PERFORMANCE OF THE WASTE COMPLIANCE PLAN AT WEST VALLEY

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ABSTRACT

The mission of the West Valley Demonstration Project (WVDP) is to solidify the radioactive constituents(1) in the high-level waste (HLW) presently at the WVDP site into borosilicate glass. This vitrification process must be performed to satisfy the Waste Acceptance Preliminary Specifications (WAPS) which define the minimum requirements that the WVDP high-level waste form product must meet for acceptance at the Nuclear Regulatory Commission (NRC) licensed repository.

VITRIFICATION FLOW SHEET DESCRIPTION

The WAPS(2) are part of the overall Waste Acceptance Process depicted in simple form in Fig.1. They have been established by the Waste Acceptance Committee (WAC), consisting of representatives from the waste form producers, the repository project and DOE-OCRWM, -NE, and -DP*, and apply equally to West Valley as well as the Defense Waste Processing Facility (DWPF) Project. As can be seen in Fig.2, the Specifications can be categorized into four sections addressing the borosilicate glass waste form, the canister, the canistered waste form, and the quality assurance(3) of the Waste Acceptance Process activities. The detailed strategy and experimental approach to satisfy the WAPS can be found in the WVDP Waste Compliance Plan (WCP).

This paper reports the progress at the WVDP in carrying out the WCP and demonstrating compliance with the WAPS. The results provided here have been verified directly from the full-size, integrated vitrification process equipment (shown in Fig.3) which has been operated in an integrated fashion for approximately four years, and which is designed for radioactive service. The perspective should be kept, however, that the process has a finite mission, that is, to solidify the existing quantity of waste, resulting in approximately 300 canisters of relatively low heat (<300, watts each).

A flow diagram of the West Valley reference HLW vitrification process is shown in Fig.4. Prior to vitrification, the PUREX waste will be pretreated. The PUREX supernatant will be decontaminated of Cs-137 and other cesium radionuclides by passing through ion-exchange columns filled with zeolite IE-96. The PUREX sludge will then be washed to remove sulfate and interstitial supernatant. The wash solutions will also be treated with the zeolite process.

The zeolite and THOREX wastes will be combined and homogenized with the PUREX solids in HLW Storage Tank 8D-2, the tank where the PUREX waste is currently stored. The slurried waste will be transferred to the Concentrator Feed Make-Up Tank (CFMUT), sampled, and concentrated. Bulk glass formers will be added to the CFMUT; the amount will depend upon waste volume and the waste chemical analysis results. The reference waste loading of the glass will be about 33 weight percent waste oxides. About 23 weight percent will be from the PUREX sludge and THOREX waste, and 10 weight percent will be from the zeolite. The slurry in the CFMUT will be equivalent to about four canisters. After mixing and composition verification, the waste and glass former slurry will be transferred to the Melter Feed Hold Tank (MFHT).

PROGRESS ON MEETING THE WAPS

Glass Transition Temperature

Differential Scanning Calorimetry (DSC 4 by Perkin Elmer) and dilatometry (Dilatronic II by Theta Industries) were employed to establish the transition temperature at Alfred University(5). Two measurements each by DSC and dilatometry were averaged to obtain transition temperatures in the range of 458° to 480°C.

Crystallization Behavior

Reference glass samples were isothermally exposed to heat treatment in the temperature range of ~500° to 1000°C for times varying from 1 to 384 hours also at Alfred University(5). The crystallization phases were determined using x-ray diffraction and energy dispersive spectroscopy. Optical microscopy was utilized to more clearly discriminate any size range of crystals present.

Essentially, the crystalline phases were found in two sizes; about 2 and 0.2 μm, which were categorized as large and small crystals, respectively. Depending on the heat treatment temperature and whether the glasses were oxidized or reduced, the following sizes were obtained:

Crystal Size

Temp (°C)	Oxidized Glass	Reduced Glass
500 few large	mostly small	
600-900 mostly small, some large		mostly small
900-1000 few large	few large	

Oxidized samples tested between 700° and 800°C yielded a maximum rate of crystallization, whereas the reduced glasses exhibited most crystallization in the temperature range of 600° and 700°C.

