

Improved Alumina Loading in High-Level Waste Glasses - 8460

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ABSTRACT

Recent tank retrieval, blending, and treatment strategies at both the Savannah River Site (SRS) and Hanford have identified increased amounts of high- Al_2O_3 waste streams that are scheduled to be processed through their respective high-level waste (HLW) vitrification facilities. It is well known that the addition of small amounts of Al_2O_3 to borosilicate glasses generally enhances the durability of the waste glasses. However, at higher Al_2O_3 concentrations nepheline ($\text{NaAlSi}_3\text{O}_8$) formation can result in a severe deterioration of the chemical durability of the slowly cooled glass near the center of the canister. Additionally, higher concentrations of Al_2O_3 generally increase the liquidus temperature of the melt and decrease the processing rate. Pacific Northwest National Laboratory (PNNL), Savannah River National Laboratory (SRNL), and Khlopin Radium Institute (KRI) are jointly performing laboratory and scaled-melter tests, through US Department of Energy, EM-21 Office of Waste Processing program, to develop glass formulations with increased Al_2O_3 concentrations. These glasses are formulated for specific DOE waste compositions at Hanford and Savannah River Site. The objectives are to avoid nepheline formation while maintaining or meeting waste loading and/or waste throughput expectations as well as satisfying critical process and product performance related constraints such as viscosity, liquidus temperature, and glass durability. This paper summarizes the results of recent tests of simulated Hanford HLW glasses containing up to 26 wt% Al_2O_3 in glass.

INTRODUCTION

The U.S. Department of Energy (DOE) is currently processing (or planning to process) high-level waste (HLW) through Joule-heated melters at the Savannah River Site (SRS) and Hanford. The process combines the HLW sludge with a pre-fritted glass or mineral additives which are subsequently melted. The molten glass is poured into stainless steel canisters to produce the final

waste form. Both process and product performance issues must be addressed. The product performance issue relates to the durability of the glass waste form. Process related issues (e.g., liquidus temperature, viscosity, electrical conductivity, and melting rate) ultimately dictate the efficiency and effectiveness of the melter operation.

Recent tank retrieval and blending strategies at both the Savannah River Site (SRS) [1] and Hanford [2] have identified increased amounts of high- Al_2O_3 waste streams that are scheduled to be processed through their respective high-level waste (HLW) vitrification facilities. Current Hanford projections suggest that the Al_2O_3 concentrations in sludge could be as high as 80 wt% in waste. The US DOE's Office of Environmental Management (EM) is addressing the issues related to the high- Al_2O_3 waste streams within its International Program to support DOE-EM site cleanup needs [3].

The Al_2O_3 has an impact on three main constraints in glass formulation: the increases of Al_2O_3 in glass (1) promotes the crystallization of aluminum-containing crystals during slow cooling in the canister, which can decrease glass durability, (2) increases the liquidus temperature of spinel crystals that can interfere with melter operation, (3) and has a potential to decrease feed processing rate due to refractory property of Al_2O_3 , i.e. slow dissolution into the glass forming melt. To address these issues, crucible scale testing is initially performed to develop and characterize glass compositions to satisfy the first two constraints, i.e., crystallization during canister cooling and liquidus temperature of spinel, while meeting other property requirements such as viscosity, electrical conductivity, and glass durability. Then, the processability of the feed or processing rate is tested and verified on a larger scale through melter runs. This paper presents the results of crucible scale testing of high- Al_2O_3 glass formulations for Hanford wastes and scale-up melter testing with a selected glass formulation. The present study focuses only on the Hanford wastes although the results of this study can be applied to the development of high- Al_2O_3 loaded glasses containing SRS wastes.

GLASS FORMULATION STRATEGY

It is well known that the addition of small amounts of Al_2O_3 to borosilicate glasses generally enhances the durability of the waste glasses [4]. However, crystallization of the slowly cooled glass near the center of the canister can result in a severe deterioration of glass chemical durability [5,6]. As illustrated in Fig. 1 [5], the formation of aluminum-containing silicate crystals, such as $\text{NaAlSi}_3\text{O}_8$ (nepheline) and $\text{LiAlSi}_2\text{O}_6$, and crystalline SiO_2 in canister centerline cooling (CCC) treated glasses can strongly increase the glass release by product consistency test (PCT). The primary driver for the reduction in glass durability is the fact that these crystals removes the glass forming oxides (Al_2O_3 and SiO_2) that increase glass durability from the continuous glass phase. Therefore, formation of these crystals produces an Al_2O_3 and/or SiO_2 deficient continuous glass matrix (relative to the same glass composition without any crystals) which reduces the durability of the final product. The magnitude of the durability reduction ultimately depends on the extent of crystallization (vol% of crystals) and on the initial glass composition. Some types of crystals do not have a significant effect on glass durability because their formation does not affect the durability of continuous glass phase (e.g., acmite and olivine in Fig. 1). It has long been known that the formation of spinel crystals, $(\text{Fe}^{2+}, \text{Ni})(\text{Fe}^{3+}, \text{Cr}, \text{Al})_2\text{O}_4$, does not affect the PCT durability [7].

