Glass Formulation for Next Generation Cold Crucible Induction Melter - 11561

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ABSTRACT

Transformational melter technologies are being considered to support mission acceleration within the U.S. Department of Energy (DOE) complex. New glass formulations are required to take full advantage of the next generation melters, for example, the cold crucible induction melter (CCIM). The key advantage of CCIM technology over current reference technologies is its capability to provide higher processing temperatures, which can lead to an increased waste throughput rate by achieving higher waste loadings and by increasing the feed processing rate. Various waste compositions within the DOE complex were evaluated to determine their potential for successfully demonstrating the unique advantages of the CCIM technology. Glass formulations that satisfy a set of constraints for product quality and assumed CCIM processing conditions were developed for two Hanford waste streams, AZ-101 high-level waste (HLW) and AN-105 low-activity waste (LAW). Three glasses selected for AZ-101 HLW have waste loadings of 40, 42.5, and 45 wt%. The 45-wt% waste loading corresponds to a 22% increase from 37 wt%, which is the maximum expected waste loading based on the current reference formulation. One glass selected for AN-105 LAW has a waste loading of 31.3 wt% at 24 wt% Na_2O in glass, which is a 14% increase from the current reference formulation maximum of 21 wt% Na_2O. These four glasses are planned for scaled melter tests for initial demonstration of the CCIM technologies for Hanford wastes.

INTRODUCTION

Resolving the nation's high-level waste (HLW) legacy requires designing, constructing, and operating large and technically complex processing facilities coupled to equally complex waste treatment and vitrification facilities [1]. Vitrification technology was chosen to treat HLW at the Hanford Site and Savannah River Site (SRS) as well as the low-activity waste (LAW) at the Hanford Site, and it may potentially be applied to other defense waste streams, such as Idaho National Laboratory (INL) tank waste or calcine. Joule-heated melters (JHMs) are being used at the Defense Waste Processing Facility (DWPF) at SRS and will be used at the Hanford Tank Waste Treatment and Immobilization Plant (WTP) to vitrify tank waste fractions [2]. The loading of waste into glass and the glass production rates at WTP and DWPF are limited by the current melter technology. Significant reductions in glass volumes for disposal and shorter mission life are only possible with advances in melter technology and glass formulations [1].

Next-generation melter technologies with a higher waste throughput rate are being developed to support accelerating the cleanup mission and reducing the lifecycle cost within the U.S. Department of Energy (DOE) complex. Currently, two melter technologies are being considered [3], an advanced Joule-heated melter (AJHM) equipped with more corrosion-resistant electrodes and refractory materials and a cold crucible induction melter (CCIM). In the CCIM design, the induction coil does not contact the molten glass, and the molten glass is in contact with a frozen "skull" of glass inside a water-cooled metal crucible; therefore, there are no glass-contact materials that can corrode [4]. Both melter technologies enable higher melter operating temperatures that can lead to higher loading of waste in glass and a higher processing rate of melter feeds to achieve a higher waste throughput rate. It should be noted, however, that the CCIM technologies offer the opportunity for much higher process temperatures due to the formation of the skull layer. In addition to their capability to achieve higher operating temperatures, the CCIM technologies possess the potential for higher tolerance to crystals in the melt.

Advanced glass formulations are being developed to take full advantage of the next-generation melter technologies. This study focuses on developing new glass formulations with higher waste loadings that can be successfully processed with the advanced CCIM technologies. These glasses should possess melt properties adequate for processing and meet all product quality requirements. This paper presents the evaluation and selection of wastes for glass formulation, the results of glass formulation and testing, and the selection of glass compositions for initial CCIM demonstration tests.

SELECTION OF WASTES

The selection of wastes initially focused on Hanford waste streams because they are likely to show the highest cost benefit to implementation considering the size and cost of the Hanford tank waste cleanup program and the timing of startup. The waste compositions were evaluated for their potential to successfully demonstrate the unique advantages of the CCIM technologies over current reference technologies. The AZ-101 HLW and AN-105 LAW were selected for initial glass formulations in this study, and their oxide compositions are given in Table I.

AZ-101 HLW is relatively high in Fe, Al, and Zr, which suggests that the higher melting temperature and potential for higher tolerance to crystals of CCIM technologies could increase the loading and potentially the processing rate. The maximum expected waste loading for the reference WTP formulation is 37 wt%.

Table I. Compositions of AZ-101 HLW and AN-105 LAW.

Oxide	AZ-101 HLW	AN-105 LAW
Al_2O_3	24.58	17.88
CaO	1.40	0
CdO	2.16	0
Cl	0	2.17
Cr_2O_3	0.46	0.07
F	0	0.01
Fe_2O_3	37.67	0
K_2O	0	1.72
MnO	0.91	0
Na_2O	10.58	76.79
Nd_2O_3	0.65	0
NiO	1.66	0
P_2O_5	1.34	0
SiO_2	3.77	0.10
SO_3	0.38	0.59
ZrO_2	11.44	0
Subtotal[a]	97.00	99.33

[a] Balance is sum of other minor components.

AN-105 LAW is a low-sulfur stream and waste loading is limited by Na_2O concentration in glass that dictates the chemical durability of glass. The maximum expected waste loading for the reference WTP formulation is 27 wt% (yielding 21 wt% Na_2O in glass). This waste stream is also characterized by its high Cl content, but its loading is not limited by Cl because of its low sulfur content (the Cl limit depends on S concentration in glass). The higher melting temperature of CCIM technologies would allow higher concentrations of refractory additive components that increase chemical durability, such as ZrO_2 and SnO_2, which would enable higher waste loading.

GLASS FORMULATIONS

Table II summarizes the glass property requirements applied when designing the HLW and LAW glasses for testing. Available glass property models [5,6] were used to predict these properties whenever possible. However, the predicted values were used primarily as guidelines for glass formulation because the high-waste-loaded glasses that are considered in this study are outside the model validity composition range of these models.

Table II. Glass Property Requirements[a)] for HLW and LAW Glasses.

