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**Glass Formulation for Phase 1 High-Level
Waste Vitrification**

J. D. Vienna
P. R. Hrma

April 1996

Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest National Laboratory
Richland, Washington 99352

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1.0 Introduction

The purpose of this study is to provide potential glass formulations for prospective Phase I High-Level Waste (HLW) vitrification at Hanford. The results reported here have been generated in cooperation with Steve Lambert of Westinghouse Hanford Company. This information will be used to aid in developing a Phase I HLW vitrification request for proposal (RFP) and facilitate the evaluation of ensuing proposals. The following factors were considered in the glass formulation effort:

- impact on total glass volume of requiring the vendor to process each of the tank compositions independently versus as a blend,
- effects of imposing typical values of B_2O_3 content and waste loading in HLW borosilicate glasses as restrictions on the vendors (according to WAPS 1995, the typical values are 5-10 wt% B_2O_3 and 20-40 wt% waste oxide loading),
- impacts of restricting the processing temperature to 1150°C on eventual glass volume, and
- effects of caustic washing on any of the selected tank wastes relative to glass volume.

2.0 Waste Compositions

The projected waste compositions (on oxide basis) identified for Phase I vitrification are listed in Table I (Washenfelter 1995). Waste compositions marked WW assume sludge washing with water as a pretreatment, whereas those marked CW assume caustic washing as a pretreatment. The wastes consist of the solids from tanks AY102, AZ101, AZ102, and C106. The solids composition for C106 is given in two variations, C106A represents the composition from a core sample taken in 1986 (analyzed by Weiss), C106B represents the composition from the same core sample analyzed by Hara. The waste mass (M_w) is also reported for each in Table I.

Table I. HLW Composition Estimates for Phase I Vitrification Tanks in Mass Fractions (and mass in kg on oxide basis).

Oxide	AY102- CW	AY102- WW	AZ101- CW	AZ101- WW	AZ102- CW	AZ102- WW	C106A- CW	C106A- WW	C106B- CW	C106B- WW
SiO ₂	0.0659	0.0592	0.0306	0.0286	0.0207	0.0187	0.3483	0.3184	0.1116	0.0908
B ₂ O ₃	0.0222	0.0199	0.0023	0.0022	0.0034	0.0031	0.0001	0.0001	0.0017	0.0014
Na ₂ O	0.2177	0.1956	0.2372	0.2218	0.2272	0.2048	0.2752	0.2516	0.3574	0.2909
Li ₂ O	0.0000	0.0000	0.0004	0.0004	0.0001	0.0001	0.0000	0.0000	0.0000	0.0000
CaO	0.0504	0.0453	0.0083	0.0078	0.0087	0.0078	0.0381	0.0348	0.0053	0.0043
MgO	0.0290	0.0261	0.0025	0.0023	0.0034	0.0031	0.0249	0.0228	0.0014	0.0011
Fe ₂ O ₃	0.3082	0.2769	0.3490	0.3265	0.4056	0.3657	0.1707	0.1560	0.2365	0.1925
Al ₂ O ₃	0.0956	0.1652	0.0633	0.1138	0.1142	0.1980	0.0921	0.1619	0.2266	0.3547
ZrO ₂	0.0020	0.0018	0.1160	0.1085	0.0529	0.0477	0.0064	0.0058	0.0015	0.0013
P ₂ O ₅	0.0120	0.0317	0.0053	0.0146	0.0016	0.0044	0.0044	0.0119	0.0097	0.0232
Others*	0.1970	0.1783	0.1851	0.1736	0.1621	0.1467	0.0398	0.0367	0.0483	0.0398
NM**	0.0200	0.0179	0.0048	0.0045	0.0031	0.0028	0.0013	0.0012	0.0045	0.0037
Cr ₂ O ₃	0.0115	0.0116	0.0037	0.0039	0.0047	0.0048	0.0029	0.0030	0.0046	0.0042
Mw (kg)	29.999	33.386	79.683	85.195	132.918	147.433	465.053	508.747	252.380	310.054

* Others are minor components (i.e., Cr₂O₃, CeO₂, La₂O₃, MnO₂, etc.) see Washenfelter (1995) for complete listing.

** NM's are noble metals (i.e., RuO₂, Rh₂O₃, Ag₂O, etc.)

Several possible blend compositions from these wastes are listed in Table II (Washenfelder 1995). These blends are:

AYC-A	=	AY102 + 0.4875*C106A,
AYC-B	=	AY102 + 0.1625*C106A,
AZ	=	AZ101 + AZ102,
AZC-A	=	AZ + 0.4875*C106A,
AZC-B	=	AZ + 0.1625*C106A,
Nom	=	0.8*AZ101 + 0.8*AZ102 + 0.32*C106A + 0.15*AY102, and
Blend	=	AZ101 + AZ102 + C106A + AY102.

As with the single tank wastes, two pretreatment variations are considered, water (WW) and caustic (CW) washing.

Table II. HLW Blend Composition Estimates for Phase I Vitrification in Mass Fractions (and mass in kg on oxide basis).