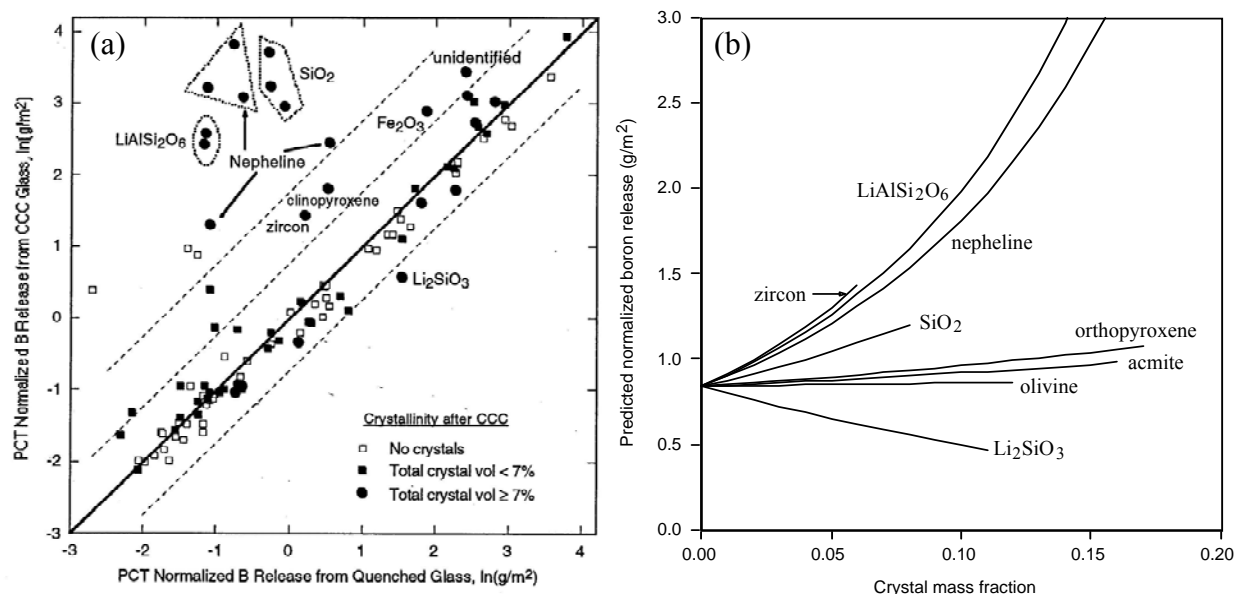


Fig. 1. Effect of crystals on PCT durability [5]: (a) comparison of PCT normalized B release between CCC treated glasses with varying content of crystals and quenched glasses without crystals, (b) predicted PCT normalized B release as a function of crystal content

Among crystals that have a strong effect on PCT, nepheline is the primary phase that forms in the waste forms for HLW dominated by sodium aluminoborosilicate glasses. To formulate glasses without nepheline precipitation after CCC, Li et al [8] suggested a rule that durable glasses with

$$\frac{g_{\text{SiO}_2}}{g_{\text{SiO}_2} + g_{\text{Na}_2\text{O}} + g_{\text{Al}_2\text{O}_3}} \geq 0.62 \quad (\text{Eq. 1})$$

where g_i is the mass fraction of the i^{th} oxide in glass, do not precipitate nepheline as their primary phase. This rule was obtained through evaluation of over 200 CCC treated HLW glasses by comparing their $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ submixtures to the nepheline primary phase field defined by the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ ternary system. The oxide mass ratio given in Eq. 1 has been referred to as the “nepheline discriminator”.

