LFCM Vitrification Technology

Quarterly Progress Report April - June 1987

**R. A. Brouns, C. R. Allen,
and J. A. Powell, Compilers**

August 1988

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LFCM VITRIFICATION TECHNOLOGY

QUARTERLY PROGRESS REPORT APRIL-JUNE 1987

R. A. Brouns, C. R. Allen, and J. A. Powell, Compilers

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SUMMARY

This report is compiled by the Nuclear Waste Treatment Program and the Hanford Waste Vitrification Program at Pacific Northwest Laboratory to describe the progress in developing, testing, applying and documenting liquid-fed ceramic melter vitrification technology. Progress in the following technical subject areas during the third quarter of FY 1987 is discussed: melting process chemistry and glass development, feed preparation and transfer systems, melter systems, and canister filling and handling systems.

Melting Process Chemistry and Glass Development - As chemical compositions of the wastes to be processed through the Hanford Waste Vitrification Plant (HWVP) are expected to vary, testing was conducted to characterize and evaluate the effects on key glass properties of variations in iron, calcium, fluorine, barium, manganese, molybdenum, and nickel in the reference HWVP waste glass. This will permit the allowable glass composition variance ranges for these components to be established.

Initial scoping variability testing determined that individual variations of up to 5 wt% BaO, 5 wt% MnO₂, 2 wt% MoO₃, and 2 wt% NiO in the glass (on an oxide basis) had no significant effects on the viscosity, electrical conductivity, or phase behavior in the HW-39 glass composition. It is recommended that these components not be included in further variability testing.

Fluorine variability testing was conducted at levels up to 4.3 wt% in the glass. Due to potential liquid-liquid phase and observed crystalline phase separation, the maximum limit for fluorine in the glass should be established at 1.73 wt% oxides.

Eight glasses based on compositional variations of the West Valley Demonstration Project glass WVCN-47 were fabricated and leach-tested to determine the effect of composition on chemical durability. The amounts of Na₂O, Al₂O₃, P₂O₅, ThO₂, and noble metal (Ru, Rh, Pd) oxides were varied from the reference. Analysis of boron release shows that durability is affected by the compositional variation. Results show also that it is not affected by a small (0.1 wt%) addition of noble metal oxides and that the specified variations in P₂O₅, ThO₂, and B₂O₃ have little, if any, effect.

Four glasses with identical oxide composition and varied redox states were batched and leach-tested to determine the effect of redox state on West Valley glass WVCN-50 chemical durability. Analysis indicates redox state does not have a large effect. Where an effect is seen, increasing the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio (i.e., more reduced) decreases chemical durability, except for cesium release.

WVCN-50 was heat-treated to simulate six cooling rates that West Valley glass may undergo in canisters. These glasses were leach-tested to determine the possible effects of canister cooling rates on durability. Crystallization and ruthenium inclusions were observed in all, with roughly a 15 to 20 wt% total crystalline content. The quickly cooled glass samples proved more durable chemically than those cooled slowly.

Based on boron release, the compositional variability studied caused a maximum 28% decrease in chemical durability; redox adjustment caused a 12% decrease, and the heat treatments had the greatest effect, causing a maximum decrease in durability of 40%.

Feed Preparation and Transfer Systems - The test plan was approved for evaluating the HWVP feed heat-transfer characteristics using a simulated neutralized current acid waste. The focus will be to establish the effects of steam pressure and temperature on the boil-off rate. Data generated will be used to determine the system's overall convective and boiling heat-transfer coefficients.

The test plan was prepared for the study of the HWVP feed forming process off gas. The objectives are primarily to characterize and quantify the gases released and relate these data to the solution kinetics and secondarily to develop a simulant that will more adequately represent the NCAW.

The test plan was approved for the large-scale feed mixing test to be performed in the West Valley concentrator/melter feed tank. Three concentrations of the simulated melter feed slurry will be used to provide data to characterize the system and verify scale-up parameters.

Melter Systems: Radioactive Testing - The design verification tests for the waste glass thermal fracturing test equipment and the resulting

modifications to it were completed. This equipment was installed in the B-Cell radiochemical test facility, and ten glass fracturing tests with radioactive canisters were completed.

Canister Filling and Handling Systems - The Nuclear Waste Treatment Program at the Pacific Northwest Laboratory is preparing 30 radioactive canisters containing borosilicate glass for use by the Federal Republic of Germany in high-level waste repository-related tests. The canisters, now filled, will be welded closed and decontaminated starting early in fiscal year 1988. Electropolishing was selected as the primary decontamination approach, and an electropolishing system with associated canister inspection equipment was designed and fabricated for installation in a large hot cell. During the reporting period, ten preliminary tests of the electropolishing system were conducted to gain information on its operating characteristics and develop operating parameters.

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INTRODUCTION

In mid-FY 1982, the U.S. Department of Energy (DOE) assigned responsibility for managing its commercial nuclear waste treatment activities in the United States to the Nuclear Waste Treatment Program (NWTP) at Pacific Northwest Laboratory (PNL).^(a) The NWTP establishes the technology for treating and immobilizing high-level waste, transuranic waste, and other related wastes from commercial nuclear fuel reprocessing. This work includes developing waste treatment system technology and components, testing treatment systems, verifying the operability of the technologies through practical applications, producing waste packages for storage and disposal testing, assisting others to resolve specific problems in transferring the developed technologies, and maintaining a resource of radioactive waste treatment capabilities and facilities for DOE.

Major current activities include developing vitrification equipment for high-level waste; operating a pilot-scale liquid-fed ceramic melter (LFCM) system under radioactive conditions; designing, fabricating, and installing canister closure, decontamination, destructive and nondestructive examination, and storage facilities for vitrified radioactive waste; providing highly radioactive glass-filled canisters as heat and radiation sources to the Federal Republic of Germany for use in their repository test program; and providing processing technology and vitrification process equipment for treating West Valley wastes.

The NWTP is multifunded with base program funds from DOE-Nuclear Energy and user funding supplied by DOE-Nuclear Energy-West Valley, DOE-Defense Programs-Richland, the Federal Republic of Germany, and Japan. During the reporting period the NWTP was managed by R. A. Brouns.

Progress in all program elements is reported through informal monthly status reports, formal annual reports (McElroy and Burkholder 1984; Burkholder and Rusin 1985; Burkholder and Jarrett 1986; Burkholder and Brouns 1987), and formal topical reports. Because of both the magnitude of the

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first-generation high-level waste program element and the large number of applications currently under way, this quarterly report series was begun in FY 1985 to facilitate the transfer of LFCM vitrification technology between and among the central source (PNL) and the various user groups: the West Valley Demonstration Project, the Hanford Waste Vitrification Plant (HWVP), and the Defense Waste Processing Facility Project.

The results of applicable technical work performed by PNL in direct support of the HWVP are included in this report. During this report period, the HWVP was managed by Rockwell Hanford Operations for DOE; PNL is providing technical support for development of vitrification system technology for application to the HWVP. The HWVP facility, one of three major U.S. vitrification facilities for high-level waste treatment, will use PNL-developed LFCM vitrification technology. This technology will also be used for the Defense Waste Processing Facility and the West Valley Demonstration Project. Progress in the development of waste- and site-specific technologies is presented in this quarterly report to complement NWTP-supported activities. The PNL HWVP work is managed by C. R. Allen.

Because the emphasis of these quarterly reports is technical rather than programmatic, the reports are organized to cover technical subject areas without regard to funding sources. This quarterly is organized as follows:

- Melting Process Chemistry and Glass Development - M. A. H. Reimus and S. O. Bates.
- Feed Preparation and Transfer Systems - M. E. Peterson et al.
- Melter Systems: Radioactive Testing - R. D. Dierks et al.
- Canister Filling and Handling Systems - G. H. Bryan et al.

Each section contains summary, introduction, and technical progress subsections. This report was compiled by R. A. Brouns, C. R. Allen, and J. A. Powell.

REFERENCES

- Burkholder, H. C., and R. A. Brouns, compilers. 1987. Nuclear Waste Treatment Program Annual Report for FY 1986. PNL-6325, Pacific Northwest Laboratory, Richland, Washington.
- Burkholder, H. C., and J. H. Jarrett, compilers. 1986. Nuclear Waste Treatment Program, Annual Report for FY 1985. PNL-5787, Pacific Northwest Laboratory, Richland, Washington.
- Burkholder, H. C., and J. M. Rusin, compilers. 1985. Nuclear Waste Treatment Program, Annual Report for FY 1984. PNL-5414, Pacific Northwest Laboratory, Richland, Washington.
- McElroy, J. L., and H. C. Burkholder, compilers. 1984. Commercial Waste Treatment Program, Annual Report for FY 1983. PNL-4963, Pacific Northwest Laboratory, Richland, Washington.

MELTING PROCESS CHEMISTRY AND GLASS DEVELOPMENT

M. A. H. Reimus and S. O. Bates

SUMMARY

HANFORD WASTE VITRIFICATION PLANT (HWVP)

The Hanford Waste Vitrification Plant will convert liquid high-level and transuranic Hanford defense waste to a solid (borosilicate glass) suitable for final disposal in a geologic repository. Chemical compositions of the wastes to be processed through the HWVP are expected to vary, resulting in a glass product that will deviate from the nominal composition of the reference glass. While borosilicate glasses are generally forgiving, changes in glass composition due to varying feed composition can adversely affect the glass physical properties and/or chemical durability. Testing was conducted to characterize and evaluate the effects, on key glass properties, of variations in Fe (in a low Cr glass), Ca, F, Ba, Mn, Mo, and Ni in the neutralized current acid waste (NCAW) to be processed through the HWVP. This will permit the ranges of allowable glass composition variation for these glass components to be established, within which there will be acceptable glass physical and chemical properties.

Initial scoping variability testing indicated that individual variations of up to 5 wt% BaO, 5 wt% MnO₂, 2 wt% MoD₃, and 2 wt% NiO in the glass (on an oxide basis) had no significant effects on the viscosity, electrical conductivity, or phase behavior in the HW-39 glass composition. It is recommended that these components not be included in further variability testing.

Fluorine variability testing was conducted at fluorine levels up to 4.3 wt% in the glass. Due to potential liquid-liquid and observed crystalline phase separation at fluorine levels of 3.0 wt% and above in the glass, the maximum limit for fluorine in the glass should be established at the next highest acceptable fluorine level tested, 1.73 wt% oxides.

WEST VALLEY DEMONSTRATION PROJECT (WVDP)

Eight glasses based on compositional variations of West Valley reference glass WVCN-47 were fabricated and leach-tested to determine the effect of composition on waste glass chemical durability. The following oxides were varied from the reference amounts: Na_2O , Al_2O_3 , P_2O_5 , ThO_2 , and noble metal (Ru, Rh, Pd) oxides. Analysis of the results of boron release shows that chemical durability of the reference glasses is statistically affected by the compositional variation. The results show also that durability is not affected by a small (0.1 wt%) addition of noble metal oxides and that the specified variations in P_2O_5 , ThO_2 , and B_2O_3 have little, if any, real effect on product chemical durability.

Four glasses with identical oxide composition and varied redox states were batched and leach-tested to determine the effect of redox state on West Valley reference glass WVCN-50 chemical durability. Analysis of the normalized elemental releases from the leached glasses indicates that the redox state of the glass tested does not have a large effect on its chemical durability. Where an effect is seen, increasing $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio (reduction of glass) decreases chemical durability, except for cesium release. Both boron and uranium releases of the individual redox-adjusted glasses are identical within experimental error, indicating that the redox state has little effect on chemical durability. Conversely, sodium releases increased between the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios of 0.24 and 0.42, and the pH of the leachate at test termination increased slightly (from 9.64 to 9.91) with $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio. These facts indicate that the redox state of the glass does slightly affect its leaching behavior.

WVCN-50 was heat-treated to simulate the six cooling rates that West Valley Nuclear Services expect their glass may undergo during cooling in the canisters. These glasses were leach-tested to determine the possible effects of canister cooling rates on glass chemical durability. Cubic spinel-type crystals $[(\text{Fe},\text{Ni})(\text{Cr},\text{Fe})_2\text{O}_4]$, hematite-type crystals $[(\text{Cr},\text{Fe})_2\text{O}_3]$, ThO_2 crystals, and ruthenium inclusions were observed in all samples, with roughly a 15 to 20 wt% total crystalline content. The ruthenium inclusions appear to act as crystal nucleation sites. The heat treatments appeared not to affect chemical durability significantly, except for uranium and thorium releases.

The quickly cooled glass samples proved to be more durable chemically than those cooled slowly. Slow cooling of the glass appears to decrease its chemical durability more than does adjusting the redox state. Although the B, Si, Na, and Al releases from the more slowly cooled glasses ($\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio of <0.06) are identical to those from a glass with identical oxide composition and a $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio of 0.4, thorium and uranium releases of the heat-treated glasses are greater.

Based on boron release, the composition variations, glass redox state, and simulated canister-cooling heat treatments affected the durability of the West Valley reference glass; the redox adjustment effect, however, was not very significant. The compositional variability studied caused a maximum 28% decrease in chemical durability. Redox adjustment had a much smaller effect on durability, causing a 12% decrease. The heat treatments had the greatest effect, causing a maximum decrease in durability of 40%.

INTROOUCION

The objectives of the melting process chemistry and glass development effort are 1) to develop glass and melter feed compositions that will produce glass products having acceptable chemical durability and 2) to design feed formulations that can be processed in a liquid-fed ceramic melter (LFCM) at an acceptable rate. Glass-forming chemicals and other chemicals used for redox control are selected to maximize melting performance and minimize problems due to foaming, metal precipitation, and other adverse phase separation. The resulting glass composition is designed to have a viscosity of 100 poise and an electrical conductivity between 0.18 and $0.5 \text{ (ohm-cm)}^{-1}$ in the temperature region between 1070°C and 1150°C . In addition, the glass is designed to minimize the tendency to form crystals above 900°C or other formation of secondary phases on the melt surface.

A key product property is chemical durability. Specifications for chemical durability of waste glass as determined by laboratory tests have not been defined. Existing regulations pertain to radionuclide release from the controlled zone of the repository. Thus a prudent development strategy is to

assume that chemical durability, as measured by laboratory tests, should be as high as possible within the other processing constraints.

The technical approach involves a close interaction among feed formulation, glass composition, and waste processing work being conducted at Pacific Northwest Laboratory (PNL). Hence a glass composition is being developed to provide the appropriate high-temperature properties (viscosity, electrical conductivity) and low-temperature properties (elemental release rate, crystallization rate). Nitrate, oxide, and hydroxide chemicals representing the waste fraction and glass-forming chemicals or frit are made into slurries in the laboratory. The redox state of the glass is then optimized using a reducing agent in the slurries until the ferrous/ferric ratios in the resultant glasses are between 0.005 and 0.3. Then the melting rates of the feeds are determined in laboratory tests by measuring the rate at which the cold cap formed melts on molten glass.