Oxide	AYC-A-CW	AYC-A-WW	AYC-B-CW	AYC-B-WW	AZ-CW	AZ-WW	AZC-A-CW	AZC-A-WW	AZC-B-CW	AZC-B-WW	Nom-CW	Nom-WW	Blend-CW	Blend-WW
SiO ₂	0.2676	0.2434	0.3153	0.2877	0.0245	0.0223	0.1919	0.1754	0.1094	0.1000	0.1709	0.1564	0.2387	0.2178
B ₂ O ₃	0.0064	0.0058	0.0027	0.0025	0.0030	0.0028	0.0015	0.0014	0.0022	0.0021	0.0019	0.0018	0.0019	0.0018
Na ₂ O	0.2584	0.2351	0.2686	0.2450	0.2306	0.2107	0.2536	0.2318	0.2417	0.2209	0.2477	0.2267	0.2585	0.2359
Li ₂ O	0.0000	0.0000	0.0000	0.0000	0.0002	0.0002	0.0001	0.0001	0.0002	0.0002	0.0001	0.0001	0.0001	0.0001
CaO	0.0416	0.0379	0.0395	0.0361	0.0085	0.0078	0.0238	0.0218	0.0163	0.0149	0.0224	0.0205	0.0298	0.0272
MgO	0.0261	0.0237	0.0254	0.0232	0.0031	0.0028	0.0144	0.0131	0.0088	0.0080	0.0132	0.0121	0.0185	0.0169
Fe ₂ O ₃	0.2094	0.1905	0.1868	0.1704	0.3847	0.3516	0.2746	0.2510	0.3285	0.3002	0.2814	0.2575	0.2404	0.2194
Al ₂ O ₃	0.0930	0.1627	0.0925	0.1623	0.0952	0.1673	0.0937	0.1647	0.0944	0.1659	0.0921	0.1621	0.0931	0.1634
ZrO ₂	0.0051	0.0046	0.0058	0.0053	0.0766	0.0700	0.0404	0.0369	0.0581	0.0531	0.0426	0.0390	0.0275	0.0251
P ₂ O ₅	0.0065	0.0175	0.0053	0.0142	0.0030	0.0081	0.0037	0.0101	0.0034	0.0091	0.0038	0.0101	0.0048	0.0130
Others*	0.0859	0.0788	0.0580	0.0534	0.1706	0.1564	0.1022	0.0938	0.1369	0.1255	0.1239	0.1138	0.0867	0.0795
NM**	0.0066	0.0060	0.0035	0.0032	0.0038	0.0035	0.0025	0.0023	0.0031	0.0029	0.0028	0.0026	0.0028	0.0026
Cr ₂ O ₃	0.0054	0.0055	0.0039	0.0040	0.0043	0.0044	0.0036	0.0037	0.0038	0.0039	0.0037	0.0038	0.0037	0.0038
Mw (Mg)	105.74	116.23	256.67	281.36	212.42	232.45	438.51	479.83	288.01	315.14	329.23	359.77	708.55	776.38

* Others are minor components (i.e., Cr₂O₃, CeO₂, La₂O₃, MnO₂, etc.) see Washenfelder (1995) for complete listing.

** NM's are noble metals (i.e., RuO₂, Rh₂O₃, Ag₂O₂, etc.)

The Phase I HLW's are generally high in Fe₂O₃ (16 to 41 wt%), Al₂O₃ (6 to 35 wt%), Na₂O (20 to 36 wt%), and in some cases SiO₂ (2 to 35 wt%). The noble metals (NM on oxide basis) and Cr₂O₃ concentrations are also high in the AY102 waste (2.0 and 1.8 wt% NMs (mostly Ag) in AY102-CW and -WW, respectively and 1.2 wt% Cr₂O₃ in each of the AY102 wastes). The weighted averages of components are equal to their mass fractions in the Blend waste (Table II) for both water and caustic washing options.

3.0 Property Models

First- and second-order mixture models have been fitted to property data obtained from the composition variation study (CVS) at Hanford (Hrma. Piepel, et al. 1994). These (Scheffé) mixture models are of the form:

$$p = \sum_{i=1}^n p_i g_i + \sum_{i=1}^{n-1} \sum_{j=i}^n p_{ij} g_i g_j \quad (1)$$

where p is the transformed property, g_i is the i -th component mass fraction, and p_i and p_{ij} are the first- and second-order model coefficients. A second-order model has a limited number of nonzero p_{ij} 's (indicating component interactions), whereas all p_{ij} 's are zero in the first-order model. The transformed properties of interest for glass formulation are the logarithm of normalized boron (r_B) and sodium (r_{Na}) release from 7-day Product Consistency Test (PCT), the melting temperature (T_M) at a viscosity of 5 Pa-s, and the liquidus temperature (T_L).

3.1 PCT Models

Models for quenched glass PCT, $\ln(r_B)$ and $\ln(r_{Na})$, have been developed, validated, and used for glass formulation and normalized release predictions (Hrma, Piepel, et al. 1994). The model coefficients are listed in Table III.

Table III. First- (1°) and Second-Order (2°) Model Coefficients for 7-day PCT Normalized Boron (r_B) and Sodium (r_{Na}) Release.

