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MAXIMIZATION OF WASTE LOADING FOR A VITRIFIED HANFORD HIGH-ACTIVITY SIMULATED WASTE

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Maximization of Waste Loading for a Vitrified Hanford High-Activity Simulated Waste

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ABSTRACT

Simulated high-level nuclear waste glasses incorporating up to 70 wt% Neutralized Current Acid Waste (NCAW) were prepared. For the waste loading (W) range of 40 to 55 wt%, alkaliborosilicate glasses were formulated with a melting temperature of 1150°C; for W>55 wt%, only silica was added to the waste and the melting temperature was 1150°C. Properties measured included durability and crystallinity of slowly cooled glasses and glasses heat treated for 24 hours at 1050°C. Acceptable durability (by the Environmental Assessment glass standard) was retained up to W=70 wt%, which is the maximum NCAW waste loading if no limit on crystallinity is imposed. If <1 vol% of spinel is acceptable in the melt at 1050°C, a waste loading of approximately 50 wt% is possible. If no crystallinity is permissible at 1050°C, W=34 wt% is the estimated maximum.

INTRODUCTION

In the originally proposed Hanford Waste Vitrification Plant (HWVP), high-level waste was to be combined with vitrifying materials (frit) in a liquid-fed joule-heated ceramic melter operating at a temperature of 1150°C. The estimated liquidus temperatures (T_L) of non-spinel crystalline phases in lower waste loading (W) glasses would satisfy the constraint T_L<1050°C, and thus prevent undesirable formation of crystalline phases in the melter provided that the settling of spinel is within tolerable limits. The plant was designed for W=0.25. However, thermodynamic predictions** indicate that T_L of non-spinel crystalline phases in the Neutralized Current Acid Waste (NCAW) glasses may satisfy the constraint of 1050°C for W≤0.50 and possibly beyond. This paper presents experimental evidence that waste loading can be substantially higher for NCAW even at the melter operating temperature of 1150°C. Because the melting technology in the

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** P. T. Fini, and P. Hrma, "Crystallinity and Liquidus Temperature Calculation of Simulated High Level Nuclear Waste Using Thermodynamic Modeling", in preparation.

final design of the high-level waste (HLW) vitrification plant will probably be substantially different from that originally conceived, glasses with melting temperatures >1150°C were also included in the study. Of primary interest were crystallinity and durability of the waste glasses as a function of waste loading. Glass compositions were formulated using empirical models for viscosity and electrical conductivity [1].

EXPERIMENTAL PROCEDURE

Glass Formulation and Preparation

All of the glasses examined in this study are based on the simulated NCAW '92 composition estimate [2], shown in Table I. The recycle composition, also shown in Table I, is an estimate for the part of the melter feed in the originally proposed HWVP, made up of plant process waste components absorbed on zeolites, particulate filtered from off-gases, and frit used to decontaminate the stainless steel canister surfaces [2]. The "Others" component is a grouping of minor oxides, sulfates and fluorides.

Table I. NCAW '92 Simulated Waste and Recycle Composition Estimates (mass fractions)

Component	NCAW '92	Recycle
SiO_2	0.0402	0.4368
Na_2O	0.2135	0.4253
B_2O_3	0.0001	0.0000
Fe_2O_3	0.2813	0.0107
ZrO_2	0.1507	0.0000
Al_2O_3	0.0901	0.0410
CaO	0.0079	0.0030
MgO	0.0020	0.0801
"Others"	0.2143	0.0801

Three series of glasses were formulated:

(A) Series A glasses had constant viscosity η_{1150}=6 Pa.s and electrical conductivity ε_{1150}=40 S/m (η_{1150} and ε_{1150} are viscosity and electrical conductivity at T=1150°C);

(B) Series B glasses had constant η_{1150}=6 Pa.s and compositions within property model validation ranges where possible, electrical conductivity was allowed to vary;

(C) Series C glasses had the highest waste loading (W=0.60 to 1.00), SiO_2 was the sole vitrifying component; both viscosity and electrical conductivity varied with W.

In all series, the ratio of the mass fraction of recycle to the mass fraction of waste was 0.122 except for W=1.00 (fused waste). To achieve desired glass properties

for each waste loading, the composition of vitrifying additives (frit) was calculated using a technique developed by Hrma [3,4]. Viscosity and electrical conductivity were obtained from Arrhenius first order models [1]. Series A compositions fell outside some of the model validation limits [1] (including those for B_2O_3 and "Others"), thus making their predicted η and ε uncertain. The highest waste loading for which the glass composition was held within the model validation limits was W=0.466 (Series B). The compositions of all glasses are shown in Table II.

