A New Approach to Glass Formulation Generates Improved Waste Loadings for Hanford HLW/LAW and Savannah River Site HLW - 11093

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ABSTRACT

This report describes the formulation and analysis of laboratory-scale samples of glass developed by GeoMatrix Solutions Inc. (GSI) to immobilize the following surrogate waste compositions:

- Hanford C-106/AY-102 (high-Fe_2O_3) high-level waste (HLW)
- Hanford 241-S-109 (high-Na_2O) low-activity waste (LAW)
- Hanford 222-S (high-Na_2O & -SO_3) composite saltcake LAW
- Savannah River Site (SRS) Sludge Batch 4 (SB4) (high-Al_2O_3) HLW

In addition to laboratory-scale work, a large-scale pilot test was conducted using the Hanford C-106/AY-102 HLW surrogate.

The objective of the work was to develop glass with high waste loadings, using GSI glass formulation methodology. Each of the glasses developed during this study successfully passed the product quality and processing requirements for its respective waste category. The cumulative results of this glass development, which was conducted between 2003 and 2009, show a significant waste loading improvement (70, 50, 38 and 9% for C-106/AY-102, 241-S-109, 222-S and SB4, respectively) over the waste loadings reached by U.S. Department of Energy (DOE) contractors at the time that our work was carried out.

Based on the technology readiness assessment (TRA) process accepted by DOE's Environmental Management (EM) as an integral part of its project management's critical decision process, the GSI formulations are considered to be at a technology readiness level (TRL) of at least 4.

INTRODUCTION

Approximately 53 million gallons of radioactive waste are stored in 177 underground tanks at the Hanford Site near Richland, Washington. This waste will be treated at the Hanford Waste Treatment and Immobilization Plant (WTP), where it will be separated into HLW and LAW. Of the radioactive waste at Hanford, the HLW consists of less than 10% of the chemical waste mass while containing over 95% of the radioactivity. The HLW will be vitrified at WTP in joule heated melters (JHM) producing between 10,000 and 14,000 HLW canisters over a 23- to 35- year period (depending on the efficiency of the waste loading increases), with operations planned to commence in 2019. The HLW canisters will be stored on site until they can be permanently disposed of in a geological repository. The predominant amount of the chemical waste mass - over 90% - will be LAW, which will be immobilized in borosilicate glass and subsequently buried on-site. The WTP is planned with a present capacity to vitrify approximately half of the LAW during the same projected operating period as the HLW vitrification. The other 50% of the LAW will either be vitrified in an additional WTP facility, or immobilized by a supplemental treatment (likely vitrification) technology [1].

At the Defense Waste Processing Facility (DWPF) in the Savannah River Site (SRS), 36 million gallons of HLW will be vitrified in a JHM producing 6,000 canisters over the next 20 to 25 years [2]. Each sludge batch (SB) contains approximately 2 million liters of HLW, which will produce approximately 500 canisters of borosilicate glass [3]. SB1 through SB5 have already been vitrified.

Increased waste loadings have a direct impact on expediting the mission by potentially accelerating the schedule and reducing the operating and disposal costs as a result of fewer canisters to be produced and disposed of [4]. At an assumed cost of approximately $2 million per canister (including production and disposal) for Hanford HLW [5] and approximately $260,000 per canister of Hanford LAW [6], increased waste loadings will have an important impact on the final costs of the project as well. In the case of Hanford LAW, increased waste loadings can potentially reduce the need for some of the planned additional LAW treatment (vitrification) facilities. Doing so will also alleviate some of the space constraints by allowing double-shell tank space to be freed up more rapidly.

GLASS FORMULATION OBJECTIVES

The primary objective of our study was to develop laboratory-scale glass formulations, using the GSI proprietary glass formulation approach, to achieve waste loadings above the levels demonstrated by DOE contractors. Concurrent with GSI's efforts, contractors had achieved a 23 wt% waste loading for Hanford C-106/AY-102 (henceforth referred to as C-106), a 20 wt% Na_2O waste loading for Hanford LAW and a 34 wt% waste loading for SRS SB4. A second objective related to C-106 was to produce GSI glass in a large-scale pilot test in order to study the scale-up effects for one of our formulations and determine its processability in a JHM.

C-106 has a high-Fe_2O_3 concentration (47.08 wt%) which has the potential to produce spinel crystallization in the glass. While crystallization rarely affects the durability of the glass, it can affect the glass processing by settling and accumulating in the melter, thereby reducing the melter's operating life. Therefore, a major challenge to increasing waste loadings for C-106 is to produce glass with minimum spinel formation. Although the permitted crystal limitation for Hanford HLW is <1 vol% at a reference temperature (typically 950^0C) [7], the target crystallinity for this work is approximately 0.4 vol% crystallinity or less.

For Hanford LAW, we began our work with a 241-S-109 simulant which has a high Na_2O content (93.25 wt%) and a low SO_3 content (1.78 wt%). The bulk of our work was related to this waste. Once that was accomplished, we did preliminary work with a 222-S composite saltcake simulant which has both a high Na_2O and SO_3 content (89.97 and 4.20 wt%, respectively).

The most challenging of the product qualifications for high sodium LAW glass is the Vapor Hydration Test (VHT). We therefore conducted relatively many VHT analyses on all of our glass. Other product quality requirements for disposal at the Hanford site (Product Consistency Test (PCT), Toxicity Characteristic Leaching Procedure (TCLP)) and processing requirements for vitrification in a JHM (viscosity and electrical conductivity) were tested with several of the representative glasses, which satisfied these requirements.