	$\ln(r_B)$ (1°)	$\ln(r_B)$ (2°)	$\ln(r_{Na})$ (1°)	$\ln(r_{Na})$ (2°)
SiO ₂	-4.317	-4.127	-4.412	-1.765
B ₂ O ₃	11.979	-2.780	9.405	-10.472
Na ₂ O	17.607	19.765	19.401	12.501
Li ₂ O	22.579	25.128	19.064	7.597
CaO	-8.711	7.894	-1.957	8.525
MgO	10.921	-51.248	11.823	-17.036
Fe ₂ O ₃	-3.201	-0.734	-4.095	-2.851
Al ₂ O ₃	-25.407	-39.690	-25.429	-32.642
ZrO ₂	-10.561	-21.813	-11.421	16.141
Others	0.159	4.356	-0.665	0.707
SiO ₂ × MgO		119.521		57.677
SiO ₂ × ZrO ₂				-53.274
B ₂ O ₃ × B ₂ O ₃		76.545		94.987
B ₂ O ₃ × CaO		-80.929		-96.621
Na ₂ O × Li ₂ O				152.352
Na ₂ O × CaO		-90.900		
Na ₂ O × ZrO ₂		70.423		
Li ₂ O × Al ₂ O ₃				-86.385
CaO × ZrO ₂		101.874		
MgO × ZrO ₂		146.706		
Al ₂ O ₃ × Al ₂ O ₃		105.282		89.997
R ²	0.911	0.911	0.946	0.924

These models have been fitted to data generated over a statistically developed composition region which is broad enough to include several nondurable glasses. However, the inclusion of nondurable glasses tends to cause the models to overpredict the release of glasses with releases ≤ 2

g/m² (Vienna and Hrma 1995 and Vienna, Hrma. et al. 1995). For Phase I glasses only compositions with predicted normalized boron and sodium releases ≤ 2 g/m² were considered.

For glass acceptance, the Canister Centerline Cooled (CCC) glass must also have acceptable durability. Accurate models do not exist to predict the durability of CCC glasses. It has been shown that CCC durability is similar to that of quenched glasses with the exception of glasses which form durability reducing crystals such as nepheline, cristobalite, or eucryptite (Kim et al. 1995). Until predictive tools are developed for crystallinity in CCC glasses, experimental measurements must be used to confirm the durability of glasses with significant crystallization.

3.2 Liquidus Temperature Models

A guideline for the T_L of glasses produced in a continuous melter is that it be at least 100°C below the operating temperature (typically equal to T_M) to avoid precipitation in cold spots and while idling. For refractory type wastes, such as those considered for Phase I vitrification, the $T_L \leq T_M - \Delta_{min}$, where Δ_{min} is the minimum temperature difference, typically taken as 100°C, restriction limits glass W. Hence, more accurate prediction of T_L enables better predictions of maximum waste loading (W_{max}) and lower laboratory costs. T_L limits waste loading when W_{max} is determined by $T_L = T_M - \Delta_{min}$. Several attempts have been made to predict T_L in HLW glasses with varying degrees of accuracy (Kim and Hrma 1994).

For this study, first- and second-order mixture models were chosen to predict T_L . Of roughly 200 CVS glasses, the T_L of only 128 were measured. These glasses cover a wide composition range (see Vienna et al. 1995) with over 20 different primary phases of crystallization. T_L is an intricate function of composition (dependent on primary phase field). Better T_L predictions result from narrowing the composition region used for T_L modelling to that which is close to the region of interest. Considering the Phase I wastes, the CVS composition region was narrowed by the following boundaries: $B_2O_3 \leq 15$, $Na_2O \geq 7$, $Li_2O \leq 7$, $CaO \leq 5$, $MgO \leq 5$, and $ZrO_2 \leq 8$ wt%. These restrictions left 74 data points with 9 primary phases (spinel, zircon, lithium silicate, clinopyroxene, nepheline, eucryptite, rare earth zirconate, chromium oxide, and sodium zirconium silicate). First- and second-order model coefficients for T_L are given in Table IV.

Table IV. First- (1°) and Second-Order (2°) Model Coefficients for T_L .

	T_L (°C) (1°)	T_L (°C) (2°)
SiO ₂	1105.956	1074.792
B ₂ O ₃	83.057	2597.870
Na ₂ O	64.624	1089.068
Li ₂ O	-1879.854	-6924.872
CaO	-27.503	304.773
MgO	2810.088	454.887
Fe ₂ O ₃	2234.924	5721.916
Al ₂ O ₃	2021.494	1598.057
ZrO ₂	1710.692	1165.960
P ₂ O ₅	1434.423	-2777.978
Others	-2136.881	1128.216
B ₂ O ₃ × Na ₂ O		-16901.340
B ₂ O ₃ × Fe ₂ O ₃		-11867.580
Na ₂ O × Li ₂ O		32790.413
Na ₂ O × Fe ₂ O ₃		-26451.550
Al ₂ O ₃ × P ₂ O ₅		92122.945
ZrO ₂ × ZrO ₂		38679.883
R ²	0.886	0.943

To assess the accuracy of the second-order T_L model, predictions were compared to measured values of high Fe₂O₃ glasses (including those not used in fitting the model). The results indicate that with few exceptions, all predicted values fall within $\pm 50^\circ\text{C}$ of the measured. The exceptions include glasses outside the composition region of interest. Hence, $\Delta_{\min} = 150^\circ\text{C}$ has been used as a W limiting criterion to insure within reasonable doubt that the T_L of the formulated glasses will fall within the prescribed limit ($T_L \leq T_M - 100^\circ\text{C}$).

