in the quenched glass, is significantly higher when the F concentration is over 8 mass%. However, there was no quantitative crystallinity information given for the 14 glasses with over 8 mass% F in this study (Table 2). Therefore, 225 glasses, with F concentrations between 0.90 and 8.00 mass%, were evaluated to determine the maximum F concentration that can be processed without potential issues (“F tolerance”).

Currently, there are no known crystallization issues in vitrifying high-F wastes reported in the open literature. One of the main reasons could be because most tests have been conducted at crucible scale only. Given the lack of criteria for F tolerance, the use of crystallinity in as-prepared crucible-scale glasses was selected as a preliminary criterion. In Table 4, the 225 glasses are categorized as pass, fail, unknown, or no data, with the latter category containing 7 glasses without crystallinity information. If a quenched glass has no crystal phase or has crystal phases but the F-containing crystal phases do not sum up to more than 5 vol% or mass%, it is placed in the “pass” category; a “fail” designation represents an ad hoc constraint of > 5 vol% or mass% of F-containing phase. Of the 225 glasses, 5 are considered to “fail”, with more than 5 vol% or mass% of F-containing crystal phases. Furthermore, the two glasses discussed before with increased PCT response after CCC heat treatment, DZr-CV-2 and DZr-CV-5, were also included in the “fail” category. The “unknown” category represents the cases in which crystallization of F-containing phase was reported but without quantitative crystallinity information. Figure 6, Figure 7, and

Figure 8, respectively, show the F tolerance groupings in plots of F mass% versus CaO mass%, NaLiK ($\text{Na}_2\text{O} + 2.07\text{Li}_2\text{O} + 0.66\text{K}_2\text{O}$ in mass%), and AlZr ($\text{Al}_2\text{O}_3 + \text{ZrO}_2$ in mass%), which are believed to have potential effects on crystallization of F-containing phases. Based on these plots, 4.5 mass% F was selected visually as a reasonable preliminary F tolerance. There was no clear correlation between F tolerance and concentration of calcium oxide, total alkali oxides, and aluminum oxide plus zirconium oxide.

Table 4. Crystallinity Data Categories for the Quenched Glasses

Category	Description	Number of Glasses
Pass	Crystal-free, or F-containing crystal phases < 5 vol% (mass%)	191
Fail	F-containing crystal phases > 5 vol% (mass%) or F-containing crystal caused significant increase of PCT response after CCC	7
Unknown	Other cases with formation of crystal phases but no quantitative data for the crystal phases	20
No data	No data to analyze, excluded	7
Total		225