SRS SB4 has a high-Al_2O_3 concentration (28.16 wt%) which has the potential to produce nepheline ($NaAlSiO_4$) crystallization in the glass. The presence of nepheline adversely affects the durability of the glass. Therefore, a major challenge to increasing waste loadings for SB4 is to produce glass while preventing nepheline formation. In addition, the main limitations for glass development at DWPF are (i) the liquidus temperature (T_L) must be 100^0 C below the melter processing temperature (typically 1150^0 C) - so T_L must be $<1050^0$ C, and (ii) the crystal fraction must be 0 vol%.

GLASS FORMULATION

GSI's glass formulation methodology is based on geochemical and petrological principles. We formulate an immobilizing borosilicate glass matrix that emulates the structural characteristics of glass found in nature. Our proprietary algorithms combine different groups of the glass components in pre-determined ratios, thus minimizing empirical trial and error. Our algorithms are based on a well-tested and unique combination of structural and compositional data that we have optimized to better predict and select highly loaded glass compositions. GSI's glass formulation methodology is distinctively different from that currently being used by the DOE and its contractors for glass development.

Waste Composition

Table I shows the surrogate waste compositions used for GSI C-106, GSI 241-S-109, GSI 222-S and GSI SB4 glasses.

Table I. Surrogate Waste Compositions Used for GSI C-106, GSI 241-S-109, GSI 222-S and GSI SB4 Glasses [8-11]

Oxide	**C-106 (Wt%) a**	**241-S-109 (Wt%)**	**222-S (Wt%)**	**SB4 (Wt%)**
Al_2O_3	13.26	1.35	1.89	28.16
B_2O_3	0.51			
BaO				0.08
CaO	1.13	0.04		3.06
Ce_2O_3				0.24
Cl		0.15	0.91	
Cr_2O_3	0.29	0.69	0.31	0.22
Cs_2O	0.19			
Cu_2O	0.17			0.06
F		0.06	0.35	
Fe_2O_3	47.08	0.22		32.03
K_2O		0.12	0.34	0.08
La_2O_3	0.90			
MgO	4.37			3.06
MnO	14.96			6.39
Na_2O	2.19	93.24	89.96	20.67
Nd_2O_3	0.56			
NiO	0.64			1.83
P_2O_5	0.35	2.35	2.04	
PbO	0.54			
SO_3		1.78	4.20	0.80
SO_4^{2-}				0.96
SiO_2	7.63			3.00
SrO_2	3.44			
TiO_2	0.53			
ZnO	0.26			0.06
ZrO_2	1.01			0.10
Total	100%	100%	100%	100%

a The full simulant included As_2O_3, I, Sb_2O_3 and SeO_2 which we did not include in our surrogate waste composition. The components listed in our waste composition have already been normalized to 100%.

Glass Fabrication

For C-106, 150 g batches of glass were prepared. The chemicals were mixed and placed into a 250-mL high- alumina crucible. The batch was placed into a furnace at the target melt temperature of 1150°C, and this temperature was held for 2.5 hours. The crucible was then removed from the furnace and the glass quenched in cold water. Part of this glass was then used for compositional analysis, phase identification, PCT, TCLP, viscosity and electrical conductivity measurements.

For 241-S-109 and 222-S, most batches of glass prepared were 700 g batches. The chemicals were well mixed and placed into a mullite vessel (a refractory material which is highly resistant to reaction with the glass). The batch was placed into a furnace at the target melt temperature of 1150°C and was held at this temperature for 2.5 hours. The furnace was then turned off, and the glass was allowed to cool to ambient temperature.

For a complete analytical suite, 500 g of product were used for the VHT, PCT and glass analysis, 100 g were used for the TCLP, and 100 g were used for viscosity and electrical conductivity measurements.

For SB4, 150 g batches of glass were prepared. The chemicals were mixed and placed into a 250-mL porcelain crucible. The batch was placed into a furnace at the target melt temperature of 1040°C (T_L), and this temperature was held for four hours. The crucible was then removed from the furnace and the glass quenched by pouring on a stainless steel plate. Part of this glass was then used for compositional analysis, phase identification and PCT. 50 g of this glass was re-melted at 1150^0C and was then heat-treated to simulate cooling along the centerline of a DWPF-type canister [12]. This cooling schedule is referred to as the centerline canister-cooled (CCC) curve.

A Systematic Approach to Glass Formulation

Table II shows some of the target characteristics of the glass formulated for C-106, 241-S-109, 222-S and SB4.