Since this model is based on limited data, additional models have been used to confirm the T_L predictions for the formulated glasses. These models are FACT (Pelton et al. 1995) and a first-order spinel T_L model (labeled "Kim") (Kim and Hrna 1994). These model predictions have been reported in Table IX for each glass composition. Because the FACT prediction for nepheline T_L may be subjected to a large error, a second primary phase was predicted wherever nepheline appeared.

3.3 Melting Temperature Models

The viscosity of 161 CVS glasses was measured as a function of temperature and the data were fitted to the Vogel-Fulcher-Tammann (VFT) equation for each glass. The VFT equation was then used to identify the temperature at which the viscosity is 5 Pa·s (T_M). The T_M values were then fitted to first- and second-order mixture models. The coefficients are listed in Table V.

Table V. First- (1°) and Second-Order (2°) Model Coefficients for T_M .

	$T_M (^{\circ}\text{C}) (1^{\circ})$	$T_M (^{\circ}\text{C}) (2^{\circ})$
SiO_2	2180.828	2210.503
B_2O_3	-85.713	-677.336
Na_2O	-385.475	-744.103
Li_2O	-3363.541	-6625.885
CaO	-193.809	185.113
MgO	21.908	24.204
Fe_2O_3	958.215	581.056
Al_2O_3	2330.672	2454.653
ZrO_2	1892.388	1893.403
P_2O_5	3307.177	2205.785
Others	1796.576	1019.346
$\text{B}_2\text{O}_3 \times \text{B}_2\text{O}_3$		3691.488
$\text{B}_2\text{O}_3 \times \text{Fe}_2\text{O}_3$		5173.637
$\text{Na}_2\text{O} \times \text{Li}_2\text{O}$		12230.849
$\text{Li}_2\text{O} \times \text{Li}_2\text{O}$		28689.792
$\text{Li}_2\text{O} \times \text{MgO}$		9954.010
R2	0.934	0.961

4.0 Formulation Method

4.1 General Methods

To vitrify a waste, one must mix it with additives that produce a durable glass on melting the mixture and cooling it down. The resulting glass composition is

$$g_i = Ww_i + (1-W)a_i \quad (2)$$

where g_i , w_i , and a_i are the i -th component mass fraction in glass, waste and additive mix, respectively, and W is the waste loading. Only those components of waste and additive mix are used which remain in the glass (mostly oxides).

Component mass fractions satisfy the balance equations $\sum g_i = \sum w_i = \sum a_i = 1$, where the summation runs over all components. By Equation (2), the first of these three identities results from the remaining two. Since $\sum w_i = 1$ is satisfied automatically through waste composition normalization, the only condition to be met is

$$\sum a_i = 1 \quad (3)$$

Generally, the $W_{\max}$ for HLW vitrification is determined by three properties: T_M , $D_T = T_M - T_L$ ($D_T \leq \Delta_{\min}$), and the normalized release of a glass key component (r_k) in 7-day PCT. To formulate glass, these properties must be known as functions of glass composition. For a small composition region, linear equations (first-order models) usually suffice as first approximations:

$$T_M = \sum T_i g_i \quad (4)$$

$$D_T = \sum D_i g_i \quad (5)$$

$$r_k = \sum r_i g_i \quad (6)$$

where T_i , D_i , and r_i are i -th component coefficients for T_M , D_T , and r_k , respectively.

Two types of waste exist according to what glass property limits the waste loading: 1) the refractory type, limited by crystallization in the melter, and 2) the flux type, limited by chemical durability. The W_{max} of the refractory type is reached when $D_T = \Delta_{min}$. The W_{max} for the flux type is reached when $r_k = r_{k,max}$, a value defined by the Environmental Assessment standard reference glass. The actual waste loading could be somewhat lower than W_{max} allowing for model and waste composition uncertainties.

According to the present estimates, most of Hanford HLW streams fall into the category of refractory wastes and all Hanford LLWs are of the flux type. Here we focus on the refractory type. The derivation shown below can be easily repeated for flux type wastes.

The baseline for W_{max} of a refractory type waste glass is that with SiO_2 as the only additive (i.e., $a_S = 1$ and $a_i = 0$ for all $i \neq S$, where the subscript S denotes SiO_2). By Equations (2), (3), and (5),

$$W_{max} = \frac{D'_{min}}{D'_w} \quad (7)$$

where $D'_{min} = \Delta_{min} - D_S$ and $D'_w = \sum D'_i w_i$. Here $D'_i = D_i - D_S$ are reduced component coefficients. The corresponding glass composition and the values of T_M and r_k are obtained from Equations (4) and (6) by substituting for g_i from Equation (2) and W_{max} from Equation (7) for W in Equation (2).

For a low-temperature melter, the operating temperature is fixed at $T_M = 1150^\circ C$. The baseline glass with a fixed melting temperature is a glass produced by adding SiO_2 and Na_2O to the waste (i.e., $a_S + a_N = 1$ and $a_i = 0$ for all $i \neq S$ or N , where the subscript N stands for Na_2O). Using Na_2O allows us to meet the condition that $T_M = 1150^\circ C$. When other additives, such as B_2O_3 , Al_2O_3 , or Li_2O , are used in addition to SiO_2 and Na_2O , their concentrations in the glass (their g_i values) can either be chosen arbitrarily or determined by additional conditions, e.g., minimization of r_k .