This rule has been proven appropriate for screening out glasses with potential precipitation of nepheline for glasses within certain composition ranges, e.g., recent SRS glasses [9]. However, because this rule is based solely on phase equilibrium without consideration of crystallization kinetics, the results may be too restrictive. More specifically, this rule has a potential of screening out the glasses that do not precipitate nepheline during HLW CCC treatment due to slow crystallization although their submixtures are within the nepheline primary phase field based on the current discriminator function. This restrictive rule is one of the reasons the maximum concentrations of Al_2O_3 in glasses have generally been limited to a maximum in the range of 11 to 17 wt% of the glass.

The glass composition would also affect the crystallization kinetics (for example, Li et al. [8] noted that boron oxide significantly lowers the tendency to precipitate nepheline on slow cooling), but there have been no tools developed to integrate other component effects. As Al_2O_3 in glass increases it becomes increasingly difficult or impossible to formulate glasses with a nepheline discriminator value higher than 0.62 while satisfying other property requirements. Therefore based on the findings of Li et al. [8], the strategy to develop high- Al_2O_3 glasses in this study was to formulate compositions that although were predicted to be within the nepheline primary phase field as defined by the current discriminator do not precipitate nepheline within the cooling rate represented by HLW CCC. Specifically, all of the glasses evaluated in this study had nepheline discriminator values less than 0.62 with the goal of demonstrating the ability to suppress nepheline formation through strategic compositional development.

FORMULATION AND SELECTION OF MELTER TEST GLASS

The composition of high- Al_2O_3 waste used in this study is given in Table I in terms of wt% of oxides and halogen. The components considered in the additive (or materials used for the frit) were B_2O_3 , CaO , K_2O , MgO , Na_2O , Li_2O , P_2O_5 , and SiO_2 . The maximum loading of this waste in glass based on the typical maximum of 17 wt% Al_2O_3 loading is 31.9 wt%.

Table I. Composition of High- Al_2O_3 Waste in Oxides/Halogen

Component	Wt%	Component	Wt%
Al_2O_3	53.27	MgO	0.26
B_2O_3	0.42	Na_2O	7.96
BaO	0.12	NiO	0.89
Bi_2O_3	2.54	P_2O_5	2.34
CaO	2.39	PbO	0.91
CdO	0.05	SO_3	0.44
Cr_2O_3	1.16	SiO_2	10.88
F	1.48	TiO_2	0.02
Fe_2O_3	13.11	ZnO	0.18
K_2O	0.31	ZrO_2	0.88
Li_2O	0.38	SUM	100.00

Glass development efforts in this study were based on an iterative process. That is, initially a small set of glasses were formulated and tested with their results applied to the next set of glasses. This process was repeated until formulations meeting all of the property acceptance criteria were identified. The glass-composition property models from literatures [10,11] were used to roughly estimate the properties, such as viscosity, electrical conductivity, and PCT normalized releases. These model predictions were used for rough guidance given the compositions being tested were outside the validity range for most existing models. The criteria for acceptable properties in glass formulation were:

- No crystallization of nepheline after CCC treatment
- Spinel after heat treatment for 24 hr at 950°C : 1 vol% or less (to avoid a potential for spinel accumulation during melter operation)
- PCT normalized releases of quenched (Q) and CCC treated glasses less than environmental assessment (EA) glass (PCT-B: 16.7 g/L, PCT-Li: 9.6 g/L, PCT-Na: 13.3 g) [12]

- Viscosity at 1150°C: of 2 – 10 Pas, [13]
- Electrical conductivity at 1150°C: 10 – 100 S/m [13]

Eighteen compositions were formulated and tested with Al₂O₃ loading ranging from 25 to 27 wt% in glass corresponding to 47 to 50 wt% waste loading. Table II summarizes the glass composition of selected glasses and their test results.

Table II. Target Glass Compositions (in Wt%) and Test Results for Selected High-Al₂O₃ Glasses

