Glass Formulation Development and Testing for Cold Crucible Induction Melter (CCIM) Advanced Remediation Technologies Demonstration Project - 9208

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ABSTRACT

Over the past few years, Cold Crucible Induction Melter (CCIM) demonstrations have been completed using SRS sludge batches 2, 3 and 4 (SB2, SB3 and SB4) simulant compositions. These campaigns demonstrated the ability of the CCIM to effectively produce quality glasses at high waste loadings. The current Advanced Remediation Technology (ART) Phase II-A Project is aimed at demonstrating the CCIM technology under representative DWPF flowsheet conditions and to demonstrate extended operations of the melter.

A glass composition development effort was completed to identify and recommend a frit composition and sludge batch 4 (SB4) simulant waste loading target for subsequent ART – Phase II-A CCIM demonstration testing. Based on the results of the glass formulation testing, it was recommended that the Frit 503-R6 composition (B_2O_3 = 14 wt %; Li_2O = 9 wt %; Na_2O = 3 wt %; and SiO_2 = 74 wt %) be utilized for the demonstration. Furthermore, a waste loading of 46 wt % was recommended. The recommended frit and waste loading would produce a glass with acceptable durability with a liquidus temperature adequately below the 1250° C nominal CCIM operating temperature. This frit composition and waste loading was found to result in a glass that met CCIM processing requirements for viscosity, electrical conductivity and thermal conductivity. The recommended frit and waste loading level should also provide a buffer for sludge product compositional variation to support the Phase II-A CCIM demonstration.

INTRODUCTION

The CCIM offers the potential to increase waste loading for High Level Waste (HLW) glasses leading to significant improvements in waste throughput rates compared to the reference Joule Heated Melter (JHM). At the Savannah River Site (SRS) this could allow the Defense Waste Processing Facility (DWPF) to complete its mission earlier and enable faster closure of the SRS waste tanks. The Advanced Remediation Technology (ART) CCIM Phase I studies concluded that the CCIM could provide significant savings (cost and schedule) in the treatment of SRS wastes. Furthermore, demonstration testing in CCIM units conducted under the auspices of the DOE Office of Environmental Management (DOE-EM) International Program and through an SRS Liquid Waste Organization (LWO) funded task has shown the feasibility of the CCIM to process SRS waste types. The ART CCIM Phase II-A project was awarded to AREVA in late FY07. The primary objective of the Phase II-A Project was to perform testing under current representative DWPF flowsheet conditions and to conduct a first set of engineering tasks.

Based on a review of previous glass formulation testing in support of the CEA Marcoule CCIM demonstrations conducted in 2007 and testing associated with other CCIM test beds, the Savannah River National Laboratory (SRNL) determined that glass composition development and testing associated with ART CCIM Phase II-A should be concentrated in a few specific areas (described below). Focusing on these emphasis areas should facilitate successful processing in the CCIM and provide the needed data to assess consistency with current DWPF operational philosophies.

APPROACH

Glass Formulation Objectives

Previous CCIM testing with SRS sludge batches 2, 3 and 4 (SB2, SB3 and SB4) simulant compositions demonstrated the ability of the CCIM to effectively produce quality glasses at high waste loadings [1,2,3]. These CCIM tests demonstrated that glasses with the necessary properties can be formulated to be processed in the CCIM. Specifically, recent pilot-scale testing of SB3 in the CEA Marcoule CCIM showed that the specified glass met acceptance requirements for viscosity, electrical conductivity, and thermal conductivity. Additionally, the formulated glasses were found to have acceptable durability as determined by the Product Consistency Test (PCT).

In support of the primary objective of the Phase II-A Project (e.g. perform testing under representative DWPF flowsheet conditions), the current processing criteria for the DWPF were utilized to guide glass formulation development activities. As discussed below, specific attention was given to liquidus temperature and durability in developing glass formulations.

An open issue remains regarding glass liquidus temperature (T_L) requirements for processing in the CCIM. The current specification for waste glass processing in the DWPF Joule Heated Melter (JHM) is the $T_{\text{melt temp.}} - T_L \geq 100°$ C. There appears to be no specific liquidus temperature criterion for CCIM processing and, in fact, previous tests were likely performed with the liquidus temperature of the glass *greater* than the melting temperature (suggesting that some volume percentage of crystals was processed through the melter during the demonstration). In short-term testing this did not appear to be a problem. In longer-term operation, the potential for crystal settling and/or build-up in the melter must be considered as well as the potential for adverse effects on melter processing or operations (e.g. pouring). Therefore, a specific criterion for liquidus temperature needs to be established.

