Glass Formulations for Immobilizing Hanford Low-Activity Wastes

D.S. Kim, M.L. Elliott, H.D. Smith, L.M Bagaasen, P.R. Hrma
Pacific Northwest National Laboratory
P.O. Box 999, Richland, WA 99352
USA

ABSTRACT

Researchers at Pacific Northwest National Laboratory (PNNL) are developing and testing glasses for immobilizing low-activity wastes (LAW) for the full Hanford mission. PNNL is performing testing for low-activity waste glasses for both the Hanford Waste Treatment Plant (WTP) and the Bulk Vitrification Plant. The objective of this work is to increase the waste content of the glasses and ultimately increase the waste throughput of the LAW vitrification plants.

This paper focuses on PNNL's development and testing of glasses for the Bulk Vitrification process. Collaborative studies are also being conducted with the Khlopin Radium Institute in St. Petersburg, Russia, to increase the solubility of sulfur in WTP glasses through the addition of trace chemicals to alter the glass chemistry. That research will be presented in a separate paper at this conference.

Bulk Vitrification was selected as a potential supplemental treatment to accelerate the cleanup of LAW at Hanford. Also known as In-Container Vitrification™ (ICV™), the Bulk Vitrification process combines soil, LAW, and chemical amendments; dries the mixture; and then vitrifies the material in a batch process in a refractory lined box. The process was developed by AMEC Earth and Environmental, Inc. (AMEC). Working with AMEC, PNNL developed a glass formulation that could incorporate a broad range of Hanford LAW. The initial glass development involved a "nominal" waste composition, and a baseline glass was formulated and tested at crucible, engineering, and full scales. The performance of the baseline glass was then verified using a battery of laboratory tests as well as engineering-scale and full-scale ICV™ tests.

Continued testing has focused on developing an acceptable operating envelope for the baseline glass. The current glass constraints are

- $17 \leq Na_2O \leq 22$ mass%
- $3 \leq B_2O_3 \leq 5$ mass%
- $8 \leq Al_2O_3 \leq 12.5$ mass%
- $5.5 \leq ZrO_2 \leq 8$ mass%; $6.4 \leq ZrO_2 \leq 8$ mass% if $Al_2O_3 \geq 9.5$ mass%
- $40 \leq SiO_2 \leq 48.5$ mass%.

Multiple samples from engineering-scale and full-scale ICV™ tests performed with a baseline glass formulation developed from crucible tests were analyzed for chemical composition, Product Consistency Test, Vapor Hydration Test, and the Toxicity Characteristic Leaching Procedure. The results show good agreement between glasses prepared in a crucible in the laboratory and the glasses from the larger scale tests. The results also show that the glass in the ICV™ box is homogeneous.

Future testing is planned for optimizing the glass waste loading and qualifying a broader range of waste streams for treatment in the Bulk Vitrification process. This paper reviews the glass development and qualification process completed to date. This includes several series of crucible studies as well as

confirmation testing at engineering-scale and full-scale. This formulation paper complements information presented by AMEC in an ICV™ processing paper.

INTRODUCTION

Baseline plans for disposition of Hanford radioactive tank waste include vitrification of the low-activity waste (LAW) fraction. The immobilized LAW will be disposed in a shallow burial facility at Hanford. Separation and vitrification operations will be performed in the Waste Treatment Plant (WTP) that is currently under construction. However, the capacity of the WTP is insufficient to process all of the tank waste and support the Hanford Federal Facility Agreement and Consent Order (Tri-Party Agreement [TPA]) milestone to complete tank waste treatment by 2028. Therefore, the U.S. Department of Energy (DOE) Office of River Protection (ORP), Washington State Department of Ecology (Ecology), and the U.S. Environmental Protection Agency (EPA) agreed to cooperatively develop approaches to accelerate tank waste treatment by providing additional LAW treatment capacity, supplemental to the WTP [1].

Bulk vitrification (BV) has been selected by ORP's tank farm contractor, CH2M HILL Hanford Group, Inc. (CH2M HILL), for a pilot supplemental treatment test and demonstration facility. The goal is to further evaluate BV through simulant and real waste testing to support a TPA milestone (M-62-11) associated with a final decision on treatment of the balance of tank waste that is beyond the capacity of the WTP.