Glass ID	HAL-01	HAL-03	HAL-04	HAL-09	HAL-11	HAL-12	HAL-17	HAL-18
Al ₂ O ₃	26.63	26.63	26.63	25.00	25.00	25.00	25.89	25.89
B ₂ O ₃	20.21	20.21	25.21	15.00	15.00	18.00	16.14	18.00
BaO	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06
Bi ₂ O ₃	1.27	1.27	1.27	1.19	1.19	1.19	1.24	1.24
CaO	3.20	3.70	5.20	10.00	6.00	8.00	7.33	8.00
CdO	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Cr ₂ O ₃	0.58	0.58	0.58	0.54	0.54	0.54	0.56	0.56
F	1.24	0.74	1.74	0.70	0.70	0.70	0.72	0.72
Fe ₂ O ₃	6.55	6.55	6.55	6.15	6.15	6.15	6.37	6.37
K ₂ O	0.16	0.16	0.16	0.15	4.00	0.15	2.72	2.72
Li ₂ O	0.19	0.19	0.19	5.00	5.00	3.50	4.00	2.75
MgO	0.13	0.13	0.13	0.12	0.12	0.12	0.13	0.13
Na ₂ O	6.48	6.48	6.48	5.00	5.75	9.50	6.07	6.66
NiO	0.44	0.44	0.44	0.42	0.42	0.42	0.43	0.43
P ₂ O ₅	6.17	8.67	1.17	1.10	1.10	1.10	1.14	1.14
PbO	0.45	0.45	0.45	0.43	0.43	0.43	0.44	0.44
SO ₃	0.22	0.22	0.22	0.21	0.21	0.21	0.22	0.22
SiO ₂	25.44	22.94	22.94	28.40	27.80	24.41	26.00	24.12
TiO ₂	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
ZnO	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09
ZrO ₂	0.44	0.44	0.44	0.41	0.41	0.41	0.43	0.43
SUM	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
WL, wt%	50.0	50.0	50.0	46.9	46.9	46.9	48.6	48.6
SiO ₂ / (SiO ₂ +Al ₂ O ₃ +Na ₂ O)	0.43	0.41	0.41	0.49	0.47	0.41	0.45	0.43
Q glass, visual observation	High vol% crystals	High vol% crystals	High vol% crystals	Clear	Clear	Clear	Low vol% crystals	Low vol% crystals
CCC glass, XRD phase w/vol% ^b	-	-	-	Spinel	Spinel	Spinel, quartz	Spinel 2.4, fluor- apatite 1.2	Spinel 2.4, fluorapatite 1.5, hematite 0.4
950°C 24 h HT, XRD phase w/vol% ^b	-	-	-	Spinel 1.0	Spinel 1.1	LiFe ₅ O ₈ 0.7	Spinel 1.0	Spinel 1.2, fluorapatite 0.6
PCT-B, Q (g/L)	-	-	-	0.182	0.387	0.532	-	-
PCT-Li, Q (g/L)	-	-	-	0.282	0.498	0.675	-	-
PCT-Na, Q (g/L)	-	-	-	0.159	0.379	0.605	-	-
PCT-B, CCC (g/L)	-	-	-	0.597	0.215	0.604	-	-
PCT-Li, CCC (g/L)	-	-	-	0.414	0.311	0.554	-	-
PCT-Na, CCC (g/L)	-	-	-	0.198	0.205	0.372	-	-

^a Empty cells with “-” represent that the tests were not performed.

^b Quantitative XRD was performed for HAL-17 and 18 glasses only.

Note that all the glasses have nepheline discriminator well below 0.62, ranging from 0.41 to 0.49, suggesting that these glasses have Na₂O-Al₂O₃-SiO₂ submixtures within the nepheline primary phase field defined by the Na₂O-Al₂O₃-SiO₂ ternary system. Some glasses formed nepheline crystals in as-prepared (quenched) glasses and were not tested further. Several compositions at 25 and 26 wt% Al₂O₃ that do not form nepheline after CCC treatment were successfully formulated, HAL-9, 11, 12, 17, and 18 in Table II. Among these glasses, three glasses (HAL-9, 12, and 17) have the spinel at 1 vol% or less after 24 h heat treatment at 950°C. The glass with higher Al₂O₃ loading, HAL-17, was selected for scale-up melter testing. Table III shows the additive composition and chemicals used to make up the glass composition given in Table II mixed with the waste given in Table I.

Table III. Composition of Additive for HAL-17 Glass Selected for Melter Testing and Source Chemicals for Additives

Component	Wt%	Chemicals
B ₂ O ₃	31.0	H ₃ BO ₃
CaO	12.0	CaCO ₃
K ₂ O	5.0	K ₂ CO ₃
Li ₂ O	7.4	Li ₂ CO ₃
Na ₂ O	4.3	Na ₂ CO ₃
SiO ₂	40.3	SiO ₂
SUM	100.0	-

PCT was performed on selected glasses with 25 wt% Al₂O₃ (HAL-9, 11, and 12), which all passed the PCT requirements by more than an order of magnitude as shown in Table II. The PCT of HAL-17 glass is being tested but was not completed before submission of this paper. However, it is unlikely that PCT of HAL-17 glass would be much different from the glasses with 25 wt% Al₂O₃. In addition, crystals observed in this glass after CCC treatment (2.4 vol% spinel and 1.2 vol% fluorapatite) are not expected to affect the PCT performance.

