VITRIFICATION PROCESS CONTROL AT THE WEST VALLEY DEMONSTRATION PROJECT

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ABSTRACT

The West Valley Demonstration Project has produced approximately 232 canisters (as of January 1999) of a glass, high-level radioactive waste form suitable for deep geologic disposal. This paper will discuss the methodology for controlling the process and final glass composition. Process control holds the key to meeting the Waste Acceptance Product Specifications as required by the Department of Energy (DOE) in order to produce an acceptable waste form for disposal in the proposed federal geologic repository. As the waste in the tank became more and more dilute, it was necessary to expand the range of acceptable glass compositions. The discussion will include the expected and unexpected successes as well as important lessons learned to improve future vitrification processes.

INTRODUCTION

The Waste Acceptance Product Specifications(1) (WAPS) provide the guidelines for producing an acceptable waste form for disposal in the proposed federal geologic repository. Using these specifications, a processing strategy was devised to demonstrate that control of critical parameters would provide adequate assurance of product quality with a minimum of sampling and testing of the final product.

BACKGROUND

The waste materials stored at the West Valley Demonstration Project (WVDP) were produced from 1966 to 1972 from the plutonium/uranium extraction (PUREX) processing of spent fuel. Most of the waste was neutralized and stored in Tank 8D-2 and had separated into a liquid layer (supernatant) on top of a layer of precipitated salts (sludge). The remaining waste was stored in Tank 8D-4 as discussed below. These wastes are generally well-known and well-characterized. There are extensive records and process flow sheets of past operations regarding the types of fuels that were processed. A number of analyses of both the sludge and supernatant have been performed. The WVDP has utilized this information in designing the glass composition and vitrification process for the waste stored at this site.

Two other waste streams have been combined with the PUREX waste in Tank 8D-2. About 15,000 L of acidic thorium extraction (THOREX) high-level liquid waste, which had been stored in Tank 8D-4, has been carefully mixed in with the supernatant in tank 8D-2. Additionally, zeolite, which was used to remove cesium from the supernatant, has also been added to Tank 8D-2. Pumps installed in the tank(2) are used to mix the combined wastes, minimizing the potential for inhomogeneities.

A five-year series of runs with nonradioactive materials and a full-scale melter and associated support systems provided the WVDP with information regarding the projection of glass composition based upon knowledge of feed composition(3). The combination of well-characterized waste materials and the various studies conducted during these runs demonstrated the ability to predict the final glass composition.

The original compositional range for the WVDP glass product composition is shown in Table I. The glasses in this region of composition space exhibit good processability characteristics and comply with the durability specification in the WAPS. The target composition selected from this range is sufficiently durable and has a viscosity between 20 and 100 poise at 1100^{o} C. The target glass composition is listed in Table II.

THE PROCESS

The blended wastes are transferred in batches into the Vitrification Facility for solidification. Waste slurry from Tank 8D-2, along with various other vitrification process recycle streams (e.g., the off-gas condensate), are combined with the heel from the previous batch in the Concentrator Feed Make-up Tank (CFMT). This waste slurry mixture is sampled and then concentrated through evaporation to remove excess water.

Samples of the slurry are obtained from a recirculating sampling loop. The samples are analyzed for pH, density, percent solids, anions, cations, and selected radionuclides. In particular, the 15 oxides listed in Table I, all of which are expected to be present in the glass at levels greater than 0.5%, are closely monitored. This criterion was established by the WAPS.

TABLE I West Valley Glass Expected Variations

	Weight Percent	
Oxide	Lower Bound	Upper Bound
Al_2O_3	5.43	6.57
B_2O_3	10.96	14.82
CaO	0.36	0.55
Fe_2O_3	10.22	13.82
K_2O	4.37	5.63
Li_2O	3.25	4.17
MgO	0.76	1.02
MnO	0.70	0.94
Na_2O	7.00	9.00
P_2O_5	1.02	1.38
SiO_2	38.73	43.23
ThO_2	2.67	4.09
TiO_2	0.68	0.92
UO_3	0.47	0.72
ZrO_2	1.12	1.52

These analyses are used to determine the chemical additions required to adjust the contents to the target feed composition. These additions are prepared in the Cold (nonradioactive) Chemical Facility. The composition of these cold chemical additions is confirmed through analysis prior to their being pumped as a slurry to the CFMT.