Bulk vitrification combines LAW and glass-forming chemicals within a large disposal container and melts the contents using electrical resistance heating. Bulk vitrification employs a disposable melter where the waste form and melter (i.e., steel container) are disposed in a LAW burial ground after the vitrified waste form has cooled. Because the bulk vitrification melter is used only once, some of the processing constraints of the baseline joule-heated, continually fed ceramic melters can be avoided. The BV In-Container Vitrification™ (ICV™)[1] process mixes and dries low-activity waste, soil, and glass forming chemicals, and then melts the mixture at 1250 to 1500°C by electrical resistance. A small amount of conductive mixture is laid between the two graphite electrodes for melt initiation. Electrical current is supplied by two graphite electrodes imbedded in the batch. The design concept used in early testing employed top-down melting of a large, single batch of waste and soil, which was surrounded by an insulating primary liner of quartz sand to protect the steel container from the glass melt. The current design uses bottoms-up melting, in which, after melt initiation of a small batch, waste is gradually loaded in increments until the container is filled with waste glass. A rigid castable refractory block is used as the primary liner to protect the steel container from the glass melt.

The testing program for the Hanford Bulk Vitrification process consists of multiple series of glass formulation studies in parallel to engineering- and full-scale testing. The current full-scale BV design uses steel containers that are 2.44 m (wide) × 2.44 m (high) × 7.32 m (long) (8 ft × 8 ft × 24 ft). Engineering-scale (ES) tests use a container that is about 1/6th linear scale relative to the full-scale melts. The ES tests are conducted to gather information on a variety of process variables that cannot be obtained with crucible-scale tests. Both ES and full-scale steel containers employ refractory materials to insulate the container walls from the high-temperature glass melt. The glass melt is in direct contact with a castable refractory block, which is surrounded by silica sand.

The studies reported in this document are focused on the glass formulation and verification testing of BV glasses. The results of the scaled equipment testing, engineering-scale and full-scale, are reported only from the standpoint of glass quality. The following sections describe the glass testing and product quality requirements, the development and testing of the baseline (nominal) glass composition followed by the

[1] In-Container Vitrification™ (ICV™) is a trademark of AMEC Inc.

development of the acceptable glass composition region, and finally the analytical results of glasses sampled from scaled tests are compared to the glasses developed in the laboratory.

GLASS TESTING AND PRODUCT QUALITY REQUIREMENTS

The waste packages from the BV process will have several product quality requirements to allow for safe storage and disposal. The glasses produced in laboratory and field tests were subjected to the following product characterizations to assure that an acceptable product is produced. The tests method used in product characterization and acceptable product quality requirements are briefly described below.

The Product Consistency Test (PCT) was performed as defined in the American Society for Testing and Materials (ASTM) C 1285 [2]. The normalized mass loss of sodium, silicon, and boron must be less than 2.0 grams/m^2 when measured using a seven-day PCT run at 90°C.

The Toxicity Characteristic Leaching Procedure (TCLP) testing was performed according to SW 846 Method 1311 [3] and quality assurance/quality control requirements. The acceptable TCLP releases used as a conservative limit in the present study are 0.6 mg/L for chromium and 21 mg/L for barium, which are the only toxic components present in the test glasses.

The vapor hydration test (VHT) was performed according to the PNNL procedure.[1] The acceptable VHT alteration rate for BV glasses is less than 50 g/(m^2·d) when measured using at least a seven day vapor hydration test run at 200 ºC.

In addition to above key properties, the amount of crystalline phase in selected glasses was determined by examining portions of the glass with the semi-quantitative x-ray diffraction (XRD), optical microscopy (OM), and scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS). Viscosity and electrical conductivity were measured on the baseline glass selected from the glass formulation development described below. More detailed information on the experimental test methods can be found in 2003 [4] and 2005[2] crucible-melt studies.

BASELINE GLASS FORMULATION DEVELOPMENT

A preliminary study [4] was performed in 2003 to identify a baseline glass that met the processing, product quality, and economic constraints of the ICV™ process applied to Hanford LAW. Hanford soil was used as the primary glass forming chemical.

Table I shows the compositions of waste simulant and soil used and the range of glass compositions tested in the baseline glass formulation, expressed in terms of oxides and halogens likely to end up in glass.

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[1] GDL-VHT. 2000. *Vapor Hydration Test Procedure*. Pacific Northwest National Laboratory, Technical Procedure.

[2] Draft report: D. Kim, P. R. Hrma, M. J. Schweiger, J. Matyáš, J. V. Crum, D. E. Smith, J. D. Vienna, M. L. Elliott, "Matrix Crucible Testing of Bulk Vitrification Glasses for Hanford Low-Activity Waste," Pacific Northwest National Laboratory, Richland, Washington, 2005

Table I. Waste Simulant and Soil Compositions and Glass Composition Range Used in Baseline Glass Formulation (in mass fractions of oxides/halogens that will remain in glass)