Table II. Target Characteristics of Glass

Characteristic	C-106	241-S-109 & 222-S	SB4
Waste loading	>34 wt%	>27 Na_2O wt%	>34 wt%
PCT	Not to exceed Environmental Assessment (EA) glass	<2g/m^2	Not to exceed EA glass
VHT	NA a	<50g/(m^2.d)	NA
TCLP	Below Universal Treatment Standards (UTS) limits	Below UTS limits	Below UTS limits
Crystallinity	<0.5 vol%	Phase identification	0 vol%
Viscosity	20 to 100 d.Pa.s at 1150^0C	10 to 150 d.Pa.s at 1100^0C	20 to 100 d.Pa.s at 1150^0C
Electrical Conductivity	0.1 to 0.7 S/cm at 1150^0C	0.2 to 0.7 S/cm at 1100^0C	0.1 to 0.7 S/cm at 1150^0C

a NA = not applicable

C-106: We began our glass formulation at a 34.0 wt% waste loading (16 wt% Fe_2O_3). Assuming that the low vol% crystallinity would be the most challenging requirement, we first analyzed our glass with X-ray Diffraction (XRD) to assess the possible formation of crystalline phases. Several glasses were formulated until we reached a composition that appeared robust. At 35.0 wt%, we conducted a PCT, TCLP and measured viscosity and electrical conductivity. As we progressed to 39.3 wt% waste loadings (18.5 wt% Fe_2O_3), we produced amorphous glass with trace amounts of crystals on the surface. For the purpose of this paper, we will discuss the analytical results of test glass GSI C-106-34.0 (i.e. glass developed by GSI using C-106 simulant, with a 34.0 waste loading) through GSI C-106-39.3.

241-S-109 and 222-S: The predominant amount of our glass development focused on the 241-S-109 simulant. We began our glass formulation at a 27 Na_2O wt% waste loading. We tested our glass for VHT, PCT, and TCLP responses, viscosity and electrical conductivity. Several glasses were formulated until we reached a composition that appeared robust. At 28 wt% Na_2O, we subjected the glass to the full battery of analyses, conducting the VHT for 7, 14 and 28 days. Afterwards, we produced glass with 30 wt% Na_2O. Finally, we developed a glass for the 222-S saltcake waste with a 27.7 wt% Na_2O waste loading with a target incorporation of 1.24 wt% SO_3, testing it for PCT and VHT response. For the purpose of this paper, we will discuss the analytical results of test glass GSI 241-S-26.8 through GSI 241-S-30, and of GSI 222-S-27.7.

SB4: We began our glass formulation at a 34 wt% waste loading. Assuming that the 0 vol% crystallinity would be the more challenging requirement, we first analyzed our glass with XRD to assess the possible formation of crystalline phases both in the T_L and the CCC-based glasses. Several glasses were formulated until we reached a composition that appeared robust. As we progressed to 36 and 37 wt% waste loadings, we produced amorphous glass with a negligible amount of crystals on the surface. At 37 wt%, we conducted a PCT for both the T_L and CCC glass. For the purpose of this paper, we will discuss the analytical results of GSI SB4-37 glass.

Determination of Glass Composition

Ground glass was mixed with lithium metaborate, the mixture melted and dissolved with nitric acid. The solution was then analyzed by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES).

GLASS TESTING & PROCESSING AND PRODUCT QUALITY REQUIREMENTS

All HLW glass developed must satisfy the processing requirements for vitrification in a JHM and the product quality requirements for disposal at a geological repository. Therefore the HLW glass was subjected to the following analyses (although due to funding constraints, not all analyses were conducted on all of the glass tested):

- Product Consistency Test
- Toxicity Characteristic Leaching Procedure
- Viscosity
- Electrical Conductivity
- Secondary Phase Identification

All LAW glass developed must satisfy the processing requirements for vitrification in a JHM and the product quality requirements for disposal at the Hanford site. Therefore, besides the analyses listed above the 241-S-109 and 222-S glass was subjected to the VHT.

Product Consistency Test

The PCT was performed as defined in the American Society for Testing and Materials (ASTM) C 1285 [13]. Samples were ground, sieved using 100 and 200 mesh sieves (to obtain particle size between 75 and 150 μm), and washed according to the procedure. Then, between 10 and 20 mL of de-ionized water were added to a corresponding clean-glass-sample size of 1.0 to 2.0 g of glass so that the ratio between the de-ionized water and the glass was exactly 10 to 1, resulting in a surface area-to-volume ratio of approximately 2000 m^{-1}. The vessels used for PCT were passivated Type 304L stainless steel. The vessel was closed, sealed, and placed into an oven at 90 ± 2°C where it remained for 7 days ± 3 hours.

After the 7-day test, the vessel was removed from the oven and allowed to cool to room temperature. The final mass of the vessel and the solution pH were recorded on a data sheet. Test solutions were then filtered through a 0.45-μm pore-size filter and acidified with concentrated, high-purity HNO_3 to 1 vol% to ensure that the analyzed elements remain in solution. Test solutions were then analyzed for major cations present in the glass, including Si, Na, B, and Li, by ICP-AES.

For HLW glass, the mean concentrations of the major cations in the leachate, after normalizing for the concentrations in the glass, must each be less than those of the benchmark glass described in the Environmental Assessment (EA) for selection of the DWPF waste form. For LAW glass, the normalized mass loss of these cations must be less than 2.0 g/m^2.

Toxicity Characteristic Leaching Procedure

The TCLP testing was performed according to SW 846 Method 1311 [14] and quality assurance/quality control requirements. Glass pieces, ≤ 9.5 mm (0.4 in.) in size and ≥ 100 g in mass, were placed in dilute acetic acid (pH value of 4.98 ± 0.05) and agitated at 30 ± 2 rpm for 18 ± 2 hours at room temperature. The concentrations of hazardous metals in solution were then measured and compared to the limits for each element. We adopted the Universal Treatment Standard (UTS) limits for the constituents.

