WEST VALLEY DEMONSTRATION PROJECT: VITRIFICATION CAMPAIGN
SUMMARY AND PATH-FORWARD TO MELTER SHUT-DOWN

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ABSTRACT

The vitrification campaign at the West Valley Demonstration Project (WVDP) is coming to a close and plans are now being made for flushing the waste-handling equipment and shutting down the melting process. This paper will discuss the performance of the waste acceptance system designed to produce an acceptable waste form, the activities planned to bring the vitrification campaign to a close, as well as some of the incidental successes and pitfalls experienced since the beginning of radioactive operations in June 1996.

The Waste Acceptance Performance Specifications (WAPS) provided the standards for vitrification processing of high-level waste (HLW) at the WVDP. Production Records for the 250+ canisters of vitrified high-level waste form suitable for deep geologic disposal (as of the summer of 2000) provide the data necessary for acceptance by the repository. This paper will review the data collected during the campaign, including waste form chemistry, radiochemistry, durability, canister fill-height, and the results of smear testing to detect contamination on the canister.

CAMPAIGN SUMMARY

The West Valley Demonstration Project (Project) has produced 254 canisters of vitrified high-level waste (HLW) form suitable for deep geologic disposal (as of December 2000). Since the completion of Phase I of the vitrification campaign on June 10, 1998, processing rates have slowed due to dilution of the remaining waste. This dilution results in the need to make many transfers from the Waste Tank Farm to the vitrification process in order to retrieve enough solid material for a complete glass batch. With more than 99.7% of the long-lived transuranic isotopes removed, the Project is now evaluating state-of-the-art equipment for the final clean-out of the waste tanks. It is estimated that 275 canisters will have been filled at the completion of the 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. A list of those oxides is presented in Table I.
Table I. Oxides to be Reported for Chemical Composition of the Waste Form

<table>
<thead>
<tr>
<th>Oxide</th>
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<tbody>
<tr>
<td>Al₂O₃</td>
<td>B₂O₃</td>
<td>CaO</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>K₂O</td>
<td>Li₂O</td>
</tr>
<tr>
<td>MgO</td>
<td>MnO</td>
<td>Na₂O</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>SiO₂</td>
<td>ThO₂</td>
</tr>
<tr>
<td>TiO₂</td>
<td>UO₃</td>
<td>ZrO₂</td>
</tr>
</tbody>
</table>

Approximately 10% of the glass-filled canisters have been sampled and analyzed for those 15 oxides. At the conclusion of the campaign, an average composition will then be calculated over the entire population and used as the value to meet this specification. The individual measurements for the major elements tested for so far are given in Figure 1.

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.

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). The WVDP will predict PCT results, based on the chemical analysis of the glass samples described for Specifications 1.1 and 1.2, and compare these predictions to measured Environmental Assessment (EA) glass data. The PCT predictions will be based on a U.S.
Department of Energy (DOE)-accepted regression model correlating measured PCT results to glass composition. The predicted normalized PCT release for B, Li, and Na will be compared to measurements from the benchmark EA glass to demonstrate compliance with this specification.

Specification 1.4 is the Specification on Phase Stability. The glass transition temperature, $T_g$, the crystallization behavior and tendency 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 to 465°C. 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) (1) using time-temperature-transformation (TTT) diagrams. The WVDP canister storage facility was designed to maintain the maximum glass temperatures well below 400°C, which has been maintained throughout the campaign.

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.
Specification 1.6 describes the International Atomic Energy Administration 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 made of 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 x 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 weld inspection has assured a leaktight weld on each canister.

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 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 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, and 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 then, during vitrification operations, has been to exclude all of these foreign materials from the Vitrification 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 had been done with nonradioactive glasses to demonstrate there are no adverse reactions between the glass composition and the 304L stainless steel at temperatures up to and beyond 500°C which would degrade the canister integrity.

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. The actual average value is more than 91 percent full. The primary method for determining the fill height of each canister is a measuring device that physically probes the height of the glass in several places after the canister has cooled and been removed from the loading turntable.

Specification 3.7 provides the limits for the 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 cm² for beta and gamma emitters and 2,200 dpm/100 cm² for alpha emitters. The external surfaces of the canistered waste forms are also visually inspected for visible glass. 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. 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. 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. The data needed to compute the 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 Years 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 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 $6.4 \times 10^3$ rem/h gamma and $8.8 \times 10^{-2}$ rem/h for neutron.

Specification 3.10 is the Subcriticality Specification. The calculated effective neutron multiplication factor, $K_{\text{eff}}$, for the canistered waste was calculated using the KENO computer code. The maximum value of $K_{\text{eff}}$, conservatively calculated using twice the anticipated amount of fissionable material, was found to be $4.89 \times 10^{-3}$.

Specification 3.11 provides for reporting 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 ship out 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 seven-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 was designed and a grapple that couples with this flange and complies with this specification was 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 reporting 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 Sr-90 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.

NEW WASTE ACCEPTANCE INITIATIVE

As the vitrification campaign at the WVDP nears its end, it becomes ever more important to prevent a situation where materials contaminated with vitrified waste resulting from processing activities, other than relating to canisters, must be disposed. One option for minimization of these materials would be to
place components from the melter and associated equipment in a WVDP canister and encapsulate these parts by pouring molten HLW glass over them. As these components are already contaminated with glass and, in addition, do not react with the glass, canister, or repository environment, this encapsulation procedure would not generate any new HLW nor would it in any way degrade the performance of the waste form package. Furthermore, it would require little or no new equipment and could very readily be processed using current operating procedures during the final stages of vitrification at the WVDP.

This class of materials includes metal insert components of the melter: thermowells, bubblers, cylindrical nozzles, etc., made of Inconel® 690. Investigations have begun on the effect of these materials on several of the WAPS. For instance, the potential for galvanic corrosion between the Inconel® 690 and the 304L stainless steel has been determined not to affect the Chemical Compatibility Specification (3.5).

A computer analysis has also been re-run on the possible effect of these materials on the drop test performance of the canisters (Specification 3.12). It has been determined that as long as the materials are surrounded by glass, there will be no detrimental effect on the canister drop test performance.

From a regulatory standpoint, comments have been received from DOE-HQ and responses from the WVDP are being resolved.

SUMMARY

The WVDP has successfully vitrified nearly all of the radioactive materials in the Waste Tank Farm. The Project is now looking toward the end of the vitrification campaign and is evaluating what is necessary to close the waste tanks and clean up or stabilize the vitrification facilities. The path forward has been defined and execution of the critical activities is now underway.

REFERENCES
