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LFCM Vitrification Technology

Quarterly Progress Report

July - September 1987

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

September 1988

Prepared for the U.S. Department of Energy
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LFCM VITRIFICATION TECHNOLOGY

QUARTERLY PROGRESS REPORT JULY-SEPTEMBER 1987

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

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September 1988

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SUMMARY

This report is compiled by the Nuclear Waste Treatment Program (NWTP) and the Hanford Waste Vittrification Program (HWVP) at Pacific Northwest Laboratory (PNL)^(a) 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 fourth quarter of FY 1987 is discussed: melting process chemistry and glass development, feed preparation and transfer systems, canister filling and handling systems, and process/product modeling and control.

Melting Process Chemistry and Glass Development - Two alternatives were evaluated for providing increased flexibility in the processing and composition of the HWVP pretreated neutralized current acid waste (NCAW). The first involved adjusting the HWVP reference frit to allow for additional sodium from the waste while maintaining the glass composition. The second alternative addressed adding SiO_2 or sodium in place of part of the frit to adjust the temperature at which the melt viscosity is 100 poise (T100P). The use of compositional ratios (the ratios of selected glass components to other glass components), such as the ratio of total alkali oxides to SiO_2 , to predict the T100P of a melt based on composition was also evaluated.

This study showed that up to 5 wt% Na_2O can be removed from the HW-39 frit composition and still maintain a commercially producible frit. This would allow for up to a 20 wt% increase of Na_2O in the NCAW'84 waste (from 11.1 to 31.1 wt% Na_2O), an approximate 16 wt% increase in the NCAW'86 waste (from 17.2 to 33.5), without changing the glass composition.

Glass compositional ratios were found to provide a good method of estimating the T100P of glass melts based on composition. The ratios using the total weight percent of alkali oxides over the sum of the weight percents of SiO_2 , Al_2O_3 , and ZrO_2 were found to predict the T100P sufficiently for glass development, feed rheology studies, melter testing, and potentially for HWVP process control.

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The addition of SiO_2 or sodium in place of some portion of the frit can adjust feed compositions. Feed compositions that would yield glass viscosities outside the range required for melter operation could be adjusted to a composition that would give a glass viscosity acceptable for melter operation.

PNL is examining the effects of composition, ferrous/ferric ratio (redox state), heat treatment, and groundwater on the chemical durability of a glass proposed for solidification of West Valley nuclear waste. Several experiments have been conducted, and preliminary results are given.

The results of the experiments conducted to date indicate that waste glass is more durable in groundwater than in deionized water; also, durability is affected by isothermal and simulated canister cooling heat treatments. However, the durability of the waste glass is not strongly affected by the variation of glass redox state. Linear mixture models were fitted to the glass compositional variation data and validated. These models may be used to predict the effects of varying specific components on durability of the reference glass within the defined composition region.

Feed Preparation and Transfer Systems - An experimental study was completed to qualify and quantify the off gases released during formic acid addition to HWVP feed simulant. An experimental study was completed to establish the heat-transfer characteristics of a simulated HWVP feed in a bench-scale system. The effect of feed composition and formic acid addition on glass redox state has been investigated and reported on. The results from these three studies are summarized here.

A statistical feed process variability study using nonradioactive feeds has been designed and a test plan issued.

Canister Filling and Handling Systems - A simple, effective method to decontaminate canister exteriors is being developed for West Valley Nuclear Services Co., Inc. It employs a reduction/oxidation system [$\text{Ce(IV)}/\text{Ce(III)}$] in nitric acid solution to chemically mill a thin layer from the canister surface, removing surface contamination as canister surface dissolves. Potential advantages of this process over others evaluated include: more effective decontamination, simpler equipment requirements, fewer support

service requirements, single-use throwaway solution, process-compatible waste stream, and compatible time-cycle requirements.

The NWTP at PNL is preparing 30 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 to install in a large hot cell. Preliminary tests of the system were conducted earlier to gain information on operating characteristics and develop operating parameters. During this reporting period, the final tests of the series were performed. In these tests, the operating parameters were further refined in preparation for electropolishing the FRG canisters filled with radioactive borosilicate glass. In addition, a series of thermal fracturing tests for the FRG was completed using two specially instrumented canisters, the data from the tests were transmitted to the sponsor, and the test facility was dismantled.

Process/Product Modeling and Control - A simulation model has been developed and tested preliminarily by applying it to approximate operation of the West Valley Demonstration Project (WVDP) vitrification system. A control logic for the WVDP process was approximated and cast in the form of an input file as required by the simulation model. Multivariate statistical techniques have been identified and described that can be applied to analyze large sets of process measurements.

The TEMPEST heat-transfer computer code was used to simulate thermal behavior of nuclear waste glass in canisters of varying dimensions. The experimental data obtained provided a sufficiently accurate basis for validation of this code.

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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; Brouns and Powell 1988), and formal topical reports. Because of both

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the magnitude of the 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 Westinghouse Hanford Company 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 - S. O. Bates and M. A. H. Reimus et al.
- Feed Preparation and Transfer Systems - M. E. Peterson et al.
- Canister Filling and Handling Systems - L. K. Holton, Jr., et al.
- Process/Product Modeling and Control - W. L. Kuhn 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

Brouns, R. A., and J. A. Powell, compilers. 1988. Nuclear Waste Treatment Program Annual Report for FY 1987. PNL-6686, Pacific Northwest Laboratory, Richland, Washington.

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

S. O. Bates, M. A. H. Reimus, G. F. Piepel, and G. B. Mellinger

SUMMARY

HANFORD WASTE VITRIFICATION PLANT (HWVP)

Two alternatives were evaluated for providing increased flexibility in the processing and composition of the Hanford Waste Vitrification Plant pretreated neutralized current acid waste (NCAW). The first alternative involved adjusting the HWVP reference frit to allow for additional sodium from the waste while maintaining the glass composition. The second alternative addressed adding SiO_2 or sodium in place of some portion of the frit to adjust the temperature at which the melt viscosity is 100 poise (T100P). The use of compositional ratios (the ratios of selected glass components to other glass components), such as the ratio of total alkali oxides to SiO_2 , to predict the T100P of a melt based on composition was also evaluated.

This study showed that up to 5 wt% Na_2O can be removed from the HW-39 frit composition and still maintain a commercially producible frit. Removing this amount of Na_2O from the frit would allow for up to a 20 wt% increase of Na_2O in the NCAW'84 waste (from 11.1 to 31.1 wt% Na_2O), an approximate 16 wt% increase in the NCAW'86 waste (from 17.2 to ~33.5), without changing the glass composition.

Glass compositional ratios were found to provide a good method of estimating the T100P of glass melts based on composition. The ratios using the total weight percent of alkali oxides over the sum of the weight percents of SiO_2 , Al_2O_3 , and ZrO_2 were found to predict the T100P sufficiently for glass development, feed rheology studies, melter testing, and potentially for HWVP process control.

The addition of SiO_2 or sodium in place of some portion of the frit can adjust feed compositions. Feed compositions that would yield glass viscosities outside the range required for melter operation could be adjusted to a

composition that would give a glass viscosity acceptable for melter operation.

WEST VALLEY DEMONSTRATION PROJECT (WVDP)

Pacific Northwest Laboratory (PNL) is examining the effects of composition, ferrous/ferric ratio (redox state), heat treatment, and groundwater on the chemical durability of a glass proposed for solidification of West Valley nuclear waste. Several experiments have been conducted, and preliminary results are given.

The results of the experiments conducted to date indicate that waste glass is more durable in groundwater than in deionized water; also, durability is affected by isothermal and simulated canister cooling heat treatments. However, the durability of the waste glass is not strongly affected by the variation of glass redox state. Linear mixture models were fitted to the glass compositional variation data and validated. These models may be used to predict the effects of varying specific components on durability of the reference glass within the defined composition region.