Viscosity

The viscosity of the glass melt was measured with the *HAAKE RV 20 Rotovisco* rotational viscometer. The glass melt in the coaxially fixed Pt cylinder was rotated with a rotating inner Pt cylinder. During rotation of the rotating body, measurement is either made of the velocity gradient at a specified shear stress or the shear stress (torque measurement with measuring spring torqueability - Verdrillwinkel) at a specified velocity gradient (constant speed). The viscosity of the fluid can be determined from the measured values and the exact geometry of the rotary body used. For calibration, a standard glass with known viscosity vs. temperature was used.

Electrical Conductivity

The specific electrical conductivity was measured in a ceramic Al_2O_3 measuring cell, in which two Pt-electrodes $10 \times 10 \times 2$ mm on opposite sides were submerged. The electrical resistance of the glass melt between the electrodes at different temperatures was measured with a conductivity bridge at 50 kHz.

The *GenRad 1689 precision RLC Digibridge®*, a microprocessor-controlled, automatic, programmable RLC measuring instrument was used for measuring.

Vapor Hydration Test

The VHT was performed as defined in the ASTM C 1663-09 [15]. Monolithic samples were exposed to water vapor at 200°C in a sealed stainless steel vessel (Type 304L). A diamond-impregnated saw was used to produce samples, 10×10×1.5 mm (0.4×0.4×0.06 in.), from glass bars. All sides were polished to 600-grit surface finishes with silicon carbide paper.

Samples, stainless steel vessels, lids, and supports were cleaned, samples were suspended from stainless steel supports on Pt wire, and 0.25 g of de-ionized water was added to the vessel. The sealed vessel was held at 200°C for a predetermined amount of time (either 7, 14 or 28 days) in a convection oven. After removal, vessels were weighed and quenched in water. The specimens were sectioned for the measurement of the average remaining glass thickness by optical microscopy/image analysis or the alteration thickness by scanning electron microscopy (SEM).

The remaining glass thickness of the VHT specimen was determined by performing at least 10 measurements distributed (roughly equally) across the crack-free cross section of the sample. This step yields the average thickness of the remaining glass and the standard deviation of the measurements. The amount of glass altered per unit surface area of specimen was determined from the average thickness of unaltered glass according to Equation 1:

$$m = \frac{1}{2}\rho(d_i - d_r) = \frac{m_i}{2w_i l_i}\left(1 - \frac{d_r}{d_i}\right) \qquad \text{(Eq. 1)}$$

where w_i, d_i, l_i = initial specimen width, thickness, and length, respectively
d_r = average thickness of remaining glass layer
m_i = initial specimen mass
m = mass of glass converted to alteration products per unit surface area
ρ = glass density.

The average rate of corrosion is calculated as $r_a = m/t$, where t is the corrosion time.

The above method of measuring the remaining glass thickness cannot accurately determine the small alteration mass from the relatively durable glasses. SEM measurements can be used for those samples with $m \leq 38$ g/m^2. The VHT alteration mass is directly calculated from the alteration thickness (t_a) measured by SEM from a relation $m = t_a\rho$. As the alteration thickness decreases, it becomes more difficult to accurately measure the alteration thickness even with SEM.

The acceptable VHT alteration rate for LAW glass is less than 50 g/(m^2·d) when measured using at least a seven-day VHT run at 200ºC.

Secondary Phase Identification

The phase identification in the glass was determined by examining portions of the glass powder with XRD. The standard used for XRD was Si-powder. The powder was mounted in an XRD sample holder. The scanning proceeds with 0.02° 2θ step size from 20 to 70° 2θ scan range, time per step was 1 sec. The secondary phase identification and quantification were aided by SEM with Energy Dispersive Spectroscopy (EDS) for selected samples. The Data Base of JCPDS-ICDD (2002) was used for the phase identification.

For C-106, we calculated the volume percent of crystallinity by measuring the image size of the glass from the SEM-EDS photos and then subtracting the area fraction with crystals.

For SB4, where the crystallinity requirement is 0 vol%, samples were run under conditions providing a detection limit of approximately 0.5 vol% for different crystal phases. That is, if crystals in glass 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 indicates that the degree of crystallization is below the detection limit.

HANFORD C-106/AY-102 HLW: ANALYTICAL RESULTS

Table III summarizes the analytical results for the Hanford C-106/AY-102 HLW glass formulated.

Table III. Summary of C-106/AY-102 Analytical Result

Parameter	**Highlight**
Glass Composition	Wt% Fe_2O_3 was within 5%, relative, of target
Crystallinity	<0.2 vol%
PCT	Significantly better than EA glass values
TCLP	Below UTS limits for As, Sb and Se
Viscosity and Electrical Conductivity	Within acceptable ranges

Glass Composition

The target concentrations of Fe_2O_3 in the GSI C-106 glasses ranged between 14.6 and 18.5 wt%. The measured concentrations were all within 5 relative % of the target, based on the reported ICP data. Normalization was not employed since the material balance was close to unity. The other elements were determined to be within 1 and 10 relative % of target.

Crystalline Phases

All glass was tested for crystallinity after a 3-day heating regimen at 950^0 C. Crystallinity was measured by SEM-EDS. From the SEM-EDS photos the volume percent of crystallinity was calculated by measuring the image size of the glass and then subtracting the area fraction with crystals. There was a thin layer of crystals visible (less than approximately 0.5 mm) on less than 5% of the surface of the glass, which comprised the majority of the crystallinity found in the glass. This surface crystallinity was caused by contact of the glass surface with air during quenching, and is not indicative of the crystallinity in the glass itself. Therefore, crystallinity was calculated both with and without this surface layer. With the surface layer, one glass with 18.5 wt% Fe_2O_3 had 0.414 vol% crystallinity, while the remainder of the glasses had less than 0.4 vol% crystallinity. Without the surface layer, all the glasses had less than 0.2 vol% crystallinity.