Several variations are examined, and the feed formulation with the best melting characteristics in this rapid, inexpensive test is recommended for short-term testing in an experimental-scale melter. If problems occur, additional laboratory glass composition or feed formulation work is conducted. A successful short-term test leads to development of an extended test in the pilot-scale ceramic melter (PSCM) or high-bay ceramic melter (HBCM).

This work has focused on glass developed and characterized for the HWVP and the WVDP.

The HWVP is dedicated to vitrification of the liquid high-level and transuranic defense wastes produced and stored at the Hanford Site, near Richland, Washington. The objectives are to accomplish the following:

- Develop and characterize reference glass formulations incorporating the different waste streams to be processed through HWVP. These glass compositions should have the required physical properties for processing in an LFCM (viscosity, electrical conductivity, and phase behavior) and maximum chemical durability.

- Evaluate the effects of possible variations of selected waste components on the physical properties and chemical durability of the reference glass.

The Product Qualification Subtask of the West Valley Support Task at PNL provides support for the waste-form qualification efforts at West Valley Nuclear Services Company, Inc. (WVNS). Testing is being conducted to determine waste-form chemical durability in support of these efforts. The effects of composition, ferrous/ferric ratio (redox state), heat treatment, and groundwater are being investigated. The results of these studies will help determine the limits under which West Valley can operate their melter system and still produce glass durable enough to meet disposal regulations.

TECHNICAL PROGRESS

HANFORD WASTE VITRIFICATION PROJECT

The chemical composition of the NCAW to be processed through the HWVP is expected to vary due to waste composition variability. The resulting glass product will therefore deviate from the nominal composition of the reference glass. While borosilicate glasses are generally forgiving, changes in the glass composition due to variation in feed composition can adversely affect physical properties and/or chemical durability of the glass. Changes in key glass physical properties such as melt viscosity, electrical conductivity, and phase behavior (crystallinity) can affect the processing of the glass in the melter. The chemical durability (leaching characteristics) of the glass product can also be affected and possibly reduce its suitability for repository disposal. The goal of HWVP composition variability testing is to characterize the effects that given variations of selected waste components have on key glass properties. The range of composition variance allowable with acceptable alteration of the physical and chemical properties of the glass can then be predicted. These ranges define an envelope of acceptable glass compositions that will be qualified for repository acceptance as the HWVP waste form rather than a single glass composition. This envelope of glass compositions will be established in a composition variability study

(CVS) as part of the waste-form and process qualification processes and will define the glass portion of the HWVP waste form.

To reduce the size of the CVS to a manageable and practical level, scoping studies have been and are being conducted to determine which candidate glass components should be included in the CVS. The scoping tests will indicate whether or not changes over a glass component's predicted variance ranges will produce significant changes in the critical glass and melt properties and will predict what extremes are allowable. Components found in the scoping studies to have little or no significant effects on the glass or melt properties will not be included in the CVS. Scoping studies began in FY 1986 to determine which components should be evaluated in the CVS to generate the data required to develop the model. These scoping studies also provide data before completion of the CVS for input to specify the HWVP feed and help identify potential processing or product difficulties.

Since development of the HW-39 glass for the vitrification of NCAW, variability scoping studies have been conducted for the following waste and glass components: zirconium, sodium, iron, aluminum, silicon, rare earths (lanthanum and neodymium), uranium, chrome, type of alkali (lithium, sodium, potassium), and waste loading. These components were chosen based on their ranges of variability and/or their potential to affect glass properties. Testing has been conducted only to evaluate the potential variability of the NCAW waste stream.

Prior tests have confirmed that wide variations in composition can be accommodated in HW-39. These studies have also determined the degree to which each component affects glass properties and have established limits for acceptable variation in HW-39. Based on these prior studies, it was recommended that the following components be included in the CVS: zirconium, waste loading, sodium, iron, aluminum, and silicon. Uranium, rare earths (lanthanum and neodymium), and potassium were found to have minor effects on glass properties over their expected ranges of variation and need not be included in the CVS.

In this series of tests, additional glass components were evaluated. The components selected for variability evaluation were F, Ba, Mn, Mo, and Ni.

The nominal compositions of the reference NCAW waste (NCAW'84) with reduced Cr_2O_3 ^(a) and of HW-39 glass are shown in Table 1 (Bates 1986). In 1986 it was determined that approximately nine-tenths of the chrome in the NCAW would be washed out during pretreatment (Wagner 1986). When the low Cr_2O_3 NCAW'84 is added to the reference frit composition at a 25 wt% oxides waste loading as shown in Table 1, the glass composition used in the testing reported here is produced.

Technical Approach

The objectives of this work were to investigate and characterize the effects that given variations of F, Ba, Mn, Mo, and Ni will have on selected key glass properties (melt viscosity, electrical conductivity, phase behavior, and leach rates), and to determine what ranges of variance were allowable without altering the physical properties of the glass unacceptably. Another objective was to establish the extreme limits of individual glass component variations if these extremes were within the tested ranges.

The evaluation of the variability effects of these components was conducted in two parts: 1) a preliminary scoping test at the maximum variation expected of each component and 2) further detailed testing. The reference NCAW'84 waste with reduced Cr_2O_3 and the resulting HW-39 glass composition (Table 1) were used as the base compositions for these studies. This provides a continuity of data with previous variability testing. As the properties of glasses produced from the NCAW'84 (low Cr_2O_3) and NCAW'86 waste composition are very similar,^(b) these data will apply to glasses produced with NCAW'86.

Preliminary tests were conducted to determine which components should be tested further to establish practical limits for these variability tests. Viscosity and electrical conductivity of glasses were evaluated at the maximum variation of the component of interest. The extreme limits tested

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- (a) Shah, K. R., Rockwell Hanford Operations, letter to J. E. Minor, Pacific Northwest Laboratory, October 18, 1984. "Recommended (NCAW/CRW Blend) Feed Stream Composition and Range for PNL FY 1985 HWVP Glass Formulation."
 - (b) Bates, S. O. 1987. "Final Letter Report: Properties of the Updated FY 1986 HW-39 Glass Composition." Pacific Northwest Laboratory, Richland, Washington.

TABLE 1. Compositions of NCAW'84 Reduced Cr₂O₃ Reference Waste and HW-39 Glass at a 25 wt% Oxides Waste Loading

Oxide	As Received, kg/MTU	Normalized Waste, Wt% Oxide	Substituted Waste, Wt% Oxide	Substituted Waste Normalized, Wt% Oxide	Substituted Waste Normalized, Mo TOC(a)	HW-39 Frit, Wt% Oxide	Glass, Wt% Oxide
SiO ₂	0.50	3.09	3.09	3.12	3.14	67.25	51.22
B ₂ O ₃	0.00	0.01	0.01	0.01	0.01	12.76	9.58
Na ₂ O	1.8	11.1	11.1	11.2	11.3	10.26	10.51
Li ₂ O	0.00	0.00	0.0	0.0	0.0	5.00	3.75
CaO	0.06	0.31	0.31	0.31	0.31	3.75	2.89
MgO	0.04	0.25	0.35	0.35	0.35	1.00	0.84
Fe ₂ O ₃	7.5	46.3	46.3	46.8	47.1	--	11.78
ZrO ₂	0.4	2.5	2.5	2.5	2.5	--	0.69
Al ₂ O ₃	2.9	17.9	17.9	18.1	18.2	--	4.55
NiO	0.40	2.47	2.47	2.50	2.51	--	0.83
La ₂ O ₃	0.37	2.28	2.28	2.31	2.32	--	0.58
TOC	0.10	0.62	0.62	0.62	--	--	0.00
Nd ₂ O ₃	0.29	1.79	2.18	2.20	2.22	--	0.55
Sb ₂ O ₃	0.25	1.54	1.54	1.58	1.57	--	0.39
F	0.20	1.23	1.23	1.25	1.26	--	0.31
MoO ₃	0.20	1.23	1.23	1.25	1.25	--	0.31
U ₃ O ₈	0.10	0.62	SUB Nd(a)	SUB Nd	SUB Nd	--	--
CoO ₂	0.10	0.62	0.62	0.62	0.63	--	0.16
Ca ₂ O	0.10	0.62	0.62	0.62	0.63	--	0.16
CuO	0.10	0.62	0.62	0.62	0.63	--	0.16
MnO ₂	0.10	0.62	0.62	0.62	0.63	--	0.16
RuO ₂	0.10	0.62	0.62	0.62	0.63	--	0.16
Cr ₂ O ₃	0.09	0.56	0.56	0.58	0.57	--	0.14
BaO	0.07	0.43	0.43	0.44	0.44	--	0.11
Pr ₆ O ₁₁	0.06	0.37	0.37	0.37	0.38	--	0.09
SrO	0.06	0.37	0.37	0.37	0.38	--	0.09
Tc ₂ O ₇	0.06	0.37	DEL(a)	DEL	DEL	--	--
PdO	0.03	0.19	0.19	0.19	0.19	--	0.05
Rb ₂ O	0.04	0.25	0.25	0.25	0.25	--	0.06
Rh ₂ O ₃	0.03	0.19	0.19	0.19	0.19	--	0.05
Su ₂ O ₃	0.03	0.19	0.19	0.19	0.19	--	0.05
Y ₂ O ₃	0.03	0.19	0.19	0.19	0.19	--	0.06
BeO	0.01	0.06	SUB Mg(a)	SUB Mg	SUB Mg	--	--
NpO ₂	0.02	0.12	DEL	DEL	DEL	--	--
TeO ₂	0.02	0.12	DEL	DEL	DEL	--	--
K ₂ O	0.00	0.00	DEL	DEL	DEL	--	--
PbO ₂	0.00	0.00	DEL	DEL	DEL	--	--
SeO ₂	0.01	0.03	--	DEL	DEL	--	--
Am ₂ O ₃	0.00	0.02	DEL	DEL	DEL	--	--
CdO	0.00	0.02	DEL	DEL	DEL	--	--
Eu ₂ O ₃	0.00	0.02	SUB Nd	SUB Nd	SUB Nd	--	--
P ₂ O ₅	0.00	0.02	DEL	DEL	DEL	--	--
PuO ₂	0.00	0.02	DEL	DEL	DEL	--	--
SnO ₂	0.00	0.02	DEL	DEL	DEL	--	--
Ag ₂ O	0.00	0.01	DEL	DEL	DEL	--	--
Gd ₂ O ₃	0.00	0.01	DEL	DEL	DEL	--	--
Nb ₂ O ₅	0.00	0.01	DEL	DEL	DEL	--	--
Pm ₂ O ₃	0.02	0.12	SUB Nd	SUB Nd	SUB Nd	--	--
Ta ₂ O ₅	0.00	0.01	DEL	DEL	DEL	--	--
TiO ₂	0.00	0.01	DEL	DEL	DEL	--	--
	16.203	100	98.889	100	100	100	100

(a) TOC = Total organic carbons; SUB = Substitute; DEL = Delete.

for each component were based upon the HWVP feed specification and upon insight from additional preliminary composition analyses of actual NCAW. If the maximum variation was found to significantly affect the viscosity, electrical conductivity, and/or phase behavior of the glass, further detailed testing was conducted. Because of the time required to evaluate durability using Materials Characterization Center procedures MCC-1 or MCC-3 (MCC 1983 and 1984) leaching tests, leach tests were not used during preliminary testing to determine whether or not to conduct further variability testing. This approach is acceptable based on previous variability test results.

If glass properties were significantly affected at the maximum variability limit tested, an efficient statistically based method employed in previous variability testing was used to model the effects of composition changes on key glass properties (Chick and Piepel 1984; Bates 1985). Using the models developed with this method, acceptable composition variability limits of selected critical waste and glass components can be determined. The composition ranges for the selected components, established with information from Rockwell Hanford Operations^(a) (Wagner 1986), define a composition field around the reference glass composition. The physical properties to be evaluated and characterized are the same ones measured in the development and characterization of HW-39 glass: viscosity, electrical conductivity, phase behavior, and chemical durability.

All glasses used in these variability tests were batched from oxides, and no adjustment of redox was attempted. To do the latter would have required that the amount of reductant (graphite) needed to produce the target redox state be experimentally determined; this amount differs for each glass composition. The effects of redox on viscosity, electrical conductivity, and durability are minimal.

Scoping Studies

Prior to in-depth testing to learn the effects of a given component on glass properties, scoping tests were conducted at a concentration beyond the range of variability expected in NCAW. In these scoping tests, glass compositions assumed a total waste loading of 25 wt%, with the remaining

(a) Now Westinghouse Hanford Company.

portion of the waste made up of the nonvarying waste components held at a constant proportion to one another. Glasses with 5 wt% fluorine, 5 wt% BaO, 5 wt% MnO₂, 2 wt% MoO₃, and 2 wt% NiO were tested in scoping tests. Table 2 summarizes their compositions. Scoping tests were not conducted for iron and calcium as previous studies and experience had shown that both elements can significantly affect glass properties over the ranges to be tested.

Except for fluorine, each waste component had no major effects on the viscosity, electrical conductivity, phase behavior, and durability of HW-39. At 5 wt% fluorine, a crystalline phase separation was observed. Because incongruent changes in viscosity, electrical conductivity, or durability can be associated with phase separation, the variability evaluation of fluorine was conducted separately. Because of the high levels of Fe₂O₃ and CaO in the glass, scoping tests were not needed for these components. Iron and calcium were included together in a single variability test. The results of the 5 wt% BaO, 5 wt% MnO₂, 2 wt% MoO₃, and 2 wt% NiO scoping tests are presented together. The results of the fluorine testing and iron-calcium testing are presented separately.

Scoping Studies Viscosity Results. Table 3 summarizes the T100P values for each scoping test glass. Over the ranges tested, no waste component produced any major change in the T100P^(a) from the value for the HW-39 (low Cr) glass. The 5 wt% variations in BaO and MnO₂ produced the largest variance but, in both cases, Δ T100P values were less than 30°C. Considering that a 5 wt% change in the waste component in the glass (20 wt% in the waste) was required to produce this Δ T100P, no waste component tested was judged to affect the viscosity significantly enough to justify including it in further detailed variability testing.

Scoping Studies Electrical Conductivity Results. Table 3 also presents the E1150 values^(b) for the scoping glasses. The electrical conductivities of all the glasses were found to be unchanged by any variation tested. This finding agrees with previous variability studies indicating that generally if

(a) The temperature at which viscosity is 100 poise.

(b) The electrical conductivity at 1150°C.