The HAL-17 glass was tested for viscosity (η) and electrical conductivity (ϵ) to confirm that they are within the boundaries for adequate processing in the Joule heated melters operated at 1150°C of nominal temperature. Fig. 2 plots the η and ϵ as a function of temperature with the ranges of acceptable η and ϵ at 1150°C overlaid to show that they are within the acceptable ranges.

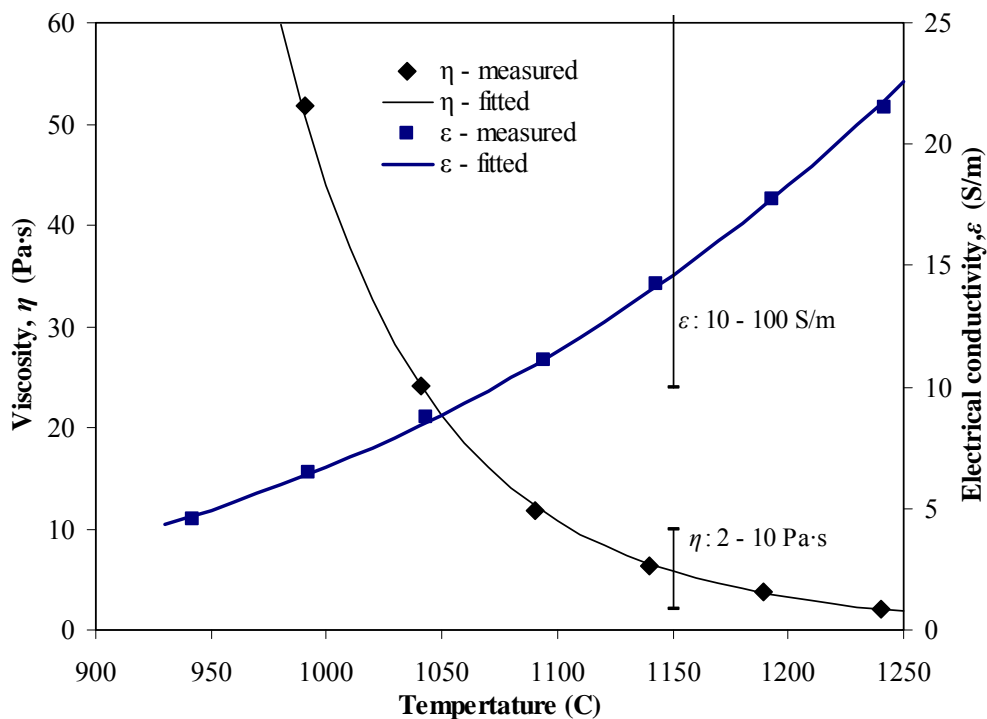


Fig. 2. Viscosity and electrical conductivity as a function of temperature for HAL-17 glass.

SIMULATED WASTE AND MELTER FEED PREPARATION

Table IV shows the source chemicals and their masses used to prepare 1 L of simulated HLW slurry with the composition given in Table I. Batches of slurry were prepared according to the procedure to simulate the pretreatment process expected at Hanford, such as additions of NaOH and Na₂CO₃ solutions, settling, and washing. The melter feed was prepared by mixing the additives given in Table III with the simulated HLW slurry.

Table IV. Source Chemicals Used for HLW Simulant

Material	Mass, g	Material	Mass, g
Fe(NO ₃) ₃ ·9H ₂ O	152.49	SiO ₂	25.02
Ni(NO ₃) ₂ ·6H ₂ O	7.94	AlOOH	144.15
ZrO(NO ₃) ₂ ·xH ₂ O, X~6	5.55	KNO ₃	1.55
Ba(NO ₃) ₂	0.47	H ₃ BO ₃	1.72
Ca(NO ₃) ₂ ·4H ₂ O	23.15	NaF	7.54
Cd(NO ₃) ₂ ·4H ₂ O	0.30	Na ₂ SO ₄	1.81
Cr(NO ₃) ₃ ·9H ₂ O	14.02	Na ₃ PO ₄ ·12H ₂ O	23.35
Mg(NO ₃) ₂ ·6H ₂ O	3.80	Li ₂ CO ₃	2.15
Pb(NO ₃) ₂	3.10	Na ₂ CO ₃	6.66
Zn(NO ₃) ₂ ·6H ₂ O	1.55	NaNO ₃	5.17
Bi(NO ₃) ₃ ·5H ₂ O	12.18	NaNO ₂	1.73
TiO ₂	0.05	Total	445.45

SMALL-SCALE MELTER TESTING

The small-scale melter testing was conducted using the SMK melter at KRI. The SMK melter consists of an insulated enclosure with silicon carbide heaters and uses a cylindrical can made of heat-resistant alloy EI-652 (~70% Cr, ~30% Ni, ~1% Fe) with melt surface area of 62 cm² and the internal volume of about 1,200 cm³ placed into the melter. Detailed information on the SMK melter is described in a paper by Gerdes et al. [3] in this issue of WM conference proceeding. The slurry feed was continuously fed to the SMK through a water cooled steel feeding tube.