TABLE II West Valley Target Glass Composition			
Oxide	Weight Percent	Oxide	Weight Percent
Al_2O_3	6.00	Nd_2O_3	0.14
B_2O_3	12.89	NiO	0.25
BaO	0.16	P_2O_5	1.20
CaO	0.48	PdO	0.03
Ce_2O_3	0.31	Pr_6O_{11}	0.04
CoO	0.02	Rh_2O_3	0.02
Cr_2O_3	0.14	RuO_2	0.08
Cs_2O	0.08	SO_3	0.23
CuO	0.03	SiO_2	40.98
Fe_2O_3	12.02	Sm_2O_3	0.03
K_2O	5.00	SrO	0.02
La_2O_3	0.04	ThO_2	3.56
Li_2O	3.71	TiO_2	0.80
MgO	0.89	UO_3	0.63
MnO	0.82	Y_2O_3	0.02
MoO_3	0.04	ZnO	0.02
Na_2O	8.00	ZrO_2	1.32

After the cold chemical additions have been mixed with the waste slurry, additional samples are obtained. The composition of these samples is determined to confirm both the attainment of the desired slurry formulation for making the glass waste form and mass balance closure. The test for verifying attainment of the desired slurry composition is to show that the prediction of glass leach resistance, based on the feed composition, exceeds the WAPS requirements. (The specific requirements are described in detail below.) If the combined waste and glass-former slurry samples fail this test, additional sampling or chemical addition operations are performed and the acceptance test is repeated. Only after the combined waste and glass former slurry sample has successfully been shown to meet the durability requirement is the slurry batch transferred to the Melter Feed Hold Tank (MFHT) for final mixing before introduction into the melter.

The glass is poured from the melter into stainless steel canisters that are two feet in diameter by 10 feet tall. Samples of the waste form are taken before the canister is welded shut in order to demonstrate compliance with the WAPS product consistency specification. These glass samples are obtained by removing shards from the top of the filled canisters.

CONTROL OF COMPOSITION

Once the composition of the batch has been shown to be within the domain of the WVDP leach rate model(4), the results from the chemical analyses are combined to form a durability index, □. This index is defined, using the oxide weight percentages, as:

(Eq. 1)
$$\Sigma = B_2O_3 - 0.3*Fe_2O_3 - \frac{3.5*[Al_2O_3 + SiO_2 + ThO_2 + ZrO_2]}{K_2O + Li_2O + Na}$$

Three modeling equations have been developed relating this durability index to the anticipated boron, lithium, and sodium leachate concentration values from the Product Consistency Test (PCT) as required by the WAPS. These equations are as follows where [B], [Li], and [Na] are defined as the boron, lithium, and sodium leachate concentrations from the PCT.

(Eq, 2) $\log [B] = 3.0722 + 0.0938\Sigma + 0.0049\Sigma^2$

(Eq. 3) $\log [Li] = 3.0529 + 0.0813\Sigma + 0.0049\Sigma^2$

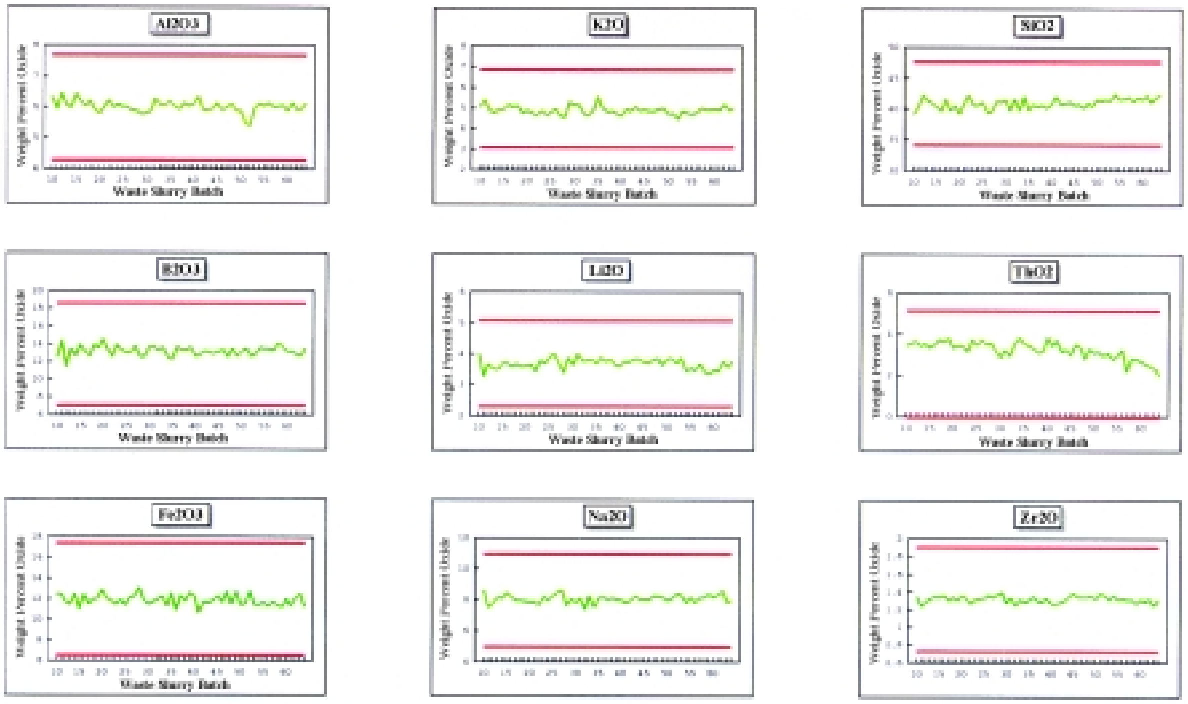
(Eq. 4) $\log [Na] = 2.9793 + 0.0852\Sigma + 0.0048\Sigma^2$