Property	AZ-101 HLW	AN-105 LAW
Crystal fraction vs. Temperature	As low as possible	NA
CCC Crystallinity	No nepheline formation after CCC	
PCT normalized release	B < 16.70, Li < 9.57, Na < 13.35 g/L	B and Na < 4 g/L
VHT alteration rate	NA	$< 50\ g/m^2/d$
TCLP Cd response	< 0.48 mg/L	NA
Viscosity	4 Pa·s at a nominal melting temperature (T_m)	
Electrical Conductivity	10 – 100 S/m at T_m	

NA: not applicable; CCC: canister centerline cooling; PCT: product consistency test; VHT: vapor hydration test; TCLP: toxicity characteristic leach procedure
a) Self-imposed for the glass development purpose except for PCT, VHT and TCLP requirements

For AZ-101 HLW, the critical information for formulating glasses with maximum possible waste loading is the crystal fraction versus temperature because the waste loading is likely limited by the crystal content within the glass melts. Currently, there is no model to predict the crystal fraction as a function of temperature. Instead, spinel $[(Fe^{2+},Ni)(Fe^{3+},Cr,Al)_2O_4]$ liquidus temperature (T_L) and temperature at which 1 vol% spinel crystal exists ($T_{1\%}$) have been used as conservative constraints to prevent the potential accumulation of crystals in the melter. Models to predict the T_L and $T_{1\%}$ have been developed [5,6]; however, they have poor predictability, especially for the glasses outside the valid composition range. Therefore, these models were used only as qualitative guidelines in selecting glasses for testing. The models for product consistency test (PCT) normalized releases [5] and toxicity characteristic leach procedure (TCLP) Cd response [5] were used to confirm that these requirements will be met. The PCT and TCLP models also suffer poor predictability outside the valid composition range. However, the performance of PCT and TCLP models is not of concern because PCT and TCLP rarely limit the waste loading of HLW glasses.

For AN-105 LAW, the key properties that limit waste loading are the PCT normalized releases and the vapor hydration test (VHT) alteration rate. Existing PCT normalized release models [5] were used considering that the PCT models provide reasonable predictability for the present purpose. Although the recent models reported in a reference [5] were developed primarily for estimating HLW glass volumes, they are considered "global" models and can be used for LAW glasses. They were developed from the compiled database that covers a large fraction of the region of waste glass compositions considered potentially of interest for Hanford including LAW glasses. However, in general, the performance of the VHT alteration rate model is poor compared to the PCT models. In addition, the recent models report [5] does not include the model for VHT alteration rates. Therefore, existing data on the VHT response in glasses with high alkali oxides ($Na_2O > 16$ wt% or $Na_2O + 0.66K_2O + 2.07Li_2O > 16$ wt%) were collected and used to develop a preliminary VHT model suited for the high-waste-loaded AN-105 based glasses in this study. A simple linear model form was applied:

$$\ln(r_{alt}) = \sum_{n=1}^{14} m_i b_i \qquad \text{(Eq. 1)}$$

where r_{alt} is the VHT alteration rate (g/m^2/d), m_i is the mass fraction of the i^{th} component in glass, and b_i is the model coefficient for the i^{th} component. Table III lists the model coefficients and R^2 value. The poor predictability of this model is evident from the low R^2 value of 0.593, which suggests that the output of this model should be used with caution.

Table III. VHT Model Coefficients.

Component	Coefficient
Al_2O_3	5.2
B_2O_3	-16.6
CaO	-16.4
Fe_2O_3	-11.6
K_2O	37.8
Li_2O	117.8
MgO	-15.7
Na_2O	45.4
SiO_2	-6.5
SnO_2	-24.4
TiO_2	-8.7
ZnO	-28.9
ZrO_2	-52.9
Others[a]	21.0
R^2	0.593

[a] Sum of all remaining components.

In both HLW and LAW glasses, crystallization of the slowly cooled glass near the center of the canister is simulated by the canister centerline cooling (CCC) treatment, which can result in a severe deterioration of glass chemical durability by PCT, especially if nepheline ($NaAlSiO_4$) is formed [7,8]. It has been known that the formation of spinel crystals that form in many HLW glasses does not affect the PCT durability [9]. To formulate glasses without nepheline precipitation, empirical rules based on nepheline discriminator (N_{Si}) [10] and optical basicity (OB) [see reference 11 for how to calculate OB from glass composition] have been developed:

$$N_{Si} = \frac{g_{SiO_2}}{g_{SiO_2} + g_{Na_2O} + g_{Al_2O_3}} \geq 0.62 \qquad \text{(Eq. 2)}$$

$$\text{OB (Optical Basicity)} \leq 0.575 \qquad \text{(Eq. 3)}$$

where g_i is the mass fraction of the i^{th} oxide in glass. The current approach for the nepheline constraint is that the glass is not likely to form nepheline after CCC if either one of the rules is met [11].

For both AZ-101 HLW and AN-105 LAW, the model for viscosity [5] was used to predict the nominal melting temperature at a predicted viscosity of 4 Pa·s. The model for electrical conductivity [5] was used to confirm that the glasses have predicted electrical conductivity within the desired range of 10 to 100 S/m [12] at a predicted nominal melting temperature.

Table IV shows the target compositions and predicted properties for AZ-101 HLW (CCIM-AZ) glasses. The predicted nominal melting temperature (T_m) at a predicted viscosity of 4 Pa·s was 1200°C for all CCIM-AZ glasses, except the CCIM-AZ-18 glass that had predicted T_m = 1150°C. The predicted electrical conductivity (EC) was within the desired range of 10 to 100 S/m at T_m for all CCIM-AZ glasses. The predicted normalized PCT releases and TCLP Cd response were all below the regulatory limits. The predicted T_L and $T_{1\%}$ were all higher than the traditional constraints (see footnotes in Table IV) that have been imposed to avoid crystal accumulation in the melter. The nepheline constraint was met for all CCIM-AZ glasses, primarily by satisfying the N_{Si} rule, except the CCIM-AZ-18 glass that failed both N_{Si} and OB rules.

Table IV. Target Composition and Predicted Properties of CCIM-AZ Glasses.