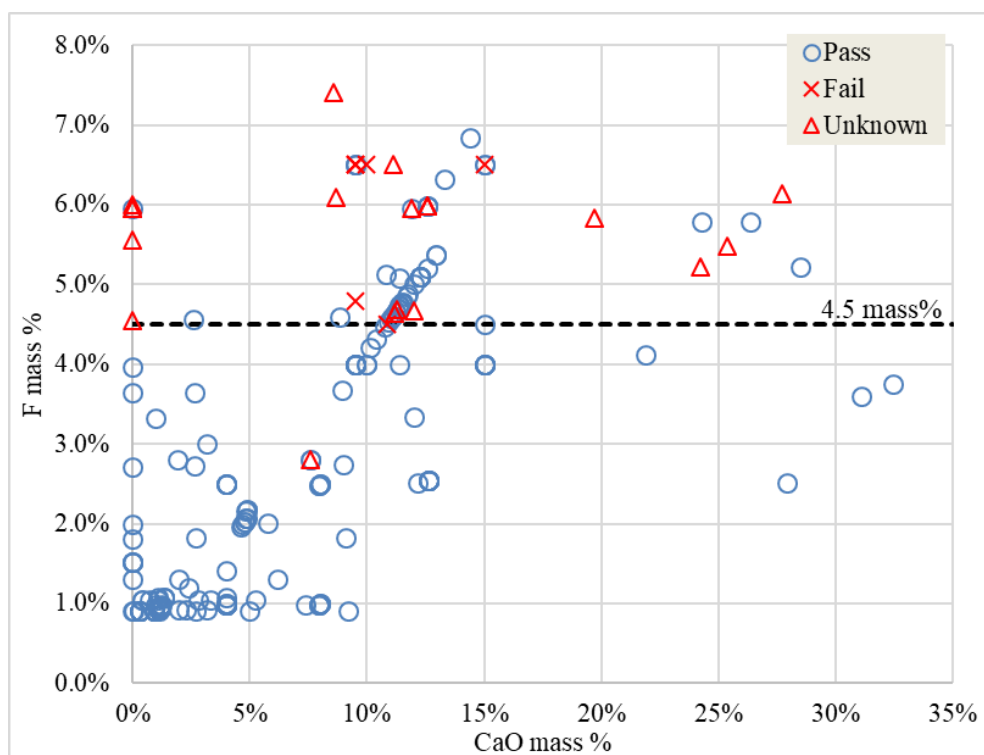


Figure 6. F Tolerance Grouping Plot. Pass/Fail/Unknown Categories Plotted with Concentration (mass%) of CaO vs. F.

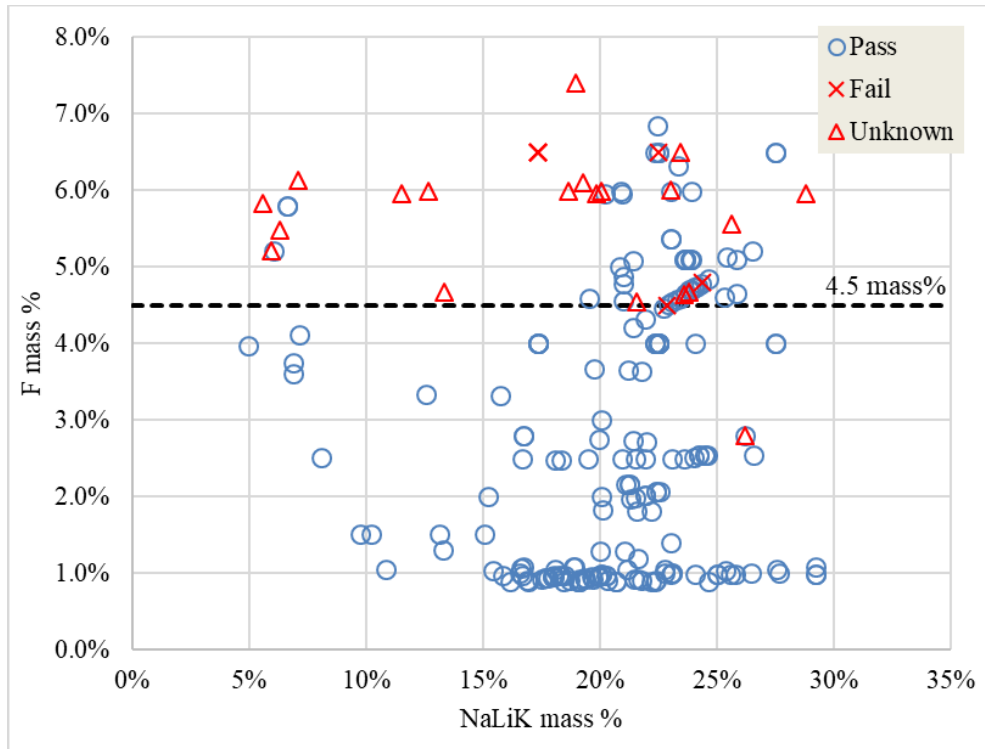


Figure 7. F Tolerance Grouping Plot. Pass/Fail/Unknown Categories Plotted with Concentration (mass%) of NaLiK ($\text{Na}_2\text{O} + 2.07 \text{Li}_2\text{O} + 0.66 \text{K}_2\text{O}$) vs. F.