INTRODUCTION

The objectives of the melting process chemistry and glass development effort are to develop glass and melter feed compositions that will produce glass products having acceptable chemical durability and 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 to form other 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 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 or high-bay ceramic melter.

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 PLANT

The HWVP will be required to process wastes with a wide range of compositions and physical properties, including pretreated NCAW, complexant concentrate waste, Plutonium Finishing Plant waste, and possibly single-shell tank waste and cladding removal waste. The HWVP reference borosilicate glass has demonstrated significant flexibility to handle variations in NCAW waste composition while maintaining the required processing properties. Additional pretreatment and processing flexibility may be required in addition to the reference glass composition's flexibility. This additional flexibility can be gained through the method by which waste and glass-forming components are added together to produce the reference glass composition.

The objective of this study was to assess the viability of potential scenarios to expand the current specifications of waste and frit components to allow for greater pretreatment and processing flexibility. This would provide B Plant with needed additional operating flexibility. These studies are based on glass and frit compositions and properties only. Before being considered fully acceptable, the scenarios identified here must be verified in slurry feed rheology and melter tests as capable of being readily processed.

The HW-39 glass, frit, and NCAW'84 (0.13 wt% Cr_2O_3) waste compositions (see Table 1) were used as a basis for these tests to allow for the use of models and data generated in previous variability testing. Where applicable, conclusions and comments with regard to the modified reference waste (NCAW'86) composition (Table 2) are also made.

The two methods evaluated to provide additional process adjustment in this study were 1) adjustment of the frit to allow for additional sodium from the waste and 2) use of SiO_2 or sodium additions in place of some portion of the frit to adjust the temperature at which the melt viscosity is 100 poise (T100P). The use of compositional ratios such as the $(\text{alkali})_2\text{O}/\text{SiO}_2$ in a glass composition to predict the T100P of a melt based on composition was also evaluated as a method of controlling process adjustments.

Frit Adjustment

Glass is an amorphous material composed of a random network of coordinated structural units. In borosilicate glasses, these networks are composed of silica and boron oxygen polyhedra. Elements such as silicon and boron, which form the network of the glass, are termed network (glass) formers. Elements such as the alkalis (e.g., lithium, sodium, and krypton) and alkaline earths (e.g., magnesium and calcium) provide additional oxygen ions that modify the network structure. These elements are called network modifiers. Cations of higher valence and lower coordination numbers than the alkalis and alkaline earths may either reinforce or further loosen the network and are referred to as intermediates. The NCAW waste is composed chiefly of glass modifiers and intermediates. Sufficient amounts of glass formers (as frit) are added to produce the glass network that will incorporate and immobilize the modifiers and intermediates from the waste. The frit also contains additional modifiers to adjust glass properties such as viscosity and electrical conductivity to meet processing requirements.

As the reference glass composition consists of 25 wt% waste and 75 wt% frit, frit modification can provide much flexibility for varying the waste. At a 25 wt% waste loading, every 1 wt% of frit component modified provides for a 4 wt% change in the same component in the waste. At present, most of the frit components are not in the waste or have small expected

TABLE 1. Compositions of the NCAW'84 (low chrome) Reference Waste, Substituted Waste, and Glass (HW-39) at 25 wt% Oxides Waste Loading

Oxide	Normalized Waste, Wt% Oxide	Substituted Waste, Wt% Oxide	Substituted Waste Normalized, Wt% Oxide	Substituted Waste Normalized, No TOC(a)	HW-39 Frit, Wt% Oxide	HW-39 Glass, Wt% Oxide
SiO ₂	3.09	3.09	3.12	3.14	67.25	51.22
B ₂ O ₃	0.01	0.01	0.01	0.01	12.76	9.66
Na ₂ O	11.1	11.1	11.1	11.3	10.26	10.62
Li ₂ O	0.08	0.8	0.0	0.0	6.00	3.76
CaO	0.31	0.31	0.31	0.31	3.76	2.89
MgO	0.26	0.35	0.35	0.35	1.00	0.84
Fe ₂ O ₃	46.3	46.3	46.9	47.2	--	11.79
ZrO ₂	2.6	2.6	2.6	2.6	--	0.63
Al ₂ O ₃	17.9	17.9	18.1	18.2	--	4.56
NiO	2.47	2.47	2.60	2.62	--	0.63
La ₂ O ₃	2.29	2.29	2.31	2.33	--	0.56
TOC	0.62	0.62	0.62	--	--	0.00
Hf ₂ O ₃	1.79	2.07	2.09	2.11	--	0.53
SO ₃	1.54	1.54	1.56	1.67	--	0.39
F	1.24	1.24	1.26	1.26	--	0.31
MoO ₃	1.24	1.24	1.26	1.26	--	0.31
U ₃ O ₈	0.62	SUB Nd (a)	SUB Nd	SUB Nd	--	--
CoO ₂	0.62	0.62	0.62	0.63	--	0.16
Ca ₂ O	0.62	0.62	0.62	0.63	--	0.16
CuO	0.62	0.62	0.62	0.63	--	0.16
MnO ₂	0.62	0.62	0.62	0.63	--	0.16
RuO ₂	0.62	0.62	0.62	0.63	--	0.16
Cr ₂ O ₃	0.66	0.66	0.66	0.67	--	0.14
BaO	0.48	0.43	0.44	0.44	--	0.11
Pr ₆ O ₁₁	0.37	0.37	0.37	0.38	--	0.09
SrO	0.37	0.37	0.37	0.38	--	0.09
Tc ₂ O ₇	0.37	DEL (a)	DEL	DEL	--	--
PdO	0.19	0.19	0.19	0.19	--	0.06
Rb ₂ O	0.26	0.26	0.26	0.26	--	0.06
Rh ₂ O ₃	0.19	0.19	0.19	0.19	--	0.06
Sr ₂ O ₃	0.19	0.19	0.19	0.19	--	0.06
Y ₂ O ₃	0.19	0.19	0.19	0.19	--	0.06
Ba ₆	0.06	SUB Mg	SUB Mg	SUB Mg	--	--
NpO ₂	0.12	DEL	DEL	DEL	--	--
TeO ₂	0.12	DEL	DEL	DEL	--	--
K ₂ O	0.00	DEL	DEL	DEL	--	--
PbO ₂	0.00	DEL	DEL	DEL	--	--
SeO ₂	0.03	--	DEL	DEL	--	--
Am ₂ O ₃	0.02	DEL	DEL	DEL	--	--
CdO	0.02	DEL	DEL	DEL	--	--
Eu ₂ O ₃	0.02	SUB Nd	SUB Nd	SUB Nd	--	--
P ₂ O ₅	0.02	DEL	DEL	DEL	--	--
PuO ₂	0.02	DEL	DEL	DEL	--	--
SnO ₂	0.02	DEL	DEL	DEL	--	--
Ag ₂ O	0.01	DEL	DEL	DEL	--	--
Gd ₂ O ₃	0.01	DEL	DEL	DEL	--	--
Nb ₂ O ₅	0.01	DEL	DEL	DEL	--	--
Pm ₂ O ₃	0.01	SUB Nd	SUB Nd	SUB Nd	--	--
Ta ₂ O ₅	0.01	DEL	DEL	DEL	--	--
TiO ₂	0.01	DEL	DEL	DEL	--	--
	100	98.869	100	100	100	100