Oxide (wt)	CCIM-AZ-10	CCIM-AZ-17	CCIM-AZ-18	CCIM-AZ-16	CCIM-AZ-29	CCIM-AZ-30	CCIM-AZ-31	CCIM-AZ-32	CCIM-AZ-33	Limits
Al_2O_3	11.09	11.09	11.09	10.44	9.79	9.79	9.79	9.79	9.79	-
B_2O_3	11.00	14.00	14.00	11.00	11.00	11.00	7.00	15.00	11.00	-
CaO	0.63	0.63	0.63	0.59	0.56	0.56	0.56	0.56	4.00	-
CdO	0.97	0.97	0.97	0.92	0.86	0.86	0.86	0.86	0.86	-
Cr_2O_3	0.21	0.21	0.21	0.20	0.18	0.18	0.18	0.18	0.18	-
Fe_2O_3	17.00	17.00	17.00	16.00	15.00	15.00	15.00	15.00	15.00	-
Li_2O	3.00	3.00	3.00	3.00	3.00	5.00	4.50	3.00	3.00	-
MnO	0.41	0.41	0.41	0.38	0.36	0.36	0.36	0.36	0.36	-
Na_2O	10.78	8.64	10.78	11.38	11.99	7.50	11.99	9.25	9.12	-
NiO	0.74	0.74	0.74	0.70	0.66	0.66	0.66	0.66	0.66	-
SiO_2	36.59	35.73	33.59	38.26	39.93	42.42	42.43	38.67	39.35	-
SO_3	0.17	0.17	0.17	0.16	0.15	0.15	0.15	0.15	0.15	-
ZrO_2	5.16	5.16	5.16	4.85	4.55	4.55	4.55	4.55	4.55	-
Subtotal[a]	97.76	97.76	97.76	97.89	98.02	98.02	98.02	98.02	98.02	-
Waste loading, wt%	45.13	45.13	45.13	42.47	39.82	39.82	39.82	39.82	39.82	-
T_m at 4 Pa·s, °C	1200	1200	1150	1200	1200	1200	1200	1200	1200	-
EC at T_m, S/m	33.1	28.9	36.6	34.3	35.7	35.5	43.6	30.2	27.1	10-100
Spinel T_L, °C	1272	1272	1226	1218	1165	1202	1182	1163	1232	<1100[b]
Spinel $T_{1\%}$, °C	1178	1184	1160	1114	1049	1077	1057	1055	1093	<1000[c]
PCT-B, g/L	0.358	0.389	0.583	0.399	0.448	0.344	0.363	0.512	0.259	<16.7
PCT-Li, g/L	0.330	0.360	0.516	0.364	0.405	0.345	0.400	0.488	0.276	<9.57
PCT-Na, g/L	0.261	0.257	0.386	0.296	0.338	0.235	0.382	0.350	0.230	<13.35
TCLP Cd, mg/L	0.184	0.193	0.280	0.181	0.178	0.129	0.143	0.194	0.170	<0.48
N_{Si}	0.626	0.644	0.606	0.637	0.647	0.710	0.661	0.670	0.675	≥0.62
OB	0.591	0.577	0.586	0.588	0.586	0.575	0.598	0.568	0.587	≤0.575

[a] The remaining components include Ce_2O_3, Cs_2O, La_2O_3, Nd_2O_3, P_2O_5, RuO_2, and SnO_2.

[b] Based on a traditional constraint: $T_L < T_m - 100°C$ (T_L limit is 1050°C for CCIM-AZ-18) [5].

[c] Based on a constraint of $T_{1\%} < 950°C$ for glasses with T_m = 1150°C ($T_{1\%}$ limit is 950°C for CCIM-AZ-18) [1].

Shaded cells indicate that the predicted or calculated value is not within the limits.

Table V shows the target compositions and predicted properties for AN-105 LAW (CCIM-AN) glasses. The predicted nominal melting temperature (T_m) at a predicted viscosity of 4 Pa·s was 1200 or 1250°C. The predicted EC was within the desired range of 10 to 100 S/m at T_m for all CCIM-AN glasses. The predicted normalized PCT releases and predicted VHT alteration rate (by Table III) are all below the regulatory limits. The nepheline constraint was met for two

CCIM-AN glasses only, CCIM-AN-02 and 09, by satisfying the N_{Si} rule; all other glasses failed both the N_{Si} and OB rules.

Table V. Target Composition and Predicted Properties of CCIM-AN Glasses.

Oxide (wt)	CCIM-AN-02	CCIM-AN-04	CCIM-AN-09	CCIM-AN-11	CCIM-AN-18	CCIM-AN-20	Limits
Al_2O_3	6.00	6.00	5.59	5.59	6.00	5.82	-
B_2O_3	10.37	10.03	9.12	11.58	7.73	8.05	-
CaO	0.00	3.00	0.00	0.00	2.00	0.00	-
Cl	0.65	0.65	0.68	0.68	0.68	0.71	-
K_2O	0.52	0.52	0.54	0.54	0.54	0.56	-
Na_2O	23.00	23.00	24.00	24.00	24.00	25.00	-
SiO_2	48.08	45.42	48.68	45.22	47.66	48.45	-
SO_3	0.18	0.18	0.18	0.18	0.18	0.19	-
SnO_2	2.50	2.50	2.50	2.50	2.00	2.50	-
ZnO	2.50	2.50	2.50	2.50	2.00	2.50	-
ZrO_2	6.00	6.00	6.00	7.00	7.00	6.00	-
Subtotal$^{a)}$	99.80	99.80	99.80	99.80	99.80	99.80	-
Waste loading, wt%	29.95	29.95	31.26	31.26	31.26	32.56	-
T_m at 4 Pa·s, °C	1250	1200	1250	1200	1250	1250	-
EC at T_m, S/m	54.3	52.5	59.8	56.9	61.0	66.3	10-100
PCT-B, g/L	1.83	1.73	2.00	2.89	1.35	1.93	<4
PCT-Na, g/L	1.78	1.99	2.13	2.56	1.89	2.33	<4
VHT, $g/m^2/d$	6.09	4.69	11.31	5.56	8.62	22.26	<50
N_{Si}	0.624	0.610	0.622	0.604	0.614	0.611	≥ 0.62
OB	0.582	0.595	0.588	0.587	0.600	0.595	≤ 0.575

a) The remaining components include Cr_2O_3, Cs_2O, F, and Re_2O_7.
Shaded cells indicate that the calculated value is not within the limits.

Key properties were measured for all formulated glasses: crystal vol% versus temperature, PCT normalized releases, the TCLP Cd response, CCC crystallinity for CCIM-AZ glasses and PCT normalized releases, the VHT alteration rate, and CCC crystallinity for CCIM-AN glasses. Based on these initial results, candidate glasses were selected for further characterization (i.e., viscosity and electrical conductivity). Chemical analyses were performed for all CCIM-AZ and CCIM-AN glasses to confirm glass batching and preparation.

RESULTS OF GLASS FORMULATIONS FOR AZ-101 HLW

Table VI summarizes the results of X-ray diffraction (XRD) analyses of CCC-treated samples of CCIM-AZ glasses. Crystals identified after CCC treatment included spinel $[(Fe^{2+},Ni)(Fe^{3+},Cr,Al)_2O_4]$ as the major phase with a smaller fraction of baddeleyite (ZrO_2) only in glasses with 16 or 17 wt% Fe_2O_3. As mentioned earlier, spinel crystals are known to have no impact on the PCT normalized releases [9]. Nepheline ($NaAlSiO_4$) was not detected in any glasses, including the CCIM-AZ-18 glass that failed the nepheline constraint (i.e., failed both N_{Si} and OB rules, see Table IV). In summary, it is expected that the PCT releases of CCIM-AZ glasses are not likely to be affected by CCC treatment.