Given the overarching ART CCIM Phase II-A project objectives, a goal was to conduct the demonstration using a glass composition that had a liquidus temperature *lower* than the nominal melter temperature. This condition is consistent with current DWPF process operations. Therefore, a primary objective of frit development and waste loading definition was to ensure that the resulting glass had a liquidus temperature below the nominal 1250° C melter operating temperature.

DWPF waste compositions with high alumina concentrations have the potential to increase nepheline ($NaAlSiO_4$) crystal formation in the glass [4]. The formation of nepheline can have a detrimental impact on glass durability because it decreases the amount of the glass forming oxides Al_2O_3 and SiO_2 in the residual glass matrix. The magnitude of the impact on durability is ultimately related to the volume percent of nepheline and the overall change in residual glass composition. The frit development effort attempted to preclude or minimize nepheline formation in the SB4 glass.

Experimental Details

Waste Composition

The DWPF SB4 surrogate waste composition was identified for testing (Table I). This sludge had a high alumina concentration and was previously found to present waste loading and melt rate challenges for the JHM.

Table I. Surrogate SB4 Waste Composition

Oxide	Weight %
Al_2O_3	28.16
BaO	0.08
CaO	3.06
Ce_2O_3	0.24
Cr_2O_3	0.22
CuO	0.06
Fe_2O_3	32.03
K_2O	0.08
MgO	3.06
MnO	6.39
Na_2O	20.67
NiO	1.83
SO_4^{2-}	0.96
SiO_2	3.00
ZnO	0.06
ZrO_2	0.10
Total	100.00

Glass Models

Glass composition models have been utilized extensively as prediction tools for waste glass formulation and for control of vitrification processes [5,6,7]. A Product Composition Control System (PCCS) was developed for DWPF based on work by Jantzen, et al. [7]. A Measurement Acceptability Region (MAR) approach was developed by Peeler and Edwards to facilitate formulation of waste glasses for DWPF [8]. The MAR approach allows for efficient evaluation of glass compositions against the PCCS constraints for various glass quality and processing properties. A "nepheline discriminator" is included as one of the MAR terms. The nepheline discriminator is based on work by Li, et al. [9] and utilizes waste glass composition to predict the potential for nepheline formation. Specifically, glasses with $SiO_2/(SiO_2+Na_2O+Al_2O_3) > 0.62$, where the chemical formula represents mass fractions in the glass, do not precipitate nepheline. The MAR approach was utilized in the formulation efforts in this study to guide identification of the initial frit compositions for testing. The MAR approach was modified, however, by the use of alternative models (e.g. alternative liquidus model) to provide guidance on properties of interest. Furthermore, model uncertainties were not applied in using the MAR approach for this study.

Glass Composition Identification

A previously developed frit composition (Frit 503) was used as a basis for identification of candidate glass formulations. Frit 503-R4 (a derivative of Frit 503) was developed and used in previous SB4 CCIM testing [10]. The liquidus temperature of this glass composition was higher than the nominal 1250° C melter temperature based on the observance of significant spinel crystallization in the glass products from the CCIM tests [3]. Therefore, the Frit 503-R4 was modified by increasing the alkali and/or boron content in an attempt to decrease the liquidus temperature. The MAR approach was then utilized to screen various frit compositions for initial laboratory testing. The candidate frit compositions identified for the initial phase of testing are shown in Table II. The compositions of Frit 503 and Frit 503-R4 are included in Table II for comparison.

Table II. Initial Candidate Frit Compositions

Oxide	503-R3	503-R6	503-R7	503	503-R4

B_2O_3	16	14	14	14	16
Na_2O	2	3	2	4	0
Li_2O	8	9	10	8	8
SiO_2	74	74	74	74	76
Total	100	100	100	100	100

Initial Frits – Fabrication

The MAR assessment tool was used to evaluate the compositions at several waste loadings (on a calcined oxide basis). Based on the MAR assessment results, it was decided to fabricate glasses using all three candidate frit compositions at 45, 50, and 55 wt % waste loading. The compositions were batched using oxide chemicals and melted at 1250° C in Pt/Rh crucibles. After nominally two hours at temperature, the glasses were quenched by pouring onto a steel plate. A portion of the glass was heat treated to simulate cooling along the centerline of the DWPF canister modified to take into account higher processing temperatures in the CCIM (i.e. Modified Canister Centerline Cooling (MCCC) profile) [11]. It must be noted that at this time the actual cooling curve for bulk quantities of glass processed in a CCIM and poured in a batch mode into a DWPF-type canister is not known. Therefore, the MCCC cooling profile was not thought to be representative of actual CCIM conditions but could provide insight into glass behavior under slow cooling conditions. It should be further noted that the MCCC initiates at a higher temperature than the CCC used to simulate JHM processing and, thus, would be expected to be more discriminating towards nepheline formation than the CCC.