Table II. Glass Composition of Series A, B and C Glasses (in mass fractions) for a Range of Different Waste Loadings (W).

	Component	W=0.40	W=0.45	W=0.50	W=0.55
	SiO_2	0.4835	0.4524	0.4215	0.3906
	Na_2O	0.1062	0.1194	0.1327	0.1460
	B_2O_3	0.0426	0.0305	0.0183	0.0061
	Li_2O	0.0515	0.0433	0.0372	0.0301
A	Fe_2O_3	0.1130	0.1272	0.1413	0.1554
	ZrO_2	0.0603	0.0678	0.0754	0.0829
	Al_2O_3	0.0380	0.0428	0.0476	0.0523
	CaO	0.0088	0.0087	0.0085	0.0084
	MgO	0.0065	0.0060	0.0056	0.0051
	"Others"	0.0896	0.1008	0.1120	0.1232
	Component	W=0.446	W=0.49	W=0.50	W=0.51
	SiO_2	0.4497	0.4146	0.4067	0.3987
	Na_2O	0.1184	0.1300	0.1327	0.1354
	B_2O_3	0.0500	0.0500	0.0500	0.0500
	Li_2O	0.0417	0.0314	0.0291	0.0267
B	Fe_2O_3	0.1260	0.1385	0.1413	0.1441
	ZrO_2	0.0672	0.0738	0.0754	0.0769
	Al_2O_3	0.0424	0.0466	0.0476	0.0485
	CaO	0.0037	0.0040	0.0041	0.0042
	MgO	0.0011	0.0012	0.0012	0.0012
	"Others"	0.0999	0.1098	0.1120	0.1143
	Component	W=0.60	W=0.70	W=0.80	W=0.90
	SiO_2	0.3929	0.2800	0.1772	0.0743
	Na_2O	0.1592	0.1858	0.2123	0.2389
C	Fe_2O_3	0.1696	0.1978	0.2543	0.2543
	ZrO_2	0.0904	0.1055	0.1356	0.1356
	Al_2O_3	0.0571	0.0666	0.0856	0.0856
	CaO	0.0050	0.0058	0.0074	0.0074
	MgO	0.0014	0.0017	0.0022	0.0022
	"Others"	0.1344	0.1568	0.2016	0.2016

Glasses were made from analytical grade chemicals. No attempt was made to prepare the frits and blend them with the simulated waste. The frits considered would be very high in silica (up to 89% in the W=0.55 glass), and hence difficult to melt. The CaO and MgO additions (Series A) would ease melting, but this compositional adjustment may be at the expense of the quality of the resulting waste glasses. As more sodium oxide is introduced from the waste as the loading increases, the frit composition approaches that of pure silica.

Source oxides, carbonates, and sulfates were mixed in an agate disc mill an melted in a platinum crucible at 1150°C (Series A and B) or at 1300°C to 1450°C (Series C) for one hour and poured onto a stainless steel plate. To increase homogeneity, glasses were crushed in a tungsten carbide disc mil and remelted at the same temperature in a covered platinum crucible. Except for glasses with W>0.70, molten glass was poured in bars and annealed for 2 hours at 500°C.

Glass Crystallization

Formation of crystalline phases may interfere with melter operation and may affect chemical durability by altering glass composition and generating residual mechanical stresses. Crystallization was tested using two heat treatments. The isothermal heat treatment (IT) was used to determine whether T_L of the glass was above or below 1050°C. Samples were heated to 1150°C for 30 minutes, transferred to a furnace at 1050°C for 24 hours, and then annealed at 500°C for 2 hours. The canister centerline cooling (CCC) treatment was performed on Series A and B glasses to simulate cooling at the center of the axis of the axis of a stainless steel canister. Glass samples were held at 1150°C for 30 minutes and cooled following the CCC schedule [5]. Crystallinity was evaluated by optical microscopy with image analysis and X-ray diffraction (XRD). Since crystalline phases in the glasses were randomly distributed, the area fraction, measured by the image analysis software and evaluated as an average of fifteen randomly-sampled measurements, was equivalent to the volume fraction [6].

Chemical Durability

The chemical durability of all glass samples was determined using the Product Consistency Test (PCT) [7]. In this test, 4 g of powdered glass was added to 40 ml of deionized water in a Teflon container and held at 90°C for seven days. The solution was analyzed using the Inductively Coupled Plasma (ICP) atomic emission spectroscopy method. The normalized mass releases were calculated as $r_i = c_i V/g_i A$, where r_i is the i-th element normalized release (g/m^2), c_i is the i-th element concentration in solution (g/m^3), V is the solution volume (m^3), g_i is the i-th element mass fraction in the glass, and A is the sample surface area (m^2). The maximum permissible release currently accepted for high-level nuclear waste glasses are those of the EA (environmental assessment) glass, developed by the Westinghouse Savannah River Technical Center [8]: $r_{Si} = 2.0$ g/m^2, $r_B = 8.37$ g/m^2, $r_{Na} = 6.66$ g/m^2 and $r_{Li} = 4.80$ g/m^2.