TABLE 2. Summary of Glass Compositions Used in Variability Scoping Tests

Element	5% Ba	5% Mn	2% Mo	2% Ni	HW-39
SiO ₂	51.06	51.07	51.16	51.17	51.21
Fe ₂ O ₃	9.46	9.54	10.97	11.10	11.77
Na ₂ O	9.94	9.96	10.31	10.34	10.50
B ₂ O ₃	9.56	9.56	9.56	9.56	9.56
Al ₂ O ₃	3.65	3.69	4.24	4.29	4.55
Li ₂ O	3.75	3.75	7.50	3.75	3.75
CaO	2.88	2.88	2.89	2.89	2.89
MgO	0.83	0.83	0.84	0.84	0.85
ZrO ₂	0.49	0.50	0.57	0.58	0.62
NiO	0.49	0.50	0.57	2.00	0.62
La ₂ O ₃	0.47	0.48	0.55	0.56	0.59
Nd ₂ O ₃	0.42	0.43	0.49	0.50	0.53
SO ₃	0.32	0.33	0.37	0.38	0.40
MoO ₃	0.26	0.26	2.00	0.30	0.32
F	0.26	0.26	0.30	0.30	0.32
RuO ₂	0.13	0.13	0.15	0.15	0.16
MnO ₂	0.13	5.00	0.15	0.15	0.16
CuO	0.13	0.13	0.15	0.15	0.16
Cs ₂ O	0.13	0.13	0.15	0.15	0.16
CeO ₂	0.13	0.13	0.15	0.15	0.16
Cr ₂ O ₃	0.11	0.11	0.12	0.13	0.13
SrO	0.09	0.09	0.10	0.10	0.11
Pr ₆ O ₁₁	0.09	0.09	0.10	0.10	0.11
BaO	5.00	0.09	0.10	0.10	0.11
Y ₂ O ₃	0.04	0.04	0.05	0.05	0.05
Sm ₂ O ₃	0.04	0.04	0.05	0.05	0.05
Rh ₂ O ₃	0.04	0.04	0.05	0.05	0.05
Rb ₂ O	0.04	0.04	0.05	0.05	0.05
PdO	0.04	0.04	0.05	0.05	0.05
Total	100	100	100	100	100

TABLE 3. Summary of Viscosity and Electrical Conductivity Data for Scoping Test Glasses

Glass Properties	Glasses				
	5% BaO	5% MnO ₂	2% MoO ₃	2% NiO	HW-39 (low Cr)
T100P, °C $\pm 10^\circ\text{C}$	1067	1058	1091	1082	1081
E1150, (ohm-cm) ⁻¹ [+0.02 (ohm-cm) ⁻¹]	0.29	0.30	0.30	0.29	0.29

the T100P of the glass is acceptable, the electrical conductivity will also be acceptable and will not be a limiting factor in variability limits.

Scoping Studies Phase Behavior Results. Thin sections of quenched samples of glass and fibers pulled during viscosity measurements were evaluated optically. These showed no observable changes in the amounts or types of crystalline material in all glasses compared to the HW-39 (low Cr) glass. The crystals in the glass are the noble metal (Ru, Rh, and Pd) phases. Analysis by x-ray diffraction (XRD) found no detectable crystalline phases except in the 5 wt% fluorine glass. It contained between 5 and 10 wt% of a crystalline identified by XRD as CaF₂. The detection limit for XRD is about 5 wt%.

Scoping Studies Discussion. The variation of 5 wt% BaO, 5 wt% MnO₂, 2 wt% MoO₃, and 2 wt% NiO in the glass produced no significant variation in viscosity, electrical conductivity, or phase behavior of the glass. Therefore, no further variability testing was conducted on any of these waste components, and it is recommended that these elements not be included in the CVS. The 5 wt% fluorine glass showed crystalline phase separation, and therefore further variability testing was started.

Fluorine Variability

The behavior of fluorine in borosilicate glasses differs in many respects from that of the other halogens. Therefore the behavior of the other halogens should not be inferred from this study. The effective radius of fluorine is very close to that of oxygen, and this permits fluorine to partially replace oxygen in the glass. The other halogens are larger and much less stable as components in the glass structure. Because of the ability to replace oxygen in the glass, fluorine has a higher solubility in

the glass than the other halogens have. Generally, most clear commercial glasses contain at the most 0.6% fluorine compared to 0.1% chlorine (Volf 1984). Above the solubility limit, both liquid and crystalline phase separation occurs, causing opacity. The presence of elements such as aluminum and boron in the glass increases somewhat the solubility of fluorine in the glass.

The 5 wt% fluorine glass evaluated in the scoping test was observed (by x-ray diffraction) to have phase separation. This is not acceptable because it can cause problems in melter operation and can lead to degradation of glass durability. Because phase separation can have incongruent effects on properties such as viscosity or electrical conductivity, the fluorine variability was evaluated independently of iron and calcium. The range of fluorine variability investigated was from the current reference level of 0.3 to 5 wt% fluorine in the glass. To cover this range, glasses with fluorine concentrations of 0.3, 2, 3, 4, and 5 wt% were tested. The waste loading of each glass remained constant at 25 wt%, with the nonvarying components remaining in the same relative weight percent proportions to each other.

During the melting of these glasses, fluorine off-gassing was noted because of odors. Analyses of the glasses showed that they retained 60 to 80 wt% of the target values of fluorine (see Table 4). The amount appears to depend on the temperature at the time of melting. During melting of the 3 wt% target fluorine glass, the melting crucible cracked, requiring transfer

TABLE 4. Target and Analyzed Fluorine Concentrations in Variability Studies

<u>F Target, wt%</u>	<u>F Analyzed, wt%</u>	<u>F Retained, %</u>
0.31	Not Analyzed	Not Analyzed
2	1.5	75
3	1.73	58 ^(a)
4	3.0	75
5	4.26	85

(a) Melting time not standard (20% longer) due to crucible failure.

of the glass to another crucible. This transfer caused a 20% increase in the standard melting time of 2 hr at which the glass was at the melting temperature of 1150°C.

Fluorine Viscosity Results. The effect of fluorine on the melt viscosity is shown in Table 5. From 0.3 to 1.5 wt% fluorine in the glass, the T100P of the glass remains unchanged. However, between 1.5 and 1.73 wt% fluorine, the T100P drops 18°C and continues to decrease as the fluorine content increases. While the magnitude of the change in T100P is not great, the drop in T100P between 1.5 and 1.73 wt% fluorine may have been due to the presence of a fluorine liquid-liquid phase separation in the glass.

Fluorine Electrical Conductivity Results. The E1150 values for the fluorine glasses are also presented in Table 5. The electrical conductivities of all the glasses were found to be unchanged due to any of the variations tested. This finding agrees with previous variability studies indicating that, in most cases, if the T100P of the glass is acceptable, the electrical conductivity will be also and will not be a limiting factor in variability.

Fluorine Phase Behavior Results. Optical analysis of the quenched glass samples found little change in the phase behavior of the glasses with 1.75 wt% or less fluorine. The glasses with 3.0 and 4.26 wt% fluorine appeared darker. No gross immiscibility was observed optically in any of the glasses. However, regions of liquid-liquid phase separation can be very small ($\leq 0.01 \mu$). Examination of possible fluorine immiscibility regions would require special techniques such as carbon replica preparation of fracture surface (Bradley 1960; Vogel 1979) or ion milling to be observed. The high cost of these techniques made their use impossible with current

TABLE 5. Summary of Viscosity and Electrical Conductivity Data for Fluorine Variability Glasses

Glass Properties	As-Analyzed F, wt%				
	0.3	1.5	1.73	3.0	4.3
T100P °C [$\pm 10^\circ\text{C}$]	1081	1085	1067	1059	Not Analyzed
E1150 (ohm-cm) ⁻¹ [± 0.02 (ohm-cm) ⁻¹]	0.29	0.31	0.31	0.32	Not Analyzed

budgeted funds. The noble metal phases were consistently present in all the glasses at the same levels observed in the reference composition.

X-ray diffraction analysis was conducted on all the fluorine glasses. A crystalline phase, 5 to 10% of CaF_2 , was identified in only the glass containing 4.8 wt% fluorine. The detection limit for XRD for most crystalline phases is about 5 wt%. Thus the 3 wt% fluorine glass may have contained some CaF_2 but at levels below detection limit.

Fluorine Durability Results. The results of 28-day MCC-1 and MCC-3 testing for the fluorine glasses are shown in Tables 6 and 7. The MCC-1 data indicate no significant changes in durability for any of the glasses. In the MCC-3 data, however, the releases for the 3.0 wt% (actual) fluorine glass are two to six times higher for boron, sodium, and lithium. The releases for the 4.3 wt% (actual) fluorine glass in both the MCC-1 and MCC-3 tests are the same as observed for all other glasses except the 3.0 wt% (actual) fluorine glass. Duplicate MCC-1 and MCC-3 tests were conducted for the 3.0 and

TABLE 6. MCC-1 Leaching Results for Fluorine Variability Testing. Test conditions: MCC-1, 28-day, deionized water, 90°C, SA/V = 10 m⁻¹

Chemical	Element	Target wt% Fluorine (actual F wt% in parentheses)				
		0.3%(0.3)	2%(1.5)	3%(1.7)	4%(3.0)(a)	5%(4.3)(a)
Leaching Results, g/m ²						
SiO ₂	Si	13.6	13.7	11.53	13.3	11.4
B ₂ O ₃	B	14.5	18.7	14.92	17.0	14.2
Li ₂ O	Li	14.9	18.2	13.7	16.5	14.2
Na ₂ O	Na	14.6	16.6	14.3	16.7	13.0
CaO	Ca	6.81	5.87	8.2	7.02	3.2
MoO ₃	Mo	16.3	17.2	15.6	19.2	11.4
SrO	Sr	5.74	3.69	5.91	5.57	3.21
Al ₂ O ₃	Al	9.54	9.05	9.14	9.86	10.2
Fe ₂ O ₃	Fe	0.32	0.18	0.52	0.34	0.3
pH	Initial	5.6	5.64	5.69	5.67	5.6
	Final	9.3	9.59	9.44	9.52	9.18

(a) Average of duplicate leaching test.

TABLE 7. MCC-3 Leaching Results for Fluorine Variability Testing.
 Test conditions: MCC-3, 28-day, deionized water, 90°C,
 SA/V = 1780 m⁻¹

Chemical	Element	Target wt% Fluorine (actual F wt% in parentheses)				
		0.3%(0.3)	2%(1.5)	3%(1.7)	4%(3.0) (a)	5%(4.3) (a)
Leaching Results, g/m ²						
0.45- μ m Filtration						
SiO ₂	Si	0.28	0.27	0.23	0.32	0.23
B ₂ O ₃	B	0.48	0.51	0.47	1.08	0.45
Li ₂ O	Li	0.59	0.59	0.55	3.88	0.65
Na ₂ O	Na	0.46	0.46	0.45	1.14	0.37
CaO	Ca	0.06	0.06	0.07	0.04	0.05
MoO ₃	Mo	NA	0.37	0.46	0.91	0.39
SrO	Sr	0.04	0.00	0.05	0.02	0.02
Al ₂ O ₃	Al	0.15	0.16	0.16	0.11	0.17
Fe ₂ O ₃	Fe	0.15	0.19	0.19	0.14	0.13
pH	Initial	5.72	5.64	5.35	5.40	5.64
	Final	10.35	10.25	10.04	10.01	9.70
18-Å Filtration						
SiO ₂	Si	0.26	0.23	0.20	0.30	0.19
B ₂ O ₃	B	0.48	0.51	0.47	1.09	0.45
Li ₂ O	Li	0.57	0.56	0.52	3.84	0.63
Na ₂ O	Na	0.45	0.45	0.44	1.13	0.36
CaO	Ca	0.01	0.01	0.01	0.02	0.01
MoO ₃	Mo	NA	0.34	0.44	1.17	0.35
SrO	Sr	0.00	0.00	0.00	0.00	0.00
Al ₂ O ₃	Al	0.05	0.05	0.04	0.03	0.06
Fe ₂ O ₃	Fe	0.00	0.00	0.00	0.00	0.00
pH	Initial	5.72	5.64	5.35	5.35	5.6
	Final	10.35	10.25	10.04	9.99	9.68

(a) Average of duplicate leaching test.

4.3 wt% fluorine glasses. A duplicate ICP^(a) analysis of the 3.0 wt% fluorine glass confirmed that the required target composition had been obtained.

The reason for the higher releases at 3.0 wt% fluorine and the decrease to previous levels at 4.3 wt% is not known. A possible theory is that a liquid-liquid phase separation had occurred in the 3.0 wt% fluorine glass (possibly an alkali-fluorine and/or a boron-fluorine phase) which is not present in the 4.3 wt% fluorine glass due to formation of CaF_2 . This also corresponds to the small but measurable drop in the T100P between 1.73 and 3.0 wt% fluorine and the observed color change in the 3.0 and 4.3 wt% fluorine glasses. The higher releases observed in the MCC-3 compared to MCC-1 tests could be because the greatly increased glass surface area contacting the leachate would expose more of a separated phase. Between 3.0 and 4.3 wt% fluorine, the CaF_2 would then form, locking up the fluorine and restricting the formation of the less durable alkali-fluorine and/or a boron-fluorine phase.

Fluorine Discussion. Viscosity and electrical conductivity data indicate that the fluorine concentration in the glass is not limited to 4.3 wt%. However, to preclude the formation of any additional crystalline phases in the glass, it is recommended that a fluorine level of 4.3 wt% be considered unacceptable. Because of the increased releases at 3.0 wt% fluorine, it is recommended that the 3.0 wt% fluorine be considered unacceptable and that the maximum allowable fluorine limit in the HWVP reference glass be set at the next highest acceptable fluorine level, 1.73 wt% in the glass.

For comparison, the fluorine level in the Defense Waste Processing Facility reference glass is less than 0.1 wt% fluorine (Jantzen et al. 1984). The low-enriched waste concentrate being vitrified at the PAMELA plant contains 6.8 wt% fluorine but with a maximum waste loading of only 14 wt% oxides. This results in a 0.95 wt% fluorine concentration in the glass (Schiewer 1985). The nominal fluorine level in glass with a 25 wt% waste loading of HWVP NCAW'86 is 0.31 wt%.

(a) Inductively coupled argon plasma emission spectroscopy.

WEST VALLEY DEMONSTRATION PROJECT

Leach Testing

All glasses were tested with a modified MCC-3 (MCC 1986) leach test method. Glass specimens were ground in an automatic mortar and pestle and then sieved to obtain -100 +200 mesh powders. These specimens were placed in Teflon® leach containers together with deaerated, deionized water. The sealed containers were placed in an airtight enclosure containing 250 g of a fresh, unused CO₂ sorbent. This enclosure was then placed in a 90°C oven for a period of 7 days. The containers were briefly removed from the enclosure and gently agitated once a day. Three duplicates and a blank were run for each glass.

At the end of the leach test period, an aliquot of the leachate was filtered through a 0.45- μ m membrane. Half of the filtered leachate was then filtered through an 18-Å filter. The leached glass was removed from the leach containers, and the containers were then rinsed with deionized water, filled with 40 mL of 1% nitric acid solution, and placed in a 90°C oven overnight. The filtered aliquots (0.45 μ m and 18 Å) and the acid-strip solutions were submitted for analysis. Comparison of the 18-Å filtered solution with the 0.45- μ m filtered solution provides information on colloid formation in the dissolution product. Analysis of the acid-strip solution may be used to determine whether dissolution products are plating out on the test container walls.