Initial Frits – Characterization and Testing

X-ray Diffraction

Both as-fabricated (AF) and MCCC glass samples were evaluated for crystallization using XRD. Samples were run under conditions providing a detection limit of approximately 0.5 vol %. That is, if crystals (or undissolved solids) were present at 0.5 vol % or greater, the diffractometer would not only be capable of detecting the crystals but would also allow a qualitative determination of the type of crystal(s) present. Otherwise, a characteristically high background devoid of crystalline spectral peaks indicated that the glass product was amorphous, suggesting either a completely amorphous product or that the degree of crystallization was below the detection limit.

Isothermal Liquidus Temperature Measurement

The T_L for a select number of glasses was determined using an isothermal liquidus determination method. In this method, a glass sample was subjected to a set temperature for nominally 24 hours. The sample was then evaluated using XRD and thin-section optical microscopy to analyze for crystallization within the sample. The isothermal heat treatment was continued until the T_L was identified as the temperature between the highest temperature at which a heat-treated sample contained crystals and the lowest temperature without crystals.

Compositional Analysis

To confirm that the AF glass corresponded to the defined target composition, a representative sample was chemically analyzed. Chemical content was analyzed by means of two dissolution techniques, sodium peroxide fusion and lithium-metaborate dissolution. The resulting dissolved samples were analyzed by Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES). Glass standards were intermittently run to assess the performance of the ICP-AES over the course of these analyses.

Product Consistency Test (PCT)

The PCT was performed in triplicate on a quenched sample and a sample heat treated using the MCCC profile to assess chemical durability using the ASTM C-1285 Procedure [12]. The method "A" procedure was followed. The PCT-A is a crushed glass leach test conducted at 90° C for 7 days. Also included in the PCT testing were the Environmental Assessment (EA) glass, the Approved Reference Material (ARM) glass, and blanks. The resulting solutions (leachates) were analyzed via ICP-AES for Si, B, Na, and Li release.

Variability Testing

The Phase II-A CCIM pilot-scale demonstration runs, utilizing a “constant” sludge composition (targeting a nominal SB4 composition – see Table I) coupled with optimized frit at a recommended waste loading, would theoretically yield a constant glass composition. Although this would support programmatic objectives, there was need to assess the potential impacts of sludge variation and/or waste loading differences on potential processing and/or product performance properties. For example, a vendor would produce a surrogate Slurry Receipt Adjustment Tank (SRAT) product targeting the nominal SB4 composition to support the CCIM testing. Recognizing the low probability of the vendor producing the exact targeted SB4 composition and/or that actual waste loading could vary ± 2% around the nominal target, led to questions regarding the impact of these variations on processing properties or perhaps more importantly on the properties of the glass waste form. To address this issue, a variability study was performed in which sludge variation was applied to the nominal SB4 composition to generate a set of extreme vertices (EVs) in order to bound the anticipated sludge variation. These EVs were then coupled with the recommended frit over waste loadings of interest to develop a glass test matrix. Glasses were fabricated and characterized to provide insight into the impacts of sludge variation and/or waste loading on specific properties of interest. The variability study included testing with the nominal SB4 sludge composition at waste loadings of 44, 46 and 48 wt % (given that data at 45, 50 and 55 wt % waste loading were already in hand). Nine EV glasses were formulated with a nominal waste loading of 46 wt %. The variability study glasses were fabricated and subjected to the MCCC profile. As-fabricated and MCCC glasses were characterized using XRD to identify crystalline phases within the glasses. The AF and MCCC glasses were tested using the PCT to assess relative durability. The XRD measurements and PCT analyses were conducted as described above.

The variability study glasses were also subjected to an isothermal heat treatment at 1225° C. The heat treated glasses were evaluated using XRD to assess crystallinity within the glass. The 1225° C temperature was selected to provide a buffer below 1250° C to account for uncertainty in the use of XRD in the determination of crystallinity within the glass. In this manner, a glass showing no indication of the presence of crystals could be confidently considered to have an estimated liquidus temperature below 1250° C.

Glass Properties Important for CCIM Processing

Since previous testing with SB4 glass compositions indicated that these compositions readily met the requirements for CCIM processing with respect to viscosity, electrical resistivity and thermal conductivity, glass formulation efforts were not specifically targeted at these properties. Validation of the properties of the recommended composition against the accepted values was made prior to final selection of a frit composition and waste loading for follow-on Phase II-A CCIM demonstrations. Viscosity, electrical resistivity and thermal conductivity measurements were made as follows.