Component	**6-Tank Composite Simulant [5]**	**Soil[(a)]**	**Glass Composition Range Tested in Baseline Glass Formulation**	
			Min	**Max**
Al_2O_3	0.0188	0.1396	0.0848	0.1248
B_2O_3			0.0000	0.0500
CaO		0.0550	0.0358	0.0462
Cl	0.0090		0.0014	0.0024
Cr_2O_3	0.0046		0.0007	0.0012
F	0.0035		0.0006	0.0009
Fe_2O_3		0.0928	0.0468	0.0868
K_2O	0.0034	0.0248	0.0168	0.0214
MgO		0.0143	0.0093	0.0120
Na_2O	0.8987	0.0321	0.1700	0.2600
P_2O_5	0.0202	0.0029	0.0053	0.0159
SiO_2		0.6242	0.4061	0.5248
SO_3	0.0418		0.0067	0.0110
TiO_2		0.0143	0.0093	0.0193
ZrO_2			0.0000	0.1000
SUM	1.0000	1.0000		
(a) From preliminary analysis of soil at AMEC site.				

Sixteen glasses were formulated, fabricated, and tested. The key parameters varied were waste loading and additive composition. The waste loading was varied from 0.159 to 0.263, which corresponds to Na_2O mass fraction in glass from 0.17 to 0.26 as shown in Table I. B_2O_3 up to 0.05 and ZrO_2 up to 0.10 (in mass fraction) were tested as additives. Glasses were prepared from raw chemicals that would yield the same composition as from simulants and additives. Each composition underwent two extreme heat treatments: a rapid cooling (quenching) and a slow cooling (following the slowest cooling the glass would experience in the full-scale ICV™ box). All quenched (Q) and slow-cooled (SC) glasses were characterized for VHT and PCT responses and crystallinity, while selected glasses were tested for TCLP responses, viscosity, and electrical conductivity. The VHT response was found to be the most restrictive property on waste loading and glass composition. The "AMBG-13" glass containing 20 mass% Na_2O (17.8 mass% from waste and 2.2 mass% from soil) and 5 mass% B_2O_3 and 7 mass% ZrO_2 (both from additive) was adopted as a glass suitable for scale up and radioactive demonstrations of the ICV™ process since it had the best mix of properties—it has outstanding PCT, VHT, and TCLP responses and does not contain any crystals after SC heat treatment. The baseline glass (AMBG-13) composition is shown in Table II. The PCT, TCLP, and VHT responses of baseline glass are summarized in Tables III through V.

The temperature required to obtain a glass viscosity of 10 Pa·s was 1238°C. The electrical conductivity at this temperature was 39.7 S/m. These are both processing requirements and are not a direct indication of product quality.

Table II. ICV™ Baseline Glass Composition (AMBG-13)

Component	Mass Fraction
Al_2O_3	0.0989
B_2O_3	0.0500
CaO	0.0375
Cl	0.0018
Cr_2O_3	0.0009
F	0.0007
Fe_2O_3	0.0633
K_2O	0.0176
MgO	0.0097
Na_2O	0.2000
P_2O_5	0.0060
ReO_2	0.0001
SiO_2	0.4255
SO_3	0.0083
TiO_2	0.0097
ZrO_2	0.0700
Total	**1.0000**
Soil	0.682
Waste	0.198
Additives	0.120

Table III. Normalized PCT Releases from Baseline Glass (g/m^2)
(limit for Na and B is 2 g/m^2)

Glass	Na	Al	B	Ca	K	Si
AMBG-13-Q	0.364	0.129	0.253	0.008	0.138	0.126
AMBG-13-SC	0.410	0.140	0.289	0.028	0.321	0.134

Table IV. TCLP Responses of Baseline Glass

	Limit (mg/L)	AMBG-13-Q	AMBG-13-SC
Boron Release (mg/L)[(a)]	NA	*0.43*	0.52
Chrome Release (mg/L)[(a)]	0.6	*0.011*	*0.0059*
(a) The italicized values are estimated results because they are below the reporting limits (0.5 and 0.25 mg/L for B and Cr respectively).			

Table V. 200°C-VHT Response of Baseline Glass (limit is 50 g/[m^2·d])

Test Number	Duration (days)	*m* (g/m^2)	r_a (g/[m^2·d])
AMBG-13-Q	6.9	6.7	0.96
AMBG-13-Q	14.0	13.5	0.97
AMBG-13-Q	28.1	223.3	7.96
AMBG-13-SC	7.0	44.6	6.39
AMBG-13-SC	13.9	5.2	0.37
AMBG-13-SC	28.0	96.9	3.46

ACCEPTABLE GLASS COMPOSITION REGION DEVELOPMENT

After determining the baseline glass composition for Bulk Vitrification, a series of crucible tests was completed to determine the acceptable glass composition region around the baseline BV glass. This latter series of tests is referred to as the Series 21 matrix crucible tests. The objective of the matrix glass formulation and testing for Series 21 glasses was to determine the acceptable glass composition region for processing S-109 tank (the first tank to be treated by BV) waste with local soil and additional additives applying the baseline formulation (soil plus boron oxide and zirconium oxide additives). Table VI shows the compositions of baseline S-109 waste simulant and soil used in the Series 21 matrix crucible testing, expressed in terms of oxides and halogens likely to end up in glass. The acceptable glass composition region is the region of glass compositions on which the bulk glass properties meet the acceptance criteria for disposal in the integrated disposal facility. The Series 21 tests were carried out in two phases.