RESULTS AND DISCUSSION

Crystallinity

In Series A and B, the degree of crystallinity was higher in the CCC treatment than in the IT treatment. Spinels as well as RuO_2 and/or RhO_2 were identified by both optical microscopy and XRD in all samples (XRD could not distinguish between RhO_2 and RuO_2 due to their almost identical lattice parameters). Spinel crystals were small (<10 μm) and well-dispersed, implying very low rate of settling in a glass melter.

As Figure 1 shows, the crystallinity (predominantly spinels) of the CCC-treated Series A glasses increased approximately linearly with waste loading in the entire W range studied, while crystallinity in the IT samples increased essentially linearly until W≈0.50. The volume fraction of crystals approaches zero at approximately W=0.33 assuming that the linear relationship between the fraction of crystallinity and W holds at lower waste loadings. As waste loading increased, error bars of the volume fraction measurements also increased due to a visibly higher degree of agglomeration of spinels. Baddeleyite (ZrO_2) was observed as transparent elongated single crystals at W=0.50 and W=0.55 for both treatments.

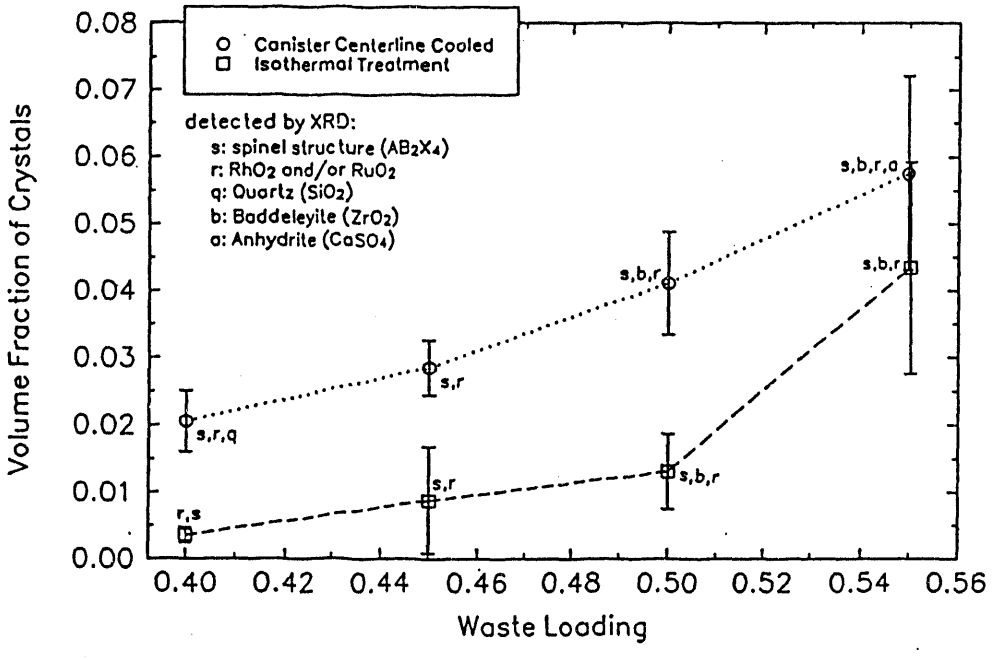

Figure 1. Total Volume Fraction of Crystalline Phases vs. Waste Loading for Series A Glasses.

The volume fraction of crystals remained nearly constant (~0.03 for CCC and ~0.01 for IT) over the range 0.44≤W≤0.51 in the Series B glasses (Figure 2) and lower than in Series A. Baddeleyite was identified in the IT W=0.50 and W=0.51 samples only. This indicates that although T_L of ZrO_2 in these samples was higher than 1050°C, the CCC-cooling was too rapid to allow precipitation of the crystals.