Normalized elemental mass releases were calculated using the following equation:

$$NR_i = C_i / (F_i \times (SA \times W) / V) \quad (1)$$

where NR_i = normalized mass release of element i, g/m²
 C_i = concentration of element i in leachate, g/m³
 F_i = fraction of element i in glass, dimensionless
 SA = surface area of glass/g of glass, m²/g^(a)
 W = g of glass sample leached, g
 V = volume of leachant, m³

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(a) Value of 0.02 m²/g used.

Glass Heat Treatments

West Valley Nuclear Services specified the heat treatments (TA #400) for the glasses. Programmed furnaces were used. The controller was "programmed" with a series of linear cooling or heating rates, an approach that closely approximates cooling curves. Figures 1 through 6 are plots representing the actual cooling history of the glass samples. The furnace was programmed to shut off and cool down once a temperature of 400°C was reached. It took about 5 hr for the furnace to cool to room temperature (25°C). The glass structure is essentially frozen at 400°C, and a subsequent 5-hr cooling heat treatment to 25°C does not affect the microstructure of the glass.

The cooling curves used were simulated versions of actual glass cooling curves obtained from thermocouple readouts of two processed glass test canisters (TC-18 and TC-23) as poured and allowed to cool. Figures 7 and 8 show the thermocouple positions in the canisters. Samples HT-S-1 and 2 were cooled with cooling curves simulating temperatures observed with thermocouples placed ~30 in. from the bottom of canister TC-18. These thermocouples happened to be placed near pour batch boundaries; the glass was poured into the canister in batches, not continuously. This is why the glass is seen to start to cool, then suddenly heat up, and then cool again. The cooling scheme used to treat HT-S-1 is the slowest cooling of the six schemes used.

The cooling scheme used to treat sample HT-S-3 simulates the temperature readings observed about 20 in. from the top of canister TC-23; it gives the fastest cooling of the six schemes used. Cooling schemes used for samples HT-S-4, 5, and 6 were simulated temperatures observed about 30 in. from the bottom of canister TC-23.

The glass was treated in the following manner. A specified amount of crushed glass was placed in a fused silica crucible and put in the furnace at 1200°C. When the glass was molten (after about 20 min), the furnace controller program was activated. The temperature of the furnace was monitored over time with a thermocouple with continuous strip-chart readout. The crucible was removed from the furnace at a temperature of roughly 100°C;

FIGURE 1. Sample HT-S-1 Cooling History

FIGURE 2. Sample HT-S-2 Cooling History

FIGURE 3. Sample HT-S-3 Cooling History

FIGURE 4. Sample HT-S-4 Cooling History

FIGURE 5. Sample HT-S-5 Cooling History

FIGURE 6. Sample HT-S-6 Cooling History

FIGURE 7. Thermocouple Locations in Canister TC-18 (taken from TA #400).
Simulated by heat-treatment samples HT-S-1 and 2

FIGURE 8. Thermocouple Locations in Canister TC-23 (taken from TA #400).
Simulated by heat-treatment samples HT-S-3, 4, 5, and 6

then it was sectioned and a vertical slice removed and polished. The slice was then examined and analyses taken with scanning electron microscopy/energy dispersive x-ray (SEM/EDX) and x-ray diffraction (XRD). A portion of the remaining glass, not including the glass/crucible interface, was crushed and sieved for leach testing.

Compositional Variability Effect Results

Eight glasses, DG-WV1 through DG-WV8, were batched according to guidance from West Valley Nuclear Services and directions from PNL. The following oxides were varied from their reference amounts: Na_2O , Al_2O_3 , P_2O_5 , ThO_2 , and noble metal (Ru, Rh, Pd) oxides. The target oxide and "as analyzed" compositions of these glasses are given in Table 8. The glasses were analyzed using ICP and laser fluorescence. It should be noted that the ThO_2 weight percent levels of all glasses batched are lower than the target levels by 0.6 to 1.6 wt%. All other oxides are within roughly 10% of their respective target values.

These eight glasses were subjected to modified MCC-3 test methods. Table 9 lists the normalized elemental mass releases of B, Cs, Na, Si, Th, U, and those other elements whose oxide contributed at least 1 wt% of the glass composition. Each value given represents the average obtained from three duplicate tests. These releases were calculated from the 0.45- μm filtered solutions.

Analysis of these releases shows that the chemical durabilities of the reference glass (DG-WV1) and of the reference glass containing 0.1 wt% noble metal (Rh, Ru, Pd) oxides (DG-WV2) are essentially identical. The least chemically durable glass appears to be the "high Na_2O " glass (11.47 versus 9.13 wt%), DG-WV4, as was expected. Increasing amounts of alkali decrease chemical durability. The glasses containing relatively low amounts of Al_2O_3 , DG-WV3 and DG-WV5 (7.16 and 6.87 versus 8.74 wt%, respectively), are less durable chemically than the reference glass, as is expected. Increasing amounts of Al_2O_3 increase chemical durability. The "high P_2O_5 and ThO_2 " and "low B_2O_3 " glasses, DG-WV6, DG-WV7, and DG-WV8, respectively, appear to be as chemically durable as the reference glass. DG-WV6 contains 3.56 versus 2.58 wt% P_2O_5 ; DG-WV7 contains 3.83 versus 2.86 wt% ThO_2 ; and DG-WV8 contains 7.51 versus 12.15 wt% B_2O_3 . This finding indicates that these variations in

TABLE 8. Compositions of First Set of Eight Compositional Variability Glasses, wt%

Oxide	DG-WV1		DG-WV2		DG-WV3		DG-WV4		DG-WV5		DG-WV6		DG-WV7		DG-WV8	
	Target	Analyzed	Target	Analyzed	Target	Analyzed	Target	Analyzed	Target	Analyzed	Target	Analyzed	Target	Analyzed	Target	Analyzed
Al ₂ O ₃	8.05	8.74	8.04	8.81	8.50	7.18	7.79	8.38	8.00	8.90	7.97	8.55	7.90	8.84	8.49	9.01
B ₂ O ₃	12.08	12.15	12.07	12.17	9.25	9.33	11.89	11.77	12.35	12.41	11.98	12.15	11.86	12.15	7.30	7.51
BaO	0.05	0.05	0.05	0.05	0.05	0.07	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
CaO	0.60	0.68	0.60	0.83	0.58	0.63	0.58	0.68	0.61	0.68	0.59	0.69	0.59	0.65	0.63	0.67
CeO ₂	0.07	0.07	0.07	0.07	0.07	0.10	0.07	0.07	0.07	0.09	0.07	0.05	0.07	0.07	0.07	0.10
Cr ₂ O ₃	0.20	0.19	0.20	0.20	0.29	0.29	0.19	0.20	0.20	0.21	0.20	0.19	0.20	0.20	0.21	0.19
Cs ₂ O	0.08	0.05	0.08	0.05	0.07	0.06	0.08	0.05	0.08	0.05	0.08	0.05	0.08	0.04	0.08	0.14
Fe ₂ O ₃	12.20	11.74	12.19	11.72	11.30	10.81	11.81	11.08	12.41	11.91	12.08	11.55	11.98	11.55	12.87	12.29
K ₂ O	1.29	1.18	1.29	0.91	3.33	1.92	1.25	1.71	1.32	1.50	1.28	0.70	1.27	1.27	1.38	1.71
La ₂ O ₃	0.03	0.04	0.03	0.04	0.03	0.05	0.03	0.04	0.03	0.04	0.03	0.04	0.03	0.04	0.03	0.03
Li ₂ O	2.03	1.74	2.03	1.76	2.82	2.34	1.97	1.71	2.08	1.78	2.01	1.71	1.99	1.71	2.14	1.84
MgO	1.33	1.32	1.33	1.30	1.21	1.70	1.29	1.29	1.36	1.35	1.32	1.29	1.31	1.28	1.40	1.39
MnO ₂	1.31	1.30	1.31	1.32	1.22	1.78	1.27	1.30	1.34	1.36	1.30	1.30	1.29	1.29	1.38	1.37
MoO ₃	0.01	0.01	0.01	0.01	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Na ₂ O	9.27	9.13	9.28	9.04	10.18	9.82	12.20	11.47	9.48	9.10	9.18	9.13	9.10	8.68	9.78	9.38
Nd ₂ O ₃	0.12	0.12	0.12	0.11	0.17	0.16	0.12	0.14	0.12	0.12	0.12	0.11	0.12	0.09	0.13	0.13
NiO	0.28	0.31	0.28	0.27	0.32	0.36	0.27	0.27	0.29	0.30	0.28	0.28	0.28	0.28	0.30	0.30
P ₂ O ₅	2.52	2.58	2.52	2.60	2.33	2.41	2.44	2.54	2.58	2.63	3.50	3.56	2.48	2.51	2.66	2.68
PdO ₂	0.00	0.00	0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pr ₆ O ₁₁	0.03	0.03	0.03	0.03	0.00	0.00	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
RhO ₂	0.00	0.00	0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
RuO ₂	0.00	0.00	0.08	0.08	0.07	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SiO ₂	42.59	43.25	42.55	43.60	44.87	45.46	41.22	41.94	43.54	44.43	42.18	43.42	41.80	43.03	44.91	45.83
Sm ₂ O ₃	0.03	0.03	0.03	0.03	0.00	0.00	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
SO ₃	0.30	0.30	0.30	0.30	0.27	0.27	0.29	0.29	0.31	0.31	0.30	0.30	0.29	0.29	0.32	0.32
SrO	0.03	0.03	0.03	0.03	0.03	0.04	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
ThO ₂	3.61	2.86	3.61	2.80	3.34	2.73	3.50	2.94	3.69	3.11	3.58	2.75	5.40	3.83	3.81	2.75
TiO ₂	0.99	0.96	0.99	0.96	0.91	1.22	0.96	0.90	1.01	0.97	0.98	0.93	0.97	0.96	1.05	1.01
UO ₂	0.58	0.54	0.58	0.53	0.52	0.54	0.54	0.54	0.57	0.00	0.58	0.53	0.55	0.46	0.59	0.58
Y ₂ O ₃	0.02	0.02	0.02	0.02	0.02	0.03	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
ZrO ₂	0.29	0.59	0.29	0.58	0.27	0.64	0.28	0.54	0.30	0.60	0.29	0.56	0.28	0.62	0.31	0.57
Total	99.97	100	99.99	100	100	100	100.01	100	99.91	100	100.01	100	100.01	100	99.99	100

TABLE 9. Average Normalized Mass Releases of Glasses DG-WV1 Through DG-WV8, g/m²

Element	DG-WV1	DG-WV2	DG-WV3	DG-WV4	DG-WV5	DG-WV6	DG-WV7	DG-WV8
Al	0.106	0.109	0.098	0.110	0.097	0.115	0.109	0.113
B	0.186	0.191	0.237	0.239	0.229	0.188	0.188	0.187
Cs	0.104	0.092	0.137	0.092	0.082	0.093	0.120	0.040
Fe	0.002	0.003	0.004	0.003	0.003	0.003	0.003	0.003
K	0.021	0.022	0.043	0.014	0.022	0.006	0.033	0.026
Li	0.301	0.305	0.300	0.294	0.328	0.301	0.323	0.319
Mg	0.000	0.000	0.008	0.000	0.000	0.000	0.000	0.005
Mn	0.001	0.003	0.003	0.002	0.002	0.002	0.002	0.003
Na	0.158	0.163	0.218	0.239	0.204	0.155	0.170	0.176
P	0.105	0.107	0.196	0.182	0.147	0.097	0.108	0.133
Si	0.116	0.117	0.129	0.123	0.127	0.123	0.119	0.118
Th	0.001	0.002	0.001	0.001	0.001	0.002	0.001	0.002
Ti	0.001	0.002	0.002	0.001	0.001	0.002	0.001	0.002
U	0.026	0.031	0.031	0.029	0.030	0.033	0.038	0.037
pH	9.15	9.27	9.41	9.22	9.37	9.02	8.78	9.33

P₂O₅, ThO₂, and B₂O₃ have little, if any, real effect on the product's chemical durability. Based on boron release, the maximum decrease in chemical durability caused by the composition variations was 28% (high Na₂O - DG-WV4).

Figures 9 through 11 graphically represent Th and U, B and Si, and Al and Na releases, respectively. Figure 9 shows the average normalized mass releases of Th and U to be relatively consistent among the glasses tested. The limited Th release is probably caused by a low solubility limit, which appears to have been reached in these tests. Figure 10 shows that the silicon release is also relatively consistent among the glasses tested, indicating that its solubility limit has been reached during the test period. The boron release data show that DG-WV3, DG-WV4, and DG-WV5 are the least durable chemically, the other five compositions exhibiting higher and very similar chemical durability. Figure 11 shows that aluminum also appears to be solubility-limited.

Analyses of the 18-Å filtered aliquots and acid-strip solutions are not presented here. Analysis of the 18-Å filtered solution indicates that very

FIGURE 9. Comparison of Thorium and Uranium Normalized Mass Releases from DG-WV1 Through DG-WV8. Modified MCC-3 test, 90°C, deaerated deionized water, 7-day.

FIGURE 10. Comparison of Boron and Silicon Normalized Mass Releases from DG-WV1 Through DG-WV8. Modified MCC-3 test, 90°C, deaerated deionized water, 7-day.

FIGURE 11. Comparison of Aluminum and Sodium Normalized Mass Releases from DG-WV1 Through DG-WV8. Modified MCC-3 test, 90°C, deaerated deionized water, 7-day.

few, if any, colloidal dissolution products were formed during the test period. Analysis of the acid-strip solutions indicates that dissolution products did not plate out on the test container wall.

Glass Redox State Effects Results

Four glasses, DG-WV11R through DG-WV14R, were batched according to guidance from West Valley Nuclear Services (TA #394). The redox state of the glasses, as measured by the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio, was varied over a range of 0.07 to 0.42. The target oxide and "as analyzed" compositions of these glasses are given in Table 10; $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios are given in Table 11. The glasses were analyzed using ICP, laser fluorescence and spectrophotometric techniques. It should be noted that the ThO_2 weight percent levels of all glasses batched are lower than the target levels by 1.0 to 1.4 wt%. This is most probably due to analytical error. All other oxides are within roughly 10 relative weight percent of their respective target values.