Table VI. Composition of Baseline S-109 Simulant and Horn Rapids Test Site (HRTS) Soil and Composition Range of Glasses Tested in Series 21 Matrix Crucible Testing

Component	Baseline S-109 Simulant[(a)]	HRTS Soil	Glass Composition Range Tested	
			Min	Max
Al_2O_3	0.0135	0.1294	0.0800	0.1679
B_2O_3			0.0167	0.0600
BaO		0.0007	0.0004	0.0005
CaO	0.0004	0.0404	0.0250	0.0550
Cl	0.0015		0.0001	0.0010
Cr_2O_3	0.0064	0.0001	0.0012	0.0058
F	0.0006		0.0001	0.0010
Fe_2O_3	0.0022	0.0627	0.0395	0.1100
K_2O	0.0012	0.0217	0.0090	0.0250
MgO		0.0197	0.0090	0.0300
MnO		0.0010	0.0006	0.0010
Na_2O	0.9331	0.0272	0.1800	0.2400
P_2O_5	0.0234	0.0021	0.0020	0.0160
SiO_2		0.6830	0.3900	0.5475
SO_3	0.0177		0.0010	0.0095
SrO		0.0004	0.0002	0.0003
TiO_2		0.0116	0.0070	0.0200
ZrO_2			0.0200	0.0800
SUM	1.0000	1.0000		

(a) From Table 1 in PNNL Document No. ST04.010 (Baseline S-109 Chemical Simulant Recipe for AMEC Tests, Jan. 21, 2004): Attachment 1 to CH2M HILL Correspondence No. CH2M-0400444 (Feb. 2004).

The Phase 1 test matrix of 12 glass compositions was formulated applying a one-parameter-at-a-time change approach to account for variations in soil composition, waste loading, waste composition, and refractory liner incorporation. The glasses were fabricated in an atmosphere-controlled furnace to simulate the redox conditions of the BV process. Both quenched and slow cooled glasses were characterized with the VHT and TCLP, and secondary phase formation in SC glasses was determined. The Phase 2 test matrix of 16 glasses was designed applying a statistical approach to account for the variations of multiple parameters (soil composition, waste loading, waste composition, and refractory liner incorporation) and to cover the possible glass composition region for S-109 waste treatment. The Phase 2 matrix glasses were prepared under ambient atmosphere. The glasses were also characterized with the PCT in addition to the VHT and TCLP for both quenched and SC glasses and with the secondary phase identification for the SC glasses.

The Series 21 matrix crucible testing was neither intended to develop an optimum glass composition for S-109 waste nor to define an acceptable glass envelope for the treatment of any waste other than S-109 salt-cake. Optimizing and evaluating larger waste composition regions will be the focus of future laboratory testing in the Bulk Vitrification program. In addition, the Series 21 matrix studies were not aimed at addressing any waste acceptance criteria other than those associated with bulk glass responses to VHT, TCLP, and PCT.

The main results from the VHT and PCT tests of Phases 1 and 2 matrix glasses are summarized below [3].

Vapor Hydration Test Results – Crucible Tests

Fig. 1. and Fig. 2. summarize the VHT results of Phases 1 and 2 matrix glasses. Fig. 1. summarizes the 14-day VHT alteration rates in quenched and SC-treated samples of all the Phase 1 glasses. Overall, except for three high-Al_2O_3 glasses (as noted in Fig. 1.), there is no noticeable effect of slow cooling showing a reasonably good agreement between quenched and slow-cooled samples. Three out of 12 glasses tested failed the 50 $g/(m^2 \cdot d)$ requirement in both quenched and cooled samples while 2 glasses failed in slow-cooled samples only. Fig. 2. compares the 14-day alteration rate in quenched and SC Phase 2 glasses. SC treatment significantly increased the alteration rate in seven glasses, significantly decreased the alteration rate in three glasses, and did not significantly affect the alteration rate in six glasses. All the quenched glasses passed the VHT requirement while the SC treatment caused one glass to fail the requirement and two glasses to nearly fail. The increased alterations rates in seven slow-cooled glasses were attributed to the crystallization during slow cooling, but the decreased alteration rates in three slow-cooled glasses were not understood.