The SMK melter tests with HAL-17 feed were performed in four test segments producing roughly 6 kg of glass with 24 hr of total test duration. Table V summarizes the conditions used in each test segment. The melt temperature was maintained at 1150°C for test segments #1 through #3 and at 1050°C for test segment #4. The purpose of test segment #4 was to evaluate the effect of melt temperature on spinel settling if it happens. The bubbling rate was kept 5 and 0.6 L/min throughout the test. The initial feed rate was 1.2 L/hr in the test segment #1. Using this feed rate, the melter was unable to handle evaporation and cold cap melting during the later stages of test segment #1. Therefore, the feed rate was reduced to ~0.5 L/hr in test segments # 2 and #3. The glass production rate during the test segments # 2 and #3 was 194 g/hr on average which corresponds to a production rate per unit melter surface area of 0.75 MT/(d·m²).

Table V. Summary of Small-Scale Melter (SMK) Test Results

Test segment	#1		#2		#3			#4				
Melt temperature, °C	1150		1150		1150			1050				
Bubbling rate, L/min	0.5 - 0.6		0.5 - 0.6		0.5 - 0.6			0.5 - 0.6				
Duration, hr	3		7		11			3.3				
Feed rate, L/hr	1.23		0.53		0.48			0.33				
Glass poured, g	305		620		1430			14				
Glass produced, g	1415		1420		2035			1000				
Production rate, g/hr	472		203		185			N/A				
Spinel content in glass, vol%												
Sample ^a	Pour 1	Melter	Pour 1	Pour 2	Melter	Pour 1	Pour 2	Pour 3	Pour 4	Melter	Pour 1	Melter
Top	2.5	3.3	2.6	1.4	1.7	1.6	1.1	1.1	1.3	1.2	1.6 ^b	1.5
Middle	3.2	4.1	3.1	1.8	1.3	1.8	1.1	1.1	1.2	1.5		1.4
Bottom	3.0	2.5	1.9	1.2	1.6	1.6	1.2	1.2	1.2	1.4		1.8
Average	2.9	3.3	2.5	1.5	1.5	1.7	1.1	1.1	1.2	1.4	1.6 ^b	1.6

^a “Pour” represents samples taken from the glass pour canister and “Melter” represents samples taken from glass block remained in the melter crucible at the completion of each test segment.

^b From one sample only.

Glass was poured after roughly every 3 hr of feeding. About 2.4 kg of glass was poured from total eight pours. For test segment #4, the glass pouring was very slow due to high viscosity of glass and only 14 g of sample was obtained compared to roughly 340 g glass per pour on average for the other 7 pours. At the end of each test segment, the melter can was removed from the melter and the remaining glass was allowed to cool. The poured glass samples and the glass samples from the melter can were analyzed for the content of crystals. Table V shows the results of spinel vol% determined by image analysis of scanning electron microscopy (SEM) photos. The glasses from the test segment #1 had the highest spinel fraction compared to the rest three

segments, which may be attributed to the high feed rate used. There was no clear difference in the spinel contents between the pour glass and the glass remained in the melter can. No trend in the distribution of spinel was observed in the glass remained in the melter can (i.e., no systematic change between top, middle, and bottom samples) for all test segments, indicating that there was no settling of the spinel crystals within the time frame of this test at both 1150 and 1050°C. The glasses from test segment #4 that was melted at 1050°C showed comparable spinel contents to those processed at 1150°C suggesting that there was no difference in spinel contents between the melts at 1150 and 1050°C. The spinel crystals observed in these glasses are likely formed during cooling. The glass samples collected from pour glasses for selected test segments are planned to be CCC heat treated and the as-received and CCC treated glasses are planned to be tested for crystals by XRD and PCT.