Table VI. Crystal Vol% after CCC Treatment for CCIM-AZ Glasses.

Crystal	AZ-10	AZ-17	AZ-18	AZ-16	AZ-29	AZ-30	AZ-31	AZ-32	AZ-33
Spinel	4.9	5.0	4.8	4.6	5.1	6.1	4.9	N/A	5.0
Baddeleyite	1.0	1.3	0.8	0.5	0	0	0	N/A	0

AZ-10, 17, and 18 have 17 wt% Fe_2O_3, AZ-16 has 16 wt% Fe_2O_3, and AZ-29 through AZ-33 have 15wt% Fe_2O_3
N/A: not analyzed

Fig. 1 displays the PCT normalized releases after 7-day tests at 90°C for B, Li, and Na (Fig. 1a-c) and TCLP Cd response (Fig. 1d) for CCIM-AZ glasses. The PCT normalized releases of all the quenched and CCC-treated glasses were well below the limits of the Environmental Assessment (EA) glass [13]. All quenched and CCC glasses passed the TCLP Cd requirement of 0.48 mg/L. Note that the AZ-101 waste is one of the small number of Hanford waste streams with high Cd content. For all PCT normalized B, Li, and Na releases and TCLP Cd response, the measured values (for quenched samples) were equal to or slightly higher than the predicted. The CCC treatment had mixed effects on PCT normalized releases and the TCLP Cd response, but did not show a significant difference from quenched samples as expected from CCC crystallinity.

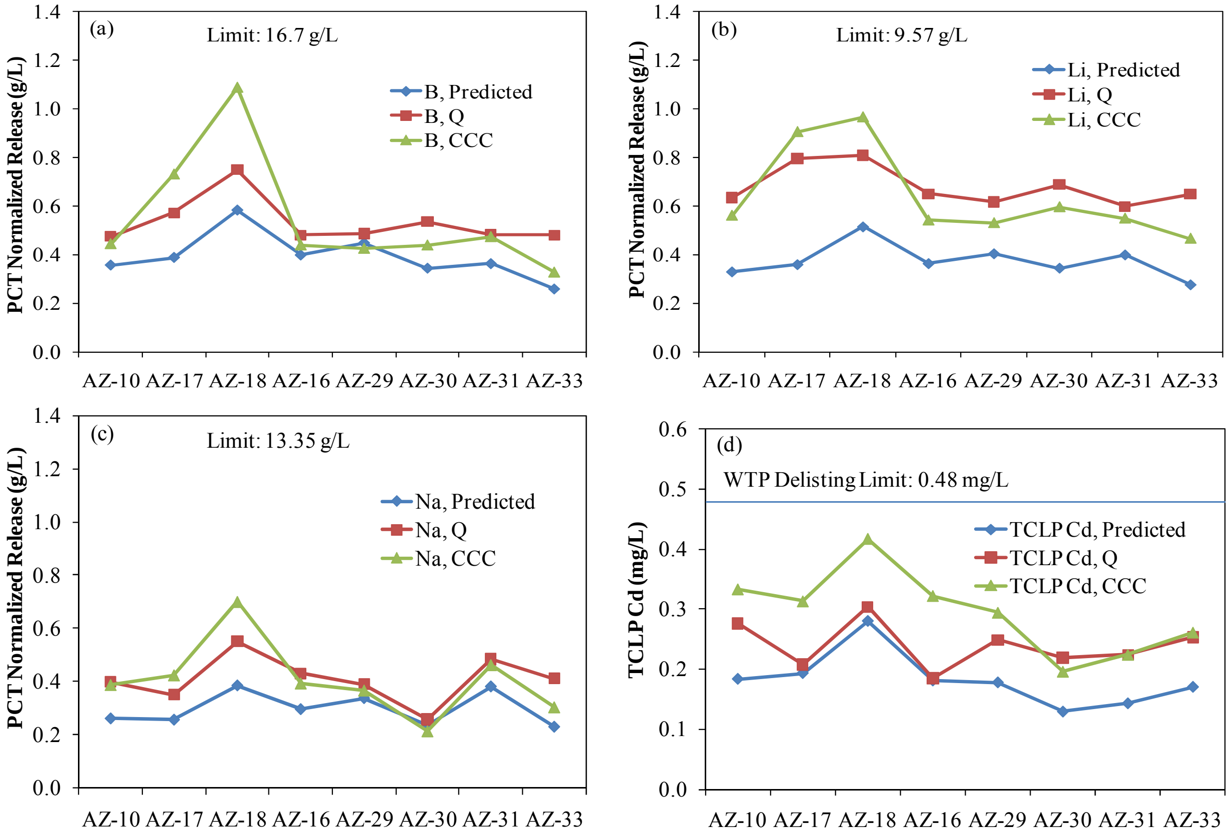

Fig. 1. PCT Releases and TCLP Cd Response of CCIM-AZ Glasses (AZ-10, 17, and 18 glasses have 17 wt% Fe_2O_3, AZ-16 has 16 wt% Fe_2O_3, and AZ-29 through AZ-33 have 15 wt% Fe_2O_3).

Table VII summarizes the results of XRD analyses of isothermal heat-treated samples at temperatures from 900 to 1250°C and CCC-treated samples of CCIM-AZ glasses. Four crystalline phases were identified for isothermal heat-treated AZ-101 glasses: spinel and hematite (Fe_2O_3) that contain Fe_2O_3 as a main constituent and baddeleyite and zircon ($ZrSiO_4$) that contain ZrO_2. Spinel was a primary phase for all nine CCIM-AZ glasses.

Table VII. Crystal Vol% after Isothermal Heat Treatments for CCIM-AZ Glasses.