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

TABLE 2. NCAW'86 and NCAW'84 Compositions, wt%

Oxide	NCAW'86 Normalized Waste	Reference NCAW'84 Waste	Oxide	NCAW'86 Normalized Waste	Reference NCAW'84 Waste
Fe ₂ O ₃	28.0	46.3	Rb ₂ O	0.20	0.25
Na ₂ O	17.5	11.1	Rh ₂ O ₃	0.20	0.19
ZrO ₂	15.0	2.50	Sm ₂ O ₃	0.20	0.19
Al ₂ O ₃	10.0	17.9	Y ₂ O ₃	0.20	0.19
SiO ₂	9.01	3.09	B ₂ O ₃	0.10	0.00
NiO	2.30	2.47	BeO	0.10	0.06
La ₂ O ₃	2.00	2.29	NpO ₂	0.10	0.12
TOC	2.00	0.62	TeO ₂	0.10	0.12
Nd ₂ O ₃	1.90	1.79	K ₂ O	0.05	0.00
SO ₃	1.80	1.54	PbO ₂	0.05	0.00
F	1.20	1.24	SeO ₂	0.03	0.03
MoO ₃	1.20	1.24	Am ₂ O ₃	0.02	0.02
U ₃ O ₈	0.70	0.62	CdO	0.02	0.02
CeO ₂	0.60	0.62	Eu ₂ O ₃	0.02	0.02
Cs ₂ O	0.60	0.62	P ₂ O ₅	0.02	0.02
CuO	0.60	0.62	PuO ₂	0.02	0.02
MnO ₂	0.60	0.62	SnO ₂	0.02	0.02
RuO ₂	0.60	0.62	Ag ₂ O	0.01	0.01
Cr ₂ O ₃	0.50	0.56	Gd ₂ O ₃	0.01	0.01
BaO	0.40	0.43	Nb ₂ O ₅	0.01	0.01
Pr ₆ O ₁₁	0.40	0.37	Pm ₂ O ₃	0.01	0.01
SrO	0.40	0.37	Ta ₂ O ₅	0.01	0.01
Tc ₂ O ₇	0.40	0.37	TiO ₂	0.01	0.01
CaO	0.30	0.31	Li ₂ O	0.00	0.00
MgO	0.20	0.25			
PdO	0.20	0.19	Total	100	100

variabilities. The exception is sodium: changes in washing efficiency at B Plant significantly affect the amount of sodium in the waste. Laboratory tests were conducted to determine the minimum of Na_2O required in the frit. This made it possible to determine how much flexibility there may be for increasing sodium in the waste by removing Na_2O from the frit.

For large-scale commercial frit producers, the frit composition must be workable below 1250°C . A good indication of workability is the temperature at which the viscosity of the glass is 100 poise (T100P). Other factors are also important, such as the rate the viscosity of the frit increases with decreasing temperature and the devitrification characteristics. Furthermore, the frit composition must be submitted to commercial frit producers to determine whether the frit can be produced. For this study it was assumed that if a frit composition had a T100P of below 1250°C it would be considered viable. However, even if a frit can be produced, it would not necessarily have the processing qualities required for the HWVP process. Factors such as melting behavior, cold-cap morphology, and melting rates must be confirmed in engineering-scale melter tests. The HW-39 reference frit has a T100P of 1108°C and has proved very processible in melter tests.

To start testing, a frit composition was formulated by removing all the Na_2O from the HW-39 reference frit and renormalizing the modified frit composition to 100%. This composition, designated Frit #1, is presented in Table 3. The melting point of Frit #1 was between 1250°C and 1300°C . At 1300°C the viscosity of the melt was about 200 poise. As the Frit #1 melt was removed from the furnace to be poured into bars, the viscosity was observed to increase very rapidly and glass crystallized immediately. The

TABLE 3. Compositions of Test Frits

Oxide	HW-39	Frit #1	Frit #2
SiO_2	67.25	74.93	70.98
B_2O_3	12.75	14.21	13.46
Na_2O	10.25	0.00	5.28
Li_2O	5.00	5.57	5.28
CaO	3.75	4.18	3.96
MgO	1.00	1.11	1.06

melt temperature had to be increased to 1400°C so that a melt could be easily poured from the melt crucible. The bars of Frit #1 looked like a totally crystalline white ceramic similar to porcelain. Frit #1 was deemed unacceptable based on the required melting temperature and viscosity properties.

For Frit #2 (Table 3), about half of the Na_2O (5 wt% of the reference 10.25 wt% total) was removed from the HW-39 reference frit and the composition renormalized to 100 wt%. Frit #2 melted at ~1200°C, but it was necessary to raise the temperature of the melt to 1300°C to allow for the fining of many bubbles in the melt. The T100P of Frit #2 was determined to be 1211°C. The rate of increase in the viscosity as the melt was poured was much less than with Frit #1, and the melt poured easily at 1300°C. While the air-quenched glass remained vitreous, the anneal bar was observed to have little crystallization. Based on melting point and viscosity, this frit composition was judged acceptable.

A commercial frit producer tentatively confirmed that Frit #2 would be viable.^(a) The general guideline obtained from the producer was that the SiO_2 remain below 72 to 73 wt% for a producible frit. Frit #2 meets this criterion. Frits, however, with SiO_2 concentrations above 68 wt% become difficult to produce because of the "shortness" of the glass. (The greater the change in viscosity versus temperature, the "shorter" the glass.) The producer would have to conduct limited testing before making a bid to produce Frit #2.

Removing up to 5 wt% Na_2O from the frit provides for the potential addition of sodium in the waste from 0 to 20 wt% as Na_2O . For the NCAW'84 waste, this would mean a Na_2O increase of from 11.1 wt% to as high as 31.1 wt% in the waste. The latest update of the NCAW composition, NCAW'86, has higher concentrations of Na_2O and ZrO_2 but lower concentrations of Fe_2O_3 and Al_2O_3 (see Table 3). All other differences in oxide concentration are too small to be of major significance in the glass. At a 25 wt% waste loading of NCAW'86, and using the HW-39 reference frit composition, the T100P of the resulting glass was 1086°C. If the revised NCAW composition for

(a) Personal communication with Bob Long of American Porcelain Enamel Co., Muskegon, Michigan, on July 17, 1987.

FY 1988 also has a similar level of alkali, the increased alkali could easily be compensated for by reducing the Na_2O by ~ 1 wt% and increasing the SiO_2 by 1 wt% in the frit. This change in frit composition should increase the T100P of the nominal glass composition nearer the center of the 1070°C to 1150°C range required for HWVP processing. Adjusting the T100P nearer the center of the acceptable range will provide more flexibility in melt viscosity as a result of waste composition variability. The ~ 1 wt% reduction of Na_2O required to increase the viscosity would mean that only 4 wt% Na_2O would be available for removal from the frit. Therefore the potential increase of sodium in NCAW'86 of 0 to 16 wt% as Na_2O would expand the Na_2O range in the waste from 17.5 to 33.5 wt%.

Because these potential modifications to the waste and frit would result in no net change in the final glass composition, glass variability ranges identified in previous variability studies would still be valid. The glass flexibility provides for an additional 2.7 wt% increase in Na_2O in the glass (10.8 wt% in the waste) before the T100P limits are exceeded. At an extreme, both the glass flexibility and the frit adjustment could be used to accommodate a maximum of about 42 wt% Na_2O in the NCAW'84 waste. However, it still needs to be verified in an engineering-scale melter test that the modified waste and frit compositions can be processed.

The removal of Na_2O from the frit would result in a harder, more durable frit. The rheology properties of the frit in the melter feed should be very similar to the reference frit. The effects of the increasing sodium in the waste on waste rheology should be investigated. The effects of frit adjustment on canister decontamination (frit blasting) also need to be evaluated.

Melter Feed Adjustments

If waste composition were to vary so much that critical glass processing properties would not be met, it may be possible to adjust the out-of-limits glass property to an acceptable value by adding certain elements to the melter feed to modify the feed and resulting glass composition. Variability studies have shown that the limiting glass property is usually melt viscosity and that if the viscosity of any of this family of waste glasses is acceptable, the other required processing properties also will be acceptable. For this reason, the two main scenarios evaluated were for a low- and

high-viscosity waste/glass composition. To keep process additions as simple as possible, only two types of additives were considered, one to raise melt viscosity (SiO_2) and one to lower it (sodium).