TABLE 10. Compositions of Redox-Adjusted Glasses,
wt% as analyzed(a)

Oxide	Target	DG-WV11R	DG-WV12R	DG-WV13R	DG-WV14R
Al ₂ O ₃	9.99	10.46	10.52	10.58	10.58
B ₂ O ₃	10.69	10.97	10.82	10.78	10.98
BaO	0.05	0.05	0.05	0.05	0.05
CaO	0.60	0.62	0.63	0.61	0.61
CeO ₂	0.07	0.07	0.07	0.07	0.07
Cr ₂ O ₃	0.18	0.17	0.17	0.17	0.17
Cs ₂ O	0.08	0.09	0.10	0.12	0.13
Fe ₂ O ₃	12.19	11.90	11.82	11.90	11.99
K ₂ O	2.44	2.67	2.85	2.87	2.19
La ₂ O ₃	0.03	0.03	0.03	0.03	0.03
Li ₂ O	2.63	2.63	2.57	2.59	2.61
MgO	1.33	1.25	1.25	1.26	1.25
MnO ₂	1.31	1.32	1.31	1.31	1.31
MoO ₃	0.01	0.01	0.01	0.01	0.01
Na ₂ O	9.58	9.52	9.58	9.38	9.51
Nd ₂ O ₃	0.12	0.07	0.08	0.09	0.08
NiO	0.28	0.31	0.29	0.31	0.29
P ₂ O ₅	2.52	2.48	2.52	2.50	2.50
PdO ₂	0.01	0.01	0.01	0.01	0.01
Pr ₆ O ₁₁	0.03	0.03	0.03	0.03	0.03
RhO ₂	0.01	0.01	0.01	0.01	0.01
RuO ₂	0.08	0.08	0.08	0.08	0.08
SiO ₂	39.96	40.61	40.16	40.18	40.20
Sm ₂ O ₃	0.03	0.03	0.03	0.03	0.03
SO ₃	0.30	0.31	0.30	0.31	0.30
SrO	0.03	0.03	0.03	0.03	0.03
ThO ₂	3.61	2.20	2.53	2.48	2.59
TiO ₂	0.99	0.95	0.94	0.96	0.96
UO ₂	0.56	0.63	0.65	0.69	0.64
Y ₂ O ₃	0.02	0.02	0.01	0.02	0.02
ZrO ₂	0.29	0.46	0.54	0.52	0.73
Total	100.02	100.00	100.00	100.00	100.00
Fe ²⁺ /Fe ³⁺ (b)		0.068	0.126	0.236	0.424

(a) ICP and laser fluorescence analyses (uranium analysis).

(b) Analyzed with spectrophotometric technique.

TABLE 11. $\text{Fe}^{2+}/\text{Fe}^{3+}$ Ratios of Glasses Tested

	DG-WV11R	DG-WV12R	DG-WV13R	DG-WV14R
	0.068	0.131	0.237	0.409
	0.068	0.124	0.237	0.427
	0.068	0.123	0.233	0.429
	0.069	0.126	0.238	0.429
Average	0.068	0.126	0.236	0.424
Standard Deviation	5.00E-04	3.56E-03	2.22E-03	9.71E-03

These four glasses were tested using the modified MCC-3 method. Table 12 lists the normalized elemental mass releases of B, Cs, Na, Si, Th, U, and those other elements whose oxide contributed at least 1 wt% of the glass composition. Each value given represents the average obtained from three duplicate tests. These releases were calculated from the $0.45\text{-}\mu\text{m}$

TABLE 12. Average Normalized Elemental Mass Releases, g/m^2

Element	$\text{Fe}^{2+}/\text{Fe}^{3+}$			
	0.068	0.126	0.236	0.424
Al	0.119	0.113	0.114	0.121
B	0.212	0.209	0.212	0.237
Cs	0.092	0.101	0.081	0.067
Fe	0.003	0.002	0.003	0.003
K	0.020	0.056	0.026	0.095
Li	0.274	0.269	0.269	0.295
Mg	0.000	0.000	0.000	0.003
Mn	0.002	0.002	0.002	0.003
Na	0.209	0.203	0.215	0.249
P	0.177	0.173	0.171	0.182
Si	0.116	0.112	0.112	0.121
Th	0.000	0.000	0.000	0.000
Ti	0.001	0.001	0.000	0.001
U	0.024	0.023	0.021	0.025
pH ^(a)	9.64	9.76	9.82	9.91

(a) pH measured at test termination.

filtered solutions. Analyses of the 18-Å filtered aliquots and acid-strip solutions are not presented here. Analysis of the 18-Å filtered solution indicates that very few, if any, colloidal dissolution products were formed during the test period. Analysis of the acid-strip solutions indicates that dissolution products did not plate out on the test container wall.

Figures 12 through 14 graphically represent U, B and Si, and Cs and Na releases, respectively. The error bars represent experimental error of plus or minus two standard deviations. Figure 12, presenting the average normalized mass release of uranium, shows the releases to be within experimental error of each other. These could represent a solubility limit; however, slightly higher uranium releases (~10%) were observed from the compositional variability glasses. Figure 13 shows that the silicon release of each glass tested is identical, within experimental error, indicating either similar chemical durability or that the silicon solubility limit has been reached during the test period. The boron release data, being identical within

FIGURE 12. Comparison of Uranium Normalized Mass Releases from Redox-Adjusted Glasses. Modified MCC-3 test, 90°C, deaerated deionized water, 7-day

FIGURE 13. Comparison of Silicon and Boron Normalized Mass Releases from Redox-Adjusted Glasses. Modified MCC-3 test, 90°C, deaerated deionized water, 7-day

experimental error, show the durability of each glass to be very similar. Figure 14 shows that cesium release decreases with increasing glass reduction and that sodium release increases between $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios of 0.24 and 0.42.

Analyses of the release data indicate that the redox state of the glass tested does not have a large effect on its chemical durability. The maximum decrease in durability, based on boron release, is 12%. Where an effect is seen, increasing $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio (reduction of glass) decreases chemical durability, except for cesium release. Cesium releases decreased with increasing $\text{Fe}^{2+}/\text{Fe}^{3+}$. The normalized mass releases of silicon of each glass were all within two standard deviations^(a) of each other. This represents

(a) Standard errors were used as an estimate of standard deviation. The standard errors were obtained from Table 3 in the Appendix of: Piepel, G. F., and G. B. Mellinger. 1987. "Statistical Analysis of Leach Data from First Stage Testing and Evaluation of Test Matrix." Letter report to J. M. Pope from J. R. Carrell, February 27, 1987, Pacific Northwest Laboratory, Richland, Washington.

FIGURE 14. Comparison of Cesium and Sodium Normalized Mass Releases from Redox-Adjusted Glasses. Modified MCC-3 test, 90°C, deaerated deionized water, 7-day

roughly a 95% confidence interval, which represents experimental error and indicates that the releases are identical. Silicon is the major component of the glass matrices, and it appears that either the chemical durability of the four redox-adjusted glasses is not affected by the redox adjustment or that the silicon solubility limit in the leachate is being approached. Boron releases are also within experimental error of each other. These identical boron releases indicate that the chemical durability of the glass is scarcely, if at all, affected by the redox adjustment as boron is a major component of the glass matrix and is not solubility-limited as silicon is. The uranium releases are also within two standard deviations of each other. All but one of the sodium releases fall within two standard deviations; the greatest release was observed at the highest $\text{Fe}^{2+}/\text{Fe}^{3+}$. The thorium releases were found to be negligible.

The final pH of the leachate appears to increase with increasing $\text{Fe}^{2+}/\text{Fe}^{3+}$ of the glass leached. This could be caused by oxidation of Fe^{2+} in

the leachate. As Fe^{2+} goes into solution, it is oxidized by dissolved O_2 . This reaction consumes H^+ ion, which in turn increases the pH. With greater $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios, more Fe^{2+} is available for oxidation. The greater the amount of Fe^{2+} oxidized, the greater the increase in solution pH. Calculations comparing available Fe^{2+} concentrations and H^+ depletion support this theory.

Cooling Rates Effects Results

Six samples of a 1.5-kg batch of WVCN-50 (made as specified in TA #394) were heat-treated and cooled to simulate canister cooling rates. The target oxide and "as analyzed" compositions of these glass samples are given in Table 13. The glasses were analyzed using ICP, laser fluorescence, and atomic adsorption techniques. The slight differences in composition of the glasses are due primarily to analytical uncertainty. It should be noted that the ThO_2 weight percent levels of all glass samples are lower than the target levels by 1.0 to 1.1 wt%. This is currently attributed to a combination of batching and analytical error. All other oxides are within roughly 10 relative weight percent of their respective target values.

Glass Microstructure

Cubic spinel-type crystals $[(\text{Fe},\text{Ni})(\text{Cr},\text{Fe})_2\text{O}_4]$ were observed in all heat-treated glasses with SEM/EDX and verified with XRD. These crystals contained Cr, Ni, and Fe; some also contained small amounts of Mn. They were scattered evenly throughout the glass and ranged from about 5 to 10 μm across. Ruthenium inclusions and fluorite crystals (ThO_2) were also observed in all glasses. The ruthenium inclusions appeared to act as sites for crystal nucleation. The fluorite crystals measured about 25 to 50 μm across; the ruthenium inclusions measured about 0.3 to 0.8 μm . Crystals that appear to be hematite $[(\text{Cr},\text{Fe})_2\text{O}_3]$ were observed in all glasses with SEM/EDX. They were not detected in four of the samples with XRD, probably due to relatively low crystalline concentrations.

The XRD analysis results are given in Table 14, which lists approximate amounts of crystals identified. Roughly, a total crystalline content of 10 to 15 wt% was estimated to be in the glass samples.

TABLE 13. Compositions of Slow-Cool^(a) Heat-Treated Glasses, wt% as analyzed^(a)

Oxide	Target	HT-S-1	HT-S-2	HT-S-3	HT-S-4	HT-S-5	HT-S-6
Al ₂ O ₃	9.99	10.60	10.32	10.41	10.37	10.33	10.35
B ₂ O ₃	10.69	10.81	10.93	10.82	10.87	10.96	10.90
BaO	0.05	0.04	0.05	0.04	0.05	0.05	0.05
CaO	0.60	0.64	0.64	0.66	0.62	0.64	0.63
CeO ₂	0.07	0.07	0.07	0.07	0.07	0.07	0.07
Cr ₂ O ₃	0.18	0.19	0.18	0.19	0.19	0.17	0.19
Cs ₂ O	0.08	0.08	0.07	0.07	0.06	0.07	0.07
Fe ₂ O ₃	12.19	11.85	11.67	11.76	11.81	11.58	11.74
K ₂ O	2.44	2.30	2.33	2.42	2.20	2.43	2.21
La ₂ O ₃	0.03	0.04	0.04	0.03	0.03	0.04	0.04
Li ₂ O	2.63	2.57	2.56	2.55	2.53	2.59	2.55
MgO	1.33	1.29	1.29	1.30	1.30	1.28	1.30
MnO ₂	1.31	1.34	1.33	1.36	1.35	1.33	1.36
MoO ₃	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Na ₂ O ₃	9.58	9.06	9.23	9.15	9.26	9.19	9.13
Nd ₂ O ₃	0.12	0.11	0.13	0.11	0.13	0.11	0.13
NiO	0.28	0.29	0.27	0.29	0.28	0.29	0.28
P ₂ O ₅	2.52	2.54	2.54	2.51	2.53	2.52	2.56
PdO ₂	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Pr ₆ O ₁₁	0.03	0.03	0.03	0.03	0.03	0.03	0.03
RhO ₂	0.01	0.01	0.01	0.01	0.01	0.01	0.01
RuO ₂	0.08	0.12	0.13	0.12	0.13	0.11	0.13
SiO ₂	39.96	41.15	41.41	41.31	41.39	41.22	41.40
Sm ₂ O ₃	0.03	0.03	0.03	0.03	0.03	0.03	0.03
SO ₃	0.30	0.31	0.32	0.31	0.31	0.31	0.31
SrO	0.03	0.02	0.02	0.02	0.02	0.02	0.02
ThO ₂	3.61	2.51	2.48	2.49	2.52	2.62	2.56
TiO ₂	0.99	0.94	0.91	0.93	0.94	0.92	0.91
UO ₂	0.56	0.49	0.49	0.49	0.49	0.51	0.50
Y ₂ O ₃	0.02	0.02	0.02	0.02	0.02	0.02	0.02
ZrO ₂	0.29	0.52	0.46	0.47	0.43	0.50	0.49
Total	100.02	100.00	100.00	100.00	100.00	100.00	100.00

(a) ICP, atomic absorption and laser fluorescence analyses.

TABLE 14. Amounts of Crystals Identified by XRD in Heat-Treated Glasses, %^(a)

Sample(b)	Spinel(c)	Hematite(d)	Fluorite(e)
HT-S-3	14.00	<0.87	3.50
HT-S-4	14.00	1.75	1.75
HT-S-2	15.75	<0.87	1.75
HT-S-5	14.88	<0.87	1.75
HT-S-6	16.62	<0.87	0.87
HT-S-1	7.00	7.00	3.50

- (a) Based on total crystalline content of 17.5%
 (b) Ordered from fastest to slowest overall cooling rates
 (c) $(\text{Fe,Ni})(\text{Cr,Fe})_2\text{O}_4$
 (d) $(\text{Cr,Fe})_2\text{O}_3$
 (e) ThO_2

Glass Chemical Durability

Table 15 lists the normalized elemental mass releases of B, Cs, Na, Si, Th, U, and those other elements whose oxide contributed at least 1 wt% of the glass composition. Each value given represents the average obtained from three replicate tests. These releases were calculated from the 0.45- μm filtered solutions. Analysis of the 18- $\text{\AA}$ filtered aliquots and acid-strip solutions are not presented here. Analysis of the 18- $\text{\AA}$ filtered solution indicates that very few, if any, colloidal dissolution products were formed during the test period. Analysis of the acid-strip solutions indicates that dissolution products did not plate out on the test container wall.

Normalized elemental mass releases of DG-WV11R and DG-WV14R are reported in Table 15. DG-WV11R has the lowest $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio (0.06) of the redox-adjusted glasses tested. DG-WV14R has the highest $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio and is the least chemically durable of the redox-adjusted glasses. The $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio of the heat-treated glasses is less than 0.06. The redox-adjusted glasses have the same oxide composition as the heat-treated glasses, their releases given here for comparison. DG-WV11R may be treated as a control glass as its redox state is fairly close to that of the heat-treated glasses.

TABLE 15. Average Normalized Elemental Mass Releases, g/m²

Element	Glass Code							
	HT-S-1	HT-S-2	HT-S-3	HT-S-4	HT-S-5	HT-S-6	DG-WV11R	DG-WV14R
Al	0.144	0.131	0.121	0.144	0.148	0.142	0.119	0.121
B	0.246	0.204	0.192	0.175	0.228	0.218	0.212	0.237
Cs	0.113	0.123	0.119	0.158	0.133	0.132	0.092	0.067
Fe	0.005	0.003	0.002	0.002	0.005	0.005	0.003	0.003
K	0.132	0.121	0.097	0.125	0.116	0.164	0.020	0.095
Li	1.030	0.581	0.408	0.295	1.000	0.930	0.274	0.295
Mg	0.025	0.015	0.007	0.006	0.022	0.023	0.000	0.003
Mn	0.009	0.004	0.003	0.002	0.006	0.005	0.002	0.003
Na	0.265	0.217	0.206	0.188	0.249	0.237	0.209	0.249
P	1.472	0.749	0.461	0.294	1.450	1.329	0.177	0.182
Si	0.142	0.124	0.117	0.109	0.141	0.136	0.116	0.121
Th	0.009	0.004	0.003	0.003	0.007	0.007	0.000	0.000
Ti	0.007	0.004	0.003	0.002	0.007	0.007	0.001	0.001
U	0.062	0.045	0.039	0.048	0.070	0.073	0.024	0.025
pH(a)	10.14	9.89	9.81	9.77	10.20	10.14	9.64	9.91

(a) pH measured at test termination.