Connecting Equations (4) and (5) with Equation (2), we get

$$T_M = WT_W + (1-W)\sum T_i a_i \quad (8)$$

$$D_T = WD_W + (1-W)\sum D_i a_i \quad (9)$$

where $T_W = \sum T_i w_i$ and $D_W = \sum D_i w_i$.

Equations (8) and (9) can also be written in the form

$$T'_M = WT'_w + (1-W)\sum T'_i a_i \quad (8')$$

$$D'_T = WD'_w + (1-W)\sum D'_i a_i \quad (9')$$

where the prime denotes the relative properties and component coefficients, i.e., $T'_M = T_M - T_S$, $D'_T = D_T - D_S$, and $T'_i = T_i - T_S$.

For low-temperature melter glass formulation, it is convenient to rewrite Equations (8') and (9') as

$$T' = WT'_w + (1-W)T'_{NaN} \quad (8'')$$

$$D'' = WD''_w + (1-W)D'_{NaN} \quad (9'')$$

where $T' = T' - \sum T'_k g_k$, $D'' = D' - \sum D'_k g_k$, $T'_w = T' - \sum T'_i w_i$, $D''_w = D' - \sum D'_i w_i$, and $i \neq k$; here the summation runs over all components used in the additive mix except SiO_2 and Na_2O . Equations (8'') and (9'') are convenient when prescribed g_i values are used for these additional additive components.

By Equations (8'') and (9''), one obtains

$$W_{\max} = \frac{T'_N D'' - D'_N T''}{T'_N D''_w - D'_N T''_w} \quad (10)$$

The glass and additive mix compositions (i.e., g_i and a_i values) can be obtained from Equations (2) and (3); the value of a_N can be obtained from Equations (8'') or (9''). Once a glass composition is defined, property values (r_k , etc.) can be calculated using any predictive model, such as the first- or second-order models represented by Equation (1).

Generally, property predictions are more accurate with second-order models within the model validity region. Thus second-order models are used to further narrow glass compositions after first-order estimations are completed. The relative complexity of second-order equations (Equation 1) prohibit analytical solutions to $W_{\max}$ and g_i . Iterative solutions were restricted by the composition constraints shown in the following Section.

4.2 Constraints

Glass formulation constraints fall into three general categories: 1) property constraints on glass product, 2) glass processing constraints, and 3) model validity constraints. Processing restrictions have been discussed in Sections 3.2 and 4.1. Model validity constraints were imposed on g_i values for B_2O_3 , SiO_2 , Li_2O , Na_2O , and Fe_2O_3 (Table VI). Experience has shown that glasses with sufficient alkaline oxides so that $T_M = 1150^\circ\text{C}$ will have acceptable electrical conductivity for processing in a Joule-heated melter.

Glass product constraints are given by Waste Acceptance Product Specification (WAPS 1995) which specifies that the normalized release of B, Na, and Li from a glass subjected to a 7-day PCT be less than that of the environmental assessment glass. These releases have been measured to be 8.5, 6.6, and 4.9 g/m² for r_B , r_{Na} , and r_{Li} , respectively. In this study the

constraints of $r_B, r_{Na} \leq 2 \text{ g/m}^2$ was imposed. This conservative constraint will accommodate model uncertainty and sample to sample variations. It will not, however, insure acceptable CCC durability.

Table VI. Constraints Used for Formulation of Phase I Glasses. The Validity Region for T_L Models are Discussed in Section 3.2 and Did Not Constrain Waste Loading or Glass Composition.

	Acceptance or validity criteria	Formulation criteria	Alternate formulation criteria
$r_B \text{ (g/m}^2\text{)}$	$r_B \leq 8.5$	$r_B \leq 2.0$	
$r_{Na} \text{ (g/m}^2\text{)}$	$r_{Na} \leq 6.6$	$r_{Na} \leq 2.0$	
$r_{Li} \text{ (g/m}^2\text{)}$	$r_{Li} \leq 4.9$		
$T_M \text{ (}^\circ\text{C)}$	$T_M = 1150$	$T_M = 1150$	$T_M \leq 1550$
$T_M - T_L$	$T_M - T_L \leq 100^\circ\text{C}$	$T_M - T_L \leq 150^\circ\text{C}$	
SiO_2	$g_S \geq 0.42$	$g_S \geq 0.40$	$g_S \geq 0.37$
B_2O_3	$0.05 \leq g_B \leq 0.20$	$g_B \geq 0.05$	$g_B \geq 0.00$
Na_2O	$0.05 \leq g_N \leq 0.20$	$g_N \leq 0.22$	$g_N \leq 0.25$
Li_2O	$0.01 \leq g_L \leq 0.07$	$0.01 \leq g_L \leq 0.06$	$g_L \geq 0.00$
Fe_2O_3	$0.02 \leq g_F \leq 0.15$	$g_F \leq 0.15$	
NMs*		$g_{NM} \leq 0.0025$	$g_{NM} \leq 0.01$

* Noble metal oxide concentration of 0.01 was considered acceptable because AgO_2 has been incorporated in glass to a high concentration. In addition, the total glass volume with $g_{NM} > 0.0025$ is small.