Viscosity Prediction

To determine whether an additive is needed and how much, a method to predict the melt viscosity based on composition must be available. The composition variability study (CVS) to be conducted for the HWVP process and waste-form qualification will be able to determine melt viscosity based on the feed composition. Both SiO_2 and Na_2O , as well as ZrO_2 , Al_2O_3 , Fe_2O_3 , CaO , and waste loading, will be included in the CVS. The CVS, however, is not projected to be completed until the end of FY 1989 and could be delayed until further data are available on the actual NCAW composition.

Other methods of varying accuracy are being evaluated to estimate the viscosity of nuclear waste glasses (Ilham and Hrma 1987). The Defense Waste Process Facility (DWPF) is evaluating the alkali/silicon ratio as a method of maintaining a constant melt viscosity. The DWPF is planning to use the alkali/silicon ratio to determine how much precipitate hydrolysis waste (high in alkali) to add to the sludge and frit. The DWPF, however, is not planning to use this ratio to adjust for compositional variations in the sludge.

To evaluate whether other compositional ratios similar to the alkali/silicon ratio could be used to predict the viscosity of HWVP glass compositions, various ones, as follows, were plotted against measured T100P values and evaluated:

- $\text{alk}_2\text{O}/\text{SiO}_2$ molar basis
- $\text{alk}_2\text{O}/(\text{SiO}_2+\text{Al}_2\text{O}_3+\text{ZrO}_2)$ molar basis
- $\text{alk}_2\text{O}/\text{SiO}_2$ wt% basis
- $\text{alk}/(\text{Si}+\text{Al}+\text{Zr})$ molar basis
- alk/Si molar basis
- $\text{alk}_2\text{O}/(\text{SiO}_2+\text{Al}_2\text{O}_3+\text{ZrO}_2)$ wt% basis

where alk is the sum of the lithium and sodium concentrations. The glasses used for this evaluation were previously studied HWVP glasses with low Cr_2O_3 concentrations (≈ 0.13 wt%). No previously studied high- Cr_2O_3 HWVP glasses were used so as to avoid the higher unstable viscosities caused by chrome crystalline phases. The glasses used are presented below, and their compositions are listed in Table 4.

TABLE 4. Glass Compositions Used in Compositional Ratio Evaluation, wt%

Oxide	HW-39	HW-43	HW-44	HW-45	HWVP-14 Melter Test Glass			
					Low Al ₂ O ₃	High ZrO ₂	High Na ₂ O	Low Fe ₂ O ₃
SiO ₂	51.21	52.76	49.86	46.97	51.37	50.91	51.12	51.43
B ₂ O ₃	9.56	9.59	8.96	8.32	9.56	9.56	9.56	9.56
Na ₂ O	10.48	12.21	12.60	12.99	11.05	9.41	13.18	11.27
Li ₂ O	3.75	3.75	3.50	3.25	3.75	3.75	3.75	3.75
CaO	2.89	2.89	2.72	2.55	2.91	2.86	2.88	2.91
MgO	0.85	0.84	0.81	0.78	0.87	0.81	0.83	0.87
Fe ₂ O ₃	11.72	7.23	8.68	10.12	14.08	7.20	10.29	8.00
ZrO ₂	0.61	3.87	4.65	5.42	0.74	10.00	0.54	0.78
Al ₂ O ₃	4.53	2.58	3.10	3.62	0.40	2.78	3.98	5.79
NiO	0.61	0.59	0.71	0.83	0.74	0.38	0.54	0.78
La ₂ O ₃	0.59	0.52	0.62	0.72	0.70	0.36	0.51	0.75
Nd ₂ O ₃	0.56	0.61	0.73	0.85	0.67	0.34	0.49	0.71
SO ₃	0.48	0.46	0.56	0.65	0.58	0.29	0.42	0.61
F	0.32	0.31	0.37	0.43	0.38	0.20	0.28	0.41
MoO ₃	0.32	0.31	0.37	0.43	0.38	0.20	0.28	0.41
CeO ₂	0.16	0.15	0.19	0.22	0.19	0.10	0.14	0.20
Cs ₂ O	0.16	0.15	0.19	0.22	0.19	0.10	0.14	0.20
CuO	0.16	0.15	0.19	0.22	0.19	0.10	0.14	0.20
MnO ₂	0.16	0.15	0.19	0.22	0.19	0.10	0.14	0.20
RuO ₂	0.16	0.15	0.19	0.22	0.19	0.10	0.14	0.20
Cr ₂ O ₃	0.14	0.13	0.15	0.18	0.17	0.09	0.12	0.18
BaO	0.11	0.10	0.12	0.14	0.13	0.07	0.09	0.14
Pr ₆ O ₁₁	0.11	0.10	0.12	0.14	0.13	0.07	0.09	0.14
SrO	0.11	0.10	0.12	0.14	0.13	0.07	0.09	0.14
PdO	0.05	0.05	0.06	0.07	0.06	0.03	0.05	0.07
Rb ₂ O	0.05	0.05	0.06	0.07	0.06	0.03	0.05	0.07
Rh ₂ O ₃	0.05	0.05	0.06	0.07	0.06	0.03	0.05	0.07
Sm ₂ O ₃	0.05	0.05	0.06	0.07	0.06	0.03	0.05	0.07
Y ₂ O ₃	0.05	0.05	0.06	0.07	0.06	0.03	0.05	0.07
Total	100	100	100	100	100	100	100	100

- HW-39, the HWVP (0.13 wt% Cr_2O_3) glass incorporating the NCAW'84 waste at a 25 wt% waste loading
- HW-43, the HW-39 frit and the NCAW'86 waste at a 25 wt% waste loading
- HW-44, the HW-39 frit and the NCAW'86 waste at a 30 wt% waste loading
- HW-45, the HW-39 frit and the NCAW'86 waste at a 35 wt% waste loading
- HWVP-14 melter test glasses based on the HW-39 glass composition at 25 wt% waste loadings (Nakaoka et al. 1986):

low Al_2O_3

high ZrO_2

high Na_2O

low Fe_2O_3

Table 5 summarizes the measured T100P values and the compositional ratios. Figure 1 is a plot of the compositional ratios versus T100P. It shows that $\text{alk}_2\text{O}/(\text{SiO}_2+\text{Al}_2\text{O}_3+\text{ZrO}_2)$ molar ratio, the $\text{alk}/(\text{Si}+\text{Al}+\text{Zr})$ ratio, and $\text{alk}_2\text{O}/(\text{SiO}_2+\text{Al}_2\text{O}_3+\text{ZrO}_2)$ wt% ratio appear to have the best linear fit to T100P. The $\text{alk}_2\text{O}/(x\text{SiO}_2+y\text{Al}_2\text{O}_3+z\text{ZrO}_2)$ ratio will be discussed later and is a

TABLE 5. Compositional Ratios and T100P Values for Evaluated Glass Compositions

Ratios	HW-30	HW-43	HW-44	HW-45	Low Al_2O_3	High ZrO_2	High Na_2O	Low Fe_2O_3
$\text{Alk}_2\text{O}/\text{SiO}_2$, mole	0.3457	0.3872	0.3861	0.4073	0.3553	0.3272	0.3978	0.3590
Alk/Si , mole	0.7959	0.8763	0.9423	1.0164	0.8284	0.7333	0.9654	0.8410
$\text{Alk}_2\text{O}/\text{SiO}_2$, wt%	0.2779	0.3024	0.3228	0.3458	0.2881	0.2584	0.3313	0.2920
$\text{Alk}_2\text{O}/(\text{SiO}_2+\text{Al}_2\text{O}_3+\text{ZrO}_2)$, mole	0.3268	0.3449	0.3568	0.3897	0.3513	0.2901	0.3783	0.3343
$\text{Alk}/(\text{Si}+\text{Al}+\text{Zr})$, mole	0.6935	0.6568	0.6774	0.6982	0.7272	0.4801	0.7485	0.6010
$\text{Alk}_2\text{O}/(\text{Al}_2\text{O}_3+\text{SiO}_2+\text{ZrO}_2)$, wt%	0.2528	0.2695	0.2794	0.2900	0.2818	0.2065	0.3044	0.2589
$\text{Alk}_2\text{O}/(x\text{SiO}_2+y\text{Al}_2\text{O}_3+z\text{ZrO}_2)$, wt%	0.6720	0.6986	0.7313	0.7651	0.7442	0.4624	0.8526	0.7021
T100P, °C	1081	1086	1078	1074	1075	1158	1048	1104

