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Advanced Waste Form and Melter Development for Treatment of Troublesome High-level Wastes

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Abstract

A number of waste components in US defense high level radioactive wastes (HLW) have proven challenging for current Joule heated ceramic melter (JHCM) operations and have limited the ability to increase waste loadings beyond already realized levels. Many of these “troublesome" waste species cause crystallization in the glass melt that can negatively impact product quality or have a deleterious effect on melter processing. Recent efforts at US Department of Energy laboratories have focused on understanding crystallization behavior within HLW glass melts and investigating approaches to mitigate the impacts of crystallization so that increases in waste loading can be realized. Advanced glass formulations have been developed to highlight the unique benefits of next-generation melter technologies such as the Cold Crucible Induction Melter (CCIM). Crystal-tolerant HLW glasses have been investigated to allow sparingly soluble components such as chromium to crystallize in the melter but pass out of the melter before accumulating. The Hanford site AZ-101 tank waste composition represents a waste group that is waste loading limited primarily due to high concentrations of Fe_2O_3 (also with high Al_2O_3 concentrations). Systematic glass formulation development utilizing slightly higher process temperatures and higher tolerance to spinel crystals demonstrated that an increase in waste loading of more than 20% could be achieved for this waste composition, and by extension higher loadings for wastes in the same group. An extended duration CCIM melter test was conducted on an AZ-101 waste simulant using the CCIM platform at the Idaho National Laboratory (INL). The melter was continually operated for approximately 80 hours demonstrating that the AZ-101 high waste loading glass composition could be readily processed using the CCIM technology. The resulting glass was close to the targeted composition and exhibited excellent durability in both the as poured state and after being slowly cooled according to the canister centerline cooling (CCC) profile. Glass formulation development was also completed on other Hanford tank wastes that were identified to further challenge waste loading due to the presence of appreciable quantities (>750 g) of plutonium in the waste tanks. In addition to containing appreciable Pu quantities, the C-102 waste tank and the 244-TX waste tank contain high concentrations of aluminum and iron, respectively that will further challenge vitrification processing. Glass formulation testing also demonstrated that high waste loadings could be achieved with these tank compositions using the attributes afforded by the CCIM technology.

Introduction

The US is currently vitrifying defense HLW at the Savannah River Site (SRS) in South Carolina and plans to vitrify defense wastes currently stored in underground tanks at the Hanford Site. To date, over 15 million liters of HLW has been treated and vitrified in the Defense Waste Processing Facility (DWPF) at SRS. Although, significant advances have been made to increase waste loading and throughput in the DWPF over the 19 years of operation, practical limits have been reached regarding waste loading. At the Hanford site, projections using models based on JHCM processing show that waste loading will be limited for several waste groups due to crystallization in the glass melt and the resulting negative impacts on glass quality or melter processing. Several chemical constituents have been identified in both SRS and Hanford wastes that challenge waste loading due to crystallization concerns. High Al_2O_3 and Na_2O concentrations in the wastes have the potential to increase nepheline ($NaAlSiO_4$) crystal formation in the glass as shown by Peeler et al. (2006). The formation of nepheline can have a detrimental impact on glass durability because nepheline crystals deplete the residual glass matrix of glass forming oxides Al_2O_3 and SiO_2 (Kim et al. 1995). Mika et al. (1997) showed that high iron oxide, nickel oxide and chromium oxide (as well as other metal oxides) lead to the formation of spinel phases in waste glasses. Jain et al. (1991) described how spinel phase formation can adversely affect JHCM processing by causing pouring problems. In severe instances, Jain et al. described how significant spinel and noble metal accumulation in the melter can cause electrical conductivity issues in a JHCM.

Efforts are underway at US DOE laboratories to better understand crystallization behavior in waste glasses and to identify means to preclude crystallization in the glasses or mitigate the deleterious effects of crystallization. At Pacific Northwest National Laboratory (PNNL), researchers have studied the behavior of crystals in the melt in an attempt to develop models that predict crystal formation and settling. Studies by Hrma (2010) and Matyas et al. (2010) resulted in increased understanding of the effects of nucleation, crystal size and crystal agglomeration on settling and accumulation of crystals in the melt. The terminal objective of this work is to develop "crystal tolerant" glass formulations that can be processed using the JHCM technology at increased waste loadings allowing crystals to form in the melter and harmlessly pass from the melter without impacting melter operations. A second approach being evaluated is to leverage advances in melter technologies that allow for higher processing temperatures and improved crystal tolerance. The CCIM affords the opportunity to significantly increase processing temperatures. The CCIM melts glass inductively by creating an eddy current inside the glass pool using a water-cooled, high-frequency electrical coil that surrounds the outer walls of the CCIM. Due to a steep temperature gradient that exists near the walls, a frozen glass layer forms along the inside walls of the CCIM that separate the walls and the heating coil from the molten glass, thus, minimizing corrosion. Alternative to the CCIM, advances in JHCM technology using improved melter electrode materials will allow for modest increases in melter operating temperatures. Additionally, the introduction of bubblers into JHCMs can enhance mixing and temperature uniformity within the melter. Smith and Iverson (2011) describe the installation and operation of bubblers in the DWPF melter.

The Hanford site has developed system models called the Hanford Tank Waste Operations Simulator (HTWOS) to assist in planning for future plant operations (Bergmann 2010). These models include modules that sequence the various wastes and predict glass quantities using existing glass composition property models and relationships to specify waste loading in the glass (Vienna et al. 2009 and McCloy et al. 2010). There are also the baseline Waste Treatment and Immobilization Plant (WTP) glass property models and constraints that were developed for initial operation of WTP (Vienna and Kim 2008). The WTP constraints are more conservative than those used in HTWOS and hence typically project larger quantities of glass to be produced. The high Fe_2O_3 waste group represents about 1300 MT out of total waste of 11,000 MT at Hanford on a calcined oxides basis. The WTP baseline model predicts that approximately 3100 MT of glass will result from processing the waste group while the HTWOS model predicts about 3000 MT of glass will be produced. The AZ-101 tank waste is representative of the high Fe_2O_3 waste group. The AZ-101 tank waste has relatively high concentrations of Fe_2O_3 (38 wt %) and Al_2O_3 (25 wt %) and, thus, can be waste loading limited due to spinel or nepheline formation. This waste also includes high ZrO_2 concentrations (11%) that can lead to further crystallization concerns. Another small waste group provides further challenges to waste loading due to the unique characteristics of the waste. In these tanks, appreciable concentrations of plutonium is present in the tank farms as >10 μm particulate Pu oxide and Pu metal.

This report summarizes results from three years of work on the IAEA Coordinated Research Project on "Processing technologies for high level waste, formulation of matrices and characterization of waste forms" (T21027), and the specific task "Advanced Waste Form and Melter Development for Treatment of Troublesome High-Level Wastes" (17207). In the first phase of this Coordinated Research Project (CRP) glass formulation development activities focused on the AZ-101 composition to demonstrate increased waste loading (over the baseline maximum of 37 wt %) by taking advantage of higher processing temperatures and crystal tolerance afforded by the CCIM technology. The second phase of the CRP focused on a CCIM demonstration campaign with the AZ-101 waste glass composition. The final phase focused on development of glass formulations that could be processed using the CCIM technology to treat Hanford tank wastes that contain appreciable amounts of plutonium and also contain high concentrations of aluminum (C-102 waste tank) and iron (244-TX waste tank).