Nepheline [$NaAlSiO_4$, $K(Na,K)_3Al_4Si_4O_{16}$] was the main crystalline phase observed in slow-cooled samples. Other major crystals identified were baddeleyite [ZrO_2], sodium-zirconium silicate [$Na_4Zr_2(SiO_4)_3$), $Na_{14}Zr_2Si_{10}O_{31}$)], combeite [$Na_{15.78}Ca_3(Si_6O_{12})$, $Na_4(Ca,Al,Fe)_3Si_6O_{16}(OH,F)_2$], and sodium-aluminum silicate [$Na_{1.45}Al_{1.45}Si_{0.55}O_4$]. Some slow-cooled glasses grossly crystallized and contained over 50 wt% crystals based on semi-quantitative analysis. These glasses were not included in the acceptable glass composition range.

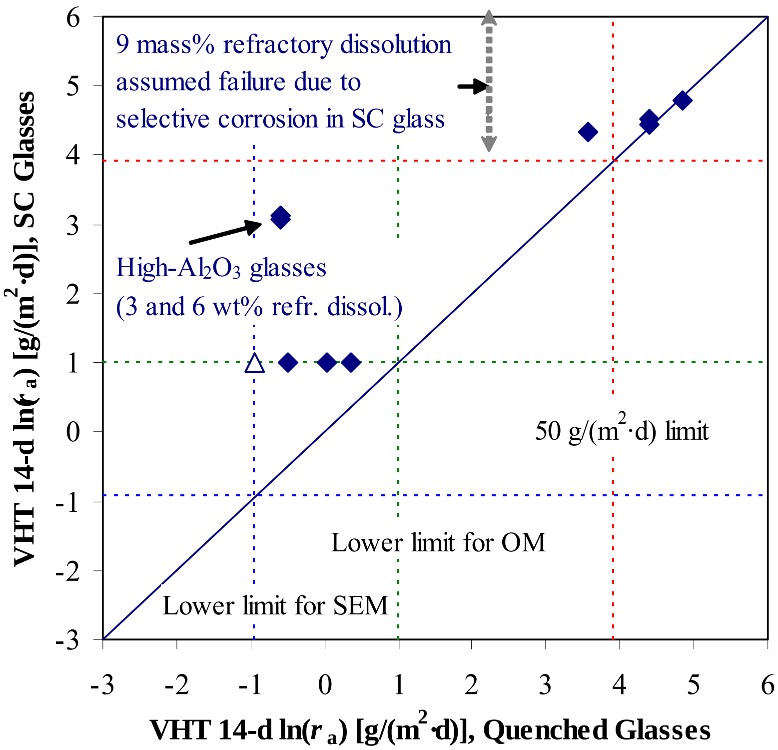

Fig. 1. Comparison of VHT alteration rates in Phase 1 quenched and slow cooled glasses

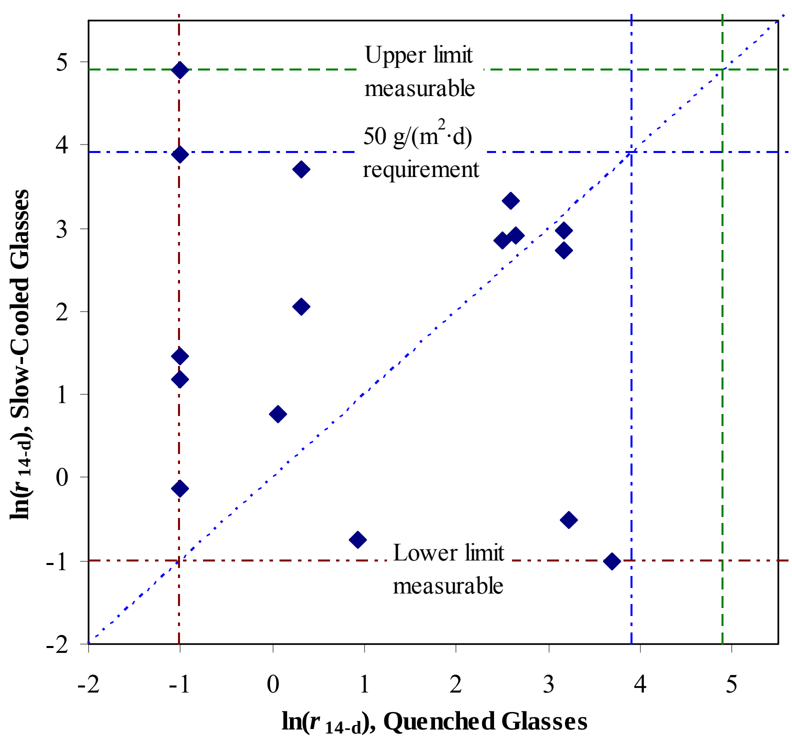

Fig. 2. Comparison of 14-day VHT alteration rates in Phase 2 quenched and slow cooled glasses