FIGURE 1. Compositional Ratios for HWVP Glasses Versus T100P

weighted $\text{alk}_2\text{O}/(\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{ZrO}_2)$. Using the fit line function in the RS1[®] program, lines were fitted to each of these three ratios. The linear fits have an equation in the form:

$$y = A(T100P) + B$$

where A and B are the unknown coefficients and y is the compositional ratio. The values of A and B with the R^2 (the fraction of the variation in the properties that is accounted for by the fitted line) values for each fitted line are presented in Table 6. These lines are also plotted in Figure 1.

Caution should be used with any of the above ratios to estimate T100P when the major changes in composition are not Na_2O , SiO_2 , Al_2O_3 , or ZrO_2 . As

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TABLE 6. Summary of Fitted Linear Coefficients and R² Values

Compositional Ratio	A	B	R ²
Alk ₂ O/SiO ₂ , wt%	-2.1411 x 10 ⁻³	3.2044	0.53
Alk/Si, mole	-6.6677 x 10 ⁻⁴	1.0288	0.54
Alk ₂ O/SiO ₂ , mole	-6.3135 x 10 ⁻⁴	1.0551	0.56
Alk ₂ O/(SiO ₂ +Al ₂ O ₃ +ZrO ₂), molar	-7.9245 x 10 ⁻⁴	1.2062	0.85
Alk/(Si+Al+Zr)	-2.6928 x 10 ⁻³	3.5751	0.88
Alk ₂ O/(SiO ₂ +Al ₂ O ₃ +ZrO ₂)	-9.9029 x 10 ⁻⁴	1.2256	0.90
(24•alk ₂ O) (7•SiO ₂)+(5•Al ₂ O ₃)+(13•ZrO ₂)	-3.3410 x 10 ⁻³	4.3385	0.93

these elements are the only ones used in the ratios, other elemental variations may not be accounted for. The HW-43, HW-44 and HW-45 glasses are based on NCAW'86 instead of NCAW'84, but the T100Ps for these glasses are predicted well by the fitted lines. However, the only major difference between these two waste compositions is the Na₂O, Al₂O₃, ZrO₂ and Fe₂O₃ concentrations. Iron has been found to have only minor effects on viscosity at the lower Cr₂O₃ concentration.

The above composition ratio/viscosity relationships also assume that the relative effect on viscosity of each of the components is the same and the effect of Na₂O on viscosity per weight percent has the same magnitude but in the opposite direction. Variability scoping tests that have evaluated Na₂O, SiO₂, Al₂O₃, and ZrO₂ have shown that each component will affect the melt viscosity to a different degree per weight percent change in concentration. Using the models developed from the variability scoping studies, the change in T100P per weight percent change in each was estimated. These estimates were made by maintaining a 25 wt% waste loading and exchanging each component individually with frit until a 1 wt% increase of the component was achieved in the glass composition. The predicted T100P was then subtracted from the predicted T100P for the reference glass to calculate the ΔT100P/wt% oxide for each component. These estimates of ΔT100P/wt% oxide values are summarized in Table 7.

TABLE 7. Estimated Change in T100P per Weight Percent Change in Glass Components

Component	$\Delta T100P/\text{wt\% Oxide, } ^\circ\text{C}$
Na_2O	-24
SiO_2	7
Al_2O_3	5
ZrO_2	13

To compensate for the different $\Delta T100P/\text{wt\% oxide}$ for each component, the $\text{alk}_2\text{O}/(\text{SiO}_2+\text{Al}_2\text{O}_3+\text{ZrO}_2)$ relationship was modified by multiplying the wt% of each component by its $\Delta T100P/\text{wt\% oxide}$ (i.e., only the Na_2O in the alk_2O was multiplied by 24). The compositional relationship now becomes

$$\frac{(\text{alk}_2\text{O} \cdot 24)}{(\text{SiO}_2 \cdot 7) + (\text{Al}_2\text{O}_3 \cdot 5) + (\text{ZrO}_2 \cdot 13)}$$

The resulting value for the above ratio for each glass is also listed in Table 6 and plotted in Figure 1 with its fitted line. The R^2 for this line is 0.93. Therefore, it can be concluded that the weighted ratio is only slightly better in predicting T100P than the other ratios evaluated.

All four ratios listed in Table 6 should provide a good estimate of T100P based on composition. However, because weight percent oxide is generally used to report glass compositions, the $\text{alk}_2\text{O}/(\text{SiO}_2+\text{Al}_2\text{O}_3+\text{ZrO}_2)$ wt% and the $\Delta T100P/\text{wt\% oxide weight alk}_2\text{O}/(x\text{SiO}_2+y\text{Al}_2\text{O}_3+z\text{ZrO}_2)$ relationships will be the most convenient to use and have the best fitted functions. As further data are generated, these $\text{alk}_2\text{O}/(\text{SiO}_2+\text{Al}_2\text{O}_3+\text{ZrO}_2)$ wt% versus T100P relationships should be further refined and quantified statistically. This relationship could be used in conjunction with the CVS models and assist in glass and feed development until the CVS is completed.

Low-Viscosity Compositions

If an HWVP feed composition is found to result in a melt viscosity too low for processing within the melter ($T100P < 1070^\circ\text{C}$), the following three options will be available: 1) reduce the waste loading until the resulting

melt composition will have the proper viscosity, 2) blend the feed with one predicted to result in a high-viscosity glass if available, and/or 3) add SiO_2 as a partial replacement for frit.

Because the T100P of the reference frit (1108°C) is at the center of the acceptable viscosity range for HWVP melter operation, the waste composition will determine whether the melter feed composition will produce a glass with a high or low viscosity. Thus, with a feed that reduces the melt viscosity, increasing the waste loading would lower the melt viscosity further out of acceptable range. Decreased waste loading would bring the viscosity closer to an acceptable value. Reduced waste loading, however, increases the required number of canisters and the subsequent cost for production, handling, and repository storage. Therefore, it should be avoided if at all possible, but is available as an option.

It may be possible to blend a feed composition that produces a low-viscosity glass with one that would produce a high-viscosity glass. The logistics for blending, such as the availability of an alternative blending feed, tank space, and a feed transport system would determine whether this option is possible. The blended feed could then be routed for processing in the HWVP.

Silica, which comprises over 50 wt% of the glass composition, is preferred as the additive to increase melt viscosity. As a network former, SiO_2 would also minimize potential devitrification of the melt compared with the other potential viscosity-increasing additives such as Al_2O_3 or ZrO_2 , which are network intermediates. The SiO_2 would be added to the feed as SiO_2 sand with the same size distribution as the frit. This procedure would minimize the impacts on feed rheology, as the SiO_2 sand would behave very much like the frit.

Adding SiO_2 would also increase the viscosity of the composition once it was melted. The SiO_2 could be added in place of part of the 75 wt% frit, and the waste loading could remain constant. It would be added to the waste at the same time as the frit is added. Because the frit contains 67.25 wt% SiO_2 , the replacement of 1 wt% frit with 1 wt% SiO_2 sand would result in a net gain in SiO_2 of only about 0.33 wt%. This replacement would reduce the

amount of other frit components, but on a much smaller scale because of their lower concentrations in the frit.