To accept a feed batch, the 95% confidence interval is calculated for the mean Σ from the nine chemical analyses performed to determine the batch oxide weight percentages. This upper 95% limit Σ value is used to determine the boron, lithium, and sodium leachate concentrations for comparison to the WAPS standard, the EA glass. Specifically, we demonstrate that the upper 97.5% multiple-use confidence limit for the model predictions for the upper 95% confidence limit Σ value is less than the lower 95% confidence interval of the EA glass PCT measurements to satisfy the WAPS statistical demonstration requirements.

PRODUCTION EXPERIENCE

The primary vitrification process control parameter is the chemical composition of the batch to be fed to the melter. The feed materials are sampled and analyzed at three different points in the process to ensure that the final glass composition will meet the specifications required by the DOE.

Figure 1 shows the batch-to-batch variability of the final waste slurry prepared for the melter as well as the valid domain of the PCT model. (Solid lines in the figure indicate the limiting values tested in the model.) Through individual chemical additions to the waste, the feed composition has remained very consistent. Thorium, which is one of the elements that is controlled but cannot be added with the nonradioactive raw materials, has been decreasing in concentration over the vitrification campaign. This is because the thorium hydroxide was found to be much easier to suspend within the waste tank than the other waste components. The ease of thorium suspension has produced a slightly preferential transport to the Vitrification Facility, thus higher depletion and the decreasing waste slurry feed concentration shown in the figure.



Note: Solid lines on the individual graphs indicate the PCT model domain limit for that oxide

Figure 1. Waste Slurry Melter Feed Batch Variability

The PCT performance of the glass waste form has stayed fairly constant over the course of the campaign. (See Figure 2.) These PCT data are based on glass shard samples removed from randomly selected canisters. The samples are analyzed and the PCT model employed to calculate the values plotted in the figure. This shows the WVDP glass product performing at a level that is an order of magnitude better than the WAPS requirement.

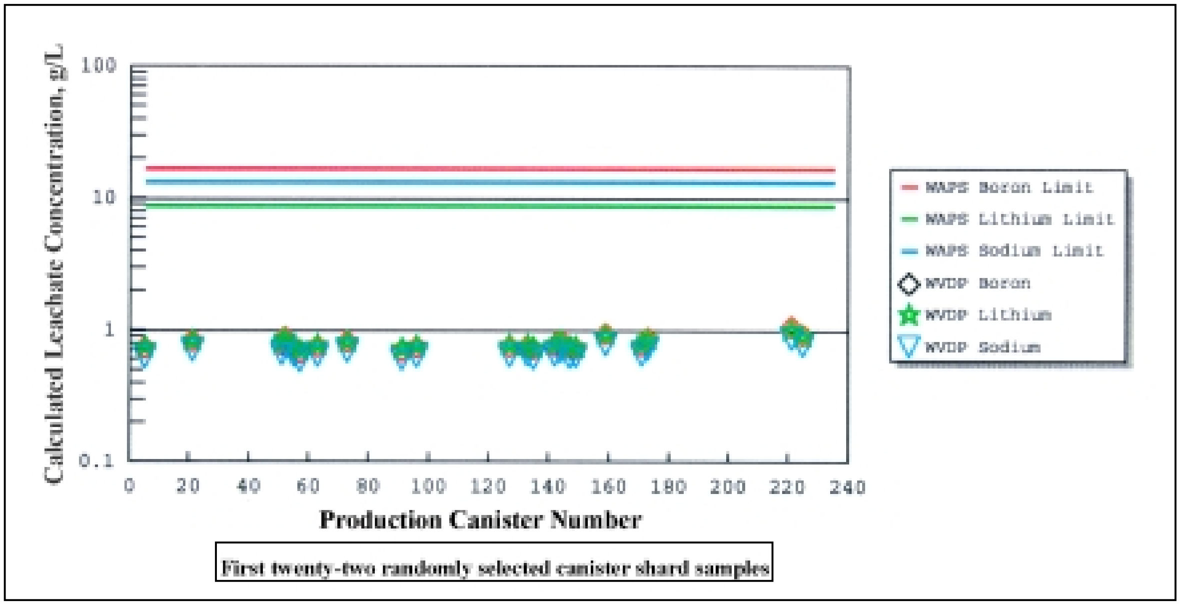


Figure 2. Product Consistency Test response from the WVDP high-level waste glass production campaign.

SUMMARY

The vitrification process control program, as instituted by the West Valley Demonstration Project, has delivered an excellent waste form with a predictably consistent product quality. It is this overall philosophy of combining the requirements of the WAPS for waste qualification and the general requirements for proper operation of the facility that has resulted in the successful operation of the Vitrification Facility.

REFERENCES

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