The primary crystal phases found were spinel (Fe_3O_4 type phase with small amounts of Cr, Ni, and/or Mn) and cerium-thorium oxide. Spinel was found at all heat treatment temperatures, over the time range of about 96 to 384

* DOE Offices of Civilian Radioactive Waste Management, Nuclear Energy, and Defense Programs, respectively.

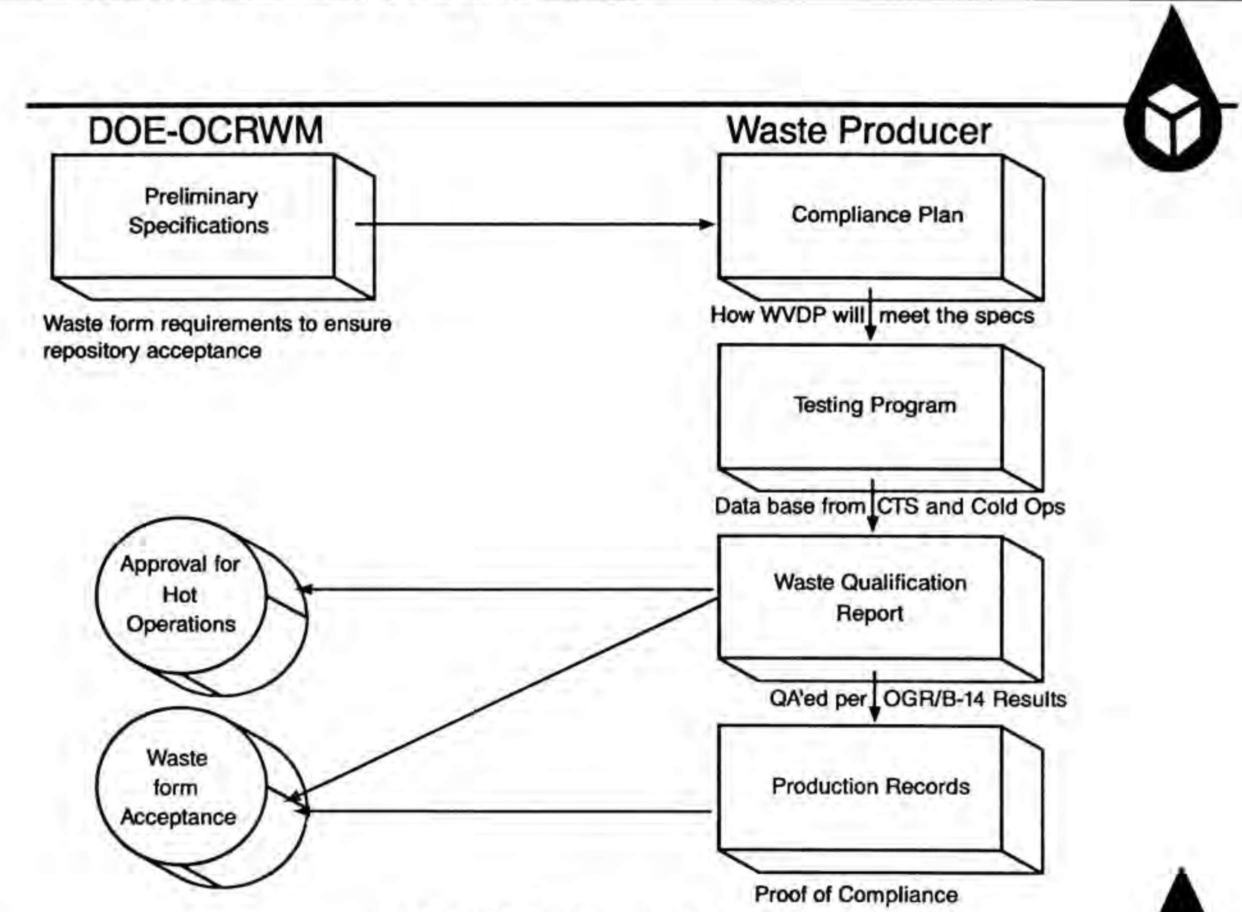

Fig. 1. Waste Acceptance Process.