Figure 1 shows an SEM photo of the surface layer of GSI C-106-39.3 glass. The gray is the amorphous glass, the white are the crystals, and the green is the epoxy sample background.

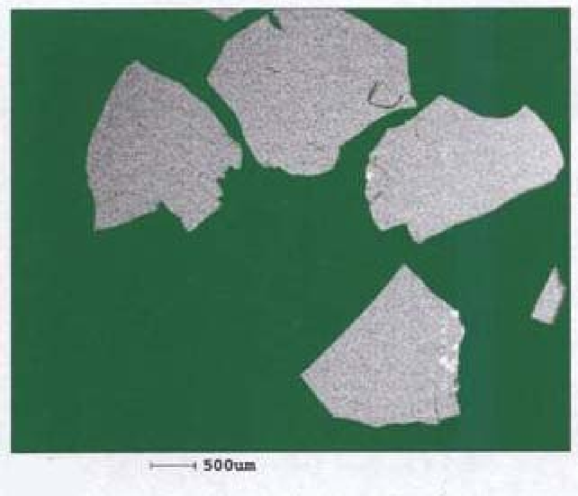

Fig.1. SEM photo showing the surface layer of C106-39.3 glass with crystals

Product Consistency Test

GSI C-106-34.8 was subjected to the 7-day PCT and met the specifications for B, Li, Na and Si releases (normalized mass loss must be less than that for EA reference glass) under PCT conditions. Table IV lists the normalized mass loss for these cations in this test, and compares it to EA reference glass.

Table IV. 7-Day 90^0C PCT Normalized Mass Loss for GSI C-106-34.8 Glass and Comparison to EA Reference Glass (g/L)*

	B	**Li**	**Na**	**Si**
GSI C-106-34.8-PT**	0.14	0.33	0.26	0.07
EA	16.7	9.6	13.3	3.9

*Uncertainty of up to 5%
**Glass from large-scale vitrification pilot testing

Toxicity Characteristic Leaching Procedure

GSI C-106-34.8 (both from the large-scale pilot test and laboratory-scale glass), was subjected to the TCLP. Generally, we did not include antimony, arsenic or selenium (trace components found in the waste) either for laboratory- or large-scale testing. However, for one of the TCLP analyses of laboratory-scale glass these elements were included. The TCLP results were far below the stringent UTS limits.

Viscosity and Electrical Conductivity

Viscosity and electrical conductivity measurements were taken for GSI C-106-34.8 (both from the large-scale pilot test and the laboratory-scale glass). The measurements at 1150^0C for viscosity were 31.8 and 33.3 d.Pa.s., and for electrical conductivity 0.12 and 0.14 S/cm, which are within the acceptable ranges for vitrification in a JHM.

Large-Scale Vitrification Pilot Test

Based on cooperation between GSI and Institut für Nukleare Entsorgung (INE) of the Forschungszentrum Karlsruhe, a large-scale pilot test was performed, using a ceramic-lined liquid fed JHM located at one of INE’s test facilities. The purpose of the pilot test was to demonstrate the suitability of GSI C-106-34.8, and its processability in a large-scale vitrification run.

Approximately 3000 L of waste simulant were immobilized in about 1500 kg of glass product by continuous melting operation during a net feeding time of 113 hours. The glass formers were added to the waste simulant prior to feeding into the melter. The glass loading with waste oxides was adjusted to 34.8 wt%. Other than during the initial phase, the feed rate was maintained at 30-35 L/hr.

The melter used for the test is characterized by a glass pool surface of 0.88 m^2 and a glass capacity of 1000 kg. It is equipped with three pairs of power electrodes arranged in two levels. For glass pouring, a bottom drain system was used for the test. The slurry-like melter feed had to be mobilized to prevent settling; the slurry was circulated by a loop arrangement around the storage vessel. A mechanical pump continuously transferred the slurry to the melter.

The main objectives of the pilot test, namely, the melting operation and subsequent pouring of the glass by a bottom drain into 4 European standard canisters (400 kg), were successfully achieved. The melting process proved to be very smooth and stable. Also, the glass pouring did not show any operational restrictions.

Initial inspection of glass samples taken from the glass pouring stream did not show separate phases. The glass had a shiny, smooth surface. SEM analysis showed a crystalline-free structure of the glass sample.

HANFORD 241-S-109 and 222-S LAW: ANALYTICAL RESULTS

Table V summarizes the analytical results for the Hanford 241-S-109 and 222-S LAW glass formulated.

Table V. Summary of 241-S-109 and 222-S Analytical Results

Parameter	**Highlights**
Glass Composition	Wt% Na_2O and SO_3 within 0-10%, relative, of target
VHT	Almost all samples < 50g/(m^2.d)
PCT	<2 g/m^2 for B, Na and Si
TCLP	Below UTS limit for Cr
Viscosity and Electrical Conductivity	Within acceptable ranges

Glass Composition

Table VI lists the target versus the measured concentrations of Na_2O in the various glasses, and the SO_3 concentration in the GSI 222-S-27.7 glass. The measured Na_2O concentration is based on the reported ICP data. Normalization was not employed since the material balance was close to unity. The other elements for the most part were determined to be within 5 and 10 relative % of target, for major and minor components, respectively.