Table 16 lists the normalized releases of DG-WV1 glass as leached at two separate times. DG-WV1 was first leached with the set of compositional variability glasses. DG-WV1 was later leached as a control at the same time that the heat-treated glasses were leach-tested. Comparison of these test results can be used to determine true test-to-test variability. Table 16 shows that the test variability is greater than the replicate variability. This information will be used in statistical analyses of the data generated by West Valley compositional variability glass leach tests. The results of these analyses will be reported in a future document.

Figures 15 through 17 graphically represent B and Si, U and Th, and Na and Al releases, respectively. The error bars represent experimental error of plus or minus two standard deviations. The figures demonstrate that the heat treatments do not have a strong significant effect on the chemical durability of the glass except for U and Th releases. Based on boron

TABLE 16. Normalized Elemental Releases of DG-WV1, g/m²

Element	DG-WV1		DG-WV1 - Control(a)		
	Normalized Release, (b) g/m ²	Replicate Standard Deviation	Normalized Release, (b) g/m ²	Replicate Standard Deviation	Test Standard Deviation(c)
Al	0.106	6.52E-04	0.096	4.71E-04	6.60E-03
B	0.186	1.33E-03	0.148	1.33E-03	2.62E-02
Cs	0.104	1.21E-02	0.107	1.01E-02	1.98E-03
Fe	0.002	3.46E-05	0.002	2.88E-05	5.27E-04
K	0.021	5.20E-03	0.081	3.00E-03	4.29E-02
Li	0.301	2.57E-03	0.221	4.11E-03	5.63E-02
Mg	0.000	0.00E+00	0.003	2.28E-03	1.86E-03
Mn	0.001	6.08E-05	0.001	0.00E+00	4.30E-05
Na	0.158	4.26E-04	0.134	7.38E-04	1.74E-02
P	0.105	2.56E-03	0.063	1.12E-03	2.98E-02
Si	0.116	5.15E-04	0.103	5.15E-04	8.86E-03
Th	0.001	2.24E-04	0.002	9.18E-05	5.53E-04
Ti	0.001	1.20E-11	0.001	1.20E-11	1.39E-11
U	0.026	1.04E-03	0.039	1.59E-03	9.33E-03
pH	9.15		9.22		

(a) Leached concurrently with heat-treated glasses.

(b) Average of three replicates.

(c) Calculated standard deviation based on the average normalized releases of the two separate tests, DG-WV1 and DG-WV1-Control leaching.

release, the maximum decrease in durability is 40% (comparing the least durable sample with the most durable sample). Figure 15 shows the average normalized mass releases of B and Si from the heat-treated samples and DG-WV11R and DG-WV14R. The B and Si releases of the more quickly cooled glasses (HT-S-2, -3, and -4) are within experimental error of each other and are lower than the more slowly cooled glasses. This result is expected, as slow cooling allows the time required for crystalline growth while the glass attempts to achieve a lower free energy state. This crystalline growth often degrades chemical durability: formation of crystals depletes the glass matrix of elements that form the crystals, and this depletion causes it to be less durable. The releases from DG-WV11R are within experimental error of the quickly cooled glasses, indicating that this cooling does not affect

FIGURE 15. Comparison of Silicon and Boron Normalized Mass Releases from Slow-Cool Heat-Treated Glasses. Heat-treated glasses are arranged in order from fastest to slowest relative cooling rates. (Modified MCC-3 test, 90°C, deaerated deionized water, 7-day.)

chemical durability any more than slight glass reduction does. The releases of DG-WV14R and the more slowly cooled glasses are within experimental error of each other, indicating that their chemical durabilities are statistically identical. This gives evidence that slow cooling and glass reduction similarly degrade chemical durability. Figure 16 shows the releases of uranium and thorium. Error bars are not shown for thorium release, as its standard deviation is very small (0.00025). This figure demonstrates that the more quickly cooled glasses are more durable chemically than the more slowly cooled. Also, it appears that slow cooling lowers durability more than the redox state does, as shown by the lower releases of DG-WV11R and DG-WV14R. Figure 17 shows the releases of Na and Al. The release behavior observed in Figure 15 appears to repeat itself here. The releases of the more quickly cooled glasses are lower than the more slowly cooled glasses, and the more highly reduced redox-adjusted glass has releases statistically identical to the more slowly cooled glasses.

FIGURE 16. Comparison of Uranium and Thorium Normalized Mass Releases from Slow-Cool Heat-Treated Glasses. Heat-treated glasses are arranged in order from fastest to slowest relative cooling rates. (Modified MCC-3 test, 90°C, deaerated deionized water, 7-day.)

The observed microstructure provides no further insight into the effect of the slow cooling treatments on chemical durability. There appears to be no correlation between type and amount of crystalline formation and chemical durability or heat treatment. Forty percent of the crystalline content of HT-S-1, treated with the slowest cooling rate, consists of hematite-type crystals. This sample's chemical durability is statistically similar to that of HT-S-5 and 6, slowly cooled glass samples which contain relatively low levels of this crystal. Similarly, no correlation is observed with spinel-type crystalline content and chemical durability or heat treatment.

FIGURE 17. Comparison of Sodium and Aluminum Normalized Mass Releases from Slow-Cool Heat-Treated Glasses. Heat-treated glasses are arranged in order from fastest to slowest relative cooling rates. (Modified MCC-3 test, 90°C, deaerated deionized water, 7-day.)

CONCLUSIONS AND RECOMMENDATIONS

HANFORD WASTE VITRIFICATION PLANT

Based on the results and observations from the HWVP work, the following conclusions are made:

- Variations of up to 5 wt% BaO, 5 wt% MnO₂, 2 wt% MoO₃, or 2 wt% NiO in the glass had no significant effects on the viscosity, electrical conductivity, or phase behavior in the HW-39 reference glass composition. The total waste loading in the glass was maintained at 25 wt%.
- Crystalline phase separation of CaF₂ occurred at fluorine levels of 4.3 wt% in the HW-39 glass.

- At 3.0 wt% fluorine in the glass, MCC-1 and MCC-3 release rates increase by 2 to 6 times for the alkalis and boron. However, at 4.3 wt% fluorine the releases returned to about the same release values observed at fluorine levels below 3.0 wt%. The reason for this increase is not known but could be due to micro liquid-liquid phase separation.

Based on the results, observations, and conclusions from this work the following recommendations are made:

- If the concentrations of the BaO, MnO₂, MoO₃, and NiO in the NCAW are maintained below the maximum levels tested, these waste components should not be included in the composition variability study (CVS).
- The glass specifications for BaO, MnO₂, MoO₃, and NiO in the NCAW should be increased to the maximum levels tested in this study - 5 wt% BaO, 5 wt% MnO₂, 2 wt% MoO₃, and 2 wt% NiO in the glass.
- Due to possible liquid-liquid and observed crystalline phase separation at fluorine levels of 3.0 wt% and above in the glass, the glass specification for fluorine should be established at a maximum of 1.73 wt%.
- Fluorine should not be included in the main CVS if fluorine levels are not expected to exceed 1.73 wt% in the glass.

WEST VALLEY DEMONSTRATION PROJECT

Based on boron release, the compositional variations, glass redox state adjustment, and simulated canister cooling heat treatments affected the West Valley reference glass compositions, although the redox adjustment effect was not significant. The compositional variability studied caused a maximum 28% decrease in chemical durability under that of the reference glass. Redox adjustment had a much smaller effect on durability, causing a 12% decrease. The heat treatments had the greatest effect on the glass durability, causing a maximum decrease in durability of 40%.

REFERENCES

- Bates, S. O. 1985. Hanford Waste Vitrification Plant Interim Milestone HWVP-85-020202C: Results of Composition Variability Studies (CVS) to Date. Pacific Northwest Laboratory, Richland, Washington.
- Bates, S. O. 1986. HWVP DOE Milestone: Issue Glass Formulation of Neutralized Current Acid Waste (NCAW). Pacific Northwest Laboratory, Richland, Washington.
- Bradley, D. E. 1960. Br. J. Phys. 11:506-509.
- Chick, L. A., and G. F. Piepel. 1984. "Statistically Designed Optimization of a Glass Composition." Am. Cer. Soc. J. 67(11):763-768.
- Jantzen, C. M., D. F. Bickford, and D. G. Karraker. 1984. "Time-Temperature-Transformation Kinetics in SRL Waste Glass." In Nuclear Waste Management. Advances in Ceramics, 8:30-38, eds. G. C. Wicks and W. A. Ross, American Ceramic Society, Columbus, Ohio.
- Materials Characterization Center. 1983. MCC-1P Static Leach Test Method. Pacific Northwest Laboratory, Richland, Washington.
- Materials Characterization Center. 1984. MCC-3 Agitated Powder Leach Test Method. Pacific Northwest Laboratory, Richland, Washington.
- Materials Characterization Center. 1986. Test Methods Submitted for Nuclear Waste Materials Handbook. PNL-3990, Pacific Northwest Laboratory, Richland, Washington.
- Schiewer, E. 1985. "The Borosilicate Glass for 'PAMELA'." Radioactive Waste Management and the Nuclear Fuel Cycle, 7(2):121-138.
- Vogel, W. 1979. Chemistry of Glass, trans. N. Kriedl. 1985. The American Ceramic Society, Inc., Columbus, Ohio.
- Volf, M. B. 1984. "Chemical Approach to Glass." In Glass Science and Technology, Vol. 7, Elsevier, New York.
- Wagner, R. N. 1986. Hanford Waste Vitrification Plant Feed Specification: Pretreated NCAW Feed. RHO SD-HWV-OCD-001, Rev. 0, Rockwell Hanford Operations, Richland, Washington.

FEED PREPARATION AND TRANSFER SYSTEMS

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SUMMARY

The test plan was approved for evaluating the Hanford Waste Vitrification Plant (HWVP) feed heat-transfer characteristics using a simulated neutralized current acid waste (NCAW). The focus of the test will be to establish the effects of steam pressure and temperature on the boil-off rate. Data generated will be used to determine the overall convective and boiling heat-transfer coefficients for the system.

The test plan was prepared for the study of the HWVP feed forming process off gas. The objectives are primarily to characterize and quantify the gases released and relate these data to the solution kinetics. A second objective is to develop a simulant that will more adequately represent the NCAW.

The test plan was approved for the large-scale feed mixing test that will be performed at the West Valley Nuclear Services Co. in the West Valley concentrator/melter feed tank. The tests, using three concentrations of the simulated melter feed slurry, will be performed to provide useful data for characterizing their feed mixing system and to verify the scale-up of the bench-scale mixing study results using their melter feed tank.

INTRODUCTION

Feed preparation and transfer systems consist of the equipment used to contain and process the high-level liquid waste between the point of entry into the vitrification facility and the melter chamber. The equipment includes tanks, concentrators, agitators, pumps, process monitors, transfer lines, and the cooled melter feed nozzle. These systems also include the equipment used to batch the glass-forming additives and to convey them into the feed makeup tank for blending with the high-level liquid waste.

TECHNICAL PROGRESS

EVALUATION OF THE HEAT-TRANSFER CHARACTERISTICS FOR HWVP FEED SIMULANTS

The test plan for the evaluation of the simulated feed heat-transfer characteristics was approved. This study will evaluate the heat-transfer characteristics of a simulated NCAW. In the HWVP process the waste will be heated, concentrated, and cooled in the slurry receipt and adjustment tank (SRAT). The testing sequence will simulate portions of the proposed SRAT concentration cycle. The primary focus of the investigation will be to establish the effects of steam pressure and temperature on the boil-off rate. In addition, data generated will be used to determine the overall convective and boiling heat-transfer coefficients for the system.

The SRAT concentration cycle is a major operational step in the HWVP vitrification process. During the cycle, NCAW slurry is heated, boiled and cooled using steam through an internal coil bundle. Based on the information presented here, it is apparent that process efficiency may be affected by the operating steam pressure selected.

The effect of temperature difference, ΔT , on heat flux for pool boiling (no agitation) of a pure fluid is illustrated in Figure 1.

In this application ΔT , or the difference between the temperature of the heat-transfer medium and the bulk fluid, determines the boiling mechanism and thus the heat flux. At low values of ΔT (line AB), natural convection controls heat transfer. Bubbles form on the heat-transfer surface, are released, and rise to the surface of the liquid without significantly disturbing normal convection currents. As the temperature difference increases (line BC), the rate of bubble production increases and begins to affect the velocity of circulation currents. The boiling mechanism in this section of the curve is termed nucleate boiling, and heat flux continues to increase with ΔT until most of the heat-transfer surface becomes covered by a layer of insulating vapor. Above this critical ΔT (point C), increasing temperature difference shifts the mechanism to transition and finally to film boiling. Operating in these regimes is generally not desirable due to the large temperature differences required with little or no gain in heat transfer.

FIGURE 1. Effects of ΔT (temperature difference between steam and fluid) on Heat Transfer

Information obtained from literature sources indicates that the effects of agitation on boiling heat-transfer mechanisms are minimal. Heat flux may be increased, but the mechanisms outlined above should be examined for agitated systems. Also, as seen in Figure 1, the use of a tube bundle in place of a single tube seems to stabilize heat flux during transition boiling.

Therefore, operation of a system using a specific slurry concentration system will be optimized in terms of achieving a maximum heat flux if a critical temperature difference is maintained. Also, if the critical ΔT lies outside the capabilities of a given system, an economic evaluation of design changes versus operational limitations may be warranted.

Testing to be conducted during this evaluation will be divided into two major segments, each directed at a specific objective. These objectives are described below:

- Establish the effects of steam pressure on boil-off rate during concentration of simulated NCAW using bench-scale equipment.

In view of the relationship between boiling mechanism and temperature difference, it becomes important to evaluate the effect of increased temperature difference on boil-off rate. This segment of the study is directed at establishing a general relationship between these two parameters during the concentration of an HWVP slurry in an agitated vessel using an internal steam coil. Emphasis will be placed on determining a critical ΔT for the bench-scale system. The range of test conditions will be constrained by the available 324 Building steam supply system and the testing equipment. However, information generated by these tests will be useful in determining the effectiveness of increased steam pressure on boil-off rate. Based on these results, it will be possible to recommend parameters for full-scale testing of feed preparation equipment.

In this segment of the investigation, a series of tests will be performed. Steam pressure will be varied (range 5 to 100 psig) for each separate test while the remaining operational parameters are held constant. Feed slurry temperature will be increased to the boiling point; the feed will be concentrated and then cooled. By monitoring and recording the amount of water driven off during concentration as a function of time, a relationship between temperature difference and boil-off rate will be established.