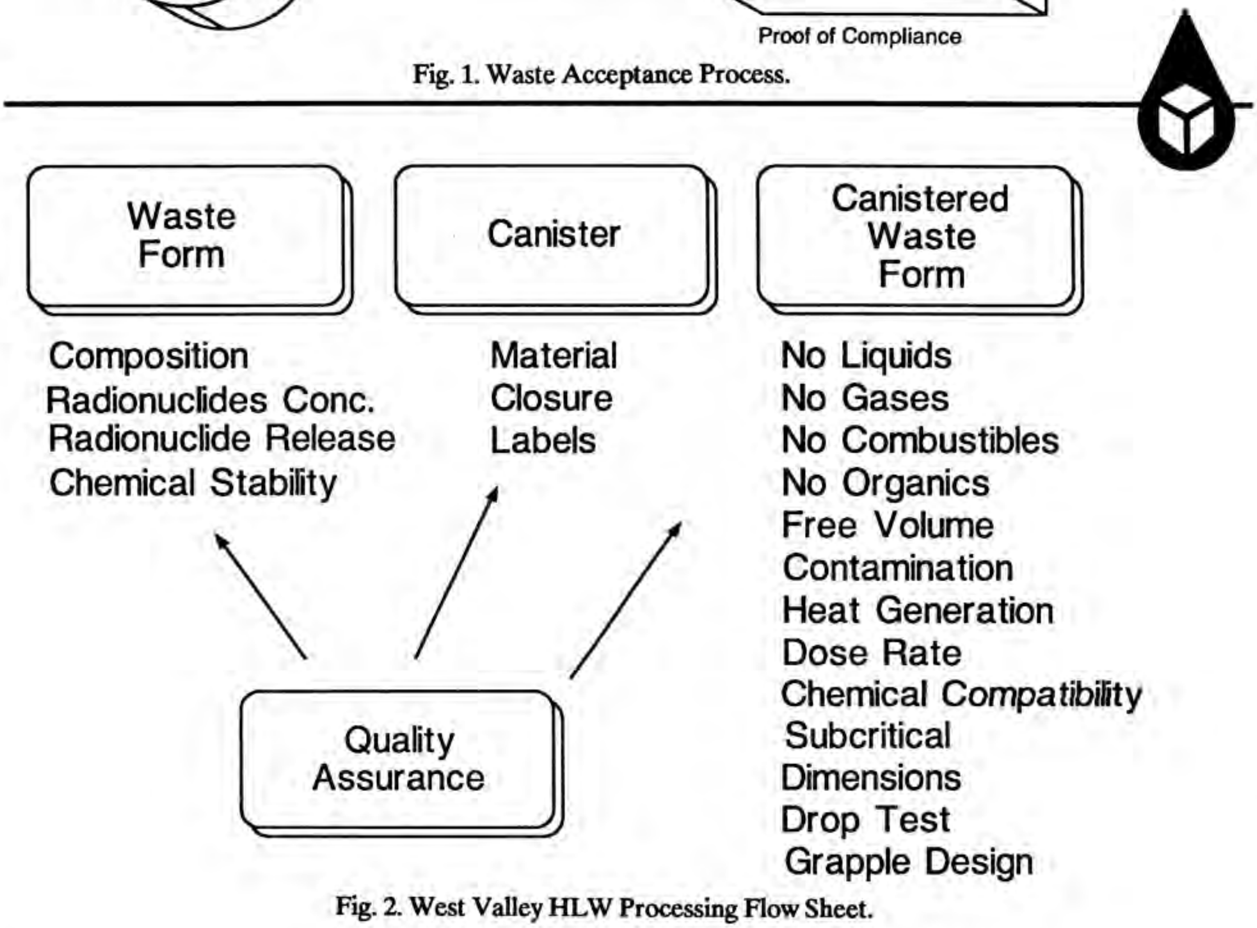

Fig. 2. West Valley HLW Processing Flow Sheet.