The pour glass samples from test segment #1 were used for chemical analyses by semi-quantitative electron probe microanalysis (EPMA) and the results are shown in Table VI. The target glass composition was also included in Table VI for comparison. For glass matrix, the total concentration was normalized to sum to 78.75 wt%, which is a sum of target concentrations of components detected by the EPMA method (i.e., the light elements (B and Li) are not detectable but constitute a significant portion of the glass). For glass samples, the analyzed iron concentrations were assigned to Fe₂O₃. For spinel crystals, the concentration of FeO and Fe₂O₃ were calculated to match the spinel chemical form, (Fe_xNi_{1-x})(Fe_yCr_zAl_{2-y-z})O₄, and the total to sum to 100 wt%. The agreement between the target and analytical results for glass samples is reasonable considering the semi-quantitative nature of the EPMA analyses. The spinel crystals in this high-Al₂O₃ glass have in general similar compositions to those formed in typical HLW glasses [10] except that relatively high concentration of Al was present.

Table VI. Chemical Composition of Glass Matrix and Spinel in Pour Glass Samples from Small-Scale Melter Test Segment #1

Comp	Glass				Spinel crystals							
	Top	Middle	Bottom	Target	Top 1	Top 2	Middle 1	Middle 2	Middle 3	Bottom 1	Bottom 2	
Al ₂ O ₃	25.61	26.76	26.01	25.89	18.37	20.88	25.18	12.12	22.83	30.96	12.16	
Bi ₂ O ₃	1.93	-	2.15	1.24	-	-	-	-	-	-	-	
CaO	7.12	7.24	7.13	7.33	-	-	-	-	-	-	-	
Cr ₂ O ₃	0.28	0.15	0.28	0.56	18.47	12.18	4.80	39.64	6.36	13.19	42.10	
FeO	-	-	-	-	19.13	18.68	19.62	23.15	17.65	23.30	24.50	
Fe ₂ O ₃	5.23	5.17	5.09	6.37	28.20	31.61	34.07	14.17	35.21	18.82	11.67	
K ₂ O	2.43	2.59	2.55	2.72	-	-	-	-	-	-	-	
MgO	0.32	0.49	0.32	0.13	-	-	-	-	-	-	-	
Na ₂ O	7.52	7.64	7.65	6.07	-	-	-	-	-	-	-	
NiO	-	-	-	0.43	15.83	16.65	16.33	10.92	17.95	13.73	9.57	
P ₂ O ₅	1.11	1.12	1.11	1.14	-	-	-	-	-	-	-	
PbO	0.62	0.84	-	0.44	-	-	-	-	-	-	-	
SiO ₂	25.93	26.76	25.96	26.00	-	-	-	-	-	-	-	
ZrO ₂	0.65	0.00	0.52	0.43	-	-	-	-	-	-	-	
Sum	78.75	78.75	78.75	78.75	100.00	100.00	100.00	100.00	100.00	100.00	100.00	

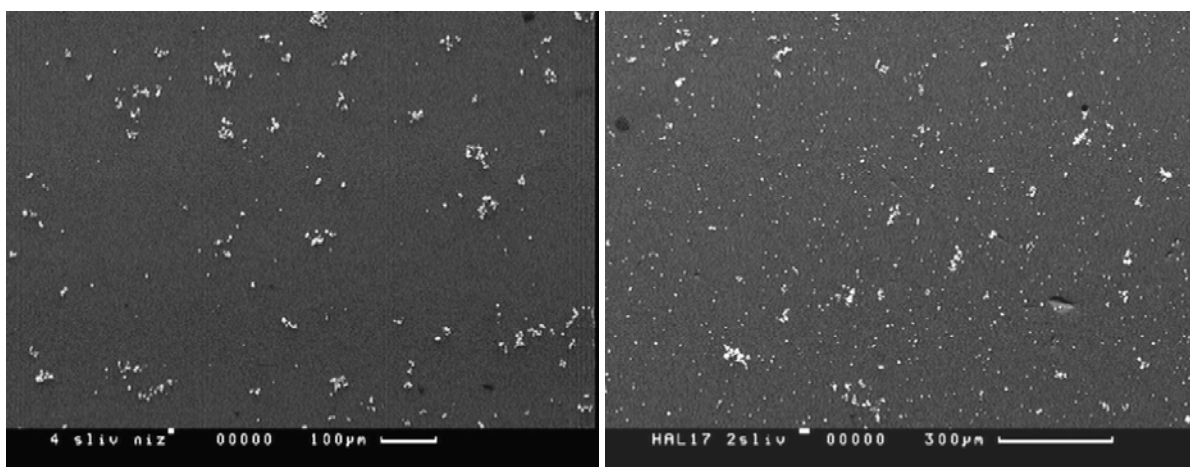
^a Empty cells with “-” represent that the component was not detected by EPMA method.