Table VI. Target versus Measured Na_2O and SO_3 in Glass

	GSI 241-S-26.8	**GSI 241-S-27.4**	**GSI 241-S-27.6**	**GSI 241-S-28**	**GSI 241-S-30**	**GSI 222-S-27.7**
Target Na_2O	26.8	27.4	27.6	28.0	30.0	27.7
Measured Na_2O	26.0	26.6	28.6	28.1	28.3	28.0
Target SO_3	--	--	--	--	--	1.24 b
Measured SO_3	NM a	NM	NM	NM	NM	1.35

a NM = not measured

b Based on the Na_2O target of 27.7 wt% and the ratio of S and Na in the waste, the target for SO_3 should be 1.29 wt%. However, the listed target for SO_3 of 1.24 wt% was calculated based on the actual composition of the test melt.

Vapor Hydration Test

A total of 47 samples from 11 batches of GSI 241-S glass were subjected to VHT. For GSI 241-S-28, 10 samples were tested for 7 days, 9 samples for 14 days, and one sample for 28 days. All remaining samples (3 for GSI 241-S-26.8, 8 for GSI 241-S-27.4, 11 for GSI 241-S-27.6 and 5 for GSI 241-S-30) were all tested for 7 days. Of all of these samples, only three samples exceeded the VHT alteration rate requirement of 50 g/(m^2.d). The predominant number of samples that passed showed alteration rates of less than 25 g/(m^2.d) (Only 6 samples exceeded this alteration rate). For GSI 222-S-27, three samples from one batch were tested for 7 days, all meeting the VHT requirement.

Based on the GSI 241-S-28 VHT experiments, enough replicate data exists to justify terminating the VHT runs for the other GSI 241-S glasses after 7 days. According to A. Jiricka, J.D. Vienna, P.Hrma and D. Strachan [16], there are four phases to steam-catalyzed corrosion of glass: dissolution in dilute solution, dissolution in concentrated solutions, precipitation of alteration products and, finally, alteration at basically a constant rate. Phase one and three are fairly sharp, while phase two is fairly flat and phase four is roughly constant (linear) with time. If GSI's VHT experimental data shows a constant corrosion rate in g/(m^2.d), then it can be deduced that the glass is corroding based on phase four, as described above. If so, then the phase four corrosion began within the first seven days of steam exposure.

Figure 2 plots alteration rate versus time for the GSI 241-S-28 glass, and the slope of the trend line is < 0.1. This is insignificant based on the repeatability of the data at 7 and 14 days, where the standard deviations were 11.0 and 22.1 g/(m^2.d), respectively, and the associated standard deviation of the means were 3.66 and 7.45, respectively.

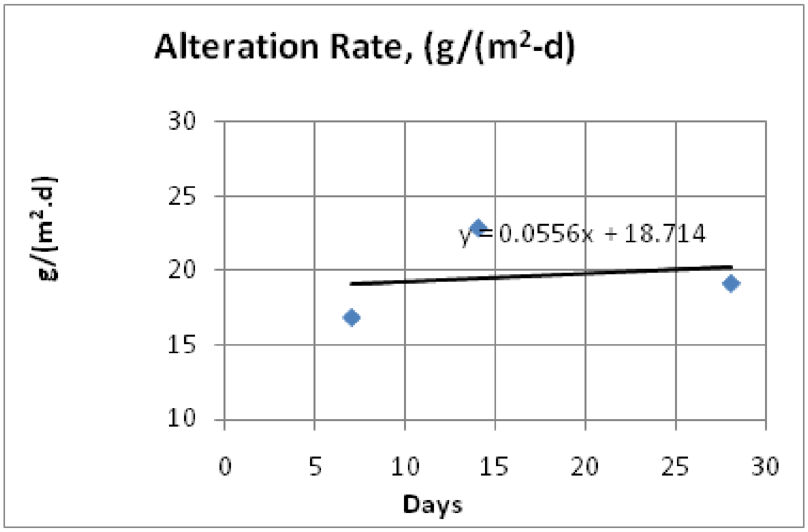

Fig. 2. Alteration rate (g/(m^2.d)) versus time for GSI 241-S-28 glass

Table VII lists the average alteration rate of the glass samples subjected to the VHT. As described above, the alteration rate is determined by a minimum of 10 measurements across the cross section of the specimen, measuring the width of the remaining unaltered glass.

Table VII. Average VHT Alteration Rates

Glass	**Duration of VHT**	**Average Alteration Rate (g/(m^2.d)) a**
GSI 241-S-26.8	7 days	5.47
GSI 241-S-27.4	7 days	7.64
GSI 241-S-27.6	7 days	15.82
GSI 241-S-28	7 days	16.84
GSI 241-S-28	14 days	22.88
GSI 241-S-28	28 days	19.14
GSI 241-S-30	7 days	7.13
GSI 222-S-27.7	7 days	20

a A bias of ≤ 2% exists in several cases resulting from deviations between the measured sample size and the 10x10 x 1.5 mm sample size dimensions assumed in the alteration rate calculations.

Figure 3 presents an SEM photo as an example of the marked cross section of a GSI 241-S-28 sample after a 7-day VHT. The glass is clear, with slight alteration visible on the top and bottom edges. The alteration rate is determined by a minimum of 10 measurements across the cross section of the specimen, measuring the width of the remaining unaltered glass.