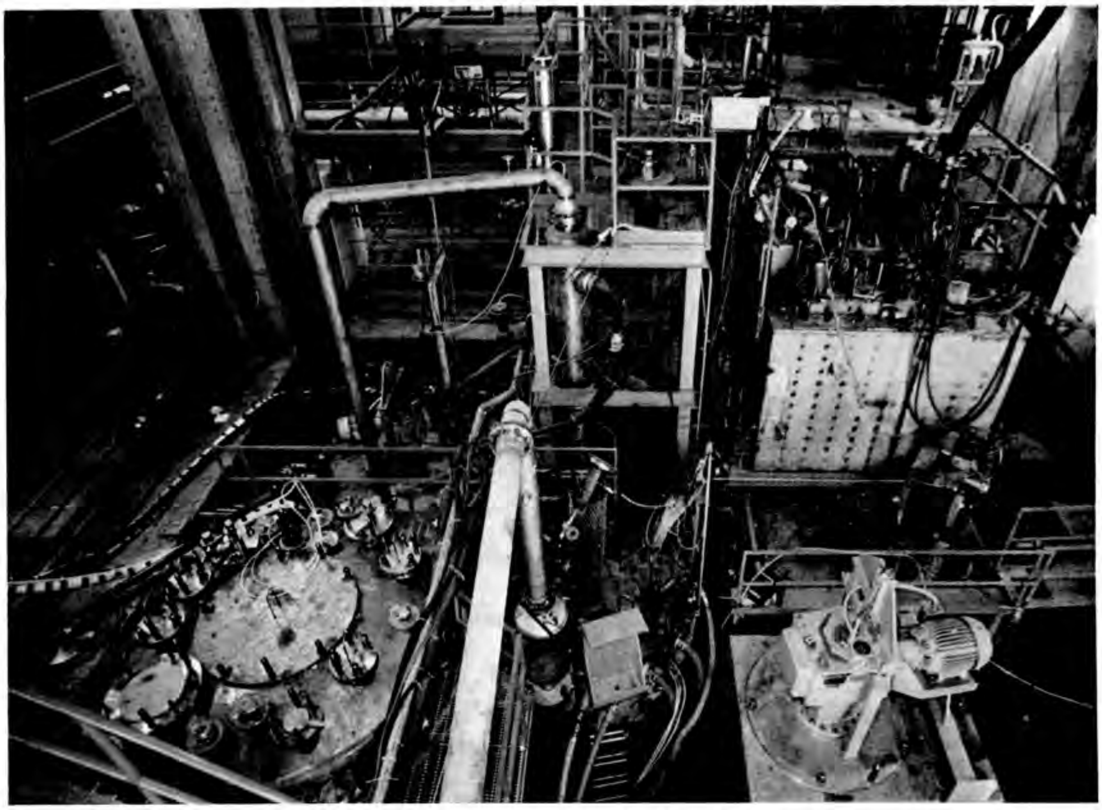

Fig. 3. Full-Size West Valley Vitrification System.