5.0 Results and Discussion

5.1 Effects of Additives and T_M on Waste Loading

Initial first-order estimates of $W_{\max}$ were generated via Equation (10) and the first-order model coefficients listed in Section 3. First, glasses with no fixed T_M were generated by the addition of SiO_2 to the waste, using Equation (7) with $\Delta_{\min} = 150^\circ\text{C}$. Baseline low-temperature glass was created using Equation (10) with $\Delta_{\min} = 150^\circ\text{C}$, $T_M = 1150^\circ\text{C}$, and $g_L = g_B = 0$. Finally, to see the effect of B_2O_3 and Li_2O on $W_{\max}$, g_L and g_B were varied as shown in Table VII with $\Delta_{\min} = 150^\circ\text{C}$, $T_M = 1150^\circ\text{C}$.

These initial calculations were performed to test the response of the glass compositions, glass properties and $W_{\max}$ to adjustable parameters (g_L , g_B , and T_M). Therefore no other limits have been imposed on glass formulation during these preliminary calculations.

Table VII. Options for $W_{\max}$ Calculations of Phase I Waste Glasses.

Case	g _B	g _L	$\Delta_{\min}$ (°C)	T_M (°C)
0	0.00	0.00	150	≤ 1550
1	0.00	0.00	150	1150
2	0.05	0.00	150	1150
3	0.00	0.01	150	1150
4	0.05	0.01	150	1150
5	0.10	0.01	150	1150
6	0.05	0.05	150	1150

The resulting $W_{\max}$ and T_M are summarized in Table VIII, which shows: 1) maximum, mean, and minimum values for 24 waste streams from Tables I and II and the Blend wastes (which represent the weighted average composition of all Phase I tank wastes).

Table VIII. Summary of $W_{\max}$ Calculations for Phase I Waste Glasses.

case	min	mean	max	Blend-CW	Blend-WW
0 T_M (°C)	1108	1346	1544	1283	1331
0 $W_{\max}$	0.51	0.74	1.00	0.79	0.82
1 $W_{\max}$	0.38	0.65	1.00	0.70	0.71
2 $W_{\max}$	0.37	0.63	0.95	0.68	0.68
3 $W_{\max}$	0.38	0.65	0.99	0.70	0.70
4 $W_{\max}$	0.37	0.62	0.94	0.68	0.68
5 $W_{\max}$	0.36	0.60	0.89	0.65	0.66
6 $W_{\max}$	0.36	0.61	0.90	0.66	0.63

For Phase I glasses with unrestricted T_M (case 0), the mean T_M was approximately 1350°C which is consistent with the average T_M seen in previous studies of Hanford HLW glasses (Kim and Hrma 1994). The mean $W_{\max}$ for case 0 is 0.74. As expected, the $W_{\max}$ values for Blend wastes were higher: 0.79 (CW) and 0.82 (WW). The maximum calculated $W_{\max}$ is 1.0, for C106A-CW and -WW. The T_M for C106A-CW was 1108°C (the only glass with T_M below 1150°C). These glasses are likely to crystallize under cooling to produce a low durability waste form.

The $W_{\max}$ is reduced by approximately ten percentage when the T_M is restricted to 1150°C except for case 0 glasses with T_M close to 1150°C (due to high Na_2O content in these wastes). This reduction is caused by the need for Na_2O additions to lower the melt viscosity at lower temperature.

At a T_M of 1150°C, an addition of 5 wt% B_2O_3 reduces $W_{\max}$ by roughly 2 wt% on average and a 10 wt% addition by 5 wt%. An addition of 1 wt% Li_2O reduces $W_{\max}$ by roughly 0.5 wt% and 5 wt% addition increases $W_{\max}$ by 5 wt%. Although the first-order models are linear, the effects of component additions on $W_{\max}$ are nonlinear because Equations (7) and (10), which relate $W_{\max}$ to composition, are nonlinear.

5.2 Glass Compositions

The criteria listed in Table VI and the second-order models with coefficients listed in Section 3 were employed to develop glass compositions for Phase I wastes. The glass compositions, predicted properties, and $W_{\max}$'s are listed in Table IX. The limiting component or property of each glass is given in bold print while points of interest are given in italics. Out of 24 glasses, 15 are limited by the model validity constraint for Fe_2O_3 ($g_F \leq 0.15$); only three glasses have a $g_F < 0.13$. Glasses with $g_F > 0.15$ have not been previously studied because these glasses are likely to precipitate spinel or hematite at high-temperatures. Extension of the current T_L database to glasses with higher Fe_2O_3 would help define the waste loading limit in terms of T_L instead of an ad hoc g_F constraint.

Table IX. Predicted Optimized Glass Compositions, $W_{\max}$'s, and Glass Properties Phase I wastes (compositions in mass fractions).