- Establish the effects of SRAT operation on boil-off rate.

A major function of the SRAT is to concentrate HWVP feed from about 2 wt% solids to 12 wt% solids. Currently it is proposed that this task be performed as a batch operation within the HWVP. The SRAT is filled with the dilute feed (2 wt% solids) and steam is applied to the coil bundle. The feed is heated to boiling, then concentrated until the liquid level approaches the top of the coil bundle. At this point, the liquid level is returned to its original value by adding dilute feed. This sequence is repeated until the solids loading of the slurry is increased to 12 wt%.

To establish an accurate cycle time for feed preparation, it is necessary to know whether or not concentration rate decreases as the cycle progresses. Also, as the feed is concentrated, the physical characteristics change. If these parameters adversely affect mixing or system operation, system constraints may have to be revised.

Testing during this segment of the evaluation will consist of a simulation of the proposed SRAT concentration cycle using the "optimum" steam pressure from segment 1. Boil-off rates will be established and compared for each step of the process. Additional information to be obtained from these tests includes characterizing the composition of the boil-off stream in terms of solids entrainment and evaluating liquid level and concentration effects on tank mixing.

Because boiling heat transfer is dependent on system characteristics that are not reproducible, the information generated in these tests will not be directly applicable to HWVP design or full-scale SRAT operation. General relationships and trends will, however, be established and can therefore be used in designing full-scale SRAT tests in the future.

STUDY OF FEED FORMATING PROCESS OFF GAS

The test plan was prepared for the study of HWVP feed forming process off gas. The primary objective of this study is to characterize the gases released during the feed forming process and to relate these data to the solution kinetics. The rate and quantity of gases released will be measured as a function of time. Factors contributing to this release, including the feed chemistry, physical properties of the feed, and system operating parameters, will be identified. Characterization and quantification of the gases are necessary for the design of safe, reliable process equipment and operating procedures. A secondary objective, which is critical to the results of this study, is to develop a simulant that will more adequately represent the chemical and physical properties of the NCAW.

More specifically, the objectives of the feed forming off-gas study are as follows:

- Design, assemble, and test a laboratory-scale system that will provide accurate and reproducible data related to the off gas generated and released during feed forming.
- Determine the effect of the total amount of formic acid added to the feed by measuring the composition and volume of off gas generated during the forming process as a function of time.
- Determine the effect of the rate at which formic acid is added on the composition and volume of off gas generated during the forming process as a function of time.

The specific activities identified to accomplish these objectives are as follows:

1. Conduct four scoping studies to evaluate the methods for
 - gas sampling using a combination of gas sampling bulbs and scrubbers and gas compositional analysis using mass spectrometry and ion chromatography
 - measuring gas pressure generated during the feed forming process as a function of time
 - on-line measurement of the feed pH during the feed forming process
 - determining the composition of formic acid vapor phase over the stock formic acid solution heated to the operating temperature.
2. Design, assemble, and test a modified feed forming system interfaced with a data acquisition system. Modifications in the feed forming system provide for collecting gases during the forming process for mass spectrometry and ion chromatographic analysis and provide a method for concentrating the feed after the heat treatment. The combined forming and data acquisition systems are designed to provide automated control of the formic acid addition rate; gas flow rate; and feed

temperature and real-time measurement of feed temperature, cover gas temperature, gas flow rate, and feed pH.

3. Determine the reproducibility of off-gas data acquired during the feed forming process conducted with the data acquisition system and modified feed forming system.
4. Conduct a one-parameter study in which the total amount of formic acid is varied and the effect of this parameter on the solution kinetics of the system is determined.
5. Conduct a one-parameter study in which the formic acid addition rate is varied and the effect of this parameter on the solution kinetics of the system is determined.

NUCLEAR WASTE TREATMENT PROGRAM LARGE-SCALE FEED MIXING TESTS

The test plan for the large-scale feed mixing study was approved. The mixing study will be performed at West Valley Nuclear Services in the West Valley concentrator/melter feed tank.

The feed mixing system is an integral part of the feed preparation system. Bench-scale mixing studies were performed by Pacific Northwest Laboratory (PNL) in FY 1986 to quantitatively describe the performance of several feed mixing systems in terms of measurable process variables. One of these systems was the West Valley melter feed tank. The nuclear waste and glass-former mixture is fed from this tank into the melter.

Figure 2 is a schematic of the feed preparation system at West Valley. The high-level liquid waste is transferred from the storage tanks to the concentrator/feed makeup tank. A sample of the waste is taken to determine the elemental concentrations. The composition of the waste is fed into a computer program (RECIPE). The computer program determines the composition of the glass formers and other additives to be blended with the waste to form the slurry that will be fed into the melter. Once the desired composition for the melter feed is prepared, the slurry is transported to the melter feed tank. The melter feed tank provides an adequate feed hold-up volume to enable continuous feeding of slurry to the melter.

FIGURE 2. Schematic of West Valley Melter Feed Preparation System

The objectives of this study are to 1) provide useful data to West Valley for characterizing their feed mixing system and 2) verify the scale-up of the bench-scale mixing study results using the West Valley melter feed tank. Specifically, the tests will be performed to: 1) determine quantitatively the homogeneity of the melter feed in the melter feed tank, 2) determine whether the liquid sampling system provides a representative sample of the feed in the tank, 3) determine the time required to agitate the melter feed tank after a power outage, and 4) determine the power number versus Reynolds number relationship for the West Valley feed mixing system.

The tests will be performed on three concentrations of the simulated melter feed slurry: the reference melter feed, the reference melter feed concentrated to 75%, and the reference melter feed diluted to 125%. The tests have been statistically designed to provide as much data as possible for the error and sensitivity analyses to add credibility to the results and conclusions.

Three of the four objectives (first, second and fourth) can be met by performing one test for each slurry concentration. This test will be referred to as the homogeneity and sampling system test. The third objective will require a separate test for each slurry concentration and will be referred to as the resuspension test. Every sample will be labeled with a unique number, the date, and the name of the collector. The samples will be obtained from the tank and analyzed in a random order.

During each of the three homogeneity and sampling system tests, 22 samples will be taken at each of six locations in the tank and from the liquid sampling system. The first sample from each location in the tank will be combined. This combined sample will be sent to PNL for rheological evaluations. The remaining samples will be analyzed at West Valley for weight percent total solids and elemental concentrations (using inductively coupled plasma spectroscopy or atomic absorption analysis). In addition, the amperage to the agitator will be monitored during testing.

For the resuspension tests, seven samples will be taken at each location in the tank. The first sample from each location will be combined and sent to PNL. The resuspension samples will be analyzed for weight percent total solids only.

MELTER SYSTEMS: RADIOACTIVE TESTING

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SUMMARY

The design verification tests of the Federal Republic of Germany (FRG) thermal fracturing test equipment and the resulting modifications to that were completed. This equipment was installed in the B-Cell radiochemical test facility, and ten glass fracturing tests were completed.

INTRODUCTION

The objective of this work is to demonstrate laboratory-developed melter concepts, first with simulated feeds in the nonradioactive engineering-scale ceramic melter, then in the nonradioactive pilot-scale ceramic melter (PSCM), and finally with actual radioactive feed compositions in the pilot-scale RLFCM. The laboratory-developed concepts include modifications of the feed formulation that affect melter performance (foaming, slag formation, free metal precipitation, scum formation) or the final glass characteristics (crack formation, leachability, devitrification).

An additional objective is to evaluate modifications of melter facility process equipment, first with simulated radioactive feeds in the PSCM and then with radioactive feeds in the RLFCM. The equipment modifications include feed tank agitation, slurry sampling, glass sampling, feed delivery systems, off-gas treatment systems, process variable sensor development, and process control concepts.

TECHNICAL PROGRESS

FRG THERMAL FRACTURING TESTS

As part of a bilateral agreement between the Federal Ministry for Research and Technology and the U.S. Department of Energy (DOE), and in

collaboration with the Karlsruhe Nuclear Research Center and the Institute for Underground Studies, the Pacific Northwest Laboratory (PNL) filled 32 German-made canisters with highly radioactive borosilicate glass. These heat and radiation sources (canisters) contained specified amounts of ^{137}Cs and ^{90}Sr to establish predetermined decay heat and radiation dose rates. Thirty of these canisters, after being sealed and thoroughly cleansed of surface contamination, will be used in FRG repository testing. Two additional canisters, specially instrumented with temperature and acoustic emission sensors, were filled with a diluted formulation of this same highly radioactive glass so that each contained about 1 kW of decay heat.

During the report period, 10 controlled cooling experiments were completed with these instrumented canisters to evaluate the effects of radionuclide self-heating on the cracking of large glass castings, and most important, its eventual effect on the steady-state centerline temperatures of canisters of nuclear waste glass in deep geologic storage.

Glass-cracking is undesirable in vitrified waste repository canisters for several reasons. However, because of the stresses that build up within the glass as it begins to cool in the waste canister, it is very difficult to produce a canister that contains no glass cracks. The extent of cracking depends mostly on the rate at which the glass cools; the more rapid the cooling rate the more extensive is the cracking.

One reason that glass-cracking in a vitrified waste canister is detrimental is that cracks act like insulating air spaces within the glass and decrease its ability to transmit heat. The more extensive the cracking, the more slowly the heat moves through the glass, or the lower is its thermal conductivity. Thus canisters of waste glass, with a significant decay heat level, can have unacceptably high centerline temperatures if their initial cooling has been rapid enough to extensively fracture the glass and decrease its thermal conductivity. With canister centerline temperatures of 500 to 600°C, typical waste glasses begin to soften to the point that molecular movement in the glass permits devitrification or possibly molecular enrichment, over very long periods of time, which could eventually compromise the waste form's integrity.

Glass studies have resulted in computer codes, TEMPEST in the United States and ADINA in Europe, that predict the extent of cracking and the decrease in the thermal conductivity of nonradioactive glasses as a function of glass cooling rates. From these data internal canister temperatures can be estimated for self-heating glasses, but with an uncertain accuracy.

The objectives of the sponsors of the FRG thermal fracturing tests are to determine the following:

1. the accuracy of existing computer codes that predict steady-state internal temperatures in canisters of nonradioactive simulated waste glasses
2. whether the cracking of the glass in the FRG canisters filled recently from the radioactive liquid-fed ceramic melter (RLFCM) was significantly reduced by a two-step cooling process that first brought the glass to a steady state in an insulated cooling pod (ICP) and then to steady state in "free air" instead of cooling to steady state in "free air" in a single step
3. whether lining the canister with a thin layer of resilient ceramic fiber insulation significantly reduced mechanical cracking by preventing undue stress on the glass from compressive force while allowing the cooling canister to contract normally.

Accordingly, the objectives of the FRG thermal fracturing tests that are being conducted in the Radiochemical Engineering facility are as follows:

1. to provide the means for remotely measuring glass temperature gradients and acoustic emissions that are associated with the cooling of canisters of high-level waste glass
2. to fill two instrumented FRG canisters to the proper level with glass containing the required amount of decay heat
3. to provide the means for accurately controlling the heating and cooling of the glass in the test canisters during the fracturing tests
4. to provide the means for remotely monitoring and recording the thermal and acoustic data acquired in the fracturing tests and transferring these data in a usable format to the sponsors of the tests.

To attain the sponsors' objectives, three cooling experiments were requested to be performed on each of two instrumented FRG canisters after they had been filled in the normal manner with radioactive glass from the RLFCM. The two instrumented canisters were identical, except that canister 13 had been lined with a 1/8-in. layer of ceramic fiber insulation and that canister 19 was unlined. Each experiment was duplicated for technique verification. Prior to each test the glass temperatures were raised to 800°C for 4 hr in a remelt furnace to "heal" the glass of all cracks produced in the previous test.

One set of experiments would allow the canisters to cool to steady-state conditions in the ICP that was used to slow the cooling of the FRG production canisters after they had been cast from the RLFCM. A second set of experiments would allow the canisters to cool to steady-state conditions in an air cooling frame (ACF) that simulated the "free air" cooling of a stack of FRG waste canisters. The third set of experiments would air-cool the canisters quickly from 800 to 600°C to minimize devitrification-induced cracking, and then control the cooling from 550 to 350°C at 2°C/hr to minimize thermal-stress cracking. Following the controlled cooling to 350°C, the canisters would then be allowed to cool to steady-state conditions sequentially first in the ICP and then in the ACF, resulting in nearly crack-free glass.

Instrument Sensors

As discussed in the prior Quarterly Progress Report, each German-built canister was fitted with an identical array of 15 dual-sensor thermocouples to monitor the internal glass temperatures. The thermocouples were arranged in three radial arrays of five each, with one array located about midway between the top and the bottom of the glass, and the other two arrays symmetrically located 82% of the distance from the middle array to the top or the bottom of the glass. Each of the three thermocouple arrays in each canister was an identical horizontal radial array, with the tip of one thermocouple positioned exactly on the centerline of the canister and the tips of the others at equal incremental radial distances between the centerline and the inner surface of the canister.

Each canister was fitted identically with two internal acoustic emission waveguides to carry the sounds of the cracking glass to external sensing devices. One waveguide was linear and extended straight to the bottom of the glass, with the other end connected to the sensor. The other waveguide formed a loop that extended to the bottom of the glass, with both ends connected to its sensing device.

Test Equipment

Following modifications to the remelt furnace (which added more insulation at the top and bottom of the furnace, a thermal baffle in the annulus between the canister and the furnace wall, and an acoustic emission sensor on the bottom of the furnace floor), the remelt furnace was moved into the Radioactive Engineering B-Cell facility in the 324 Building. There it was positioned in front of the south shielded viewing window of the first floor operating gallery.

Acoustic emission waveguides and sensors were installed in the bases of the ICP and the ACF. The two instrumented canisters are fitted with two acoustic emission sensors, one with a loop waveguide and the other with a linear waveguide, imbedded directly in the glass. The external sensors in the remelt furnace, the ICP and the ACF, are, however, of use only as back-up devices in case the primary in-glass sensors failed.

The remelt furnace was remotely controlled with a digital programmable controller located in the B-Cell operating gallery. Thermocouple data was automatically scanned with a desktop computer and a data logger once every 60 seconds. Once every 300 seconds the previous five data values for each sensor were averaged and stored on a hard disk. Once an hour a status report was automatically generated listing the sensors and their last averaged values. Graphic plots of any sensor value versus time were available on demand to operating personnel.

Acoustic emission data were automatically collected with an acoustic emission analyzer. Graphic plots of total acoustic emission events versus time were available on demand to operating personnel.

Experiment Schedule

Ten cooling experiments were completed during the report period. Table 1 shows the experiment schedule that was followed.

Although the nonisothermal characteristics of the remelt furnace noted during the design verification tests were partially corrected with the thermal baffle inserted into the furnace, it was still necessary to raise the crack-healing furnace temperature from 800 to 825°C to ensure that the very top and bottom of the canister glass was 800°C throughout the soak. It was also found necessary to introduce a continuous low flow of cooling air in the lower part of the furnace to hold down the mid-level glass temperatures. This technique reduced the temperature difference between the mid-level and the top and bottom of the glass from 150 to 50°C. However, the air was introduced at a single point in the lower furnace and did impinge directly on the canister wall, creating a relatively cool spot on one side of the canister.