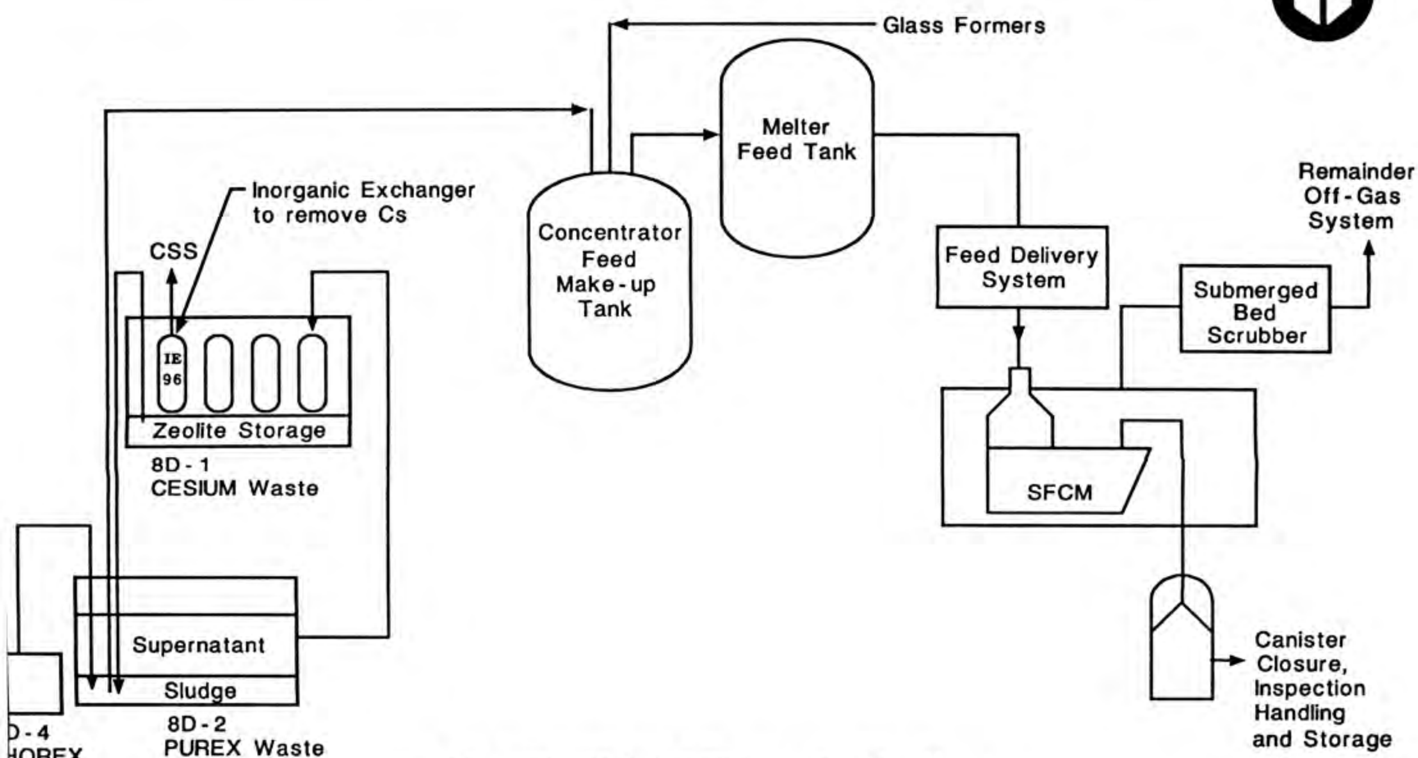

Fig. 4. West Valley HLW Processing Flow Sheet.

hours, and in both the oxidized and reduced glasses. The cerium-thorium oxide phase appeared at temperatures up to ~800°C for the reduced glasses, but not at low or high temperatures. To a secondary extent, Acmite was observed at all heat treatment temperatures and times for the oxidized glasses, but only at 600° to 700°C range for the reduced glasses(5).

The corresponding T-T-T diagrams are given in Fig.5 and Fig.6. Typically, crystals in the range of 1 to 5 volume percent were observed, which had no adverse effect on the other properties, such as leach rate.

Glass Leaching Behavior

The WAPS (1.3.1) states that the capability of the waste glass to limit releases shall be demonstrated using a MCC-1 test(6) conducted in deionized water at 90°C. The acceptance criterion is that the normalized elemental leach rate of matrix constituents B, Si, and Na, as well as the radionuclides Cs-137 and U-238 will be less than 1 g/m^2-d averaged over the 28-day test duration.

