WASTE FORM QUALIFICATION EXPERIENCE AT THE WEST VALLEY DEMONSTRATION PROJECT

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ABSTRACT

Since 1996, the West Valley Demonstration Project (WVDP) has operated a slurry-fed ceramic melter to vitrify high-level nuclear waste (HLW) for the U.S. Department of Energy (DOE). More than 65 batches of HLW were mixed with glass-forming chemicals between June 1996 and August 2002 to make a "qualified" HLW form. Each batch was tailor-made to the federal repository's Waste Acceptance Product Specifications (WAPS) (1) according to the procedures prescribed by the Waste Form Compliance Plan (WCP) (2) and Waste Form Qualification Report (WQR) (3). The nuances of this procedure and the lessons learned from the application of the process will be provided in this paper to guide future producers of immobilized HLW.

The WVDP melter was put into service in October 1995 and radioactive waste was first added in June 1996. The WAPS define the envelope of permissible properties of the WVDP's vitrified waste form, the canister, and the canistered waste form to be delivered to the federal repository. The philosophy of the WVDP is that the glass would meet the WAPS criteria by: 1) only allowing acceptable feed materials to be delivered to the melter; 2) controlling the process temperatures and redox state of the glass; and 3) predicting or determining the composition of the product.

The waste form specifications ask for the chemical composition, radionuclide inventory, waste form durability, phase stability, whether or not the glass is categorized as hazardous waste, and the uranium and plutonium content of each canister.

The canister specifications have to do with the canister material, fabrication and closure, identification and labeling, and dimensions (length and diameter). Canister integrity has been ensured by specifications of the components and method of fabrication, as well as by a rigorous program of inspection and verification. Close control of the autogenous, pulsed gas tungsten arc welding (GTAW) process and by weld inspection has assured a leaktight weld on each production canister.

There are 14 specifications for the canistered waste form. The first four have to do with exclusion of materials other than glass from the closed canisters. The precluded materials include free liquids, extraneous gases, explosive, pyrophoric, combustible, and organic materials. The vitrification process has been shown to evaporate free liquids and destroy most of the compounds in question by its very nature. The primary task during WVDP vitrification operations, then, has been to exclude all of these foreign materials from the facility as possible. This has been accomplished through administrative controls and timely permanent weld closure of the canisters.

Other specifications deal with fill height, heat generation, dose rate, plutonium content, smearable contamination, criticality, glass/steel chemical compatibility, mass and overall dimensions, drop testing (of a filled canister), and plutonium content.

Production records for the WVDP's 275 canisters of vitrified HLW will summarize the data generated by the processes designed by the WVDP to comply with these specifications. This paper will review the processes and data collected from the WVDP vitrification campaign.

MEETING THE WAPS

Glass Specifications

Specification 1.1 asks for the chemical composition of the glass waste form. All oxides present greater than 0.5 weight percent must be reported. The target glass composition and the average and range of oxide compositions are reported in Table I. Approximately 10% of the canisters of glass have been sampled and analyzed for those 15 oxides. (Data in the table are from the chemical analysis of shard samples taken from 27 canisters over the course of the vitrification campaign.)

Table I. Range of Oxides in WVDP Glass

Oxide	Measured Minimum (wt%)	Measured Maximum (wt%)
Al_2O_3	5.6	7.1
B_2O_3	11.2	14.8
CaO	0.21	0.6
Fe_2O_3	10.7	13.5
K_2O	4.1	5.3
Li_2O	3.3	4.2
MgO	0.7	1.3
MnO	0.7	0.9
Na_2O	7.1	8.6
P_2O_3	1.0	1.4
SiO_2	39.5	48.4
ThO_2	0.1	3.6
TiO_2	0.7	0.9
UO_3	0.1	0.8
ZrO_2	1.2	1.4

Specification 1.2 is the Radionuclide Inventory Specification. Again, approximately 10% of the canisters have been analyzed and an average will be reported for the population. All radionuclides that have half-lives longer than 10 years and that are, or will be, present in concentrations greater than 0.05 percent of the total radioactive inventory, indexed to the years 2015 and 3115 must be reported. To meet this specification, only Cs-137 and Sr-90 will actually be measured on the waste form itself. Other radionuclides will be calculated based on the known ratio to these two, more predominant, species. Figure 1 shows the Cs-137 and Sr-90 concentrations measured in the glass shards taken from 27 production canisters over the six-year vitrification campaign.