Glass Composition Development for AZ-101 Waste Tank

Experimental Strategy

Scoping glass composition development tests were initially conducted using the AZ-101 waste composition (Table 1) with concentrations of up to 20 wt % Fe_2O_3 with melting temperatures ranging from 1150 to 1300° C. Glass former additives included B_2O_3, Li_2O, Na_2O and SiO_2. Based on these initial results, a series of compositions with Fe_2O_3 concentrations ranging from 15-17 wt % were formulated. A subset of the compositions evaluated is provided in Table 2. The glasses were fabricated at 1250° C in platinum crucibles using reagent grade chemicals. It should be noted that a melting temperature of

Table 1. Composition of AZ-101 Waste Surrogate (wt %)

Component	Concentration
Al_2O_3	24.58
CaO	1.40
CdO	2.16
Ce_2O_3	0.80
Cr_2O_3	0.46
Cs_2O	0.50
Fe_2O_3	37.67
La_2O_3	0.89
MnO	0.91
Na_2O	10.58
Nd_2O_3	0.65
NiO	1.66
P_2O_5	1.34
RuO_2	0.15
SiO_2	3.77
SnO_2	0.66
SO_3	0.38
ZrO_2	11.44

Table 2. Targeted Glass Compositions for Select AZ-101 Glasses (wt %)

	AZ-10	AZ-16	AZ-17	AZ-18	AZ-29	AZ-30	AZ-31	AZ-32	AZ-33
Al_2O_3	11.09	10.44	11.09	11.09	9.79	9.79	9.79	9.79	9.79
B_2O_3	11.00	11.00	14.00	14.00	11.00	11.00	7.00	15.00	11.00
CaO	0.63	0.60	0.63	0.63	0.56	0.56	0.56	0.56	4.00
CdO	0.98	0.92	0.98	0.98	0.86	0.86	0.86	0.86	0.86
Ce_2O_3	0.36	0.34	0.36	0.36	0.32	0.32	0.32	0.32	0.32
Cr_2O_3	0.21	0.20	0.21	0.21	0.18	0.18	0.18	0.18	0.18
Cs_2O	0.23	0.21	0.23	0.23	0.20	0.20	0.20	0.20	0.20
Fe_2O_3	17.00	16.00	17.00	17.00	15.00	15.00	15.00	15.00	15.00
K_2O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
La_2O_3	0.40	0.37	0.40	0.40	0.35	0.35	0.35	0.35	0.35
Li_2O	3.00	3.00	3.00	3.00	3.00	5.00	4.50	3.00	3.00
MnO	0.41	0.38	0.41	0.41	0.36	0.36	0.36	0.36	0.36
Na_2O	10.78	11.38	8.64	10.78	11.99	7.50	11.99	9.25	9.12
Nd_2O_3	0.29	0.28	0.29	0.29	0.26	0.26	0.26	0.26	0.26
NiO	0.75	0.70	0.75	0.75	0.66	0.66	0.66	0.66	0.66
P_2O_5	0.60	0.57	0.60	0.60	0.53	0.53	0.53	0.53	0.53
RuO_2	0.07	0.06	0.07	0.07	0.06	0.06	0.06	0.06	0.06
SiO_2	36.59	38.26	35.73	33.59	39.93	42.42	42.43	38.67	39.35
SO_3	0.17	0.16	0.17	0.17	0.15	0.15	0.15	0.15	0.15
SnO_2	0.30	0.28	0.30	0.30	0.26	0.26	0.26	0.26	0.26
ZrO_2	5.16	4.86	5.16	5.16	4.55	4.55	4.55	4.55	4.55
WL, %	45.1	42.5	45.1	45.1	39.8	39.8	39.8	39.8	39.8

1250° C would be easily achievable in a CCIM. After fabrication, a portion of the glass was subjected to a canister centerline cooling (CCC) heat treatment intended to mimic the most extreme slow cooling profile that would be expected in glass fabricated in the plant. The glasses were analyzed using x-ray diffraction (XRD) and scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS) to assess crystallinity within the glasses in the as-fabricated state and after the CCC heat treatment. Isothermal heat treatments were used to provide a measure of the equilibrium crystal fraction vs. temperature. The liquidus temperature associated with spinel crystallization (T_L) was estimated by extrapolating the lower temperature data to 0 vol % crystal content. The Product Consistency Test – Method A (PCT-A) was used to assess the relative durability of the glasses in both the as-fabricated condition and after being subjected to the CCC heat treatment. The PCT-A is an ASTM standard test method (2002) used as a benchmark test to determine glass repository acceptability. To confirm that the as-fabricated glasses corresponded to the defined targeted composition, a representative sample was chemically analyzed. Chemical content was analyzed by means of two dissolution techniques, sodium peroxide fusion (PF) and lithium-metaborate (LM) fusion both followed by acid dissolution. The resulting dissolved samples were analyzed by Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES).

Results and Discussion

Visual observations of the glasses identified in Table 2 showed that the glasses were essentially crystal free after fabrication. After the glasses were subjected to the CCC treatment, XRD scans indicated the presence of a magnetite-type spinel crystalline phase in all of the samples. Baddeleyite phase was observed in the higher waste loading glasses (AZ-10, AZ-16, AZ-17 and AZ-18). The XRD scans showed that no nepheline was present in any of the glasses after the CCC treatment. The lack of nepheline reduces the risk that the chemical durability of the CCC glasses would be significantly worse than that of the quenched glasses.

The isothermal heat treatments showed that in general the volume percent of crystals decreased as the heat treatment temperature increased (Figure 1). An artifact of the testing was identified for some glasses in that at the higher heat treatment temperatures used (1200 and 1250° C), very fine spinel crystals formed during quenching the samples, i.e., they were not present at the heat treatment temperature but formed during cooling. Figure 1 also shows that crystal content generally increased as waste loading increased.

Table 3 provides the normalized elemental releases for B, Li and Na by PCT-A. These results show that all glasses exhibited lower normalized elemental releases than the Environmental Assessment (EA) glass by at least one order of magnitude. The EA glass is a standard glass used for qualifying US HLW glasses for repository disposal as reported by Jantzen et al. (1993). The results also indicated that CCC heat treatment had no significant effect on the PCT-A responses of the glasses, as expected. Interestingly, the normalized releases were also essentially equivalent irrespective of waste loading.

Based on total crystal vol % versus temperature data in Figure 1, the three glasses with 17 wt%, 16 wt%, and 15 wt% Fe_2O_3, CCIM-AZ-10, 16, and 29, respectively, were identified as candidates for initial CCIM demonstration testing. Figure 2 displays the total crystal vol % as a function of temperature for the selected three glasses. It was evident that the estimated crystal content increased as waste loading increased in these three glasses. At a processing temperature of 1250° C, these 3 glasses provide a range of crystal concentrations that could adequately assess the ability of the CCIM to process crystal laden melts.

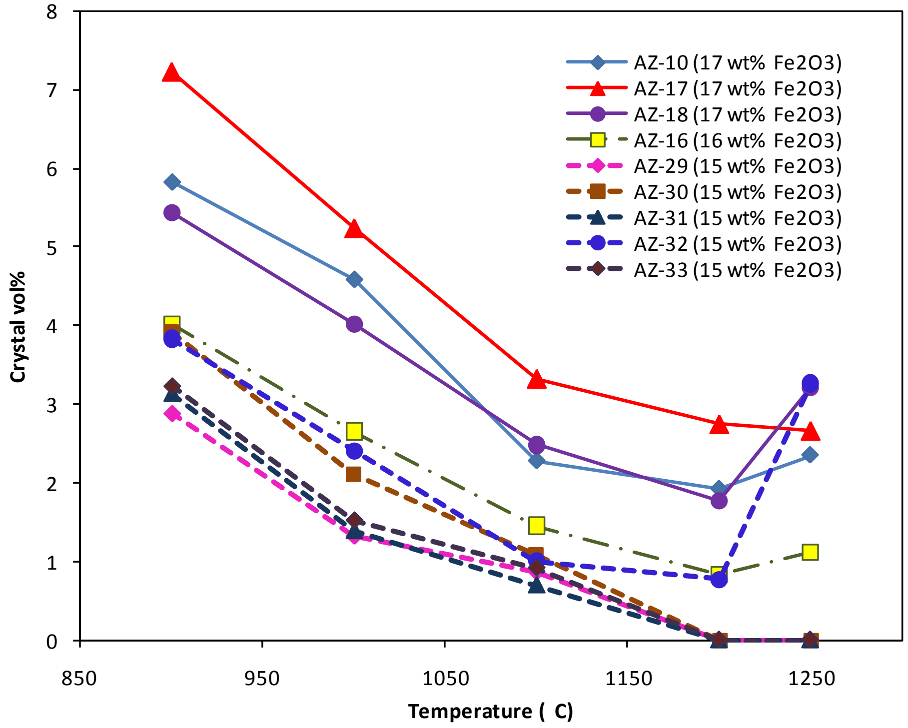

Figure 1. The volume percent of crystals in select AZ-101 HLW glasses as a function of heat treatment temperature. Note that some glasses erroneously showed an increase in crystal content at 1250° C due to spinel crystals forming during cooling from the heat treatment temperature.