T, °C	Crystal	AZ-10	AZ-17	AZ-18	AZ-16	AZ-29	AZ-30	AZ-31	AZ-32	AZ-33
900	Spinel	3.2	2.6	2.6	2.5	2.9	3.5	3.1	2.0	2.0
	Hematite	1.7	2.8	2.0	1.0	-	0.2	-	1.6	1.1
	Baddeleyite	0.9	0.3	0.9	0.5	-	-	-	-	-
	Zircon	-	1.6	-	-	-	0.3	-	0.3	0.1
1000	Spinel	2.7	1.7	2.1	2.2	1.3	1.8	1.4	1.5	1.5
	Hematite	1.0	2.1	1.1	-	-	-	-	0.2	-
	Baddeleyite	0.8	0.5	0.9	0.5	-	-	-		-
	Zircon	-	1.0	-		-	0.3	-	0.8	-
1100	Spinel	1.6	1.5	1.8	1.3	0.9	1.1	0.7	1.0	0.9
	Hematite	-	1.0	-	-	-	-	-	-	-
	Baddeleyite	0.6	0.8	0.7	0.2	-	-	-	-	-
1200	Spinel	1.5	1.9	1.5	0.8	-	-	-	0.8	-
	Hematite	-	0.3	-	-	-	-	-	-	-
	Baddeleyite	0.4	0.5	0.3	-	-	-	-	-	-
1250	Spinel	2.3	1.7	3.2	1.1	-	-	-	3.3	-
	Hematite	-	1.0	-	-	-	-	-	-	-

AZ-10, 17, and 18 have 17 wt% Fe_2O_3, AZ-16 has 16 wt% Fe_2O_3, and AZ-29 through AZ-33 have 15wt% Fe_2O_3

Fig. 2 shows the effects of the heat-treating temperature on the total crystal vol% (Fig. 2a) and spinel vol% (Fig. 2b). The crystal content in general increased as the waste loading increased and decreased as the temperature increased. However, all glasses with 17 and 16 wt% Fe_2O_3 (CCIM-AZ-10 through 18) and one glass with 15 wt% Fe_2O_3 (CCIM-AZ-32) exhibited the crystal content that increased as the temperature increased at higher temperatures. This unusual behavior is caused by formation of small crystals that occurred during "quenching," but were not present at each heat-treating temperature. The precipitation of these small spinel crystals makes it difficult to measure the T_L and $T_{1\%}$ values. Therefore, the T_L and $T_{1\%}$ values were "estimated" by extrapolating the crystal content data at lower temperatures.

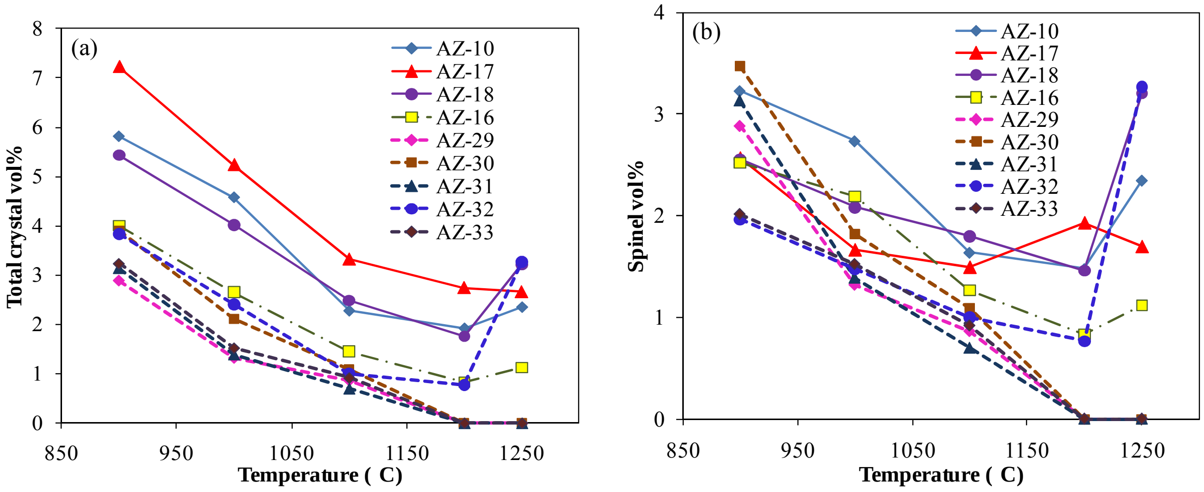

Fig. 2. Total Crystal and Spinel Vol% As a Function of Temperature (AZ-10, 17, and 18 glasses have 17 wt% Fe_2O_3, AZ-16 has 16 wt% Fe_2O_3, and AZ-29 through AZ-33 have 15 wt% Fe_2O_3).

Fig. 3 displays the estimated spinel T_L (Fig. 3a) and $T_{1\%}$ (Fig. 3b) for all CCIM-AZ glasses. The estimated spinel T_L and $T_{1\%}$ showed a similar general trend, except for three glasses marked in Fig. 3. Both the estimated spinel T_L and $T_{1\%}$ were higher than the predicted values for 17 and 16 wt% Fe_2O_3 glasses but agreed reasonably well with the predicted for 15 wt% Fe_2O_3 glasses. It is likely that the outlying results for the three glasses with high B_2O_3 concentrations marked in Fig. 3 were caused by the precipitation of small spinel crystals that interfered with the estimation of T_L and $T_{1\%}$.

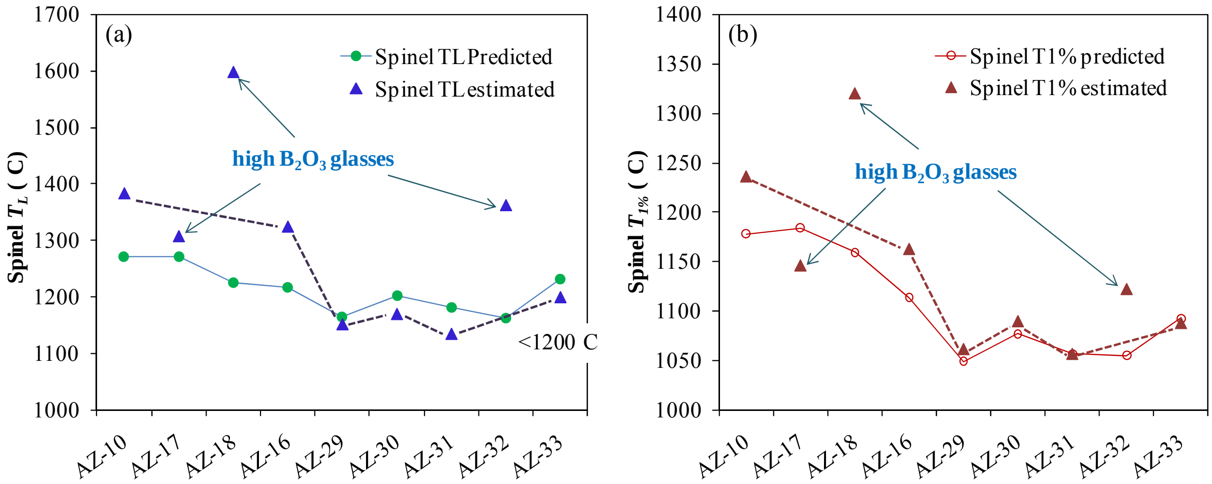

Fig. 3. Estimated Spinel T_L and $T_{1\%}$ Compared with Predicted Values (AZ-10, 17, and 18 glasses have 17 wt% Fe_2O_3, AZ-16 has 16 wt% Fe_2O_3, and AZ-29 through AZ-33 have 15 wt% Fe_2O_3).