Viscosity

The viscosity of the molten glass was measured as a function of temperature using a Couette-type rheometer. The molten glass was contained in a 29 mm, Pt/Rh 10% crucible in which a 14 mm rotor was immersed. Typically, prior to viscosity measurement, molten glass is raised to the required upper temperature inside a muffle furnace, in order to evaluate if any reboil occurs (with subsequent overflow) in the crucible due to the presence of multivalent reducible elements (such as Fe, Cr, Mn). In this case, the target upper measurement temperature was set at 1300° C, which was the maximum target temperature in the CCIM demonstration plan.

The glass was heated and held at several temperatures within a range of 1000 - 1300° C. At each temperature step, torque was measured over a range of rotation speeds, and the results plotted. The slope of this line is proportional to melt viscosity at each temperature step.

Electrical Resistivity
Electrical resistivity was measured at temperatures up to 1300° C using the 4-electrode method. The complex impedance of the specimen was measured by a Solartron SI 1260 impedance analyzer over a frequency range between 1 Hz and 1 MHz.

Thermal Conductivity
Thermal conductivity of SB4 reference glass was measured over a temperature range from 750° C to 1300° C. In the measurement cell, the glass was heated from the top and the crucible was cooled at the bottom, thus, creating a temperature gradient in the crucible. Thermal conductivity was then determined by measuring the temperature gradient in the glass as a function of the heat eliminated through the cooled bottom.

RESULTS

Initial Frits

Glass Fabrication

The three frit compositions (Table II) were utilized to prepare glasses at 45, 50 and 55 wt % waste loading using the SB4 sludge simulant (Table I). The resulting 9 glasses were characterized and tested as follows.

X-Ray Diffraction

Samples evaluated by XRD were analyzed under conditions providing a detection limit for crystalline content of ~0.5 vol %. For all three frit compositions, the XRD results for the AF glasses were amorphous at 45 wt % waste loading. The presence of spinel crystals (magnetite, Fe_3O_4)[*] was evident in AF glasses for the three frits at 50 wt % waste loading with increasing content at 55 wt % waste loading. No nepheline formation was observed in the AF glasses regardless of frit composition.

Spinel (magnetite, Fe_3O_4) crystals were evident in the MCCC glasses for the three frit compositions at all waste loadings. Nepheline was also detected in MCCC glasses for all frits at 50 and 55 wt % waste loading. The observed presence of nepheline in these glasses was consistent with the nepheline prediction equation. The spinel and nepheline content in the glasses appeared to increase with increasing waste loading. As previously discussed, the presence of nepheline in the glass can have a detrimental impact on glass durability because it depletes the residual glass matrix of the glass forming oxides, Al_2O_3 and SiO_2.

Isothermal Liquidus

Isothermal liquidus temperature measurements were made on glasses made at select waste loadings with the three frit compositions. Glasses were tested with all three frits at 50 wt % waste loading. The 503-R3 glass was also tested at 55 wt % waste loading. The 503-R3 composition had the lowest alkali content and, thus, was expected to have the highest (bounding) T_L for the three frits. Liquidus temperature results are shown in Table III.

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[*] The peaks identified in the XRD scans were indexed to the spinel structure magnetite (Fe_3O_4). It is likely that there was some substitution of both Ni and Cr for Fe in these crystals.

Table III. Liquidus Temperature Values for the Three Initial Frits

Glass ID	Liquidus Temperature (T_L)
503-R3 @ 50 wt % WL	1252° C
503-R6 @ 50 wt % WL	1229° C
503-R7 @ 50 wt % WL	1227° C
503-R3 @ 55 wt % WL	1463° C

The target CCIM operating temperature for the Phase II-A demonstration was 1250° C. Although the measured liquidus temperatures for the 503-R6 and 503-R7 compositions appeared to be below the nominal operating temperature, a margin of less than 25° C was a potential concern to meet the overarching Phase II-A demonstration objectives. As discussed previously, the current specification for waste glass processing in the DWPF Joule Heated Melter (JHM) is the $T_{\text{melt temp.}} - T_L \geq 100°$ C. Therefore, consideration was given to lowering the targeted waste loading below 50 wt % for the Phase II-A CCIM demonstration with SB4 to meet a constraint for the Phase II-A demonstration of $T_{\text{melt temp.}} - T_L \geq 25°$ C.