An early set of 16 glasses with various compositions resulting from a statistical test plan around the reference and central composition shown in Table I was exposed to the above cited leach testing conditions at Battelle Pacific Northwest Laboratories (PNL) Materials Characterization Center (MCC). These results from 8 of the glasses are given in Fig.7, and illustrate that all (including those not shown) of the glasses tested have normalized release rates below the WAPS criterion of 1 g/m^2-d. However, in estimating short- and long-term within lab and lab-to-lab (at PNL) uncertainties in the glass analyses, leach testing and leachate analysis processes, and fitting empirical models to the data, a conclusive statement that 95 percent of the glass will meet the release criterion 95 percent of the time cannot presently be made.

TABLE I
ATM-10 Glass Composition

Component		Weight Percent
Al_2O_3	7.75	
B_2O_3	9.26	
$BaO + CaO + MgO$		1.77
Fe_2O_3	12.04	
$K_2O + Li_2O + Na_2O$		16.32
MnO_2	1.30	
P_2O_5	2.48	
SiO_2	42.50	
ThO_2	3.55	
UO_2	0.54	
Others	2.49	

Quantitatively, we can multiply the 1 g/m^2-d criterion by the 28-day time of the test to give 28 g/m^2. The highest leach rate found in Fig.7, 22 g/m^2, is well within this limit. However, when estimating the within lab variability, the 95 percent upper confidence limit is estimated to increase to 29.3 g/m^2; and, between lab variability could increase to 41.1 g/m^2; both above the release limit (based upon purely statistical characterization).

Various recourses are being or will be pursued: (1) increase the replication of samples only two duplicates were used in the PNL leach testing; (2) use several laboratories to reduce the effective magnitude of the variation; (3) ensure the identical preparation including polishing the MCC-1 sample surfaces at each of the laboratories; (4) invoke the latitude in the WAPS (1.3.3) by using an alternate leach test, e.g., the product consistency test, which is a powder test, and correlate these results to MCC-1 results; and (5) revisit the basis for the MCC-1 test and the criterion of 1 g/m^2-d.

Canister Impact Test

The reference West Valley canister is 10-gauge (or ~0.13 inch), 304L stainless steel, with the top and bottom flanges made from material 0.1875 inch thick. Before impact testing, strain circles were applied on the external surfaces of the canister with particular attention being given to the areas near the weld joints where the largest strain from impact were expected. Although the canisters were seal-welded closed, this was not intended to represent a reference closure because it has not yet been finally designed for the WVDP canister.

This canister, as well as others of similar design, was dropped on its bottom and head from the WAPS height of 7 m at PNL(7). The drops were conducted primarily with the canister in a vertical orientation, but also with the canisters' center of gravity over the bottom and top corner.

The impacted canisters displayed more deformation from the top drops than from the bottom drops, as was expected because the glass within the canister resists the deformation during the bottom impact. Because the top of the canister is void of glass, much of the energy from the impact is absorbed as canister deformation. In the case of the bottom impact, the primary deformation which was not large, occurred approximately 3 to 7 inches above the bottom weld. More significant deformation resulted from the top impact. The head of the canister was pressed inward and two concentric buckles formed in the canister wall(7). Strain-circle evaluation allowed the deformation to be quantified by measuring the change in their dimensions. The strain which resulted from the bottom drop of the reference canister was less than 3 percent, which is insignificant relative to a failure condition. The outside edge of the top wall ring of deformation produced the maximum strain measured. In the worst case, the peak loop strain was approximately 8 percent while the peak axial strain was about 44 percent, which can be compared with a typical failure strain of 56 percent for 304L material.