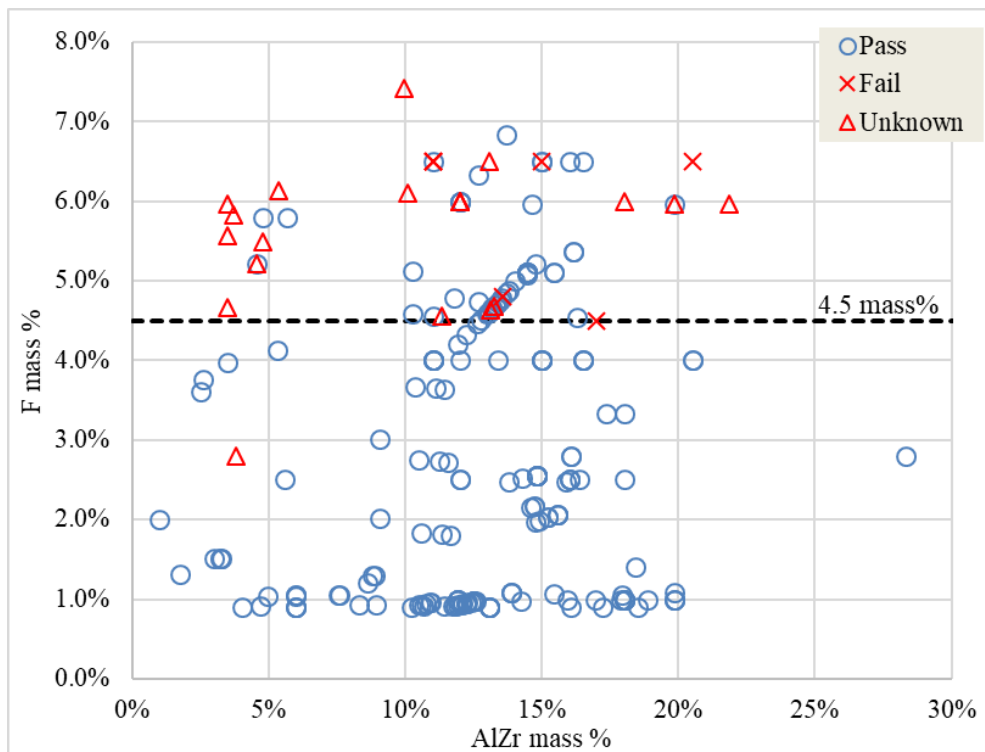


Figure 8. F Tolerance Grouping Plot. Pass/Fail/Unknown Categories Plotted with Concentration (mass%) of AlZr ($\text{Al}_2\text{O}_3 + \text{ZrO}_2$) vs. F.

5.0 Conclusions and Recommendations

The objective of this research was to determine the basis for a fluorine limit in Hanford HLW glass formulations. A dataset of 239 waste glasses was compiled, including composition and properties of waste glasses with ≥ 0.90 mass% of F (target). In this dataset, 56 glasses were designed for Hanford HLW with F concentrations of up to 2.8 mass%, 7 glasses were designed for Hanford LAW with up to 3.01 mass% F, and the others were 149 INEEL glasses and 27 Fernald glasses, with many over 2.5 mass% F (max. 17.42 mass%).

As-quenched and post-CCC crystallinity of F-containing phases and PCT response correlations were used to make pass/fail judgements. F volatility, liquidus temperature (T_L), and glass melt viscosity data were also examined, but revealed no clear basis for limiting F-loading in glass. By this effort, the F tolerance for waste glass formulation has been estimated as 4.5 mass% F based mainly on crystallization response and, to a lesser extent, on PCT response after CCC heat treatment.

Volatility of F and its downstream impacts on WTP component life in the HLW and LAW melter off-gas systems may potentially pose a concern. However, the data available were insufficient to form a F-concentration limit like that suggested for crystallinity and PCT response of CCC samples. The impacts of F in the WTP melter off-gas treatment system should be investigated, including the service life of melter-to-SBS transfer line, guard-bed to the carbon bed, AgZ, and SCO/SCR catalysts. These studies would require more-detailed system DFs and cost-benefit trade studies comparing component life to high-F waste mitigation strategies. Likewise, corrosion of glass contact materials in the melter (Inconel 690, Monofrax K-3, and Monofrax E) might be influenced by higher F concentrations in the melt (Min'ko and Nartsev 2007). However, no direct evidence was found to support or refute that hypothesis. For the candidate high-Cr K-3 refractory material for waste glass melters, test data are limited to LAW glasses and no data are available for glasses with over 0.49 mass% F (Muller et al. 2018). It is recommended that K-3 and Inconel 690 corrosion tests be conducted for high-F glass melts to address this potential issue.