Compositional Analysis

The chemical composition of a sample of each glass was measured to confirm that the AF glasses corresponded to the target formulations. The measured compositions were generally close to their target values (within +/- 10%). It should be noted that the measured values for known spinel formers (Fe_2O_3, NiO, and Cr_2O_3) all appeared to be biased low in the chemical analyses. In general, these differences were small and these deviations were not expected to impact the results of the testing.

Product Consistency Test

The PCT was performed in triplicate on a total of 18 glasses (each of the three frits at 45, 50 and 55 wt % waste loading and in the AF state and after being subjected to the MCCC profile). The ARM glass, EA glass and solution blanks were included in the test matrix. The measured values for the EA glass were consistent with the reference EA glass normalized release values [13]. Table IV provides a summary of the averaged B, Li, Na and Si normalized releases.

A review of the data in Table IV suggests:

- The glasses were all very durable in the AF state with very little change in relative durability as a function of waste loading.
- There was only a slight decrease in durability in the 45 wt % waste loading glasses after being subjected to the MCCC profile as compared to the 45 wt % waste loading AF glasses.
- A noticeable decrease in relative durability was evident in the MCCC glasses at 50 wt % waste loading and this decrease was significant in the 55 wt % waste loading glasses. It should be noted, however, that all glasses met the EA glass NL [B] benchmark value (as well as the benchmark values for NL [Li] and NL [Na]).

Table IV. PCT Data for Initial Glasses at 45, 50 and 55 wt % Waste Loading and in the AF and MCCC Conditions

Glass ID	NL [Li] (g/L)	NL [B] (g/L)	NL [Na] (g/L)	NL [Si] (g/L)
R3-45-AF	0.713	0.694	0.609	0.366
R3-45-MCCC	0.869	0.605	0.547	0.361
R6-45-AF	0.774	0.841	0.758	0.401
R6-45-MCCC	1.200	0.916	0.774	0.460
R7-45-AF	0.798	0.938	0.780	0.428
R7-45-MCCC	1.378	1.126	0.854	0.512
R3-50-AF	0.736	0.705	0.720	0.367
R3-50-MCCC	1.853	2.070	1.100	0.449
R6-50-AF	0.812	0.824	0.847	0.411
R6-50-MCCC	2.008	2.066	1.184	0.544
R7-50-AF	0.833	0.917	0.871	0.454
R7-50-MCCC	2.418	2.422	1.300	0.677
R3-55-AF	0.855	0.862	0.887	0.427
R3-55-MCCC	7.026	7.986	2.787	0.699
R6-55-AF	0.825	0.864	0.997	0.443
R6-55-MCCC	8.122	11.916	3.394	0.979
R7-55-AF	0.913	1.035	1.045	0.519
R7-55-MCCC	8.968	14.421	3.447	1.026
EA	8.628	15.874	12.399	3.440
ARM	0.661	0.606	0.596	0.292

Note: For EA Glass - NL[B] = 16.695 g/L; NL [Li] = 9.565; NL [Na] = 13.346 [13]

Based on a review of the data from the initial testing, Frit 503-R6 was the frit composition with the best combination of properties (namely T_L and durability) and was identified for follow-on variability study testing. Additionally, a 46 wt % waste loading was identified as a target waste loading for further study. The 46 wt % waste loading was expected to result in a highly durable glass with a liquidus temperature below the nominal CCIM operating temperature. Furthermore, this waste loading represented an increase in waste loading for SB4 that was comparable to the increase demonstrated in previous CCIM testing with SB3. In the SB3 testing, 50 wt % waste loading was demonstrated in the CCIM at Marcoule. This corresponded to an approximate 32% increase in waste loading over the reference 38 wt % waste loading previously run through the JHM in DWPF. Currently, the target waste loading for SB4 in DWPF is 34 wt %. Therefore, a waste loading of 46 wt % in the CCIM represents a comparable increase in waste loading (35%) to what was demonstrated with SB3.

Variability Testing

The variability study included glasses formulated with Frit 503-R6 using the nominal SB4 sludge composition at waste loadings of 44, 46 and 48 wt %. In addition, nine EV glasses (EV1-EV9) were formulated with Frit 503-R6 at a waste loading of 46 wt %. The sludge compositions used in the EV glasses varied the concentrations of the major species (Al_2O_3, Fe_2O_3 and Na_2O) of the nominal SB4 composition ±7.5% and the minor species (CaO, MgO, MnO, NiO, SiO_2 and the sum of the "others") of the nominal SB4 composition ±0.5 wt % to generate a set of extreme vertices (EVs). These variations were thought to provide reasonable margin to account for variations during the manufacture of the sludge simulant for the Phase II-A CCIM demonstration.