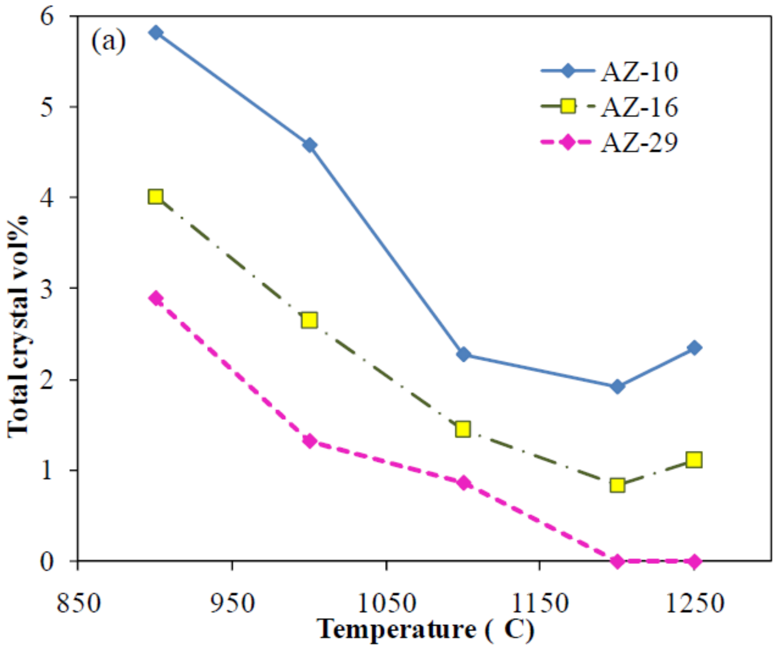

Figure 2. The volume percent of crystals for the three glasses identified as candidates for CCIM testing.

Table 3. Liquidus Temperature and PCT Normalized Elemental Releases for AZ-101 Glasses

	Glass Composition								
Normalized Elemental Release (g/L)	**AZ-10**	**AZ-16**	**AZ-17**	**AZ-18**	**AZ-29**	**AZ-30**	**AZ-31**	**AZ-33**	**EA (Jantzen 1993)**
B (quenched)	0.48	0.48	0.57	0.75	0.48	0.53	0.48	0.48	16.70
B (CCC)	0.44	0.44	0.73	1.08	0.43	0.44	0.47	0.33	--
Na (quenched)	0.40	0.43	0.35	0.55	0.39	0.26	0.48	0.41	13.35
Na (CCC)	0.39	0.39	0.42	0.70	0.37	0.21	0.46	0.30	--
Li (quenched)	0.63	0.65	0.80	0.81	0.62	0.69	0.60	0.65	9.56
Li (CCC)	0.56	0.54	0.91	0.97	0.53	0.60	0.55	0.47	--
T_L (spinel) (°C)	1398	1330	1311	1633	1146	1168	1132	1196	--

The results of the glass formulation development effort with the tank AZ-101 composition demonstrated that increased waste loading could be achieved with increasing crystal content for a given temperature. The higher operating temperature and apparent tolerance of the CCIM to crystallization within the melt could allow for processing the glass with up to 45.1 wt % waste loading (equivalent to 17 wt % Fe_2O_3) resulting in over a 20% improvement in waste loading over the current maximum projected waste loading of 37 wt % for AZ-101.

CCIM Testing on AZ-101 Glass Composition

The successful glass formulation development effort with the AZ-101 Hanford waste simulant supported CCIM testing to demonstrate that significant waste loading increases could be achieved using advance glass compositions in combination with the CCIM technology. The demonstration testing was conducted using the Idaho National Laboratory CCIM test platform.

Idaho National Laboratory Test Platform

The Idaho National Laboratory (INL) CCIM platform is comprised of liquid and solid feed systems, melter system, cooling system and off-gas system (Figure 3). The slurry feed system employs a feed tank equipped with a stirrer, sparger and recirculating loop. The slurry is fed to the melter using a recirculating pump that meters feed to the melter and recirculates excess feed to the feed tank. The 267 mm inner diameter CCIM vessel is constructed from 304L stainless steel and consists of a lower manifold, upper manifold, and cooling tubes. The cooling tubes are oriented vertically to form the crucible cylinder. The induction power system consists of a variable high frequency generator that can operate in frequency ranges from 200-400 kHz and 1.5-4 MHz to produce a maximum power of 75 kW (however, overpower interlocks limit the maximum power to 60 kW). A conductive metal (copper) cage encloses the melter and induction coil system to minimize worker exposure to electromagnetic radiation. Figure 4 provides a view of the INL CCIM melter in the protective metal cage. The molten glass is drained semi-continuously through a resistively heated bottom drain assembly. The off-gas system consists of a heated duct to the thermal reaction chamber, off-gas quench section, wet scrubber system and induced draft fan. The off-gas system is specifically designed to facilitate off-gas sampling making the INL CCIM system well suited for melter off-gas characterization tests.

The objective of the AZ-101 melter test campaign was to demonstrate CCIM operations over an extended period (in excess of 72 hours). Initially, the AZ-16 composition was targeted because the crystal content was in the middle of the range of the candidate glasses that were identified. Melter parameters were monitored over the duration of the testing. The glasses were characterized to determine chemical composition and relative glass quality as measured by the PCT.

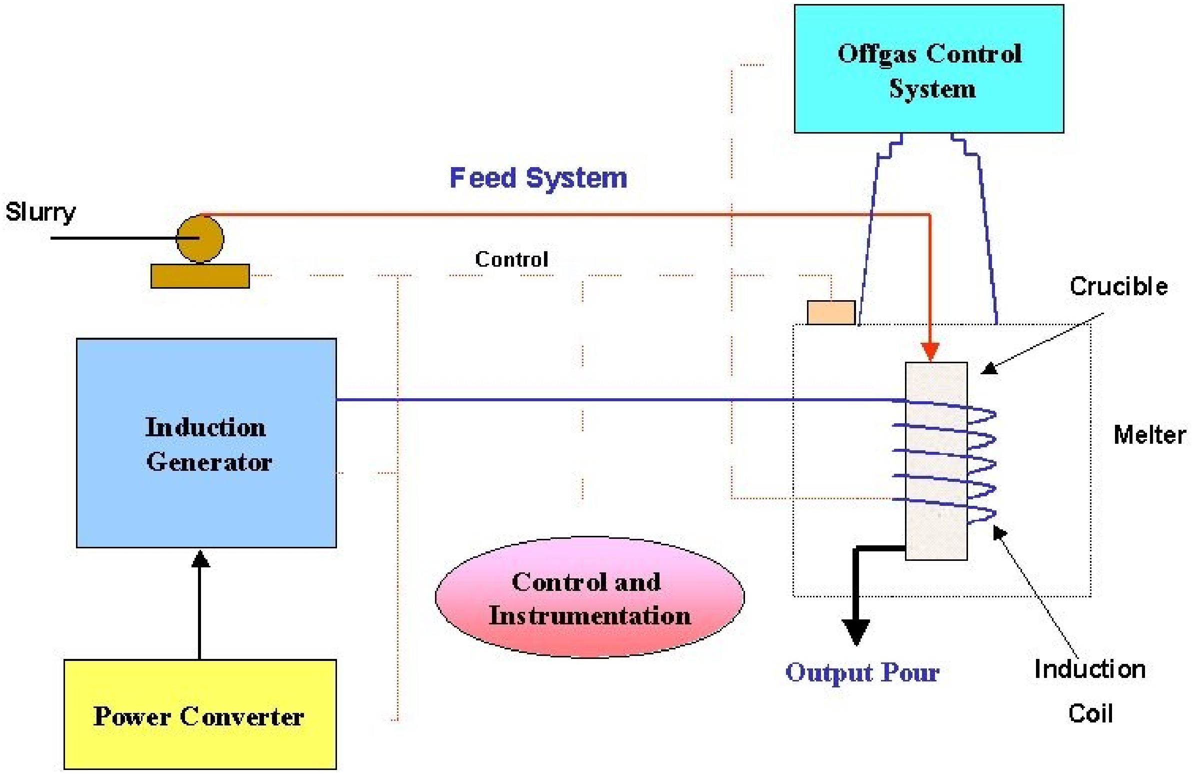

Figure 3. Simplified schematic diagram for the INL CCIM pilot-scale platform. (Soelberg 2009)