Future HLW formulation should consider the $F \leq 4.5$ mass% limit as a relatively conservative value. More testing on glasses with high F concentrations (over 0.9 mass %) specifically designed for Hanford HLW feeds will be required to refine the F-concentration limits.

6.0 References

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Appendix A – Fu et al. 1993 Report “Vitrification Development Studies for OU1 Wastes”

A report by GTS Duratek Inc. and Vitreous State Laboratory, The Catholic University of America was published in 1993. The full report is not available. The cover page and pages containing glass IDs and compositions of 18 glasses are shown below.

**Vitrification Development Studies
— for OU1 Wastes**

**FINAL REPORT
Contract No. PO 917844-00**

Prepared by

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Washington, DC 20064**

for

**The Fernald Environmental Management Project
Fernald Environmental Restoration Management Corporation
P.O. Box 398704
Cincinnati, Ohio 45239-8704**

April, 1993

GTS Duratek
PO 917844-00

Vitrification Development
Studies for OUI Wastes

Table 4.3 Analyzed and Calculated Compositions (wt%) of FEMP Crucible Melt Glasses
(analysis is from DCP results with the assumption that all of the Mg is combined with fluoride, calculated is batch composition)

	F5-5	F5-5	F5-7	F5-7	F5-8	F5-8	F5-10	F5-11	F5-11	F5-12	F5-12	F5-13	F5-13
Components	(calc)	(anal)	(calc)	(anal)	(calc)	(anal)	(calc)	(calc)	(anal)	(calc)	(anal)	(calc)	(anal)
Al ₂ O ₃	3.9	5.0	4.0	3.7	3.70	3.7	4.3	3.8	4.3	2.1	2.3	5.7	5.3
AlF ₃	0.0	NA	NA	NA	0.0	NA	NA	0.0	NA	0.0	NA	0.0	NA
B ₂ O ₃	10.1	7.6	6.2	6.1	12.0	11.5	6.2	12.2	13.4	8.3	7.9	7.2	6.7
BaO	0.7	0.7	0.9	0.8	0.71	0.8	0.8	0.8	0.8	1.1	1.0	1.1	1.0
CaO	23.5	22.7	26.5	24.4	22.4	22.8	25.8	24.4	24.2	23.5	21.8	23.5	21.2
Fe ₂ O ₃	2.6	3.0	2.9	3.2	2.5	2.9	2.9	2.7	3.8	2.2	2.9	2.2	2.6
K ₂ O	0.9	0.9	0.9	1.5	0.9	1.3	1.0	0.9	0.0	0.4	0.5	0.4	0.5
MgO	2.1	*	2.1	*	2.1	*	2.4	2.1	*	0.7	*	0.7	*
MgF ₂	15.7	20.6	19.2	25.1	14.9	21.5	17.2	17.0	21.5	22.2	28.1	22.2	28.4
Na ₂ O	8.6	8.9	5.9	5.7	10.6	10.8	5.9	5.8	5.7	5.5	5.1	3.6	3.1
NaF	0.0	NA	0.0	NA	0.0	NA	0	0.0	NA	0	NA	0.0	NA
SiO ₂	28.5	28.4	29.15	26.20	27.1	24.1	31.3	28.1	25.5	32.0	28.7	32.0	38.3
U ₃ O ₈	0.3	0.4	0.3	0.4	0.3	0.5	0.3	0.3	NA	0.4	NA	0.4	NA

* Assumes that all of the Mg is combined with fluoride rather than oxygen
NA = not analyzed

GTS Duratek
PO 917844-00

Vitrification Development
Studies for OUI Wastes

Table 4.3 (cont.)