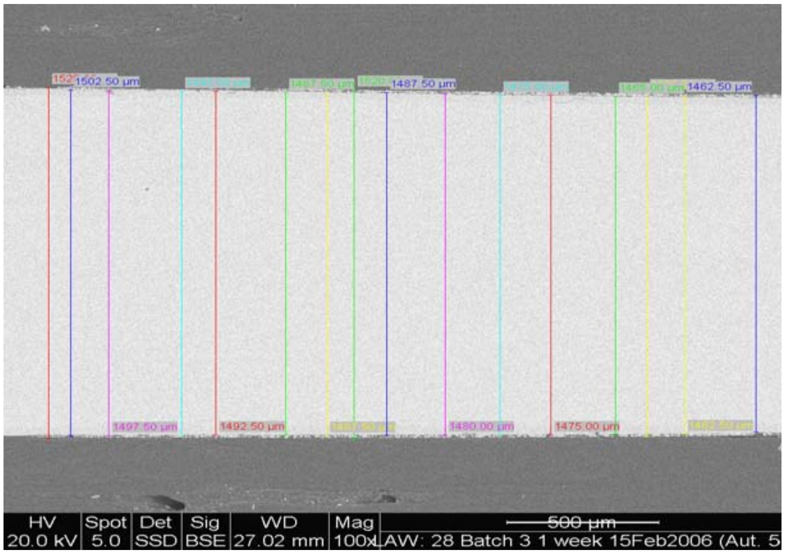

Fig. 3. SEM photo of VHT glass (GSI 241-S-28, batch 3, sample 5a, after 7-day leaching) with measurements of thickness of unaltered glass

The XRD pattern of GSI 241-S-28 before being subjected to the VHT does not show any peaks, which is representative of an amorphous material. No secondary phases were detected. The XRD pattern of the glass surface after being subjected to the VHT exhibits peaks corresponding to crystalline sodium aluminosilicate-boron hydroxide ($Na_{7.6}(AlSiO_4)_6(B(OH)_4)_{1.7}2H_2O$).

Product Consistency Test

GSI 241-S-27.6, GSI 241-S-28, GSI 241-S-30 and GSI 222-S-27.7 were subjected to the PCT. All of these glasses met the specifications for B, Na and Si releases (normalized mass loss must be less than 2.0 g/m^2) under PCT conditions. Table VIII lists the normalized mass loss for these cations in these tests.

Table VIII. 7-Day 90^{0}C PCT Normalized Mass Loss for GSI 241-S and GSI 222-S Glasses (g/m^2) a

Glass ID	B	Na	Si
GSI 241-S-27.6	1.53	1.22	0.64
GSI 241-S-28	1.73	1.98	0.35
GSI 241-S-30	1.3	0.97	1.5
GSI 222-S-27.7	1.37	1.21	0.96

a Uncertainty of up to 5%

Toxicity Characteristic Leaching Procedure

GSI 241-S-28 was subjected to the TCLP once. Cr is the only toxic component present in the test glass. The Cr release for the GSI 241-S-28 glass was 0.11 mg/L, which meets the specifications for Cr release (less than 0.6 mg/L according to the UTS).

Viscosity and Electrical Conductivity

Viscosity and electrical conductivity measurements were taken for GSI 241-S-28.5, a similar glass to GSI

241-S-28 (although with 28.5 wt % Na_2O). The viscosity measurements at 1150^0C were 38.3 d.Pa.s., and for electrical conductivity 0.48 S/cm, which are within the acceptable ranges for both vitrification in the planned JHM in Hanford.

SRS SB4 HLW: ANALYTICAL RESULTS

Table IX summarizes the analytical results of the SRS SB4 HLW glass formulated.

Table IX. Summary of SB4 Analytical Results

Parameter	**Highlight**
Glass Composition	Wt% Al_2O_3 and Fe_2O_3 within 5-10%, relative, of target
PCT	Significantly better than EA glass values
Crystallinity	0 vol%; value of nepheline discriminator = 0.64

Glass Composition

The target concentrations of Al_2O_3 and Fe_2O_3 in the GSI SB4-37 glass were 10.42 and 11.85 wt%, respectively. The measured concentrations were 11.2 wt% Al_2O_3 and 11.0 wt% Fe_2O_3, based on the reported ICP data. Normalization was not employed since the material balance was close to unity. The other elements were determined to be within 1 and 10 relative % of target.

Product Consistency Test

The GSI SB4-37 T_L and CCC glasses were subjected to the 7-day PCT and met the specifications for B, Li, Na and Si releases (normalized mass loss must be less than that for EA reference glass) under PCT conditions. Table X lists the normalized mass loss for these cations in this test.

Table X. 7-Day 90^0C PCT Normalized Mass Loss for GSI SB4-37 T_L and CCC Glasses and Comparison to EA Reference Glass (g/L) a

	B	**Li**	**Na**	**Si**
GSI SB4-37 (T_L)	0.31	0.54	0.55	0.19
GSI SB4-37 (CCC)	0.39	0.45	0.33	0.16
EA	16.7	9.6	13.3	3.9

a Uncertainty of up to 5%

Crystalline Phases

The formation of crystalline phases was determined by XRD analysis for both the T_L glass and the CCC glass from two batches of SB4-37. No crystalline phases were detected.