LARGER SCALE MELTER TESTING

The larger scale melter testing was conducted at the EP-5 melter at KRI. The EP-5 melter is a pilot-scaled rectangular bath Joule-heated melter with heat-resistant alloy EI-652 (~70% Cr, ~30% Ni, ~1% Fe) electrodes installed along the walls. The melter has a melt surface of 338 cm² with a working volume of 5 L. Detailed information on the EP-5 melter is described in a paper by Gerdes et al. [3] in this issue of WM conference proceeding.

The EP-5 melter tests with HAL-17 feed (the same as used for SMK test) were performed for 52 hr including the melter heat-up time of 5 hr, total feeding time 39 hr, and cool down time 8 hr. A constant bubbling rate of 2 L/min was maintained throughout the test. The melter feeding was started at a melt temperature of 1093°C. Operation temperature was maintained between 1120 and 1170°C. Glass was poured at a melt temperature of 1150°C. A total of 20.3 kg of glass was produced during 9 separate pours. The feeding rate was started at 1 L/hr, raised to 1.5 L/hr, lowered to 1.3 L/hr, and then the optimal feed rate of 1.4 L/hr was finalized after 6 hr of feeding. The final feed rate was determined at a rate that provides stable cold cap with 80-85% coverage and was maintained for the rest of test duration. The glass production rate at this 1.4 L/hr feed rate was 540 g/hr which corresponds to a production rate per unit melter surface area of 0.38 MT/(d·m²).

The glass samples from the first six pours were analyzed for spinel content. The spinel contents ranged from 2.0 to 3.8 vol% with an average of 2.8 vol%, which is higher than the glasses from SMK melter. Slower cooling rate of the EP-5 pour glasses may have contributed to larger amount of spinels. Fig. 3 shows examples of SEM micrographs with the spinel crystals in glass.



(a) Test #3, pour #4 bottom (1.4 vol%)

(b) EP-5, pour #2 (2.3 vol%)

Fig. 3. SEM micrographs of glass samples from SMK and EP-5 melter testing

SUMMARY AND CONCLUSIONS

Glasses with Al₂O₃ loading ranging from 25 to 27 wt% were formulated and tested at a crucible scale. Successful glass formulations with up to 26 wt% Al₂O₃ that do not precipitate nepheline during CCC treatment and had spinel crystals 1 vol% or less after 24 hr heat treatment at 950°C were obtained. The selected glass, HAL-17 with 26 wt% Al₂O₃, had viscosity and electrical

conductivity within the boundaries for adequate processing in the Joule heated melters operated at 1150°C. This HAL-17 glass was successfully processed using small-scale (SMK) and larger-scale (EP-5) melters. There was no indication of spinel settling during processing. The product glass samples from these melter tests contained 1 to 4 vol% spinel crystals that are likely formed during cooling. The PCT tests on the product glasses are underway.

The present study demonstrated that it is possible to formulate the glasses with up to 26 wt% Al₂O₃ that satisfy the property requirements and is processable with Joule-heated melters operated at 1150°C. The “nepheline discriminator” for HAL-17 glass is 0.45, which supports that claim that the current rule (“nepheline discriminator” < 0.62) is too restrictive. Considering that the cost of HLW treatment is highly dependent on loading of waste in glass, this result provides a potential for significant cost saving for Hanford. The maximum Al₂O₃ loading that can be achieved will also depend on concentrations of other components in wastes. For example, the loading of waste used in this study was also limited by the spinel crystallization after 950°C 24 hr heat treatment, which suggests that the concentrations of spinel-forming components such as Fe₂O₃, Cr₂O₃, NiO, ZnO, and MnO would be critical in addition to Al₂O₃ for the maximum Al₂O₃ loading achievable.

The observed glass production rate per unit melter surface area of 0.75 MT/(d·m²) for SMK test is comparable to the design capacity of WTP HLW melters at 0.8 MT/(d·m²). However, the test with EP-5 melter achieved 0.38 MT/(d·m²), which is roughly a half of the WTP design capacity. This result may imply that the glass with 26 wt% Al₂O₃ may not achieve the WTP design production rate. However, this hypothesis is not conclusive because of unknown effects of melter size and operational differences. Further testing is needed to quantify the effect of high Al₂O₃ loading on glass production rate.

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