X-Ray Diffraction

The XRD results for the quenched variability study glasses indicated that 10 of the 12 glasses were amorphous. There were very minor indications of spinel crystals (magnetite, Fe_3O_4) in the glass with the centroid sludge composition at 48 wt % waste loading and in the EV3 glass. The EV3 glass contained both high levels of Cr_2O_3 and NiO with moderate amount of Fe_2O_3. Spinel crystals were observed in all glasses subjected to the MCCC profile. In addition to spinel crystals, the EV4 composition subjected to the MCCC profile also contained a minor concentration of nepheline crystals. It was interesting to note that the nepheline discriminator value determined by the MAR assessment for the target EV4 glass was 0.644 implying that this composition would *not* be expected to be susceptible to nepheline formation when subjected to the reference DWPF centerline canister cooling profile. Furthermore, the nepheline discriminator based on the actual measured composition was 0.658 further indicating that this composition may be a contradiction to the nepheline discriminator criterion. It must be remembered, however, that the compositions tested in this study were subjected to the MCCC not the standard CCC for which the nepheline discriminator was developed.

Isothermal Liquidus (1225° C Heat Treatments)

The variability study glasses were also subjected to an isothermal heat treatment at 1225° C to determine if the liquidus temperature was above or below 1225° C. The heat treated glasses were evaluated using XRD to assess crystallinity. Ten of the twelve variability study glasses were amorphous after the 1225° C heat treatment indicating that the liquidus temperature was below 1225° C. This included the glasses using the nominal SB4 composition at 44, 46 and 48 wt % waste loading. EV1 and EV3 were found to have a very minor concentration of spinel (magnetite, Fe_3O_4) phase. These EV glasses had higher concentrations of iron.

Compositional Analysis

The chemical composition of a sample of each variability study glass was measured to confirm that the AF glasses corresponded to the target formulations. The measured compositions were generally close to their target values (within +/- 10%). It should be noted that CaO was not detected in 2 compositions (EV3 and EV4) due to an apparent batching error. This deviation was not expected to impact the results of the testing.

Product Consistency Test

The PCT was performed in triplicate on a total of 24 glasses (each of the three centroid sludge composition glasses at 44, 46 and 48 wt % waste loadings and the nine EV glasses with glasses in the AF and MCCC states). The ARM glass, EA glass and solution blanks were included in the test matrix. The measured values for the EA glass were consistent with the reference EA glass normalized release values [13]. Table V provides a summary of the averaged B, Li, Na and Si normalized releases.

Table V. PCT Data for Variability Study Glasses in the AF
and MCCC Conditions

Glass ID	**NL [Li] (g/L)**	**NL [B] (g/L)**	**NL [Na] (g/L)**	**NL [Si] (g/L)**
Centroid-44-AF	0.775	0.837	0.700	0.396
Centroid-44-MCCC	1.110	0.914	0.711	0.440
Centroid-46-AF	0.806	0.859	0.772	0.395
Centroid-46-MCCC	1.449	1.176	0.876	0.494
Centroid-48-AF	0.856	0.928	0.825	0.409

Centroid-48-MCCC	1.701	1.449	0.965	0.516
EV1-AF	0.884	1.398	0.862	0.406
EV1-MCCC	1.330	1.302	0.848	0.464
EV2-AF	0.769	0.889	0.675	0.363
EV2-MCCC	1.333	1.151	0.713	0.415
EV3-AF	0.737	0.813	0.572	0.385
EV3-MCCC	1.122	0.951	0.709	0.518
EV4-AF	0.840	0.926	0.658	0.395
EV4-MCCC	3.409	4.069	1.604	0.687
EV5-AF	0.857	1.085	0.771	0.394
EV5-MCCC	2.181	2.153	1.068	0.563
EV6-AF	0.901	1.046	0.778	0.383
EV6-MCCC	1.483	1.206	0.820	0.458
EV7-AF	0.974	1.185	0.908	0.438
EV7-MCCC	1.716	1.460	0.970	0.578
EV8-AF	0.839	0.930	0.748	0.368
EV8-MCCC	2.430	2.372	1.147	0.562
EV9-AF	0.872	1.102	0.848	0.397
EV9-MCCC	1.296	1.231	0.883	0.461
EA	9.70	17.97	13.92	3.73
ARM	0.58	0.50	0.52	0.26

Note: For EA Glass - NL[B] = 16.695 g/L; NL [Li] = 9.565; NL [Na] = 13.346 [13]

The normalized elemental releases for all glasses were below the Environmental Assessment (EA) glass used for repository acceptance. The highest normalized release rates were observed in the EV4 glass after being subjected to the MCCC profile. A minor concentration of nepheline was measured in the EV4 MCCC glass likely causing the decrease in relative durability.