PCT Results – Crucible Tests

Fig. 3. summarizes the PCT normalized Na and B releases for quenched and slow-cooled Phase 2 glasses (PCT tests were not performed for Phase 1glasses). Fig. 3. shows that all the quenched glasses passed the 2 g/m^2 requirement and the SC treatment increased the PCT normalized releases for most glasses causing seven glasses to fail the requirement. Similar to the effect of slow cooling on VHT alteration rate, the increased PCT releases in these glasses were also attributed to the crystallization of slow-cooled glasses.

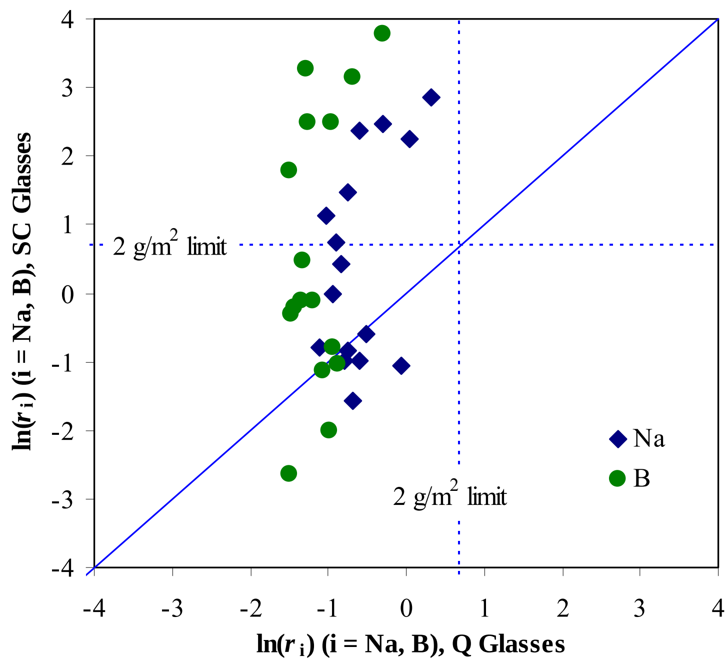

Fig. 3. Comparison of normalized PCT Na and B releases in Phase 2 quenched and slow cooled glasses

Preliminary Acceptable Glass Composition Region

The results of the Phases 1 and 2 matrix studies were combined with those from a previous study [5] on Bulk Vitrification glasses to construct a Bulk Vitrification glass database. The resulting data of all Bulk Vitrification glasses were evaluated focused on the effect of slow cooling and crystallization on the VHT, PCT, and TCLP responses to define the composition boundary of acceptable glasses. For Bulk Vitrification glasses, it has been found that the VHT response is the most restrictive requirement. Therefore, the boundary definition was primarily performed based on the VHT data. Then, the PCT and TCLP data were examined to make sure that all the glasses within the VHT acceptable composition boundary pass the PCT and TCLP restrictions and this was found to be true.

In conclusion, for the waste compositions expected from S-109 tank and soil compositions at the Hanford Site, the glass composition needs to be kept within the following range boundary to produce acceptable glasses:

- $17 \leq Na_2O \leq 22$ mass%
- $3 \leq B_2O_3 \leq 5$ mass%
- $8 \leq Al_2O_3 \leq 12.5$ mass%
- $5.5 \leq ZrO_2 \leq 8$ mass%; $6.4 \leq ZrO_2 \leq 8$ mass% if $Al_2O_3 \geq 9.5$ mass%

- $40 \leq SiO_2 \leq 48.5$ mass%.

The concentrations of other remaining components, including CaO, Fe_2O_3, K_2O, MgO, P_2O_5, and TiO_2, are not critical, but need to be kept within the ranges tested in BV glasses for the above composition boundary of major components to be valid.

GLASS ANALYSES FROM SCALED TESTING

Testing at engineering- and full-scale with simulated Hanford LAW has been conducted in parallel with the glass formulation studies. Product glasses from several of these tests have been analyzed to verify the performance of the glass. Initial testing in FY 2003 was done in a top-down process where the melt was started at the top of the feed batch and the melt progressed down during the test. Silica sand was used as a glass contact refractory for these tests. In FY2004 the process was changed to a bottom-up and feed-while-melt system where the initial batch of dried feed was melted from the bottom upward. After the initial batch was melted and subsided, feed was added and melted until the ICV™ box was full. The glass contact refractory was changed from silica sand to a castable refractory block. Although these two methods of operation are significantly different, the glasses experience nearly the same temperature heating and cooling histories. Relative to the glass quality, the main difference between the two methods of operation is that the earlier process, top-down melting with sand refractory, resulted in a glass that was higher in silica because some of the refractory sand would melt into the glass batch during processing.