	AZ102- CW	AZ101- CW	AZ101- WW	AZ102- CW	AZ102- WW	C106A- CW	C106A- WW	C106B- CW	C106B- WW	AYC-A- CW	AYC-A- WW	AYC-B- CW	AYC-B- WW
SiO ₂	0.4137	0.4333	0.4108	0.4797	0.4357	0.4396	0.3700	0.3808	0.3700	0.4278	0.3700	0.3700	0.3700
B ₂ O ₃	0.0500	0.0500	0.0500	0.0500	0.0500	0.0500	0.0500	0.0500	0.1854	0.0500	0.0500	0.0500	0.0500
Na ₂ O	0.1574	0.1773	0.1860	0.1706	0.1743	0.2117	0.2139	0.2267	0.1312	0.1851	0.1840	0.2047	0.1986
Li ₂ O	0.0110	0.0136	0.0100	0.0229	0.0228	0.0000	0.0007	0.0067	0.0351	0.0021	0.0075	0.0000	0.0046
CaO	0.0245	0.0036	0.0036	0.0032	0.0032	0.0293	0.0296	0.0034	0.0019	0.0298	0.0285	0.0301	0.0292
MgO	0.0141	0.0011	0.0011	0.0013	0.0013	0.0192	0.0194	0.0009	0.0005	0.0187	0.0179	0.0194	0.0188
Fe ₂ O ₃	0.1500	0.1500	0.1500	0.1500	0.1500	0.1313	0.1326	0.1500	0.0868	0.1500	0.1436	0.1423	0.1381
Al ₂ O ₃	0.0465	0.0395	0.0523	0.0422	0.0812	0.0800	0.1376	0.1437	0.1600	0.0666	0.1226	0.1308	0.1316
ZnO	0.0010	0.0498	0.0498	0.0196	0.0196	0.0049	0.0049	0.0010	0.0006	0.0037	0.0035	0.0045	0.0043
P ₂ O ₅	0.0058	0.0023	0.0067	0.0006	0.0018	0.0034	0.0101	0.0061	0.0105	0.0047	0.0132	0.0040	0.0115
Others	0.0959	0.0796	0.0798	0.0599	0.0602	0.0306	0.0312	0.0306	0.0179	0.0615	0.0593	0.0442	0.0433
NM's	0.0097	0.0021	0.0021	0.0012	0.0012	0.0010	0.0010	0.0029	0.0017	0.0047	0.0045	0.0027	0.0026
Cr ₂ O ₃	0.0056	0.0016	0.0018	0.0017	0.0020	0.0023	0.0026	0.0029	0.0019	0.0038	0.0041	0.0030	0.0033
$W_{\max}$	0.487	0.430	0.459	0.370	0.410	0.769	0.850	0.634	0.451	0.716	0.753	0.762	0.810
Mw (kg)	29,999	79,683	85,195	132,918	147,433	465,053	508,747	252,380	310,054	105,744	116,234	256,671	281,357
Cans	37	112	112	218	218	366	363	241	417	89	93	204	210
Model Predictions													
m (g/m ²)	1.36	2.00	1.69	2.00	0.91	0.77	0.36	0.82	1.73	0.84	0.36	0.34	0.35
rs (g/m ²)	0.76	0.78	0.63	0.93	0.44	0.57	0.30	0.32	0.69	0.55	0.28	0.27	0.29
T _m (°C)	1150	1150	1150	1150	1150	1150	1150	1150	1150	1150	1150	1150	1150
T _i (°C)	977	1000	983	924	936	794	889	799	926	882	1000	857	947
Kim T _i	1007	1004	1009	1004	1030	1037	1079	1043	992	1075	1101	1097	1092
FACT Predictions													
Phase	Eskolite	Spinel	Spinel	Spinel	Spinel	NephelindNephelindNephelindNephelindNephelindNephelindNephelindNephelind							
T _i (°C)	1042	968	971	981	1004	1099	1143	1136	1103	1052	1103	1146	1125
Phase	Spinel	Acmite	Nephelinc	Acmite	Nephelinc	Eskolite	Hematite	Hematite	Eskolite	Spinel	Spinel	Spinel	Spinel
T _i (°C)	1002	944	963	960	969	943	858	897	844	1004	924	907	899

Table IX continued. Predicted Optimized Glass Compositions, $W_{\max}$'s, and Glass Properties
Phase I wastes (compositions in mass fractions).