The normalized PCT boron release from the 503-R6 glass compositions vs. SB4 waste loading is shown in Figure 1. The normalized boron release was essentially constant for all waste loadings in the AF glasses. However, it was apparent that an increase in normalized release occurred with increasing waste loading in the MCCC glasses (consistent with the formation of nepheline in the glasses).

It can be concluded from the variability study testing that the 503-R6 composition was robust with respect to simulant and frit composition variations at the recommended 46 wt % waste loading. Additionally, small variations in SB4 waste loading (46 wt % ± 2 wt %) would not significantly impact anticipated product performance.

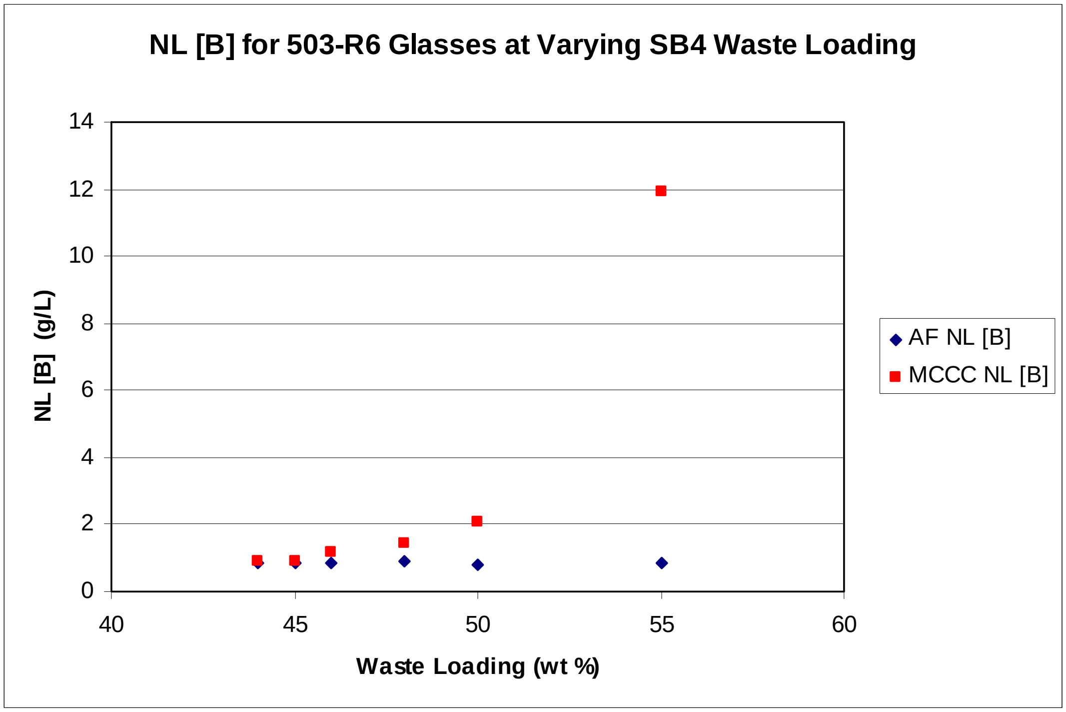

Figure 1. Normalized PCT boron release for 503-R6 glass compositions at varying SB4 waste loadings.

Glass Properties Important for CCIM Processing

Viscosity, electrical resistivity and thermal conductivity were measured for the recommended 503-R6 composition at 46 wt % waste loading.

Viscosity

The viscosity of the Frit 503-R6 – SB4 glass at 46 wt % waste loading was measured as a function of temperature using a Couette-type rheometer. Prior to viscosity measurement, the glass was raised to 1300° C (maximum target temperature for the CCIM demonstation) inside a muffle furnace, in order to evaluate any reboil phenomenon that might occur in the crucible due to the presence of multivalent reducible elements (such as Fe, Cr, Mn). No glass foaming was observed in the platinum crucible up to a temperature of 1300° C.

Initial measurements were performed while ramping the temperature down from 1300° C to 1000° C. At the lower value, the viscosity was too high to obey a VFT law of variation of melt viscosity with respect to temperature. This result indicated a possible crystallization in the glass melt during the measurement. The glass was then heated to 1250° C to dissolve the crystals, and a second set of measurements was performed while ramping down again from 1250° C to 1030° C. The measurement sequence was as follows:

1300 – 1200 – 1100 – 1000 – 1250 – 1150 – 1050 – 1030 °C

At each temperature step, torque was measured over a range of rotation speeds, and the results plotted. The slope of this line is proportional to melt viscosity at each temperature step. Results are summarized in Table VI. The viscosity at the nominal CCIM melt temperature (1250° C) was deemed to be acceptable for processing.