The post-test characterizations of engineering- and full-scale glasses are compared with glasses produced in crucibles under laboratory conditions. As noted earlier, the laboratory glasses were either cooled by quenching or slow cooling to simulate the cool down of a full-scale ICV™ block. Both quenched and slow-cooled crucible glasses are shown for comparison.

PCT Results for Scaled Tests

Table VII presents the PCT results for the first two ICV™ large scale tests (LS-2 and LS-3), engineering-scale ICV™ test ES-1, the quenched and slow cooled baseline crucible glasses, and the Environmental Assessment (EA) glass [6]. The EA glass was developed as a "standard" for high-level waste glasses in that it establishes the minimum allowable durability for that class of waste glasses. The two things to note are 1) the LS and ES sample results indicate a uniformly good durability and 2) the LS and ES samples have better performance than the baseline crucible glasses. This is due to the higher silica content of the glasses from the scaled tests as a result of partial incorporation of the silica sand refractory. As is also readily observed, all of the glasses easily meet the product quality requirement that the normalized mass loss of the LAW waste glasses produced be < 2 g/m^2.

Table VII. Average Seven-Day 90ºC PCT Normalized Mass Loss

	Element (g/m^2)		
Glass	**B**	**Na**	**Si**
Large-Scale Test LS-2 Glasses [6]			
LS-2-01	0.117	0.076	0.055
LS-2-02	0.099	0.076	0.057
LS-2-03	0.099	0.075	0.054
LS-2-05	0.099	0.077	0.062
LS-2-07	0.096	0.078	0.059
Large-Scale Test LS-3 Glasses [6]			
LS-3-01	0.081	0.103	0.077
LS-3-02	0.088	0.124	0.078
LS-3-03	0.077	0.11	0.079
LS-3-05	0.072	0.109	0.08
LS-3-07	0.073	0.109	0.078
Engineering-Scale Test ES-1 Glasses[(a)]			
ES-1-6	0.073	0.152	0.126
ES-1-7	0.071	0.140	0.120
ES-1-8	0.073	0.150	0.129
ES-1-9	0.063	0.132	0.126
ES-1-10	0.073	0.143	0.124
(a) Values reported in *Engineering-Scale In-Container Vitrification Test Results, Final Report*. August 2003. AMEC, Earth & Environmental, Inc.			

TCLP Test Results for Scaled Tests

Table VIII presents TCLP results for the Resource Conservation and Recovery Act (RCRA) metals barium and chromium for several scaled tests and the baseline crucible glasses. The concentration of boron was also measured for the TCLP solutions to give an additional indication of durability of these glasses. The release values are comparable for the scaled tests and the crucible glasses. The values are also uniform within each scaled test indicating that the glasses within the ICV™ boxes were uniform and homogeneous. Note that the values that are reported are well below the Universal Testing Standard values also shown in the table. This is necessary to meet RCRA land disposal requirements.

Table VIII. TCLP results for B, Ba and Cr

	B	**Ba**	**Cr**
Test	**Concentration, mg/L**		
UTS[(a)]	n/a	21	0.6
Large-Scale Test LS-2 Glasses [6]			
LS-2-01	0.37	Nr[(b)]	0.0051
LS-2-02	0.30	nr	nr
LS-2-03	0.30	nr	nr
LS-2-05	0.33	nr	nr
LS-2-07	0.29	nr	0.0068
Large-Scale Test LS-3 Glasses [6]			
LS-3-02	0.18	nr	nr
LS-3-04	0.25	nr	nr
LS-3-05	0.35	nr	0.044

	B	Ba	Cr
Test	Concentration, mg/L		
LS-3-06	0.29	nr	nr
LS-3-07	0.42	nr	nr
Engineering-Scale Test ES-1 Glasses(c)			
ES-1-6	0.23	nr	0.0052
ES-1-7	0.36	nr	ND(d)
ES-1-8	0.33	nr	ND
ES-1-9	0.20	nr	0.01
ES-1-10	0.24	nr	ND
FY2004 ES Tests (bottom up tests)			
ES-31A	0.38	0.026	0.029
ES-31B	0.36	0.026	0.027
ES-32A	0.44	0.041	0.025
Baseline Crucible Glasses			
AMBG-13-Q	0.43	nr	0.011
AMBG-13-SC	0.52	nr	0.0059