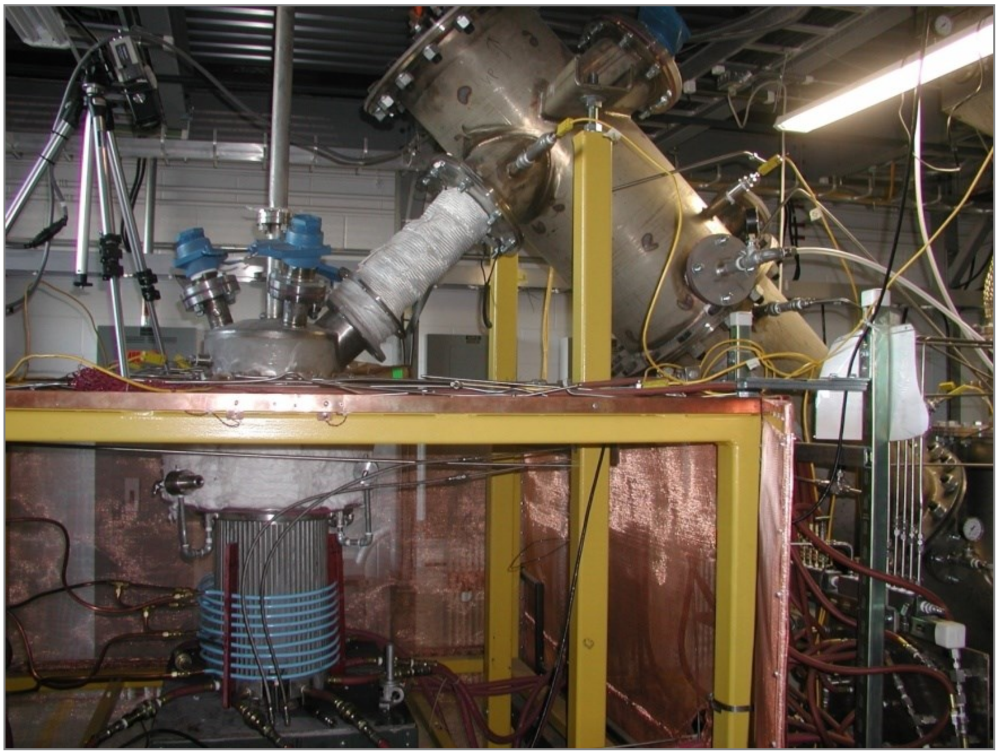

Figure 4. INL CCIM melter in the copper protective metal cage (INL 2011).

Glass Property Data to Facilitate Melter Testing

Prior to conducting CCIM testing, the viscosity and the electrical conductivity of the candidate glass compositions were measured to ensure these properties were in the range needed from successful melter operations. Figure 5 displays the results of viscosity (Figure 5a) and electrical conductivity (Figure 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 Figure 5a). The measured viscosities agreed 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 presence of crystals in the glass (the measured viscosities were higher than predicted, and the low-temperature viscosity increased as the waste loading increased). The measured viscosity was ~2 to 4 Pa·s in the range of 1200 – 1250 ° C (i.e., the recommended melting temperature range for all three glasses). These viscosity values were deemed to be acceptable for CCIM processing (Marra, et al. 2008). For electrical conductivity, three glasses had different predicted values as shown in Figure 5b. Figure 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 to support CCIM operations (Marra, et al. 2008).

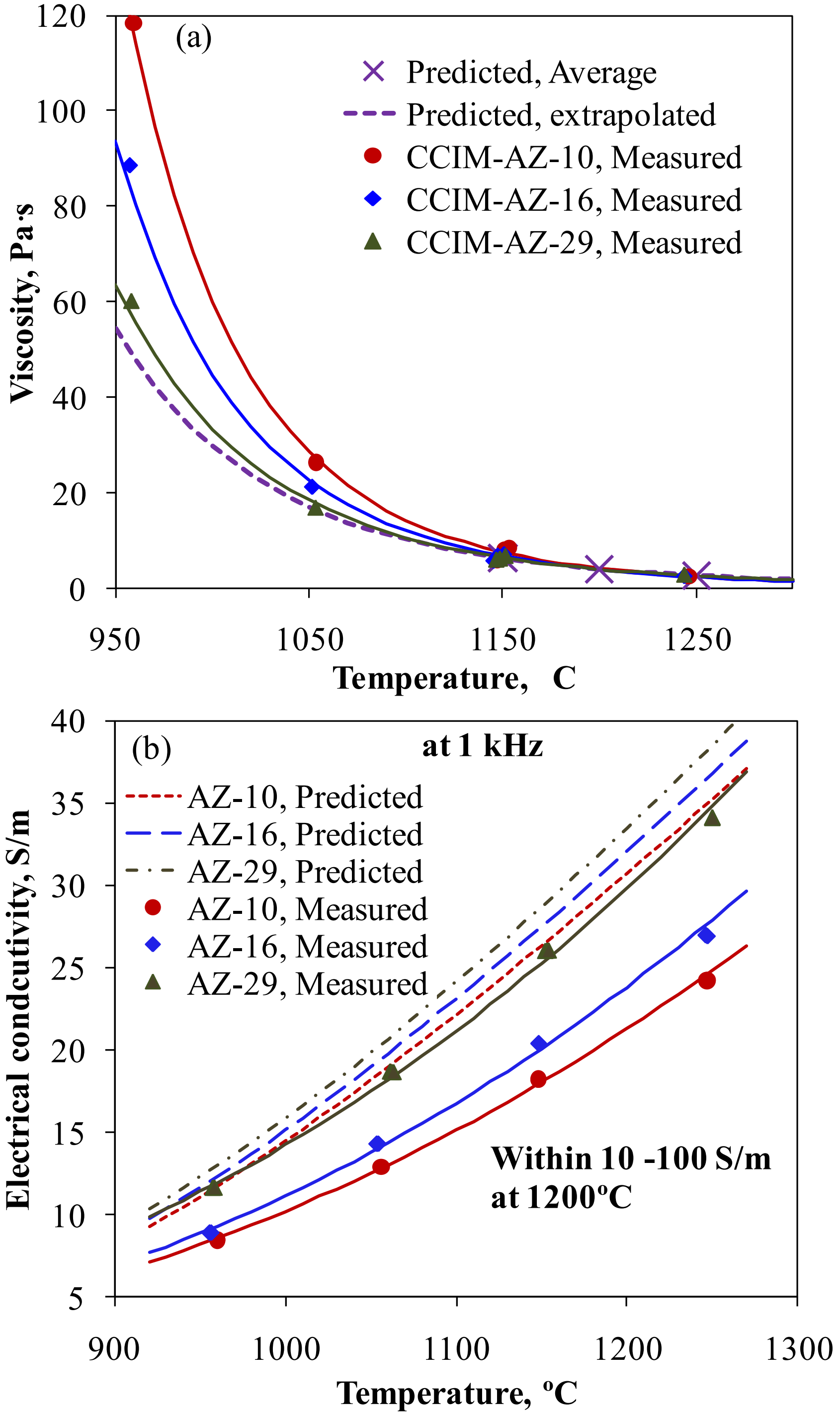

Figure 5. Viscosity (a) and electrical conductivity (b) of three glasses selected for CCIM testing (AZ-10, 16, and 29 glasses have 17, 16, and 15 wt% Fe_2O_3, respectively).