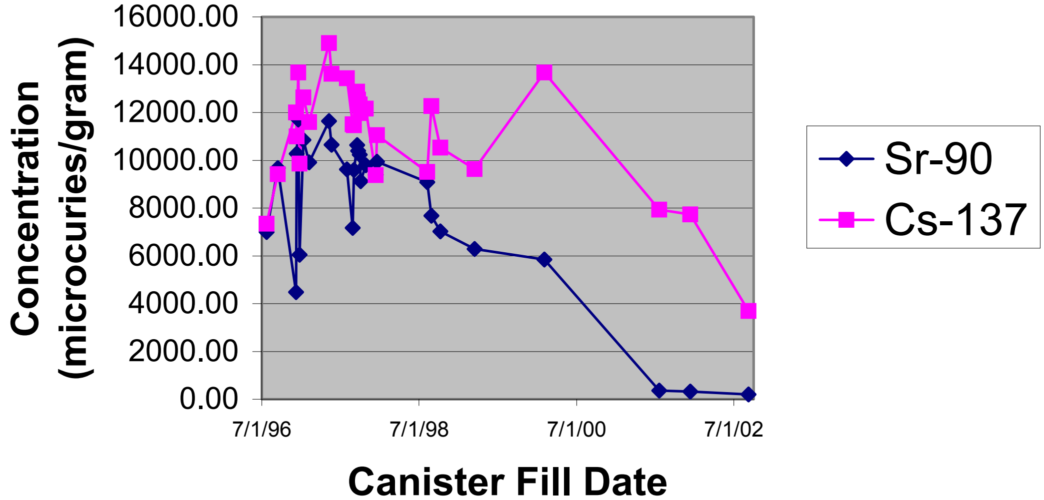

Figure 1. Sr-90 and Cs-137 in Glass Shards

Specification 1.3 is, essentially, the waste form durability specification. The glass must be shown to be more durable than a standard glass as measured by the Product Consistency Test (PCT). To show compliance with this specification, the WVDP predicts PCT results based on the chemical analysis of the production glass samples described for Specifications 1.1 and 1.2, and compares these predictions to measured EA glass data. The PCT predictions are based on a DOE-accepted regression model correlating measured PCT results to glass composition. The predicted normalized PCT releases for B, Li, and Na are compared to measurements from the benchmark EA glass to demonstrate compliance with this specification. Typical results are given in Table II.

Table II. Product Consistency Test Results

Glass	Cation Release, mg/L		
	Boron	Sodium	Lithium
Benchmark EA Glass	16,780	13,274	9036
Typical Production Glass (Shard Analysis)	1009	929	783

Specification 1.4 is the Specification on Phase Stability. The glass transition temperature, T_g, the crystallization behavior of the glass, and the storage temperature conditions must be reported. The T_g for target glass composition, as well as several others in the same range, was measured and found to be in the range of 450- 465EC. The effect of redox and thermal history on the glass transition temperature was found to be not significant. The crystallization behavior was reported in the Waste Form Qualification Report (WQR) (3) using time-temperature-transformation (TTT) diagrams. The West Valley canister storage facility was designed to maintain the maximum glass temperatures well below 400EC, which has been maintained throughout the campaign. Typical crystalline phases found in nonradioactive test glasses include spinels, lithium phosphate, and hematite. Under typical cooling conditions, the amount of crystallinity, determined by both x-ray diffraction (XRD) and optical microscopy image analysis is about 2 vol%. Even under extreme conditions of long times (96 hours) at relatively high temperatures (700^{o}C), the amount of crystalline materials present never exceeded 9 vol%.

Specification 1.5 is the Hazardous Waste Specification. The WVDP glass waste form is not a "listed" hazardous waste. To assess whether the vitrified glass product is a "characteristic" waste, prototypical WVDP glass compositions containing three times the expected amounts of silver, arsenic, barium, cadmium, chromium, lead, and selenium were prepared and evaluated using the Toxicity Characteristic Leaching Procedure (TCLP) leach test. In all cases, the metal extraction levels for hazardous metals were significantly below the regulatory limit. Table III shows the results of these tests (3) for the WVDP target glass and the spiked glass.