Following the impact testing, the canisters were subjected to leak testing to verify that they had not breached. Helium leak testing of these canisters showed rates less than 3×10^{-8} atm-cc/sec which satisfies the WAPS required level of 1×10^{-7} atm-cc/sec(7). Although the canisters had not been breached, this result will be verified for canisters

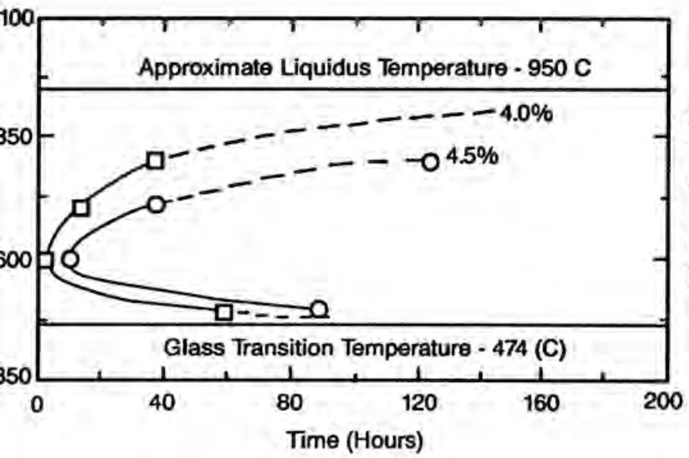

Fig. 5. T-T-T- Diagram for the Oxidized WVDP Reference Glass (5).

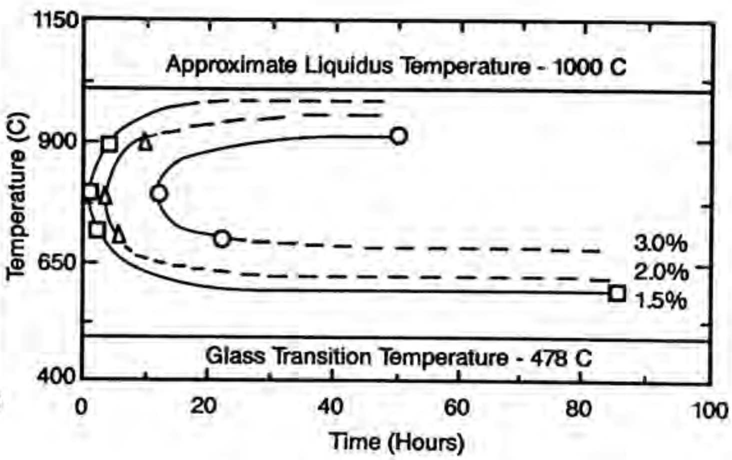

Fig. 6. T-T-T- Diagram For The Reduced WVDP Reference Glass (5).