AZ-101 Glass CCIM Test Campaign Summary

The AZ-101 borosilicate glass feed at 43.5 wt % waste loading was vitrified in a campaign lasting about 80 hours in the INL 267 mm CCIM. The CCIM operated at 1250° C with temperatures in the pour valve estimated to be about 1175° C (Maio 2013). A new drain design that incorporated helium and nitrogen cooling for remote stopping of the pour stream was demonstrated. Glass samples were obtained from canisters that cooled under ambient conditions and canisters that were placed in a clam-shell furnace to be cooled slowly according to the CCC profile. The glass composition results are provided in Table 3-31. The measured compositions were very close to the targeted values with the exception of sulfate. There was no sulfate detected in the glasses indicating that volatility of this anionic species was prevalent under the CCIM operating conditions. Interestingly, boron and alkali volatility appeared to be minor. These observations should be evaluated in more detail in future CCIM campaigns. The durability of the glass samples was also evaluated using the PCT and showed that both atmosphere cooled and control cooled glasses exhibited elemental releases that were lower than the EA glass by better than an order of magnitude and that cooling conditions did not affect PCT response (Table 3-32).

Unfortunately, due to funding issues, off-gas samples that were collected during the test were not able to be analyzed. Therefore, an attempt to perform a mass balance (e.g. evaluate volatility observations discussed above) around the melter was not possible.

The CCIM test campaign was successful in demonstrating that the high waste loading AZ-101 glass (AZ-16) could be processed using the CCIM technology. Follow-on testing is suggested with the AZ-29 composition to further demonstrate the tolerance of the CCIM to crystals within the glass.

Table 4. Measured Chemical Compositions for AZ-101 Borosilicate Glass Produced using the INL 216mm CCIM

Oxides	Target Composition	Ambient Cooling	Controlled Cooling
B_2O_3	11.00	12.4	12.7
Li_2O	3.00	2.72	2.78
Na_2O	11.38	10.8	10.9
Al_2O_3	10.44	10.7	10.8
SiO_2	38.26	37.8	38.1
SO_3	0.16	0.00	0.00
CaO	0.60	0.62	0.58
SnO_2	0.28	0.28	0.29
Cr_2O_3	0.20	0.19	0.19
MnO	0.38	0.38	0.38
Fe_2O_3	16.00	16.3	16.5
NiO	0.70	0.52	0.51
ZrO_2	4.86	4.04	4.05
CdO	0.92	0.83	0.84
Ce_2O_3	0.34	0.42	0.42
La_2O_3	0.37	0.31	0.31
Nd_2O_3	0.28	0.26	0.25
P_2O_5	0.57	0.44	0.45

Table 5. PCT Results for AZ-101 Borosilicate Glass Produced using the INL 216 mm CCIM

Glass ID	Normalized release, g/L			
	B	Li	Na	Si
Ambient Cooling	0.57	0.62	0.39	0.26
Controlled Cooling	0.50	0.61	0.37	0.27
EA glass	17.8	9.64	13.66	3.99

Glass Composition Development for C-102 and 244-TX Waste Tanks

The selection of wastes for the glass formulation and testing efforts to demonstrate increased waste loading 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 AZ-101 glass composition development effort was the first Hanford HLW stream evaluated. Several tank wastes have been recently identified that provide further challenges to waste loading due to unique characteristics of the wastes.

Settling of plutonium-bearing particles > 10 µm in WTP process vessels is a concern for the WTP pretreatment facility (PTF) (Sams 2012). Recently it was estimated that approximately 30 kg of plutonium present in the tank farms was delivered as >10 µm particulate Pu oxide and Pu metal. This inventory is located in 16 tanks; eight with minimal quantities, and eight with appreciable quantities that could challenge the Criticality Safety Evaluation Report (CSER). The eight tanks with appreciable quantity (> 750 g) are TX-105, TX-109 and TX-118, 244-TX, SY-102, C-102, AN-101, and S-108.

Alternative treatment approaches for these tanks with safety concerns for processing within the WTP PTF are being considered. Direct vitrification using a near-tank CCIM unit is one candidate.

The tank wastes 244-TX and C-102 were identified for glass formulation development using the CCIM technology for the following reasons. The 244-TX composition has an exceedingly high iron oxide concentration (>59 wt %). This high iron concentration would significantly limit waste loading using the current JHCM technology with a process temperature limit of 1150° C and relatively low crystal tolerance. The C-102 composition has a high Al_2O_3 concentration (>60 wt %). The high alumina concentration in the waste limits waste loading due to the propensity to form nepheline and spinel in glasses with high alumina contents. These wastes also represent Hanford HLW composition families in general. Therefore, the information gained from this study may also be helpful for future glass formulation development efforts for Hanford HLWs in general. Table 6 shows the composition of these two wastes after adjusting the full composition by removing radioactive components (UO_3), by replacing PuO_2 and ThO_2 with ZrO_2 and lanthanide and actinide oxides with La_2O_3 (molar equivalent), and by removing minor components with <0.01 wt %. Each waste is also spiked with Cs_2O to ensure adequate analysis of this key volatile component.

Experimental Strategy

Glass property models were initially used to identify candidate glasses for both the C-102 and 244-TX waste compositions. Based on the modeling results, series of glass compositions were prepared in an iterative manner with the intent to build on the results from the previous series. The glasses were prepared in Pt crucibles using reagent grade chemicals. As described above, the glasses were analyzed using XRD and SEM-EDS to assess crystallinity. Liquidus temperature measurements, PCT and chemical composition determination were also conducted on select glasses.

Table 6. Composition of 244-TX and C-102 Waste Surrogates (wt %)

Comp.	244-TX	C-102
Ag_2O	0.01	--
Al_2O_3	0.81	62.5
As_2O_5	0.07	--
Bi_2O_3	--	0.32
CaO	0.37	1.10
Cl	0.38	0.21
Cr_2O_3	0.23	0.11
Cs_2O	0.20	0.20
F	0.06	0.49
Fe_2O_3	60.8	3.01
K_2O	0.94	0.17
La_2O_3	0.02	0.02
MgO	3.36	--
MnO	--	0.23
Na_2O	31.5	17.1
NiO	--	0.97
P_2O_5	0.38	1.46
PbO	0.04	0.21
SiO_2	--	8.96
SO_3	0.83	0.71
SrO	--	0.02
ZrO_2	--	2.21

Results and Discussion for C-102 Glasses

As mentioned, testing was conducted in a sequential manner with the intent to identify new compositions based on the results of previous crucible melts. In this manner, six of the 22 glass formulations were identified as “preferred” compositions for the C-102 waste and were fully characterized including performing chemical composition measurements and PCT measurements. These 6 compositions are shown in Table 7.

One series of six glasses was formulated based on the idea that the precipitation of spinel crystals in quenched glasses may improve PCT performance. It was suggested from a previous set of glasses that the addition of MgO may promote the formation of spinel in quenched samples. All six glasses with 3 to 7 wt % MgO formed 1 to 10 vol % spinel in quenched samples. All CCC glasses formed nepheline between 3 and 42 vol % along with spinel and/or various other crystals. Two glasses with low nepheline, C36-17 (4 vol %) and C36-20 (3 vol %), were tested for PCT for both quenched and CCC treated samples. In this study, one half of the PCT responses for the EA glass were used as a “provisional” pass/fail for the glass formulations (Jantzen et al. 1993). That is, the “provisional” PCT limits of 8.4 g/L for B, 4.8 g/L for Li, and 6.7 g/L for Na were used. The C36-17 glass failed but the C36-20 passed the “provisional” PCT constraints for both quenched and CCC samples. The PCT results on these two quenched samples suggested that the idea of precipitating spinel crystals in quenched glasses to improve PCT performance does not always work. The C36-20 glass, although it formed a small fraction of nepheline, is a potential candidate for a CCIM melter test as it is the only glass that passed the PCT constraints out of 14 glasses tested at 36 wt % Al_2O_3.