Based on crystal versus temperature data in Fig. 2 and the estimated spinel T_L and $T_{1\%}$ in Fig. 3, the three glasses with 17, 16, and 15 wt% Fe_2O_3, CCIM-AZ-10, 16, and 29, respectively, were selected for initial CCIM demonstration tests. The estimated spinel T_L and $T_{1\%}$ increase as waste loading increases in these three glasses (Fig. 3). Fig. 4 displays the total crystal vol% (Fig. 4a) and spinel vol% (Fig. 4b) as a function of temperature for the selected three glasses, which shows that the crystal content in general increases as waste loading increases.

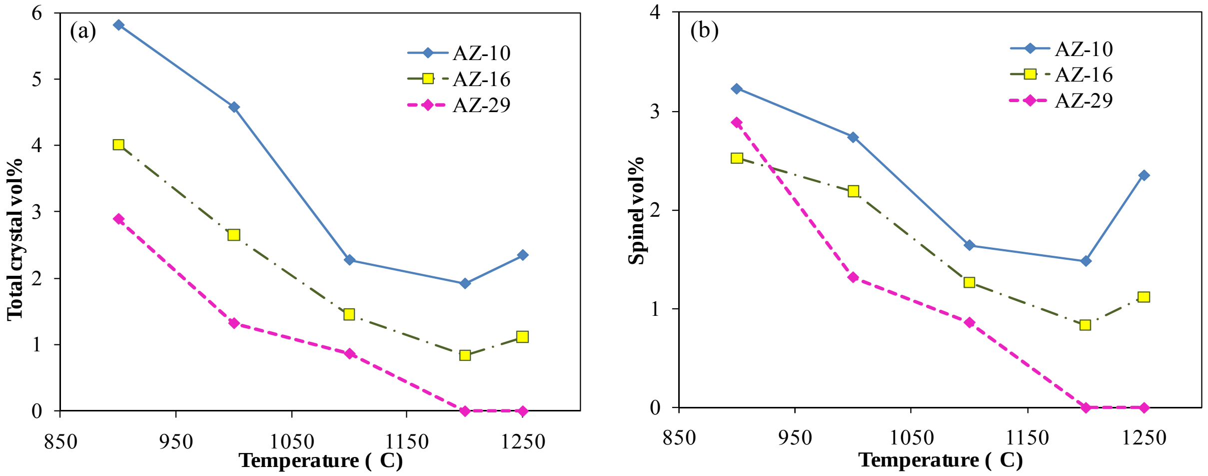

Fig. 4. Total Crystal Vol% and Spinel Vol% As a Function of Temperature for Selected Three Glasses (AZ-10, 16, and 29 glasses have 17, 16, and 15 wt% Fe_2O_3, respectively).

Table VIII summarizes the composition of three selected glasses. They all have the same B_2O_3 and Li_2O concentrations. As the waste loading increases, the concentrations of major waste components (Al_2O_3, Fe_2O_3, and ZrO_2) increase, and the concentration of Na_2O, which was adjusted to keep the predicted viscosity constant, gradually decreases. The CCIM technologies possess the potential for higher tolerance to crystals in the melt. By processing these glasses during the CCIM demonstration tests starting at 39.8 wt% waste loading (15 wt% Fe_2O_3) and increasing to 42.5 wt% (16 wt% Fe_2O_3) and to 45.1 wt% (17 wt% Fe_2O_3), it would be possible to evaluate the CCIM's tolerance to crystals in the melt within the range of crystal contents summarized in Fig. 4.

Table VIII. Target Compositions Major Components in Three Selected Glasses.

Glass	AZ-29	AZ-16	AZ-10
Al_2O_3	9.79	10.44	11.09
B_2O_3	11.00	11.00	11.00
Fe_2O_3	15.00	16.00	17.00
Li_2O	3.00	3.00	3.00
Na_2O	11.99	11.38	10.78
SiO_2	39.93	38.26	36.59
ZrO_2	4.55	4.85	5.16
Subotal[a]	95.26	94.94	94.63
Waste loading, wt%	39.8	42.5	45.1

[a] Balance is remaining waste components

Fig. 5 displays the results of viscosity (Fig. 5a) and electrical conductivity (Fig. 5b) as a function of temperature for three glasses selected for the CCIM demonstration tests. All three glasses had almost the same predicted viscosity (average predicted value is included in Fig. 5a). The measured viscosities agree reasonably well with the predicted value for all three glasses at temperatures equal to or higher than 1150°C. The viscosities at lower temperatures were likely to be affected by the crystal contents given in Fig. 4, i.e., the measured viscosities were higher than predicted, and the low-temperature viscosity increased as the waste loading increased. The measured viscosity was ~4 Pa·s at 1200°C; i.e., the recommended melting temperature is 1200°C for all three glasses. For electrical conductivity, three glasses had different predicted values as shown in Fig. 5b. Fig. 5b shows that the measured electrical conductivities were lower than predicted, and the measured differences between glasses were greater than predicted. However, the measured electrical conductivities for all three glasses were within the desired range of 10 to 100 S/m [12] at a recommended melting temperature of 1200°C.

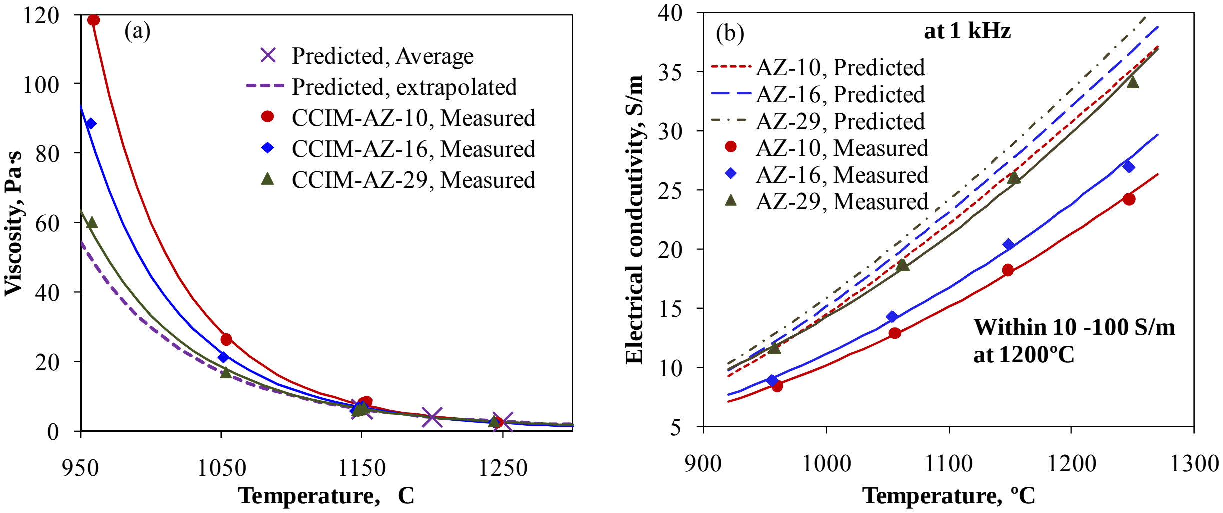

Fig. 5. Viscosity and Electrical Conductivity of Three Glasses Selected for CCIM Tests (AZ-10, 16, and 29 glasses have 17, 16, and 15 wt% Fe_2O_3, respectively).