Table VI. Measured viscosity for SB4 reference glass

Temperature (°C)	Viscosity (dPa.s)	Temperature (°C)	Viscosity (dPa.s)
1300.6	14.0	1251.8	19.7
1202.3	27.5	1153.6	41.8
1103.8	62.0	1052.8	106.0
1000.2	268.5	1030.4	148.5

Electrical Resistivity

Electrical resistivity was measured at temperatures up to 1300° C using the 4-electrode method. The results are reported in Figure 2.

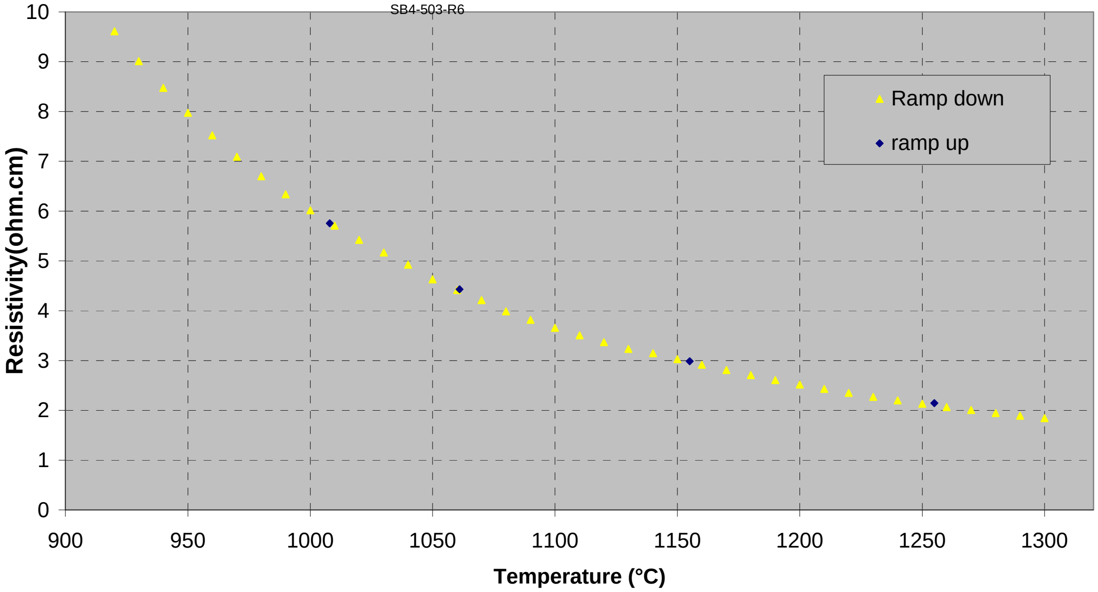

Figure 2. Measured electrical resistivity of SB4 reference glass as a function of temperature.

Resistivity at 1250° C was approximately 2 Ω.cm. The acceptable range for operating the cold crucible induction melter is between 1 and 10 Ω.cm. The 503-R6 reference glass was, thus, within the acceptable range down to a temperature of about 900° C.

Thermal Conductivity

Thermal conductivity of SB4 reference glass was measured over a temperature range from 750° C to 1300 ° C. The variation of thermal conductivity values was found to be insignificant over the temperature range considered. The mean value measured was close to 4.1 +/- 0.2 $W.m^{-1}.K^{-1}$. Just a small increase of this value to about 5 $W.m^{-1}.K^{-1}$ was observed during ramp up and ramp down at temperatures between 1100° C and 1200° C. A value of 4.1 $W.m^{-1}.K^{-1}$ was measured at 1250° C. The thermal conductivity was determined to be acceptable for CCIM processing.

CONCLUSIONS

A glass composition development effort was completed to identify and recommend a frit composition and SB4 simulant waste loading target for subsequent Advanced Remediation Technology – Phase II-A

CCIM demonstration testing. Based on the results of the glass formulation testing, it was recommended that the Frit 503-R6 composition (B_2O_3 = 14 wt %; Li_2O = 9 wt %; Na_2O = 3 wt %; and SiO_2 = 74 wt %) be utilized for the demonstration. Furthermore, a waste loading of 46 wt % should be targeted. The recommended frit and waste loading should produce a glass with acceptable durability with a liquidus temperature adequately below the 1250° C nominal CCIM operating temperature. The recommended frit and waste loading level should also provide a buffer for SRAT product compositional variation to support the Phase II-A CCIM demonstration.

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