Table 7. Targeted Glass Compositions for Preferred Candidate C-102 Glasses (wt %)

Glass ID	**C36-17**	**C36-20**	**C36-21**	**C34-4**	**C34-5**	**C32-3**
Al_2O_3	36.00	36.00	36.00	34.00	34.00	32.00
B_2O_3	16.00	13.00	17.00	15.00	17.00	17.00
Bi_2O_3	0.18	0.18	0.18	0.18	0.18	0.16
CaO	0.63	2.50	4.80	7.00	5.50	5.50
Cl	0.12	0.12	0.12	0.12	0.12	0.11
Cr_2O_3	0.064	0.064	0.064	0.061	0.061	0.057
Cs_2O	0.12	0.12	0.12	0.11	0.11	0.10
F	0.28	0.28	0.28	0.27	0.27	0.25
Fe_2O_3	1.73	1.73	1.73	1.63	1.63	1.54
K_2O	0.099	0.099	0.099	0.093	0.093	0.088
La_2O_3	0.010	0.010	0.010	0.009	0.009	0.008
Li_2O	6.00	4.50	4.20	4.50	4.50	4.82
MgO	5.00	3.00	0.00	0.00	0.00	0.00
MnO	0.13	0.13	0.13	0.12	0.12	0.12
Na_2O	9.82	9.82	9.82	9.28	9.28	8.73
NiO	0.56	0.56	0.56	0.53	0.53	0.50
P_2O_5	0.84	0.84	0.84	0.79	0.79	0.74
PbO	0.12	0.12	0.12	0.11	0.11	0.11
SiO_2	20.59	25.22	21.50	24.60	24.10	26.66
SO_3	0.41	0.41	0.41	0.39	0.39	0.36
SrO	0.013	0.013	0.013	0.012	0.012	0.011
ZrO_2	1.27	1.27	2.00	1.20	1.20	1.13
WL %	0.57563	0.57563	0.57563	0.54365	0.54365	0.51167

A final set of four glasses were tested at 36, 34, and 32 wt % Al_2O_3. All four quenched glasses were crystal free by XRD. None of the four glasses formed nepheline after CCC treatment, and formed spinel only at 2 to 5 vol %. For the C36-21 glass with 36 wt % Al_2O_3, the quenched sample failed the "provisional" PCT constraints although the CCC sample passed. However, the high PCT releases in quenched samples can be partly attributed to a potential batching error (both higher Li_2O and lower ZrO_2 concentrations were found in the chemical composition measurements – higher Li_2O concentration and lower ZrO_2 concentration would tend to increase PCT releases). The two glasses with 34 wt % Al_2O_3 and one with 32 wt % Al_2O_3 all passed the "provisional" PCT constraints for both quenched and CCC samples. These results suggest that the maximum Al_2O_3 concentration in the glass that can be achieved while satisfying the PCT constraints is roughly 36 wt %. Considering the likeliness that the glass with this maximum loading may be susceptible to failing the property requirements upon relatively small change of composition, the glass with 34 wt % Al_2O_3 was recommended for CCIM melter testing. Out of two glasses with 34 wt % Al_2O_3, the C34-5 was selected because its higher B_2O_3 is preferred for nepheline tolerance although neither glass formed nepheline after CCC. This C34-5 glass was characterized for crystal vs temperature, viscosity, and electrical conductivity.

Figure 6 shows the effect of the heat treatment temperature on the spinel vol% determined by XRD for the C34-5 glass. Linear extrapolation of the data to 1 vol% results in the $T_{1\%}$ value of 1138 °C, which is the same as the predicted value by the model (Vienna et al. 2009) as given in Table 21.

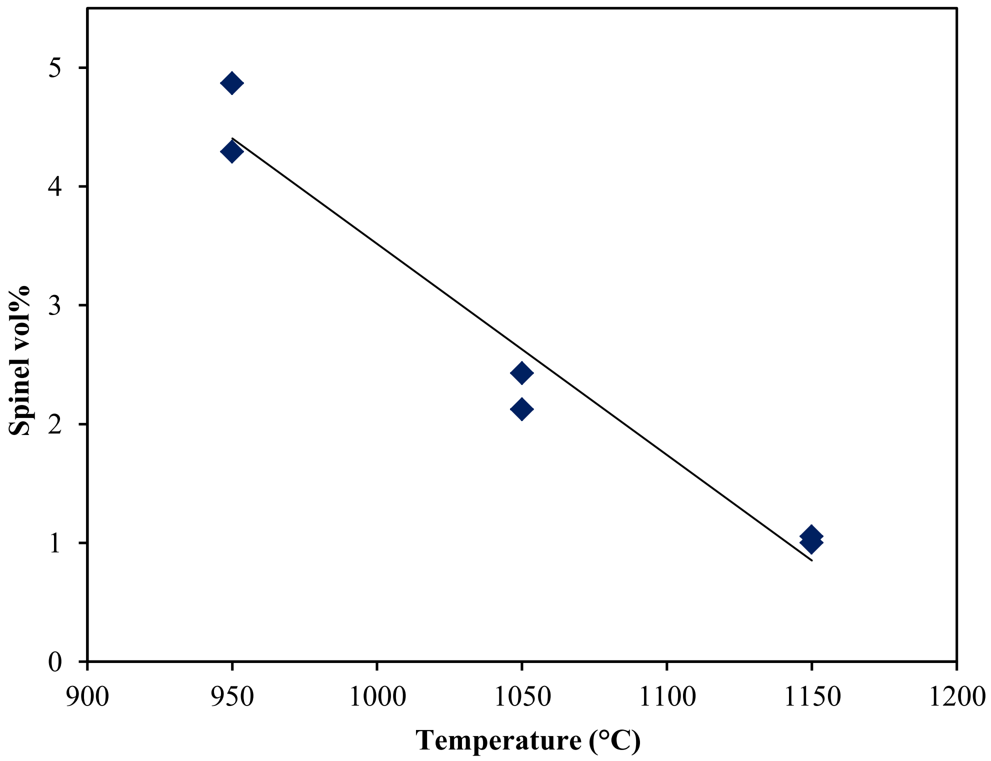

Figure 6. Spinel Vol% as a Function of Temperature of the C34-5 Glass

Table 8 summarizes the viscosity and electrical conductivity of the C34-5 glass. Figure 7 and Figure 8 display the results of viscosity and electrical conductivity of this glass as a function of temperature. Also shown in Figure 7 and Figure 8 are the curves of fitted data (Arrhenius form) to the measured values and of predicted data by the model (Vienna et al. 2009). The measured viscosities were significantly lower than the predicted values (Figure 7). The large difference between measured and predicted viscosities was understandable because the composition of this glass was well outside the model validity range. The recommended processing temperature is 1200° C based on the measured (interpolated) viscosity of ~3 Pa·s. The measured electrical conductivities agree reasonably well with the predicted values, which is likely due to the fact that the electrical conductivity is primarily affected by the alkali oxides, i.e., the concentrations of alkali oxides are well within the model validity range although other components, especially Al_2O_3 and SiO_2, are outside the model validity range. The measured (interpolated) electrical conductivity at 1200° C is 29.7 S/m, which is well within the desired range of 10 S/m to 100 S/m according to Marra et al. (2008).