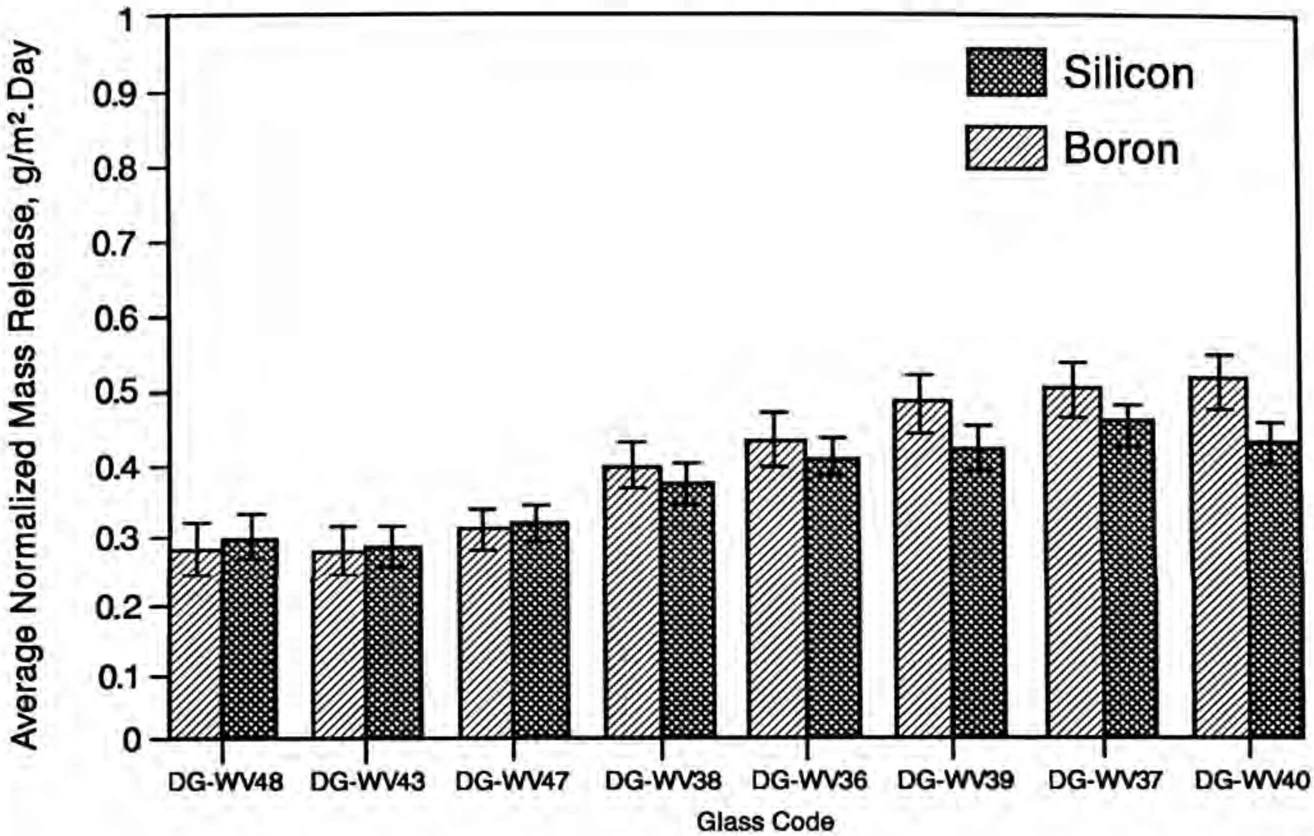

Fig. 7. Statistically Varied Compositions.

sealed using the reference welding technique after it is selected.

Canister Decontamination

It is anticipated that during filling, the exterior surface of the canister will become contaminated with volatile radionuclides, primarily Cs-137. The radionuclides will be bound with tenacity as part of the oxide film formed on the canister during filling.

The reference method to be used at the WVDP is basically an etching process, similar to an electhropolishing process, but without the need for an applied electric current. Specifically, an oxidation reaction system utilizing Ce^{+4} in a dilute nitric acid carrier solution will be employed based upon Bray's work at PNL(8). This can be represented by the following reaction:
$3Ce^{4+} + Fe^{0} \rightarrow Ce^{3+} + Fe^{3+}$. The decontamination station will remove sufficient material from the canister exterior to reduce the smearable contaminate below the level of 220 dpm alpha per 100 cm^2, and 2200 dpm beta plus gamma per 100 cm^2. Current PNL experimental results show that this can be achieved by removing about 1.5 to 3μm of metal surface. Three moles of Ce^{+4} are required to dissolve one mole of iron, and approximately 0.65 to 1.4 moles of Ce^{+4} will remove the aforementioned layer of stainless steel from about 1 m^2 of surface. The contact time is 3 to 6 hours at a temperature of at least 45°C.

Verification tests were also performed using coupons placed on canisters in the PNL B-Cell facility where a Radioactive Liquid Fed Ceramic Melter was operated. When the coupons were etched once to remove ~3μm of surface, the samples satisfied the WAPS requirements(8). Scanning electron microscopy indicated that intergranular attack is not significant even with surface removal of ~6μm which is twice that needed to meet the required smearable levels(2).

In the WVDP flow sheet, the spent cerium solution is returned to the high-level waste tank becoming part of the slurry incorporated in the waste-glass product. The Ce^{+4} is essentially consumed in the decontamination process; however, the $NaNO_2$ in the HLW tank will reduce any residual cerium to Ce^{+3}, which is inert relative to the tank and piping materials of construction.

CONCLUSIONS

Results continue to indicate that those expecting to vitrify HLW (the "Producers") will satisfy the same Specifications(2) with their glass product. Similarly, the canistered glass will be accommodated by the same transportation cask. Standardization in a quality product is being demonstrated.

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