High-Viscosity Compositions

The same three options listed above for the disposition of the feeds that would result in low-viscosity glasses also exist for feeds that would produce high-viscosity glasses, but sodium would be used as an additive instead of SiO_2 . As stated, waste loading reduction is not desirable and should be used only in extreme circumstances.

To lower the melt viscosity, sodium would be the additive recommended. Alkaline earths decrease viscosity but also increase the potential for devitrification. The alkalis are very effective in lowering melt viscosity. If lithium concentration is high, liquid-liquid phase separation can occur. Sodium has the highest concentration of the alkalis in the glass and is the most inexpensive and most easily available of the alkalis. Sodium has a long history of uses in the commercial glass industry. For these reasons, sodium is the additive recommended. The form in which it would be added needs to be evaluated based on feed rheology and melter performance. Some forms that should be investigated are Na_2CO_3 , NaCOOH , NaOH , and NaNO_3 . Because NaOH would add no additional carbon or NO_x to the melter, it should be evaluated first. The effects of the additional sodium on the forming process of the waste also should be investigated.

Sodium has a very strong influence on the viscosity of the glass, and therefore smaller amounts will be needed to change the T100P compared with SiO_2 . Because Na_2O comprises 10.25 wt% of the frit composition, the replacement of 1 wt% frit with 1 wt% equivalent of Na_2O would result in a net gain in Na_2O of about 0.9 wt% in the glass.

WEST VALLEY DEMONSTRATION PROJECT

Pacific Northwest Laboratory is conducting tests (Reimus et al. 1988) to determine the chemical durability of nuclear waste glass proposed for production by the West Valley Demonstration Project, West Valley, New York. These tests are being performed by the West Valley Support Task at PNL, which is providing support for the waste-form qualification work at West Valley.

Specifically, the effects of composition, ferrous/ferric ratio (redox state), heat treatment, and groundwater on glass durability are being investigated. The results of these studies will help determine the limits under which West Valley Nuclear Services can operate its melter system and still produce glass that meets disposal regulations. Preliminary results for both boron and silicon releases are discussed. The leach test results are interpreted based primarily on boron releases because, for the types of glasses studied, boron behavior is assumed the best indicator of overall glass dissolution.

Experimental Approach

The glasses used in the durability experiments were prepared primarily with carbonate and oxide sources. Each batch was melted at a temperature at which glass viscosity was ~100 poise. When oxidation state control was required, a small amount of graphite was added to the batch during melting.

Composition

Two sets of compositional variation glasses were tested at PNL; the first set consisted of eight glasses designated DG-WV1 (reference glass WVCN-47) through DG-WV8, and the second set consisted of 16 glasses designated DG-WV15 through DG-WV30 (reference glass WVCN-50). The reference glass compositions are given in Table 8.

The first set of glasses was based on variations of the WVCN-47 reference glass composition developed by Catholic University of America (CUA). This set has the following descriptions:

<u>Glass Code</u>	<u>Description</u>
DG-WV1	CUA reference glass - WVCN-47
DG-WV2	WVCN-47 glass with Ru, Rh and Pd oxides
DG-WV3	Alternate glass (designated ATM-10)
DG-WV4	WVCN-47 with higher Na ₂ O (12.20 versus 9.27)
DG-WV5	WVCN-47 with lower Al ₂ O ₃ (6.00 versus 8.05)
DG-WV6	WVCN-47 with higher P ₂ O ₅ (3.50 versus 2.52)
DG-WV7	WVCN-47 with higher ThO ₂ (5.40 versus 3.61)
DG-WV8	WVCN-47 with lower B ₂ O ₃ (7.30 versus 12.08).

TABLE 8. Composition of West Valley Reference Glasses, wt%

Oxides	DG-WV1; WVCN-47	DG-WV30; WVCN-50
Al ₂ O ₃	8.05	9.86
B ₂ O ₃	12.08	12.27
BaO	0.05	0.19
CaO	0.60	0.82
CeO ₂	0.07	0.72
Cr ₂ O ₃	0.20	0.14
Cs ₂ O	0.08	0.07
CuO	0.00	0.04
Fe ₂ O ₃	12.20	11.93
K ₂ O	1.29	1.61
La ₂ O ₃	0.03	0.04
Li ₂ O	2.03	2.22
MgO	1.33	0.79
MnO ₂	1.31	1.21
MoO ₃	0.01	0.04
Na ₂ O	9.27	9.79
Nd ₂ O ₃	0.12	0.14
NiO	0.28	0.31
P ₂ O ₅	2.52	2.47
PdO ₂	0.00	0.00
Pr ₆ O ₁₁	0.03	0.04
RhO ₂	0.00	0.00
RuO ₂	0.00	0.00
SiO ₂	42.59	39.60
Sm ₂ O ₃	0.03	0.02
SO ₃	0.30	0.23
SrO	0.03	0.02
ThO ₂	3.61	3.52
TiO ₂	0.99	0.84
UO ₂	0.56	0.61
Y ₂ O ₃	0.02	0.02
ZnO ₂	0.00	0.03
ZrO ₂	0.29	0.40
Total	99.97	99.99

The second set of glasses consisted of another reference glass (WVCM-50), also developed by CUA, and 15 vertices of a polyhedral composition variation region centered around WVCM-50. The 15-vertex compositions were chosen using computer-aided experimental design techniques (Piepel 1988; Snee 1985) to provide optimum information for fitting linear mixture models (Cornell 1981). The glasses chosen were within an explicitly defined compositional region given in Table 9. The target compositions are given in Table 10.

TABLE 9. Definition of Compositional Variation Region (based on WVCM-50)

Multiple-Component Constraints			
48	$\leq$	$\text{SiO}_2 + \text{Al}_2\text{O}_3$	≤ 54
23.6	$\leq$	$\text{Alkalis} + \text{B}_2\text{O}_3$	≤ 27.6
3.3	$\leq$	$(\text{SiO}_2 + \text{Al}_2\text{O}_3) / \text{Alkalis}$	≤ 4.1
3.7	$\leq$	$(\text{SiO}_2 + \text{Al}_2\text{O}_3) / \text{B}_2\text{O}_3$	≤ 4.7
Single-Component Constraints			
9.0	$\leq$	Al_2O_3	≤ 12.0
10.0	$\leq$	B_2O_3	≤ 14.0
1.0	$\leq$	$\text{BaO} + \text{CaO} + \text{MgO}^{(a)}$	≤ 3.0
9.0	$\leq$	Fe_2O_3	≤ 15.0
11.6	$\leq$	$\text{K}_2\text{O} + \text{Li}_2\text{O} + \text{Na}_2\text{O}^{(a)}$	≤ 15.6
0.5	$\leq$	MnO_2	≤ 2.5
1.5	$\leq$	P_2O_5	≤ 3.5
36.0	$\leq$	SiO_2	≤ 44.0
2.0	$\leq$	ThO_2	≤ 5.25
0.1	$\leq$	UO_2	≤ 1.0
1.0	$\leq$	Others	≤ 8.0

(a) The $\text{BaO}:\text{CaO}:\text{MgO}$ and $\text{K}_2\text{O}:\text{Li}_2\text{O}:\text{Na}_2\text{O}$ wt% ratios were held constant at their levels in the WVCM-50 glass.