Table8. Viscosity and Electrical Conductivity of the C34-5 Glass as a Function of Temperature

Viscosity	
T, °C	***η*, Pa·s**
1052	13.91
1148	4.50
1260	1.72
1374	0.854
1383	0.815
Electrical Conductivity	
T, °C	***ε*, S/m**
950	9.14
1050	16.04
1150	25.30
1250	36.53
1350	47.41

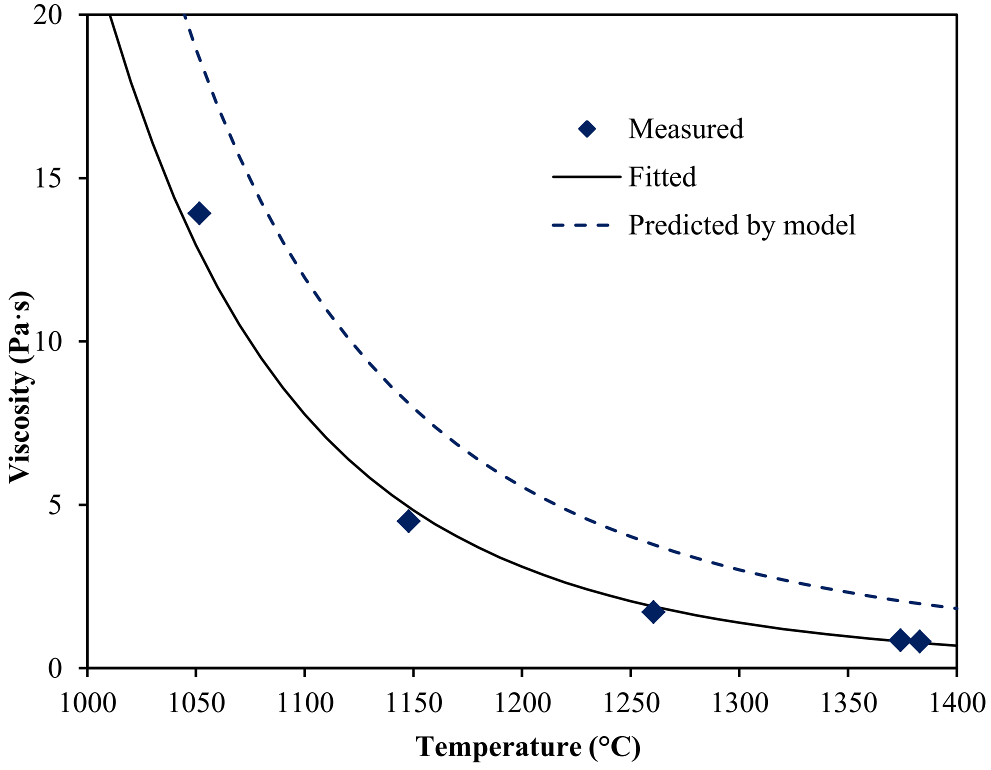

Figure 7. Viscosity of C34-5 Glass as a Function of Temperature

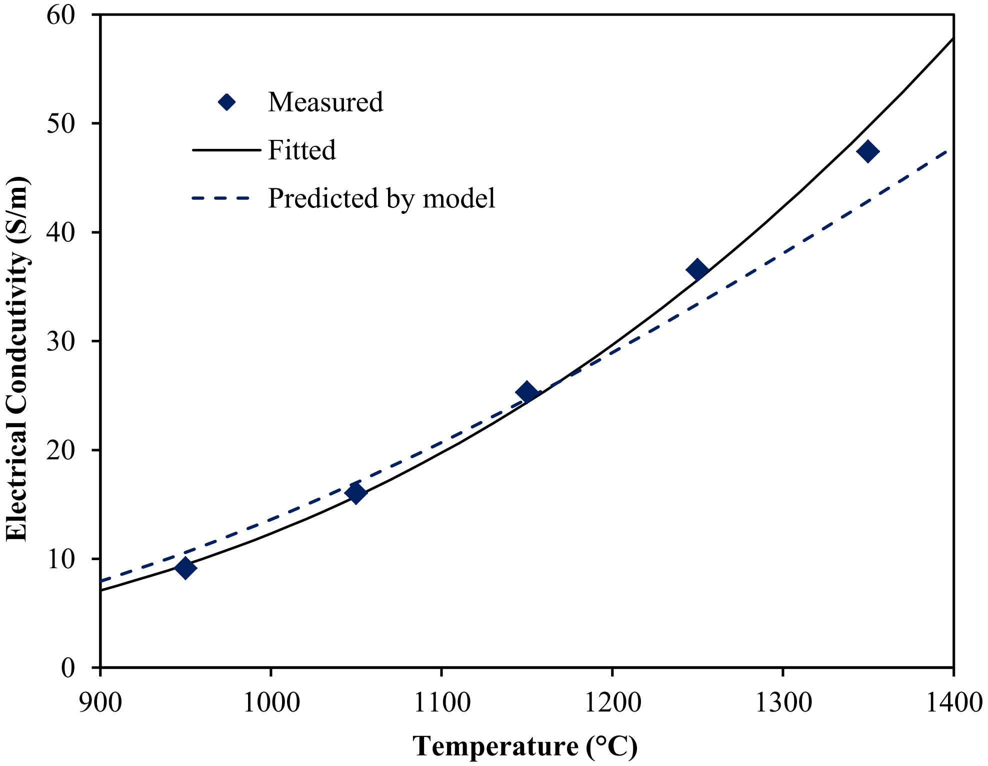

Figure 8. Electrical Conductivity of C34-5 Glass as a Function of Temperature

Results and Discussion for 244-TX Glasses

An iterative glass formulation development process was also used for the 244-TX waste composition. A set of four glasses (TX36-1 through TX36-4) were initially formulated at 36 wt % Fe_2O_3 (59.2 wt % waste loading). The first glass (TX36-1) was formulated with SiO_2 as the only additive; the TX-244 waste has already high concentration of Na_2O (31.5 wt % Na_2O in waste and 18.7 wt % Na_2O at 36 wt % Fe_2O_3 loading). The next three glasses were formulated focusing on improving PCT performance considering that the TX36-1 glass may fail the "provisional" PCT requirements. These three glasses were formulated with the addition of Al_2O_3 alone (TX36-2) or Al_2O_3 combined with B_2O_3 (TX36-3) or CaO (TX36-4). The PCT of quenched samples performed on two glasses, TX36-1 and TX36-2, showed that the addition of 6 wt % of Al_2O_3 decreased the PCT Na releases (B and Li are not present in these glasses) from 9.8 g/L (fail) to 2.8 g/L (pass). This suggests that the PCT requirements can readily be met by the addition of Al_2O_3 to these high-Fe_2O_3 glasses. However, all four glasses formed a significant amount of a separate salt layer after the first and second melts (re-melted after grinding the glass from the first melt). Although it was not possible to conclude that these glasses will form a salt layer during processing in a CCIM melter, it was likely that salt formation could be a limiting factor. The TX36-3 was characterized for crystallinity after a 24 h heat treatment at 950° C resulting in 7.4 vol % hematite. The TX36-4 was fabricated but not characterized for any property.

The second set of five glasses (TX36-5 through TX36-9) at 36 wt % Fe_2O_3 was focused on eliminating or decreasing the salt phase. The TX36-7 composition did not form salt after the first or second melt. The remaining four glasses all formed salt after the first melt, but only one glass (TX36-6) formed salt after the second melt. However, the amount of salt formed in the first melt of the four glasses (TX36-5 and

TX36-7 through TX36-9) was significantly smaller than the first set of four glasses (TX36-1 through TX36-4). These four glasses (TX36-5 and TX36-7 through TX36-9) were tested for crystallinity after a 24 h heat treatment at 950° C and three glasses (TX36-5, TX36-7, TX36-8) formed 5 to 6 vol % hematite with a small fraction of spinel and one glass (TX36-9) had 8 vol % spinel. Since spinel has a higher potential for settling, the three glasses (TX36-5, TX36-7, and TX36-8), which formed hematite after 24 h at 950° C and did not form salt in the second melt, were preferred CCIM melter glass candidates. Four glasses (TX36-5 through TX36-8) were tested for CCC crystallinity and all formed 4 to 8 vol % hematite without forming nepheline. PCT was performed on four quenched glasses (TX36-5 through TX36-8) and these all passed the "provisional" PCT requirements. However, the three preferred candidate glasses (TX36-5, TX36-7, and TX36-8) all failed the "provisional" PCT requirements for the CCC treated samples. It was surprising that these glasses formed hematite only after CCC treatment but they all had increased PCT releases after CCC.