(a) UTS – Universal Testing Standard [7]
(b) Nr – not reported
(c) All TCLP values for the ES-1 test are estimated results because they are below the reporting limits of 0.25 mg/L for Cr and 0.5 mg/L for B. Values reported in *Engineering-Scale In-Container Vitrification Test Results, Final Report*. August 2003. AMEC, Earth & Environmental, Inc.
(d) ND – below detection limit

VHT Test Results for Scaled Tests

Table IX presents the VHT results for ES-1 and the LS Tests 1, 2, and 3 (all top-down melts). The results for all of the top-down melt specimens except ES-1-10 were less than the estimated accuracy of the test (±10 g/m^2). Hence little if any corrosion occurred during the VHT exposure to any of the glass specimens. The exception was ES-1-10, which was taken near a graphite electrode and contained metal inclusions. Although the sample has a higher VHT response, it is still well below the limit of 50 g/m^2/d. The VHT response of ES Test 31B (bottom-up melt with S-109 simulant) is also included in the table. This response was slightly higher than the top-down melts, but agrees with the baseline crucible glass. All of the glasses are well below the specification of 50 g/m^2/d.

Table IX. VHT Responses of Scaled Tests and Baseline Glass

Test and Sample	t (days)	m_a (g/m^2)(a)	r_a (g/m^2/d)
Specification Limit	14	700	50
Large-Scale Test LS-2 Glasses [6]			
LS-2-01-VHT-014	14.0	2.5	0.2
LS-2-02-VHT-014	14.0	-1.3	-0.1
LS-2-03-VHT-014	14.0	-3.8	-0.3
LS-2-05(1)-VHT-014	14.0	5.0	0.4
LS-2-05(2)-VHT-014	14.0	1.3	0.1
Large-Scale Test LS-3 Glasses [6]			
LS-3-02-VHT-014	14.0	-1	-0.1
LS-3-04-VHT-014	14.0	4	0.3

Test and Sample	**t (days)**	**m_a $(g/m^2)^{(a)}$**	**r_a $(g/m^2/d)$**
LS-3-05-VHT-014	14.0	-1	-0.1
LS-3-06-VHT-014	14.0	-2	-0.2
LS-3-07-VHT-014	14.0	-1	-0.1
Engineering-Scale Test ES-1 Glasses(b)			
ES-1-6	14.1	5.06	0.36
ES-1-7G	13.9	3.74	0.27
ES-1-8G	14.0	3.79	0.27
ES-1-9	14.1	1.27	0.09
ES-1-10	14.1	66.20	4.68
FY2004 ES Test (bottom up tests)			
ES-31B	14	nr(c)	1.7
Baseline Crucible Glasses			
AMBG-13-Q	14.0	13.5	0.97
AMBG-13-SC	13.9	5.2	0.37

(a) Estimated measurement uncertainty is ±10 g/m^2
(b) Values reported in *Engineering-Scale In-Container Vitrification Test Results, Final Report*. August 2003. AMEC, Earth & Environmental, Inc.
(c) nr – not reported

FUTURE TESTING

The Bulk Vitrification glass development and testing program is partially complete. Continued testing has focused on evaluating the impact of variable waste streams on the Bulk Vitrification glass. A study was performed to identify the range of waste feeds expected to be produced during tank retrieval and pretreatment operations for the full Hanford mission. An expanded series of crucible tests to investigate this broader range of wastes is partially complete. These crucible tests are coupled with engineering-scale process tests conducted by AMEC to establish process limitations. Process limitations from the engineering-scale tests and glass performance results from crucible scale tests are combined to establish an acceptable set of glass formulations for bulk vitrification.

CONCLUSIONS

A baseline glass composition and an acceptable composition region have been developed for the bulk vitrification process for treating Hanford low-activity waste. Experiments have been carried out at the crucible scale, engineering-scale and full-scale and the results consistently indicate that the bulk glass within the ICV™ box is homogeneous and the glass will meet product quality constraints for VHT, PCT and TCLP response.

ABBREVIATIONS AND ACRONYMS

ASTM	American Society for Testing and Materials
BV	bulk vitrification
CRB	castable refractory block
DOE	U.S. Department of Energy
EA	Environmental Assessment
EDS	energy dispersive spectroscopy
EPA	U.S. Environmental Protection Agency
ES	engineering scale
IM	image analysis
ICV™	In Container Vitrification™
LAW	low-activity waste
LS	large scale
OM	optical microscopy
ORP	DOE Office of River Protection
PCT	Product Consistency Test
PNNL	Pacific Northwest National Laboratory
Q	quenched
RCRA	Resource Conservation and Recovery Act
SC	slow cooled

SEM	scanning electron microscopy
TCLP	Toxicity Characteristic Leaching Procedure
TPA	Tri-Party Agreement
VHT	Vapor Hydration Test
WTP	Hanford Waste Treatment Plant
XRD	x-ray diffraction

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