RESULTS OF GLASS FORMULATIONS FOR AN-105 LAW

All CCIM-AN glasses were crystal free after CCC treatment, although only two glasses, CCIM-AN-02 and 09, satisfied the nepheline constraint (i.e., met either N_{Si} or OB rule, see Table V), which indicates the conservativeness of the current constraint. As a result, CCC treatment is not likely to have a significant impact on PCT normalized releases and VHT responses. Negligible corrosion was observed after 7-day and 24-day VHTs at 200°C for all quenched and CCC samples based on optical microscopic examination. All 7-day VHT samples were observed by scanning electron microscopy (SEM) to confirm the negligible corrosion by optical microscopy. Table IX summarizes the results of VHT alteration rates measured by SEM after 7-day tests at 200°C. The alteration rate was more than an order of magnitude smaller than the limit of 50 g/m^2/d and significantly lower than predicted by the model (Table III) for all glasses. Fig. 6 is an example SEM micrograph showing the VHT alteration layer formed on the CCIM-AN-09 CCC glass after the 7-day VHT at 200°C. Due to negligible corrosion by VHT, glasses for further testing were selected based on PCT normalized releases, discussed below.

Table IX. VHT Alteration Rates for CCIM-AN Glasses after 7-Day Test at 200°C.

Glass	CCIM-AN-02	CCIM-AN-04	CCIM-AN-09	CCIM-AN-11	CCIM-AN-18	CCIM-AN-20
Quenched, g/m^2/d	0.7	0.4	2.9	2.3	0.6	2.4
CCC, g/m^2/d	1.0	<0.4	3.0	1.9	2.6	1.0

AN-02 and 04 glasses have 23 wt% Na_2O, AN-09, 11 and 18 have 24 wt% Na_2O, and AN-20 has 25 wt% Na_2O

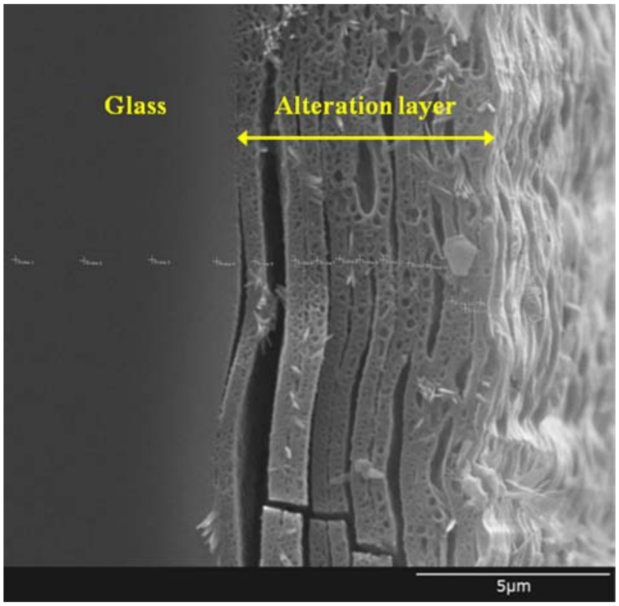

Fig. 6. SEM Micrograph Showing the VHT Alteration Layer of CCIM-AN-09 CCC Sample After 7-day VHT at 200°C

Fig. 7 shows the results of PCT normalized B (Fig. 7a) and Na (Fig. 7b) releases from quenched and CCC-treated CCIM-AN glasses. All glasses but one (CCIM-AN-11 quenched) passed the PCT requirements for B and Na. The measured PCT normalized releases showed reasonable agreement with the predicted values, and there were no undesirable effects on PCT by CCC treatment. The CCC-treated samples showed equal to or slightly lower PCT B and Na releases than quenched samples for all glasses. Based on PCT results, two glasses, CCIM-AN-09 and 18, were selected for further testing for viscosity and electrical conductivity. The CCIM-AN-20 glass with 25 wt% Na_2O passed all requirements, but its analyzed composition significantly deviated from the target composition and was not selected for further testing. Additional tests to identify the source of composition discrepancy were not performed.

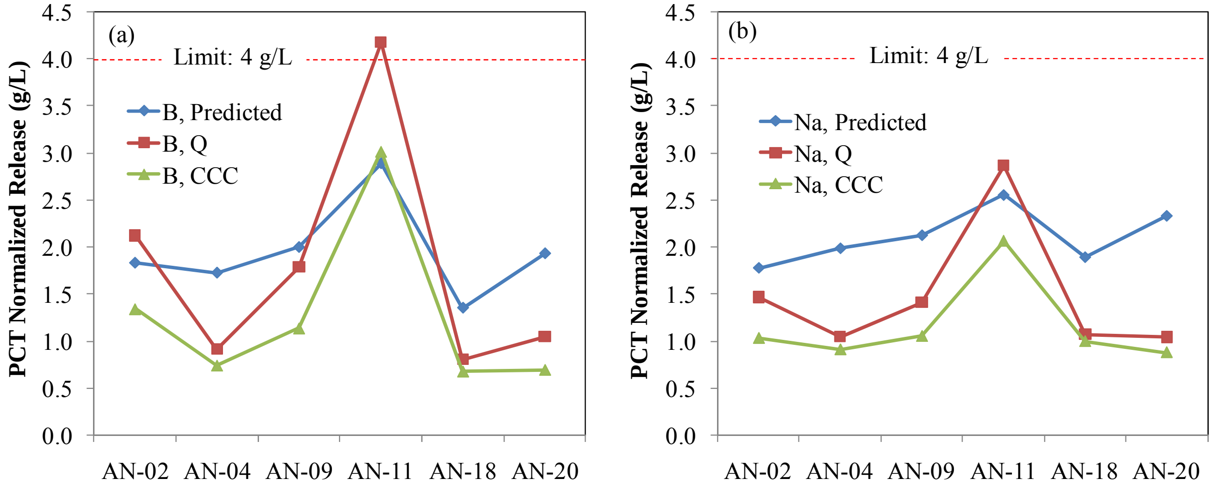

Fig. 7. PCT Normalized Releases for CCIM-AN Glasses after 7-Day Test at 90°C (AN-02 and 04 have 23 wt% Na_2O, AN-09, 11, and 18 have 24 wt% Na_2O, and AN-20 has 25 wt% Na_2O).