Examination of the thermal data collected during the controlled cooling experiments suggested that some of the cooling techniques initially requested were resulting in short-term temperature changes of more than 2°C/hr that could be causing some glass-cracking instead of resulting in a crack-free

TABLE 1. Schedule of FRG Thermal Fracturing Tests

Canister	Air Cooling Frame		Insulated Cooling Pod		Controlled Cooling	
	#1	#2	#1	#2	#1	#2
19 (unlined)	1(a) 4/27/87	3 5/04/87	7 6/01/87	11	5 5/07/87	6 5/25/87
					13	9 6/12/87
	14	--	2 4/29/87	4 5/05/87	8 6/02/87	10 6/22/87
13 (lined)						12

(a) Experiment numbers are indicated. Below these are the dates the experiments were started.

glass. To improve the reference "crack-free" thermal data, experiments 5 and 10 were scheduled to be repeated (as experiments 12 and 13).

FRG HEAT AND RADIATION SOURCE PRODUCTION

As reported in the prior Quarterly Progress Report, the third and final FRG canister production campaign (RLFCM-9) was completed during the last of March 1987. Table 2 summarizes the major technical statistics of the 30 isotopic heat and radiation sources produced for the FRG during these three production campaigns.

TABLE 2. Summary Canister Data Estimated for the FRG Isotopic Heat Sources

	<u>Sequence</u> <u>Number</u>	<u>FRG Canister</u> <u>Number</u>	<u>Glass</u> <u>Volume, L</u>	<u>Glass</u> <u>Mass, kg</u>	<u>Cs-137</u> <u>Content, kCi</u>	<u>Sr-90</u> <u>Content, kCi</u>	<u>Decay</u> <u>Heat, W</u>	<u>Surface</u> <u>Dose, R/hr</u>
<u>RLFCM-7</u>	1	1	80.9	189	190	100	1578	238,000
	2	2	59.3	187	194	109	1864	286,000
	3	4	59.4	159	176	99	1500	233,000
	4	5	59.8	158	192	88	1515	273,000
	5	6	59.3	153	198	75	1449	293,000
	6	7	83.5	149	198	73	1435	284,000
	7	8	59.4	183	237	88	1723	282,000
	8	12	83.1	171	197	77	1482	235,000
	9	17	80.8	157	178	87	1299	238,000
	10	14	80.8	156	190	70	1380	282,000
<u>RLFCM-8</u>	11	21	80.2	153	187	90	1499	255,000
	12	28	84.2	186	170	130	1687	219,000
	13	34	83.8	183	137	147	1840	172,000
	14	33	81.8	144	55	148	1248	95,000
	15	36	84.2	182	74	158	1417	106,000
	16	37	58.8	151	47	158	1271	79,000
	17	41	80.9	159	38	159	1247	58,000
	18	42	80.2	168	28	148	1108	44,000
	19	43	80.2	155	18	150	1093	33,000
	20	44	58.8	152	17	145	1058	28,000
<u>RLFCM-9</u>	21	10	59.8	158	182	142	1827	275,000
	22	18	80.2	180	197	143	1908	284,000
	23	20	59.8	159	194	142	1877	289,000
	24	38	59.3	159	198	142	1892	277,000
	25	45	59.7	159	191	137	1832	320,000
	26	46	59.1	157	218	138	1961	286,000
	27	47	59.3	181	212	128	1882	290,000
	28	48	82.9	185	233	120	1924	313,000
	29	49	81.0	154	221	103	1747	283,000
	30	50	59.8	155	221	105	1785	287,000

CONCLUSIONS

In general, the programmable temperature controllers performed very well in regulating the temperature of the glass in the canisters. The two controllers used the outside thermocouples of the top and bottom thermocouple arrays as feedback for the controllers regulating the power to the upper and lower heating elements of the remelt furnace. While this arrangement introduced some lag in the control system, the automatic tuning capability of the controllers provided almost flawless control in ramping the temperatures both up and down at their prescribed rates. There was some problem, however, with the furnace's nonisothermal characteristics: the mid-level was always 50 to 150°C hotter than the top and bottom levels, which were controlled. Introducing cooling air into the lower furnace area appears to reduce this temperature difference effectively.

Operation of the data acquisition and display system has been very satisfactory, with the historical data plotting capability showing very clearly the performance of the temperature control system. Canister 19, used extensively in the design verification tests, has lost significantly more thermocouple sensors than has canister 13. It is suspected that flexing of the bundle of thermocouple extension cable wires causes the failures.

CANISTER FILLING AND HANDLING SYSTEMS

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SUMMARY

The Nuclear Waste Treatment Program (NWTP) at the Pacific Northwest Laboratory (PNL) is preparing radioactive canisters containing borosilicate glass for use by the Federal Republic of Germany (FRG) in high-level waste repository-related tests. The canisters, now filled, will be welded closed and decontaminated. Electropolishing was selected as the primary decontamination approach, and an electropolishing system with associated canister inspection equipment was designed and fabricated for installation in a large hot cell.

During the reporting period, ten preliminary tests of the electropolishing system were conducted, as described here, to gain information on the operating characteristics of the electropolisher and to develop operating parameters.

INTRODUCTION

The Department of Energy has a project agreement with the Federal Ministry for Research and Technology in the FRG to provide canisters of radioactive waste for the German repository testing program. PNL is providing the vitrified waste in sealed stainless steel canisters. Before shipment, the filled canisters will be inspected and decontaminated: the smearable surface radionuclides will not exceed 22,000 dis/min-100 cm² beta-gamma. (Because transuranic radionuclides are not contained in the waste, no alpha contamination will be present.)

An electropolishing system was constructed for canister decontamination. Electropolishing is an electrochemical process that has been used extensively by industry for many years to produce a smooth, polished surface on a variety

of metals and alloys. It is also a rapid, versatile, and effective technique for removing a variety of radionuclides, including plutonium, uranium, radium, cobalt, strontium, cesium, and americium. Moreover, it is very effective at removing baked-on and ground-in contamination, which has proved difficult to remove with other procedures.

TECHNICAL PROGRESS

The electropolishing system at PNL is a complex and unique piece of equipment designed and fabricated for remote operation. Since an electropolishing system of sufficient size to process the canister of glass produced by the radioactive liquid-fed ceramic melter has not been previously designed or demonstrated, a sizable effort is necessary to verify the performance of engineered design features. The system requires extensive nonradioactive testing before it is installed in A-Cell.

Functional testing of the canister electropolisher system was performed in the high-bay extension of 324 Building. Experiments were started in April 1987 and continued throughout the reporting period, with ten tests performed. There were two primary objectives in this quarter's testing. The first was to determine the operating characteristics of the electropolisher system. The system was tested using FRG canisters filled with sand or nonradioactive glass to determine the handling characteristics. The second objective was to accomplish the electropolishing of an oxidized FRG canister. In this testing the removal of the oxide from the surface was evaluated as well as the appearance of the canister surface. An acceptable electropolished FRG canister will have 1 to 3 mils of material removed from the surface and have a spectral emissivity of at least 0.4. Some tests used thermally oxidized FRG canisters to simulate actual conditions.

The first operation of the electropolisher was to check electrical continuity and operation of the power supply. It showed that the system operated correctly with no electrical shorts except that expected due to electrolyte conductance.

In the second test a nonoxidized canister was electropolished at three positions on the canister wall. At the first two positions the system was

operated at an anodic current density (the current density in amperes per square decimeter on the canister surface) of 35 A/dm^2 , and these areas were slightly polished. The third position was electropolished at 70 A/dm^2 , which resulted in a highly polished surface. It was noted that the areas previously electropolished changed in appearance when the canister was repositioned and electropolished.

The third test electropolished an oxidized canister at three positions and at the bottom. Current densities were up to 104 A/dm^2 . The first pass removed the oxide from the canister in a 6-to-7-in. band around the canister. This band indicated good current directional patterns. After electropolishing at the second position, almost all oxide was removed from the entire canister. This indicated that stray currents were acting on the canister surface although current densities were low at positions other than directly opposite the cathode. The bottom of the canister was only slightly polished, and the dimple in the bottom was not polished. The power cables became quite hot with operation at 104 A/dm^2 .

In the fourth test, an attempt to electropolish an oxidized canister, it was found that the electrically insulating material had not adhered to the cathode cage surface and that electrical short circuiting was causing the current to be distributed over the entire canister. Testing revealed that stray currents originating from the back side of the uncoated cathode ring would result in uncontrolled electropolishing of the sides of the canister. The canister was only slightly polished after operation at a current density of 35 A/dm^2 . It was noted that the cathode cage was polished in areas, and stray currents could also potentially be electropolishing areas on the electropolisher tank. Therefore, electrically nonconductive coatings were tested in the laboratory in a mini-electropolisher to evaluate their behavior. Based upon these tests, neoprene and a retort cement were selected to evaluate in the electropolisher. Laboratory tests revealed that unacceptable coatings failed because hydrogen bubbles formed on the cathode surface. If the coating was even slightly porous, hydrogen generation beneath the surface caused the coating to separate from the metal cathode.

Experiments 5 and 6 were performed to evaluate coatings for the cathode cage in order to prevent the electrical short circuiting. First an

unoxidized canister was electropolished to evaluate neoprene coating on the cathode cage. The canister was electropolished satisfactorily, but the neoprene coating did not adhere to the cathode cage. Next a test canister was electropolished to evaluate a retort cement coating on the cathode cage. The canister was electropolished satisfactorily, and the retort cement coating on the cathode cage adhered well.

The seventh test was performed on an unoxidized canister to evaluate the effect of current density on the electropolished canister surface. Current density settings of 7, 17.5 and 35 A/dm² were tested. One area of the surface was electropolished at 35 A/dm², which produced a moderately polished surface. Electropolishing at a position near the canister center was performed first at 35 A/dm², and resulted in a very polished surface. The canister was then electropolished at the lower current densities of 17.5 and then 7 A/dm². Although polishing occurred at the 17.5 A/dm², the surface appeared less polished than with the 35 A/dm² setting. At 7 A/dm² the surface appeared to be electropolished, but the finish was flat and dull.

In the eighth test an oxidized canister was processed to determine the characteristics achieved when an entire canister wall is electropolished from top to bottom in 6-in. increments. Current densities were 35 and 70 A/dm². First the top 6 in. of canister wall were electropolished for 5 min and inspected. Since not all the oxide was removed in this period, the area was electropolished 5 min more at the same current density, 35 A/dm². The result was a shiny polished surface. The canister was then electropolished by lifting the canister in 6-in. increments and electropolished at each position for 5 min at 70 A/dm². The canister surface appeared darker near the top than did the lower canister wall (Figure 1). The darkened surface was nearly the color of iron rust, or a golden brown. It is thought that lifting the canister from the electrolyte and exposing each successive 6-in. length to the air above the electrolyte caused the discoloration, but the exact mechanism by which the surface was discolored is not known.

In experiment 9, the canister used in experiment 8 was electropolished in an attempt to reverse the discoloration of the surface. It was first lowered into the electrolyte, electropolishing in incremental 6-in. lengths at a current density of 17.5 A/dm². Then the canister wall was

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FIGURE 1. Test Canister Showing Bands and Discoloration Following Electropolishing Experiment 8

electropolished by incrementally raising the canister 6 in. at a time and electropolishing at 35 A/dm^2 . Inspection after electropolishing at 17.5 A/dm^2 showed that the surface was no longer discolored and that the entire canister wall had an even polish. After electropolishing at 35 A/dm^2 the canister appeared more evenly polished, although not so highly as when electropolished at 70 and 104 A/dm^2 as in previous experiments. The lowest

6 in. of the canister wall was shiny compared to the rest above that position. To attempt to matte that 6-in. band, the canister was positioned so that the bottom was above the cathode ring and the current density would be lower on this portion of the wall. After polishing in this position for 5 min at 35 A/dm^2 , the lowest 6 in. showed a more matte-like finish but was still not as dull as the rest of the canister wall. The lid was electropolished at 70 A/dm^2 and was very shiny and polished after 5 min.

In the final experiment of the quarter, an oxidized canister was electropolished to determine whether results achieved in experiment 9 could be accomplished with one pass through the cathode ring but at a current density of 70 A/dm^2 . The resulting surface appeared shiny, but two distinct rings were observed on the canister wall, one exactly 6 in. from the lid and the other 12 in. from it. This phenomenon was believed to be caused by the same mechanism as in experiment 8. The canister had been electropolished while incrementally raising the canister 6 in. at a time, exposing it to the atmosphere while electropolishing at positions lower on the canister wall. The exact 6-in. separation between rings confirmed that the rings formed because the canister was raised out of the electrolyte.

At this time the anode grapple malfunctioned, requiring repair. After this repair, testing will continue in order to define operating parameters.

CONCLUSIONS

These initial tests provided preliminary information on the operating characteristics of the electropolisher. They were also important in the early development of operational parameters to produce acceptable canister surfaces. Additional work remains to be done on electropolishing of the canister lid and bottom, and operating parameters will be further refined to achieve the required 0.4 spectral emissivity.

After these tests are completed, the electropolisher system will be installed in A-Cell for decontaminating the radioactive FRG canisters.

APPENDIX

ACRONYMS AND ABBREVIATIONS

°C - degrees centigrade
Å - angstrom
ACF - air cooling frame
cm - centimeter
CRW - cladding removal waste
CVS - composition variability study
DG - doped glass
DOE - Department of Energy
E1150 - electrical conductivity at 1150°C
FRG - Federal Republic of Germany
g - gram
HBCM - high-bay ceramic melter
HT-S - heat-treated sample
HW - Hanford waste
HWVP - Hanford Waste Vitrification Plant
ICP - inductively coupled argon plasma emission spectroscopy
ICP - insulated cooling pod
kCi - kilocurie
kg - kilogram
kW - kilowatt
L - liter
LFCM - liquid-fed ceramic melter
μ - micron
m - meter
MCC - Materials Characterization Center
min - minute
mL - milliliter
MTU - metric ton of uranium
NCAW - neutralized current acid waste
NWTP - Nuclear Waste Treatment Program
PNL - Pacific Northwest Laboratory
PSCM - pilot-scale ceramic melter
redox - chemical reduction oxidation
RLFCM - radioactive liquid-fed ceramic melter
SA/V - surface area to volume (ratio)
SEM - scanning electron microscopy
SEM/EDX - scanning electron microscopy/energy dispersive x-ray
SRAT - slurry receipt and adjustment tank
T100P - the temperature at which viscosity is 100 poise
TA - Technical Advisory
TC - test canister
TOC - total organic carbons
W - watts
wt% - weight percent
WVDP - West Valley Demonstration Project
WVNS - West Valley Nuclear Services Company, Inc.
XRD - x-ray diffraction

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