TABLE 10. Target Compositions of Second Set of Compositional Variation Glasses

Glass Code	Oxides, wt%										
	Al ₂ O ₃	B ₂ O ₃	BaO + CaO + MgO	Fe ₂ O ₃	K ₂ O + Li ₂ O + Na ₂ O	MnO ₂	P ₂ O ₅	SiO ₂	ThO ₂	UO ₂	Others
DG-WV15	9.00	12.97	3.01	9.00	14.55	2.50	1.50	39.00	2.00	1.00	5.47
DG-WV16	9.00	12.97	3.01	15.00	11.71	2.22	3.50	39.00	2.00	0.10	1.49
DG-WV17	9.00	10.21	3.01	9.00	14.55	2.50	1.50	39.00	5.14	0.10	5.99
DG-WV18	9.00	10.95	1.01	15.00	15.60	0.50	1.50	42.48	2.37	0.10	1.49
DG-WV19	12.00	10.35	3.01	15.00	13.25	0.50	1.50	36.65	5.25	1.00	1.49
DG-WV20	12.00	11.06	3.01	9.00	12.54	0.50	3.50	39.40	2.00	1.00	5.99
DG-WV21	12.00	10.32	1.01	15.00	14.68	2.50	3.50	36.49	2.00	1.00	1.50
DG-WV22	12.00	11.82	1.01	15.00	11.78	2.50	1.50	36.30	2.00	0.10	5.99
DG-WV23	9.00	12.97	1.01	14.57	11.71	0.50	3.50	39.00	5.25	1.00	1.49
DG-WV24	12.00	14.00	1.01	9.00	13.60	2.50	1.50	42.00	2.00	0.90	1.49
DG-WV25	9.00	11.28	1.01	9.00	12.94	2.45	3.50	44.00	5.25	0.10	1.47
DG-WV26	12.00	14.00	3.01	9.00	12.77	0.50	1.50	40.38	5.25	0.10	1.49
DG-WV27	12.00	13.01	1.01	9.00	14.59	0.50	3.50	36.14	4.16	0.10	5.99
DG-WV28	9.00	11.00	1.01	12.72	12.60	0.50	1.50	42.68	2.00	1.00	5.99
DG-WV29	9.00	12.00	3.01	9.00	15.60	0.50	3.30	44.00	2.00	0.10	1.49
DG-WV30	9.86	12.27	1.80	11.93	13.62	1.21	2.47	39.60	3.52	0.61	3.11

Glass Redox

Four redox-adjusted glasses, DG-WV11R through DG-WV14R, were fabricated for this study. The target composition of these glasses varied slightly from the WVCM-50 composition, with ~1 wt% less B₂O₃ and 1 wt% more K₂O. This target composition was used also in the heat-treatment and groundwater effects experiments. The redox state of the glass, as measured by the Fe²⁺/Fe³⁺ ratio, was varied over a range of 0.07 to 0.42.

Heat Treatment

Heat-treating was done to determine the effects of simulated canister cooling and specified isothermal heat treatments on the chemical durability of the target composition used in the redox experiments. From these results,

information can be obtained on the appropriate processing conditions, e.g., canister cooling rates and melter idling conditions, to produce a durable product. Six specimens of the glass were treated with simulated canister cooling rates. Fifteen specimens were treated isothermally. No volatility losses of the specimen glasses or other compositional changes due to the heat treatments were observed.

The simulated canister cooling was performed with a programmed furnace. The furnace controller was "programmed" with a series of linear cooling/heating rates. The cooling rates used were simulated versions of actual glass cooling curves obtained from thermocouple readouts on two full-sized cooling glass canisters processed by West Valley Nuclear Services. For the experiment, crushed glass was melted at 1200°C in a fused-silica crucible; then the furnace controller program was activated. Table 11 gives representative programmed temperature ranges and cooling rates used.

The isothermal heat treatment consisted of five different treatment temperatures and holding times varying from 6 to 240 hr (Table 12). Crushed glass was melted at 1200°C in a covered fused-silica crucible, which was

TABLE 11. Representative Cooling Rates and Temperature Ranges Used in Simulated Canister-Cooling Heat Treatment

<u>Temperature Range, °C</u>	<u>Cooling Rate, °C/hr</u>
1000 - 720	-70
720 - 690	-7.5
690 - 500	-15.8
500 - 400	-7.7

TABLE 12. Test Matrix for Isothermal Heat Treatment

<u>Specimen</u>	<u>Temperature, °C</u>	<u>Holding Time, hr</u>
HT-S-7 - 8	500	120, 240
HT-S-9 - 11	600	12, 48, 240
HT-S-12 - 16	725	6, 12, 48, 120, 240
HT-S-17 - 19	800	12, 48, 240
HT-S-20 - 21	900	120, 240
HT-S-22 (test standard)	500	2

removed and placed in an oven heated to the specified treatment temperature, where it remained for a specified holding time. The crucible was then annealed for 2 hr at 500°C.

Groundwater

Four leachants representing repository groundwaters were used in this study. One of these leachants, J-13, is actual groundwater recovered from a well at the Yucca Mountain tuff repository site, and is now used as reference water chemistry for experimental work (Oversby 1985).

The other three leachants are synthetic groundwaters, prepared with specific compositions, used in testing the effects of these repository groundwaters on the nuclear waste package. Permian Basin Brines No. 1 (PBB1) and No. 3 (PBB3) represent salt-site repository groundwater (McGrail and Reimus 1987). The GR-4 water is chemically representative of groundwater found in the reference repository location area of the Grande Ronde basalt formation underlying the Hanford Site near Richland, Washington (Dill 1985).

Leach Testing

All glasses were tested with the Materials Characterization Center (MCC)-3 leach test method (MCC 1986). These 7-day tests were conducted in deaerated, deionized water (DIW) at 90°C in a CO₂-free environment. The containers were briefly removed from the enclosure and gently agitated once a day in lieu of continuous agitation. Three replicates and a blank were run for each glass.

At the conclusion of the leach test period, an aliquot of the leachate was sequentially filtered through 0.45- μ m and 18-Å filters. The leach containers were then rinsed with DIW and filled with 1% nitric acid solution (acid strip) and placed in a 90°C oven overnight. The filtered aliquots and the acid-strip solutions were then analyzed.

Results and Discussion

Inductively coupled plasma (ICP) and laser fluorescence were used to analyze all glass specimens. Redox states were determined with spectrophotometric techniques. Solution analyses were performed with ICP, laser fluorescence, and atomic absorption techniques. All normalized releases reported

were calculated from the elemental concentrations of the 0.45- μm filtered solutions. The results from these analyses are given below. Analyses of the 18- $\text{\AA}$ and acid-strip solutions are not presented here because they indicated that very few, if any, colloidal dissolution products formed during the test periods, and none plated out on the test container walls.

Compositional Variability

The normalized elemental mass releases of Al, B, Cs, Li, Na, Si, Th, and U from the first set of glasses are given in Table 13. Each value given represents the average obtained from three replicate tests. Analysis of these releases showed that chemical durabilities of WVCN-47 (DG-WV1) and the glass containing noble metal (Rh, Ru, Pd) oxides (DG-WV2) are essentially identical, indicating that durability is not affected by noble metal addition. The "high P_2O_5 and ThO_2 " and "low B_2O_3 " glasses (DG-WV6, -WV7, and -WV8, respectively) appear to be as chemically durable as the reference glass. This similarity indicates that these variations in P_2O_5 , ThO_2 , and B_2O_3 have little, if any, real effect on chemical durability of the product.

Table 14 lists the normalized elemental mass releases of Al, B, Cs, Li, Na, Si, Th, and U from the second set of glasses. Again, each value given represents the average obtained from three replicate tests. Roughly half of these glasses had greater chemical durability than the nominal WVCN-50 composition. The compositional variation caused maximum boron releases that were 34% higher and 29% lower than WVCN-50.