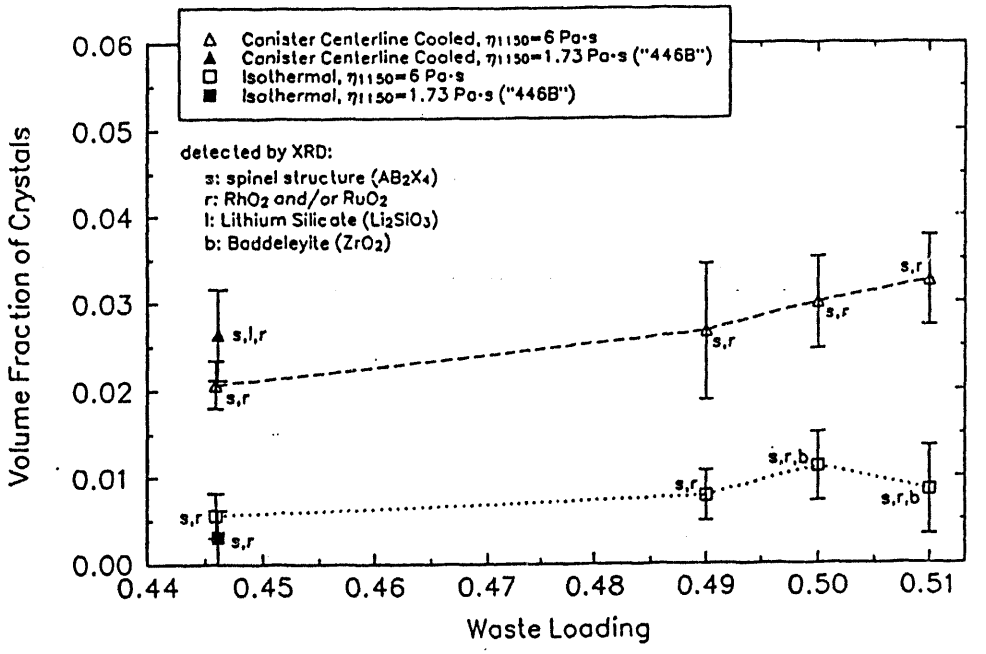

Figure 2. Total Volume Fraction of Crystalline Phases vs. Waste Loading for Series B Glasses.

Series C samples exhibited molten salt segregation (most likely of sulfates) and settling of dense phases during processing. Except the W=0.60 sample, the samples were too opaque to be viewed in transmission optical microscopy. As the waste loading increased, the quantity and complexity of crystalline phases increased. The W=0.90 and W=1.00 (fused waste) samples were almost entirely crystalline, but no definite solution to their patterns could be made by XRD due to large number of possible matches to reference data.

Glass Durability

The normalized PCT releases from Series A samples for all elements except Na (Figure 3) remained relatively constant as waste loading increased and were an order of magnitude lower than the EA limits. The elemental releases of the CCC glasses were close to those of IT glasses at each waste loading and thus virtually independent of differing levels of crystallinity between the two treatments.

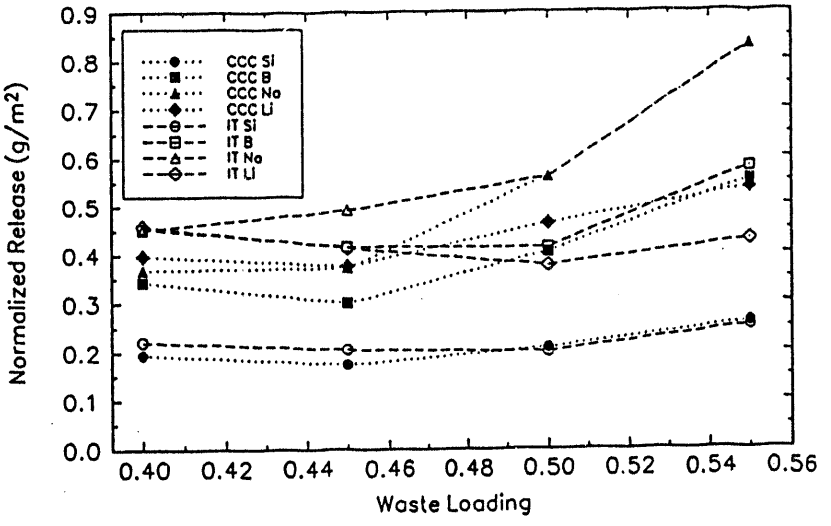

Figure 3. PCT 7-Day Normalized Elemental Release vs Waste Loading for Series A Glasses.

The normalized releases of Series B glasses subjected to the CCC and IT treatments, shown in Figure 4, were comparable with the Series A results, but the release of Si was slightly lower and the Li and Na releases significantly lower for Series B glasses, to which no CaO and MgO were added.