Table III. Results of TCLP Testing of WVDP Glass

Metal	EPA Limit (ppm)	Amount Extracted (ppm)	
		Target Glass	Spiked Glass
Ag	5.0	<0.030	<0.030
As	5.0	<0.30	<0.30
Ba	100	0.39	0.36
Cd	1.0	<0.015	<0.015
Cr	5.0	0.038	0.030
Pb	5.0	<0.15	<0.15
Se	1.0	<0.30	<0.30

Specification 1.6 describes the IAEA safeguards regarding the uranium and plutonium content of each canister. The total amount (in grams) as well as concentration (in grams per cubic meter) of ten of the isotopes of these elements will be reported along with the radionuclide content as described in Specification 1.2.

Canister Specifications

Specifications 2.1, 2.2, 2.3, and 2.4 have to do with the canister material, fabrication and closure, identification and labeling, and length and diameter, respectively. The canisters were fabricated from austenitic stainless steel 304L. The canister heads and barrel were made of ASTM A240 plate type 304L stainless steel and the flange was 304L stainless steel pipe per ASTM A312, plate per ASTM A240, or forging per ASTM 182. The composition of ASME SFA5.9 ER308L austenitic stainless steel, the weld filler metal, was used to assemble the canister from its component parts. This 308L alloy was also used for the weld beaded canister identification labels.

Canister integrity has been ensured by specifications of the components, by specification of the method of fabrication, and by a rigorous program of inspection and verification. One major component of the canister receipt inspection is a test of the leaktightness of the as-manufactured, unfilled canister. Final, leaktight (1×10^{-4} atm-cc/sec helium, as defined in this specification) weld closure of the canisters has been performed as soon as practical after filling. Close control of the autogenous, pulsed gas tungsten arc welding (GTAW) welding process and by weld inspection has assured a leaktight weld on each production canister. Over the entire campaign, which filled 275 canisters, fewer than 10 needed to go through a second welding procedure.

The code used for identifying the canistered waste forms is a five character alphanumeric code consisting of two letters and three numbers. The reference labeling technique is bead-welding the alphanumeric characters directly onto the canister surface using 308L. This labeling technique was shown to be suitable by fabricating full-sized weld-bead labeled canisters, handling and decontaminating the labeled canister in a manner similar to that used in the WVDP process, and then establishing that the labels are still readily legible and not subject to preferential obliteration.

The specified maximum and minimum length and diameter of the unfilled WVDP canister has been designed to be safely within those required by this specification. As-built canister lengths and diameters have been provided for all production canisters.

Canistered Waste Form Specifications

Specifications 3.1, 3.2, 3.3, and 3.4 have to do with the exclusion of materials other than glass from the closed canisters. The precluded materials include free liquids, extraneous gases, explosive, pyrophoric, combustible, and organic materials. The vitrification process has been shown by its very nature to evaporate free liquids and destroy most of the compounds in question. The primary task then, during vitrification operations has been to exclude all of these foreign materials from the facility as much as possible. This has been done by administrative controls and timely permanent weld closure of the canister.

The canisters were inspected prior to entry into the WVDP Vitrification Facility as well as after filling and just before closure to ensure they contain no prohibited materials.

Specification 3.5 is the Chemical Compatibility Specification. Testing was done with nonradioactive glasses to demonstrate that there are no adverse reactions between the glass composition and the 304L stainless steel at temperatures up to and beyond 500EC which would degrade the canister integrity. In one test (4), crucibles made of 304L stainless steel held typical borosilicate waste glass for 10,000 hours at 350°C. A metallographic examination of the cross sections of the crucibles in contact with the glass showed no significant corrosion had occurred.

Specification 3.6 requires that the canisters be at least 80 percent full. The WVDP planned for its canisters to be at least 85 percent full and the actual average production value is more than 91 percent full. The primary method for determining the fill height of each production canister is a measuring device which physically probes the height of the glass in several places after the canister has cooled and been removed from the loading turntable. The average fill height for the 275 canisters filled during the campaign was 91%.

Specification 3.7 is the specification for removable radioactive contamination on the outside surface of the canister. The canistered waste form is decontaminated with a nitric acid and Ce^{+4} solution prior to transfer to the interim storage facility. The canister's external surfaces are smeared according to 10 CFR 71.87(i) before transfer to the interim storage facility on site. The limits are 22,000 dpm/100 cm^2 for beta and gamma emitters and 2,200 dpm/100 cm^2 for alpha emitters. The external surfaces of the canistered waste forms are also visually inspected for visible glass. The smear surveys have resulted in only three of 250 canisters being decontaminated a second time. No visible glass has ever been detected on any canister. Typical values found during production are about 1000 dpm/100 cm^2 for beta and gamma emitters and <20 dpm/100 cm^2 for alpha emitters. A second decontamination process will be utilized just before the canisters are packaged for final shipment.