	AZ-CW	AZ-WW	AZC-A- CW	AZC-A- WW	AZC-B- CW	AZC-B- WW	Nom- CW	Nom- WW	Blend- CW	Blend- WW
SiO ₂	0.4734	0.4234	0.4520	0.3965	0.4252	0.4084	0.4471	0.3938	0.4451	0.3809
B ₂ O ₃	0.0500	0.0500	0.0500	0.0500	0.0501	0.0500	0.0500	0.0500	0.0500	0.0500
Na ₂ O	0.1631	0.1862	0.1847	0.1889	0.1924	0.1934	0.1841	0.1879	0.1825	0.1870
Li ₂ O	0.0242	0.0144	0.0112	0.0111	0.0100	0.0100	0.0100	0.0100	0.0100	0.0100
CaO	0.0033	0.0033	0.0130	0.0130	0.0075	0.0075	0.0119	0.0119	0.0186	0.0186
MgO	0.0012	0.0012	0.0079	0.0079	0.0040	0.0040	0.0071	0.0071	0.0116	0.0116
Fe ₂ O ₃	0.1500	0.1500	0.1500	0.1500	0.1500	0.1500	0.1500	0.1500	0.1500	0.1500
Al ₂ O ₃	0.0371	0.0714	0.0512	0.0984	0.0703	0.0829	0.0491	0.0944	0.0581	0.1117
ZrO ₂	0.0299	0.0299	0.0221	0.0221	0.0265	0.0265	0.0227	0.0227	0.0171	0.0171
P ₂ O ₅	0.0012	0.0035	0.0020	0.0060	0.0015	0.0046	0.0020	0.0059	0.0030	0.0089
Others	0.0665	0.0667	0.0558	0.0561	0.0625	0.0627	0.0660	0.0663	0.0541	0.0544
NM's	0.0015	0.0015	0.0014	0.0014	0.0014	0.0014	0.0015	0.0015	0.0018	0.0018
Cr ₂ O ₃	0.0017	0.0019	0.0020	0.0022	0.0017	0.0020	0.0020	0.0022	0.0023	0.0026
$W_{\max}$	0.390	0.427	0.546	0.598	0.457	0.500	0.533	0.583	0.624	0.684
Mw (kg)	212,420	232,447	438,509	479,827	288,018	315,144	329,230	359,768	708,541	776,379
Cans	330	330	487	487	382	382	374	374	688	688
Model Prc										
r_n (g/m ²)	1.99	1.20	1.55	0.66	1.20	0.98	1.68	0.72	1.19	0.49
r_{n^*} (g/m ²)	0.92	0.50	0.74	0.35	0.51	0.43	0.75	0.36	0.65	0.30
T_M (°C)	1150	1150	1150	1150	1150	1150	1150	1150	1150	1150
T_L (°C)	968	922	888	924	884	900	895	929	893	953
Kim T_L	1006	1019	1026	1057	1024	1033	1024	1054	1044	1079
FACT Prc										
Phase	Spinel	Nepheline	Spinel	Nepheline	Nepheline	Nepheline	Spinel	Nepheline	Spinel	Nepheline
T_L (°C)	980	990	988	1062	1014	1040	990	1062	995	1084
Phase	Acmite	Spinel	Nepheline	Spinel	Spinel	Spinel	Nepheline	Spinel	Nepheline	Spinel
T_L (°C)	959	987	959	985	986	987	958	989	988	974

5.3 Blending and Pretreatment Options

To compare the different pretreatment and blending options, the total number of glass canisters produced from each waste tank or blend was estimated as

$$c = \frac{M_w}{W_{\max} M_c} \quad (11)$$

where M_w is the mass of waste in kg, $W_{\max}$ is the calculated waste loading (from Table IX), and M_c is the mass of glass per canister, assumed to be 1650 kg. Table X shows the effect of each blend scenario on glass canister count using the blending equations found in Section 2.

Table X. Canister Count for Different Blending and Pretreatment Options.

Waste	blend CW	blend WW	tank CW	tank WW
AY102			37	37
C106A			366	363
C106B			241	417
AZ101			112	112
AZ102			218	218
AZ	330	330	330	330
AZC-A	487	487	509	507
AZC-B	382	382	390	389
AYC-A	204	210	216	214
AYC-B	89	93	97	96
Nom	374	374	387	386
Blend	688	688	734	730

Although caustic washing reduces the overall HLW volume, it also generally reduces $W_{\max}$ and does not significantly effect glass volume. An exception to this rule is C106B tank waste. For C106B-WW, $W_{\max}$ (0.44) is limited by T_L . Caustic washing removes a substantial fraction of Al_2O_3 and adds Na_2O . This allows an increase of $W_{\max}$ (0.62) which is limited by g_N .

The apparent ineffectiveness of caustic washing results from the limit imposed on g_F (≤ 0.15). Preliminary calculations of $W_{\max}$ in absence of the g_F constraint shows a possible $W_{\max}$ increase of 10 wt% (Schweiger et al. 1995).

Blending significantly reduces the volume of glass produced from Phase I wastes. Assuming the largest amount of blending occurs (i.e., Blend composition), roughly 6% of the glass volume is saved over the single can vitrification route. The savings decreases as the blending extent decreases.

6.0 Conclusions

The following conclusions and recommendations are made based on the results of this

study. These conclusions are, however, preliminary and contingent upon validated laboratory studies which are planned as an extension of this study.

The glass produced from Phase I HLW s will be contained in 688 (all tank wastes blended) to 734 (tank wastes vitrified separately) canisters. Blending in the most extensive case decreases glass volume by 6 %.

Caustic washing does not decrease HLW glass volume. This is a result of the Fe_2O_3 concentration ($g_F \leq 0.15$) limit. This conclusion may change if an accurate T_L limit is used.

The ad hoc Fe_2O_3 concentration ($g_F \leq 0.15$) constraint limits $W_{\max}$ of 15 out of 24 Phase I waste and blend compositions. An accurate $W_{\max}$ will be obtained for these wastes if this restriction is replaced by an accurate T_L limit.

Generally, $W_{\max}$ is increased by 10 wt% by relaxing $T_M = 1150^\circ\text{C}$ constraint. This will produce an average T_M of roughly 1350°C for Phase I glasses.

The addition of B_2O_3 or Li_2O reduces $W_{\max}$ by roughly 0.5 % per 1% of either g_B or g_L .

Laboratory validation is recommended to confirm glass property predictions where limited data cause high uncertainty (i.e., CCC PCT and T_L) and better define $W_{\max}$ for selected wastes and impacts of blending/pretreatment options. The experimental work outlined in an investigation plan (Schweiger et al. 1995) follows from this study.

7.0 References

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