A "nepheline discriminator" is included as one of the process control constraints at DWPF [17]. The nepheline discriminator predicts the potential for nepheline formation in the glass. According to the nepheline discriminator, glasses in which $SiO_2/(SiO_2+Na_2O+Al_2O_3) > 0.62$ (where the SiO_2, Na_2O and Al_2O_3 are weight percentages in the glass) should not form nepheline when quenched or slow cooled. The nepheline discriminator value for GSI SB4-37 was 0.64.

Figure 4 shows XRD analyses of the GSI SB4-37 T_L and CCC glass, respectively. Both analyses show absence of crystalline phases.

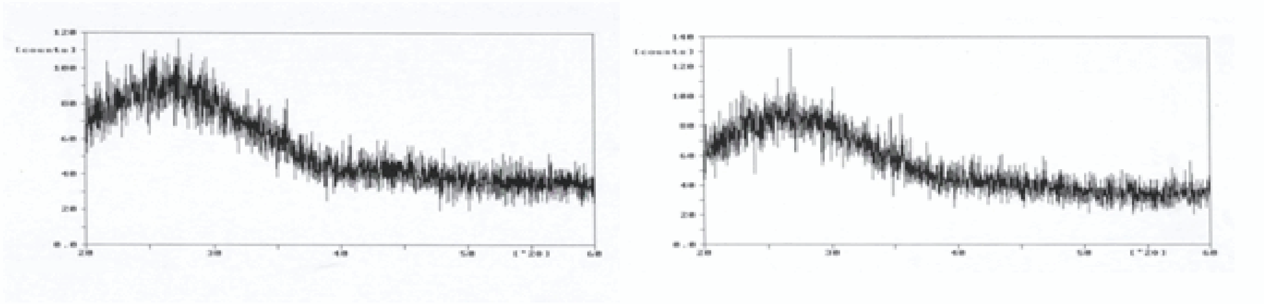

Fig. 4. XRD pattern of GSI SB4-37 T_L glass and GSI SB4-37 CCC glass showing no discernible crystal phases

CONCLUSIONS

The primary objective of this work was to use GSI's glass development methodology and proprietary formulations in order to increase waste loadings beyond those achieved by DOE contractors at the time that our work was carried out.

GSI conducted laboratory-scale testing with surrogate compositions for Hanford C-106/AY-102 HLW, Hanford 241-S-109 and 222-S LAW, and SRS SB4 HLW. In addition, a pilot-scale test was conducted with the Hanford C-106 surrogate. With all of these wastes, we have successfully demonstrated glass with high waste loadings, while meeting or exceeding the glass processing and product quality requirements. The simulants used for these tests were demonstratedly comparable to those created and tested in HLW and LAW glass formulations by the WTP and DWPF.

The results of this work were as follows:

C-106: GSI successfully demonstrated the processability of its glass in a large-scale pilot test with a 34.8 wt% waste loading compared to the then-current 23 wt% waste loading. Following the large-scale pilot test we increased the waste loading to 39.3 wt% in further laboratory-scale tests. Since the GSI C-106-34.8 and GSI C-106-39.3 glass are similar in many respects we do not anticipate that any difficulties would be encountered in a large-scale test using the higher waste loading glass.

241-S-109 and 222-S: GSI formulated 241-S-109 glass with a 30 wt% Na_2O waste loading (compared to the then-current 20 wt% Na_2O waste loading), and a 222-S glass with a 27.7 wt% Na_2O and 1.24 wt% SO_3 waste loading (compared to the then-current 20 wt% Na_2O and 0.93wt% SO_3 waste loading).

SB4: GSI formulated a SB4 glass with a 37 wt% (compared to the then-current 34 wt%) waste loading.

In March 2007, the U.S. Government Accountability Office recommended that DOE adopt the TRA process developed by the National Aeronautics and Space Administration and the U.S. Department of Defense for evaluating technology maturity. In 2008 EM established the TRA process as an integral part of its project management's critical decision process [18]. The TRA process includes the use of a TRL scale.

The GSI glass formulations are relatively mature. They have been extensively evaluated over the course of 7 years at various bench- and laboratory-scales, using a wide variety of both short and long term standardized performance tests with a range of relevant simulants. One of the GSI formulations has been successfully demonstrated at pilot-scale in a representative melter system. Based on the testing described in this paper, the GSI formulations are considered to be at a TRL of at least 4.

GLOSSARY OF ABBREVIATIONS

AES	Atomic Emission Spectrometry	PCT	Product Consistency Test
ASTM	American Society for Testing and Materials	SB	Sludge Batch
CCC	Centerline Canister-Cooled	SEM	Scanning Electron Microscopy
DOE	U.S. Department of Energy	SRS	Savannah River Site
DWPF	Defense Waste Processing Facility	T_L	Liquidus Temperature
EA	Environmental Assessment	TCLP	Toxic Characterization Leaching Procedure
EDS	Energy Dispersive X-Ray Spectrometry		
EM	DOE Office of Environmental Management	TRA	technology readiness assessment
GSI	GeoMatrix Solutions Inc.	TRL	technology readiness level
HLW	High Level Waste	UTS	Universal Treatment Standard
ICP	Inductively Coupled Plasma	VHT	Vapor Hydration Test
INE	Institut für Nukleare Entsorgung	WTP	The Hanford Waste Treatment and Immobilization Plant
JHM	Joule Heated Melter		
LAW	Low Activity Waste	XRD	X-Ray Diffraction

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