Additionally, the Project must provide an estimate of the material removed during the decontamination process and an assessment of the unfilled canister wall thickness. The decontamination process is estimated to remove between ten and fifteen micrometers of 304L stainless steel from the canister. Ultrasonic wall thickness measurements on the as-manufactured canisters have been made and found to be within the specifications required of the fabricator. The individual results for each canister will be reported in the Production Records in compliance with Specification 3.11.

Specification 3.8 is the Heat Generation Specification. The heat generation rate in a canister containing high-level waste was calculated using the Standardized Computer Analyses for Licensing Evaluation (SCALE) computer codes (5). The heat generation rate depends on the amount and type of radionuclides contained in the canister and decreases with time as a result of radioactive decay. Data needed to compute heat generation rate in the SCALE code are the concentration of radionuclides in a canister. The source of these data is in WQR Section 1.2.1. Radionuclide concentrations have been established in the WQR and the corresponding heating rates are computed with the SCALE system. The maximum amount of heat generated expected is about 362 watts, as measured by 1996 radionuclide decay. The maximum values predicted for 2015 and 3115 are 238 and 3.5 watts, respectively.

Specification 3.9 requires an estimate of the maximum gamma and neutron dose rates indexed to the year 2015 and the time of shipment. The limits are 10^5 rem/h for gamma and 10 rem/h for neutrons. Projections of gamma dose rates at the surface of high-level waste (HLW) canisters were made using the Standardized Computer Analysis for Licensing Evaluation (SCALE) system computer codes. The estimation of radionuclide inventory is described in WQR Section 1.2. The results of the calculations are reported in WQR Section 3.9 where the maximum values are given as 6.4×10^3 rem/h gamma and 8.8×10^{-2} rem/h for neutron. Actual gamma measurements on production canisters have shown a maximum of about 7.1×10^3 rem/h with a usual range of 3.0×10^3 to 5.0×10^3 rem/h. (Neutron measurements have not been made.)

Specification 3.10 is the Subcriticality Specification. The calculated effective neutron multiplication factor, $K_{eff,}$ for the canistered waste was calculated using the KENO computer code. The maximum value of $K_{eff,}$ conservatively calculated using twice the anticipated amount of fissionable material, was found to be 4.89×10^{-3}.
Specification 3.11 provides for the reporting of the mass of the overall canistered waste form and its overall dimensions. The maximum allowed mass is 2,500 kg and the canister must fit into a right-circular cylindrical cavity 64.0 cm in diameter and 3.01 m in length. These parameters will be checked before shipout and the results of the tests reported in the Storage and Shipping Records.

Specification 3.12 is the Drop Test Specification. A filled canister must withstand a drop of seven meters onto a flat, essentially unyielding surface without breaching. The WVDP strategy for compliance with this specification consisted of two approaches: 1) using engineering calculations to form a basis for the conclusion that the reference canister is capable of surviving a 7 meter drop; and 2) dropping nonradioactive glass filled canisters to confirm their ability to withstand the required drop. Both methods demonstrated that the canistered waste form would survive such a test.

Specification 3.13 is the Handling Features Specification. A flange geometry for the WVDP canister and a grapple that couples with this flange and complies with this specification were designed. The grapple has a rated capacity nearly two times that of a completely (100%) full canister and a 5000 lift cycle lifetime.

Specification 3.14 requires the reporting of the concentration of plutonium in each canistered waste form. The WVDP plans to comply with this specification using shards removed from the top of canistered glass, measuring the quantity of ^{90}Sr in the shard, and relating this value to the quantity of plutonium in the canistered waste form using scaling factors from the waste characterization program. This plutonium value will then be divided by the quantity of glass in the canistered waste form to generate the plutonium concentration value. This calculated plutonium concentration will be listed in the Production Records.

SUMMARY

The West Valley Demonstration Project has successfully vitrified all of the radioactive materials in the Waste Tank Farm. All canisters have been prepared according to the requirements of the WAPS with no non-conformances. The Production Records are now being finalized and are expected to be reviewed and ready to provide to DOE for their acceptance during CY2003. The 275 HLW canisters will remain safely stored on site until arrangements can be made for permanent disposal.

REFERENCES

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