Components	F5-32	F5-32	F5-33	F5-33	F5-33	F5-33	F5-34	F5-34	F5-34	F5-35	F5-35	F5-36	F5-36
	(calc)	(anal)	(calc)	(anal)	(anal)	(anal)	(calc)	(anal)	(anal)	(calc)	(anal)	(cal)	(anal)
Al ₂ O ₃	7.7	7.8	7.7	6.9	6.9	6.1	7.5	6.6	7.4	7.6	7.4	6.6	6.9
AlF ₃	0.0	NA	0.0	NA	NA	NA	0.0	NA	NA	0.0	NA	0.0	NA
B ₂ O ₃	10.2	10.6	10.4	10.1	10.0	9.3	10.4	8.9	10.1	10.5	10.2	9.3	8.7
BaO	0.9	1.0	0.9	0.9	0.9	0.8	0.8	0.8	0.9	0.9	0.9	0.9	0.9
CaO	20.3	20.2	19.0	18.1	16.8	15.1	18.8	15.5	18.1	19.8	19.0	19.8	19.0
Fe ₂ O ₃	2.6	3.3	2.8	3.2	3.4	2.8	3.6	3.7	4.1	3.7	4.3	5.4	5.7
K ₂ O	0.1	0.1	0.3	NA	0.4	0.2	0.7	1.1	NA	0.7	NA	0.4	NA
MgO	0.0	*	0.3	*	*	*	0.5	*	*	0.5	*	0.8	*
MgF ₂	18.3	21.5	17.9	21.1	20.1	18.4	17.5	18.4	21.4	17.7	21.2	18.1	20.5
Na ₂ O	0.4	6.3	8.5	8.6	8.9	7.8	8.0	7.2	7.9	6.2	6.1	7.5	7.4
NaF	7.9	NA	0.0	NA	NA	NA	0.0	NA	NA	0.0	NA	0.0	NA
SiO ₂	31.2	29.9	31.7	28.3	32.1	27.9	31.3	27.3	28.1	31.8	27.9	30.5	27.8
U ₃ O ₈	0.3	NA	0.3	NA	NA	NA	0.3	NA	NA	0.3	NA	0.3	NA

Components	F5-37	F5-37	F5-37B	F5-38	F5-39	F5-39	F5-40	F5-40	F5-41	F5-41
	(calc)	(anal)	(anal)	(cal)	(cal)	(anal)	(calc)	(anal)	(calc)	(anal)
Al ₂ O ₃	7.8	8.2	2.9	7.8	7.6	7.2	7.3	7.7	3.2	3.6
AlF ₃	0.0	NA	NA	0.0	0.0	NA	0.0	NA	0.0	NA
B ₂ O ₃	9.3	9.6	0.1	9.3	8.7	7.5	9.2	8.7	8.5	8.1
BaO	0.9	0.9	0.0	0.9	0.8	0.8	0.8	1.0	0.9	1.1
CaO	20.0	19.9	0.3	20.0	19.0	17.9	18.5	16.7	24.2	20.1
Fe ₂ O ₃	5.1	4.3	0.4	5.05	4.3	4.6	4.3	5.5	2.5	3.0
K ₂ O	0.8	NA	0.2	0.84	0.8	0.8	0.7	0.9	0.7	0.7
MgO	0.9	*	*	0.89	0.8	*	0.8	*	1.6	*
MgF ₂	18.1	23.4	0.3	18.08	17.2	20.5	16.9	20.3	19.1	23.7
Na ₂ O	5.3	5.5	0.5	5.30	0.6	7.9	0.6	7.9	0.7	4.7
NaF	0.0	NA	NA	0.0	9.2	NA	11.1	NA	6.0	NA
SiO ₂	30.8	29.5	7.6	30.81	29.8	28.1	28.8	24.0	31.6	26.2
U ₃ O ₈	0.3	NA	NA	0.3	0.3	0.3	0.3	0.3	0.3	0.3

* Assumes that all of the Mg is combined with fluoride rather than oxygen; NA = not analyzed

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