The third set of two glasses [TX36-10(34) and TX36-11(32)][1] formulated were initial efforts to evaluate the effect of lower Fe_2O_3 content at 34 and 32 wt% Fe_2O_3. Both glasses did not form salt from the first and second melts. After a 24 h heat treatment at 950° C, TX36-10(34) formed spinel only and TX36-11(32) formed spinel and hematite (crystal quantification was not performed). After CCC treatment, TX36-10(34) formed spinel only, but surprisingly TX36-11(32) formed 6.5 vol% nepheline along with hematite and spinel. Both glasses failed the "provisional" PCT requirements on quenched samples. However, for the CCC samples, TX36-10(34) at 34 wt% Fe_2O_3 passed the "provisional" PCT requirements but surprisingly TX36-11(32) at 32 wt% Fe_2O_3 failed. Additional tests to investigate the cause of these unexpected results were not pursued because the combination of relatively high Al_2O_3 ($\geq$ 4 wt%) and high CaO ($\geq$ 4 wt%) was a likely reason for poor performance in these two glasses.

The last set of three glasses (TX36-12, TX34-5, and TX32-7) were formulated at 36, 34, and 32 wt % Fe_2O_3, respectively with 2 to 3 wt % Al_2O_3 and 7 to 9 wt % B_2O_3 without CaO and were identified as the preferred compositions for the 244-TX waste. The compositions of these glasses are shown in Table 9. These glasses were modifications of TX36-5 that had the best PCT performance after CCC treatment among the three preferred candidate glasses in the second set of glasses tested. The TX36-12 glass had increased Al_2O_3 from 2 to 3 wt % and increased B_2O_3 from 7 to 9 wt % at the expense of SiO_2 starting from TX36-5. The TX34-5 and TX32-7 were designed to keep the same 2 wt % Al_2O_3 and 7 wt % B_2O_3 as TX36-5 while increasing SiO_2 as the waste loading decreased. These three glasses were characterized for salt formation and the crystallinity of quenched, 950° C 24 h heat treated, and CCC treated samples. The quenched glass at 36 wt % Fe_2O_3 (TX36-12) formed 1 vol % hematite and the lower waste loaded glasses (TX34-5 and TX32-7) were crystal free. After 24 h 950°C and CCC treatments only hematite formed and its amount decreased as the waste loading decreased. Similar to the second set of glasses, all quenched samples passed the "provisional" PCT requirements. For the CCC samples, the 36 wt % Fe_2O_3 glass (TX36-12) failed the "provisional" PCT requirements while the two glasses (TX34-5 and TX32-7) at lower waste loading passed, showing the decreasing trend of PCT normalized release as the waste loading decreased. The properties for these preferred 244-TX glasses are summarized in Table 10.

Based on the glasses tested in the present study it was demonstrated that a loading of 34 wt % Fe_2O_3 for the 244-TX waste compositions is possible while satisfying the major constraints evaluated. It is possible that glasses with the higher waste loading (36 wt % Fe_2O_3) could be successful for CCIM processing if additional formulation efforts are completed. Due to funding constraints, property measurements for the

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[1] Note that the ID in these two glasses had the Fe_2O_3 concentration in parenthesis unlike all other glasses that specified the Fe_2O_3 or Al_2O_3 concentration right after the tank ID abbreviations, e.g., TX36-1 is a glass with 36 wt% Fe_2O_3 formulated for 244-TX tank waste.

glasses (viscosity and electrical conductivity measurements) to support CCIM melter tests were not performed for the 244-TX glasses.

Table 9. Targeted Glass Compositions for Preferred Candidate 244-TX Glasses (wt %)

Glass ID	**TX36-12**	**TX34-5**	**TX32-7**
Ag_2O	0.006	0.006	0.006
Al_2O_3	3.00	2.00	2.00
As_2O_5	0.04	0.038	0.036
B_2O_3	9.00	7.00	7.00
CaO	0.21	0.21	0.20
Cl	0.22	0.21	0.20
Cr_2O_3	0.14	0.13	0.12
Cs_2O	0.12	0.11	0.10
F	0.035	0.033	0.031
Fe_2O_3	36.00	34.00	32.00
K_2O	0.56	0.53	0.50
La_2O_3	0.012	0.011	0.011
MgO	1.98	1.87	1.76
Na_2O	18.65	17.62	16.58
P_2O_5	0.22	0.21	0.20
PbO	0.023	0.022	0.021
SiO_2	29.28	35.54	38.80
SO_3	0.49	0.46	0.44
WL %loading	59.20	55.92	52.63

Table 10. Measured Properties of Preferred Candidate 244-TX Glasses

Glass ID	**TX36-12**	**TX34-5**	**TX32-7**	**Provisional PCT limits (g/L)**
Salt – first melt	Yes	No	No	
Salt – second melt	Yes	No	No	
Q XRD vol %		amorphous	amorphous	
950C 24h, XRD vol %		Hm 4.3	Hm 3.7	
CCC XRD vol %	Hm 6.9	Hm 5.7	Hm 5.3	
Q-PCT B, g/L	3.3	3.4	2.6	8.4
Q-PCT Li, g/L	No Li	No Li	No Li	4.8
Q-PCT Na, g/L	2.8	2.8	1.9	6.7
CCC-PCT B, g/L	9.0	8.0	4.3	8.4
CCC-PCT Li, g/L	No Li	No Li	No Li	4.8
CCC-PCT Na, g/L	7.7	6.6	3.3	6.7

Conclusions

Several "troublesome" US defense HLW chemical constituents may lead to crystallization within the melt when waste loadings are increased. The formation of these crystals can negatively impact product quality or have a deleterious effect on melter processing. Therefore, waste loading is limited due to these waste components. Efforts are underway at US national laboratories to develop "crystal tolerant" glasses that control crystallization within the melt allowing crystals to harmlessly pass from the melter. Other efforts are attempting to leverage advances in glass melter technologies to develop glass formulations that take advantage of increased melter processing temperatures, thus, leading to increased waste loading.

A case study was conducted using the Hanford tank AZ-101 waste composition (representative of a high Fe_2O_3 waste group with high Al_2O_3) to demonstrate that higher melt temperature and higher crystal content glass compositions could be developed to significantly increase waste loading yet meet product quality requirements. The results showed that waste loadings of over 50 wt % could be realized for this waste group by processing at temperatures that could be readily achieved using a CCIM. Extrapolating these higher waste loading results to model projections used in Hanford site operations planning, indicated that for the high Fe_2O_3 waste group approximately 600 MT less glass would need to be produced.

The CCIM test campaign with an AZ-101 high waste loading composition (AZ-16) demonstrated that this waste could be readily processed using the CCIM technology. The resulting glass was close to the targeted composition with only sulfate showing significant volatility. The glass product from the CCIM test was better than an order of magnitude more durable than the EA glass as measured by the PCT.

An additional Hanford waste type was identified that would prove challenging for JHM processing due to the presence of appreciable plutonium concentrations. In addition to containing appreciable Pu quantities, the C-102 waste tank and the 244-TX waste tank contain high concentrations of aluminum and iron, respectively that will further challenge vitrification processing. Glass formulation testing was conducted on these waste tank compositions to evaluate the potential benefits of the CCIM technology to vitrify these waste streams.

The major constraints that limited the waste loading in the high-Al_2O_3 loaded glasses for C-102 tank waste were crystallinity after CCC treatment and PCT responses in quenched (as-prepared) and CCC treated samples. One glass (C36-5) was successfully formulated at 36 wt% Al_2O_3 to pass the "provisional" PCT requirements for both quenched and CCC samples. However, this glass did not pass the nepheline constraint because it formed 3 vol % nepheline after CCC treatment (although this small amount of nepheline did not cause the glass to fail the PCT after CCC treatment). The glasses with 34 and 32 wt% Al_2O_3 passed both the nepheline constraint after CCC and the "provisional" PCT requirements for both quenched and CCC samples. The glass with 34 wt% Al_2O_3 (C34-5) was recommended for CCIM melter testing.

The initial focus of glass formulation for the high-Fe_2O_3 loaded glasses for 244-TX tank waste was to design the composition without sulfate salt formation that may interfere with melter operation. However, the primary focus shifted to the PCT requirements for both quenched and CCC glasses after finding the composition regions that avoid salt formation. The maximum Fe_2O_3 loading that passed all the major constraints evaluated was 34 wt% as exhibited by the TX 34-5 formulation.

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