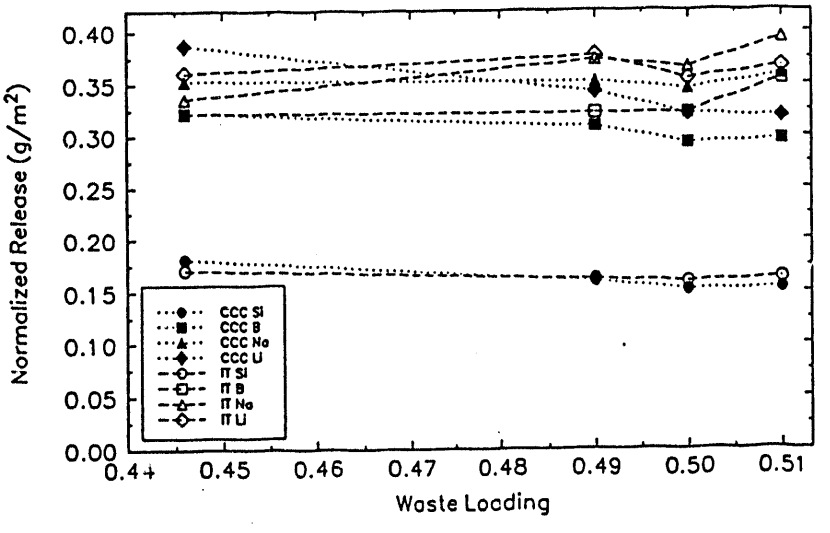

Figure 4. PCT 7-Day Normalized Elemental Release vs. Waste Loading for Series B Glasses with η_{1150}=6 Pa.s.

The Si releases of all Series C compositions were lower than that of the EA glass, and the Na releases were lower than the EA glass until approximately W=0.75 (Figure 5). Glasses with W>0.55 were found containing a high fraction of crystallinity and thus cannot be processes in continuous melters with long residence times. A different type of processing, periodic or continuous with short residence time as well as elevated melting temperature, is needed for these higher waste leading products.

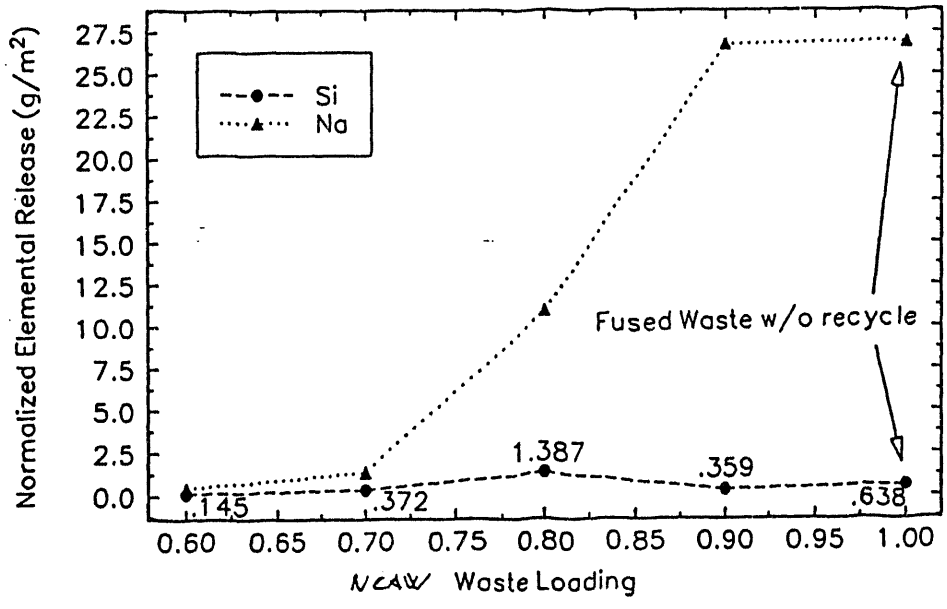

Figure 5. PCT 7-Day Elemental Release for Series C Compositions

CONCLUSIONS

The flexibility of glass formulation and potential for high waste loading in vitrifying high-level wastes has been demonstrated using the NCAW as an example. Until W=0.50, it was possible to maintain constant glass viscosity and electrical conductivity at 1150°C by varying the frit composition. Glasses with W<0.55 exhibited low levels of crystallinity, with small (<10 μm) and well-dispersed spinel-type crystals predominating. Glasses with CaO and MgO added exhibited slightly lower durability than glasses without these additions. No correlation could be made between crystallization of spinel-type and ZrO_2 phases and chemical durability. Durability was within acceptable limits (by EA glass standard) up to W=0.70. Glasses with W>0.60 (with only silica added) required processing temperatures as high as 1400°C, contained large fractions of crystals, and exhibited separation of a (most likely) sulfur-containing phase.

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