Fig. 8 displays the results of viscosity (Fig. 8a) and electrical conductivity (Fig. 8b) as a function of temperature for two selected glasses compared with the predicted values. Both glasses had almost the same predicted viscosity (average predicted value is included in Fig. 8a). The measured viscosities agree reasonably well with the predicted value for both glasses within the temperatures tested. The measured viscosity was ~4 Pa·s at 1250°C; i.e., the recommended melting temperature was 1250°C for both glasses.

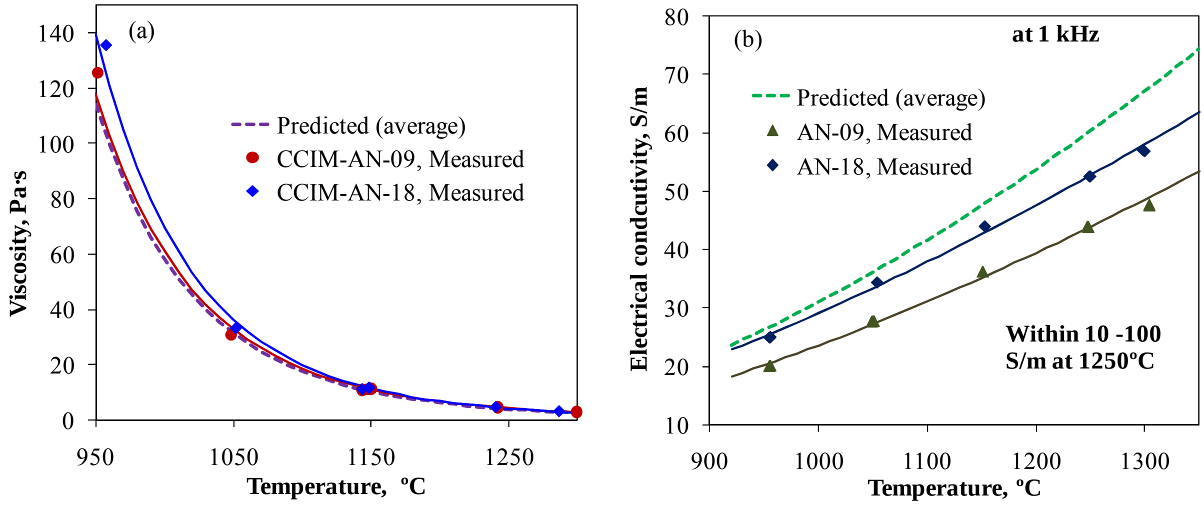

Fig. 8. Viscosity and Electrical Conductivity of Selected Two CCIM-AN Glasses with 24 wt% Na_2O.

Both glasses also had very similar predicted electrical conductivities (average predicted value is included in Fig. 8b). Fig. 8b shows that measured electrical conductivities were lower than the predicted value for both glasses with a significant measured difference between these two glasses. However, the measured electrical conductivities for both glasses were well within the desired range of 10 to 100 S/m [12] at a recommended melting temperature of 1250°C.

Since there was no preference between these two glasses based on viscosity or electrical conductivity, the CCIM-AN-18 glass that had slightly better performance for PCT than CCIM-AN-09 was selected for the CCIM demonstration test.

SUMMARY

The three glasses, CCIM-AZ-29, 16, and 10, formulated for AZ-101 simulated waste, were selected for the initial CCIM demonstration testing. The target Fe_2O_3 concentration and waste loading of these glasses are summarized in Fig. 9.

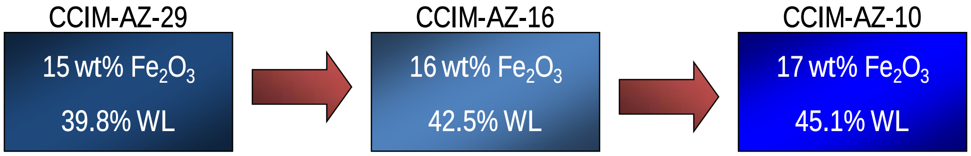

Fig. 9. Fe_2O_3 Concentration and Waste Loading in Three AZ-101 Glasses Selected for Initial CCIM Demonstration Testing.

The CCIM tests with AZ-101 simulated HLW will start with the CCIM-AZ-29 glass, and the glass melting characteristics will be evaluated (e.g., processing rates, cold cap behavior, pour stability, etc). When successful at this waste loading (39.8 wt%), a transition will be made to target the higher waste loaded (42.5 wt%) CCIM-AZ-16 glass, and then ultimately the CCIM-AZ-10 (45.1 wt%) glass. In this approach, the capability of CCIM technologies to tolerate the crystals in the melt, which increases as the waste loading increases, can be evaluated. The CCIM-AZ-10 glass at 45.1-wt% waste loading corresponds to a 22% increase from 37 wt%, which is the maximum waste loading that is likely to be achieved based on expected reference WTP formulation. The recommended nominal processing temperature for all three glasses is 1200°C based on a measured viscosity of 4 Pa·s for all three glasses. The measured electrical conductivities at 1200°C is 30, 24, and 21 S/m for CCIM-AZ-29, 16, and 10 glasses, respectively, which are within the desired range of 10 to 100 S/m. All three glasses meet the PCT and TCLP requirements regardless of thermal history (quenched or CCC treated glasses).

The CCIM-AN-18 glass targeting 24 wt% Na_2O with a waste loading of 31.3 wt% was selected for the CCIM demonstration test with AN-105 simulated LAW. This waste loading is a 14% increase from the reference WTP formulation maximum of 21 wt% Na_2O in glass. The recommended nominal processing temperature for CCIM-AN-18 glass is 1250°C based on a measured viscosity of ~4 Pa·s. The measured electrical conductivity at 1250°C is 53 S/m, which is within the recommended range of 10 to 100 S/m. The CCIM-AN-18 glass meets the PCT and VHT requirements for both quenched and CCC-treated glasses.

After successful demonstrations with initial formulations developed in this study, glass formulations and CCIM demonstration tests will be expanded to additional waste streams that have great potential to successfully demonstrate the unique advantages of the CCIM technologies over current reference technologies.

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