TABLE 13. Average Normalized Mass Releases, g/m^2 , from Glasses DG-WV1 Through DG-WV8

Glass Code	Al	B	Cs	Li	Na	Si	Th	U	pH(a)
DG-WV1	0.106	0.186	0.104	0.301	0.158	0.116	0.001	0.026	9.15
DG-WV2	0.109	0.191	0.092	0.305	0.163	0.117	0.002	0.031	9.27
DG-WV3	0.098	0.237	0.137	0.300	0.218	0.129	0.001	0.031	9.41
DG-WV4	0.110	0.239	0.092	0.294	0.239	0.123	0.001	0.029	9.22
DG-WV5	0.097	0.229	0.082	0.328	0.204	0.127	0.001	0.030	9.37
DG-WV6	0.115	0.188	0.093	0.301	0.155	0.123	0.002	0.033	9.02
DG-WV7	0.109	0.188	0.120	0.323	0.170	0.119	0.001	0.038	8.78
DG-WV8	0.113	0.187	0.040	0.319	0.176	0.118	0.002	0.037	9.33

(a) pH at test termination.

TABLE 14. Average Normalized Mass Releases, g/m², from Glasses DG-WV15 Through DG-WV30

Glass Code	Al	B	Cs	Li	Na	Si	Th	U	pH(a)
DG-WV15	0.103	0.264	0.097	0.287	0.243	0.115	0.000	0.023	7.88
DG-WV16	0.108	0.181	0.089	0.243	0.155	0.111	0.000	0.022	8.56
DG-WV17	0.110	0.273	0.097	0.296	0.248	0.117	0.000	0.019	9.26
DG-WV18	0.127	0.210	0.061	0.266	0.207	0.126	0.004	0.042	9.18
DG-WV19	0.126	0.207	0.085	0.286	0.190	0.112	0.001	0.036	9.03
DG-WV20	0.113	0.148	0.112	0.241	0.125	0.105	0.000	0.006	8.57
DG-WV21	0.150	0.205	0.099	0.252	0.205	0.136	0.010	0.044	8.86
DG-WV22	0.136	0.185	0.091	0.294	0.160	0.128	0.007	0.036	8.44
DG-WV23	0.136	0.232	0.031	0.294	0.172	0.132	0.023	0.052	9.29
DG-WV24	0.123	0.193	0.071	0.284	0.156	0.117	0.003	0.030	9.39
DG-WV25	0.125	0.179	0.082	0.264	0.153	0.119	0.002	0.031	9.50
DG-WV26	0.101	0.172	0.108	0.265	0.144	0.098	0.000	0.028	9.43
DG-WV27	0.149	0.250	0.071	0.300	0.208	0.133	0.007	0.022	9.48
DG-WV28	0.130	0.188	0.073	0.301	0.156	0.128	0.011	0.034	9.49
DG-WV29	0.101	0.207	0.103	0.260	0.194	0.113	0.000	0.033	9.80
DG-WV30	0.126	0.205	0.099	0.281	0.206	0.122	0.001	0.029	9.66

(a) pH at test termination.

After the second set of glasses was analyzed, empirical mixture models were fit to the normalized boron release data to determine whether varying the composition within the composition region studied had a statistically significant effect on normalized release. Linear mixture models were fit using the form shown in Equation (1):

$$\text{Normalized Elemental Release} = \sum_{i=1}^{11} b_i x_i \quad (1)$$

where $x_1, \dots, x_{11}$ are the weight fractions of the 11 oxide components listed under Single-Component Constraints in Table 9, and $b_1, \dots, b_{11}$ are the model parameters estimated via least squares regression.

Normalized release models were fit to the total 24 compositional variability glasses and also to the set of 16. The model fit to the 24 glasses was chosen for prediction purposes since it was obtained from a larger data

set. The fitted boron release model for the 24-glass data set is given in Equation (2):

$$\begin{aligned} \text{NBR} = & -1.3200 \text{ Al}_2\text{O}_3 + 0.6571 \text{ B}_2\text{O}_3 - 0.2333 (\text{BaO}+\text{CaO}+\text{MgO}) + \\ & 0.3999 \text{ Fe}_2\text{O}_3 + 2.0574 (\text{K}_2\text{O}+\text{Li}_2\text{O}+\text{Na}_2\text{O}) + 1.0203 \text{ MnO}_2 + \\ & 0.2260 \text{ P}_2\text{O}_5 - 0.3245 \text{ SiO}_2 + 0.9641 \text{ ThO}_2 + 1.7413 \text{ UO}_2 + \\ & 0.8085 \text{ Others} \end{aligned} \quad (2)$$

where NBR is normalized boron release from the 7-day MCC-3 leach test. This model fits the data set well, with an R^2 value of 0.90.

The model fit to the set of 16 glasses was used to predict NBR for the eight-glass set. The results were used to check the usefulness of the models as predictive tools. Table 15 lists the measured and predicted values for each glass. As shown by Table 15, the predicted NBR values compare well with the observed values. This is very good evidence that these models can be used reasonably for prediction.

Effects plots (Piepel 1982), which demonstrate the effects of varying individual oxide components, are presented in Figures 2 and 3 for boron and silicon releases. In a given effects plot, there is one effect curve for each component. Each curve displays the effect of changing the associated component over its allowable range as defined by the constraints of Table 9.

TABLE 15. Comparison of Observed Normalized Boron Release Values to Predicted Values and Prediction Intervals from the 16-Glass Linear Mixture Model

<u>Glass Code</u>	<u>Observed Values, g/m²</u>	<u>Predicted Value</u>
DG-WV1	0.1842, 0.1855, 0.1868	0.1875
DG-WV2	0.1892, 0.1918, 0.1905	0.1793
DG-WV3	0.2364, 0.2364, 0.2364	0.2210
DG-WV4	0.2339, 0.2407, 0.2407	0.2594
DG-WV5	0.2296, 0.2270, 0.2296	0.2219
DG-WV6	0.1868, 0.1882, 0.1882	0.1765
DG-WV7	0.1855, 0.1895, 0.1895	0.1849
DG-WV8	0.1869, 0.1847, 0.1865	0.1480

FIGURE 2. Effects Plot for Normalized Boron Release (linear mixture model, 24 glasses)

FIGURE 3. Effects Plot for Normalized Silicon Release (linear mixture model, 24 glasses)

The effects curves are merely a series of predicted normalized release values plotted versus weight percent changes from the value of each component in the reference glass. The WVCN-50 glass is used as the reference in Figures 2

and 3. Equation (2) was used to generate Figure 2. A similar equation relating silicon releases to composition was used to generate Figure 3.

The alkalis (K_2O , Li_2O , and Na_2O), UO_2 , and ThO_2 have the largest positive effects on boron release per unit weight percent change. Increasing their levels tends to decrease the chemical durability of the glass. Conversely, the oxides Al_2O_3 and SiO_2 have the largest negative effects on boron release. Although the per-unit effect of UO_2 is relatively large, its total effect is not as large as those of MnO_2 , "Others," and ThO_2 , which have larger ranges. From a practical standpoint, it may only be the total effects of the components that are of interest. Components such as P_2O_5 , Fe_2O_3 , B_2O_3 , and the alkaline earths (BaO , CaO , and MgO), which have nearly horizontal effects curves in Figure 2, do not have a substantial effect on boron release within the region studied.

These results compare well with those compiled from a previous glass composition effects study (Chick et al. 1984). In that study, alkali, in the form of Na_2O , also was observed to have the largest positive effect on boron and silicon release, and aluminum and silicon oxides had large negative effects (MCC-1 and -3, 28-day modeled results). These effects were large relative to the effects of the other components studied.

Glass Redox Adjustment

The normalized elemental mass releases of Al, B, Cs, Li, Na, Si, Th, and U for the redox-adjusted glasses are listed in Table 16. Each value given represents the average obtained from three replicate tests. A graphic representation of boron and silicon releases is given in Figure 4. The error

TABLE 16. Average Normalized Elemental Mass Releases, g/m^2 , from Redox-Adjusted Glasses

Fe^{2+}/Fe^{3+}	Al	B	Cs	Li	Na	Si	Th	U	pH(a)
0.068	0.119	0.212	0.092	0.274	0.209	0.116	0.000	0.024	9.64
0.126	0.113	0.209	0.101	0.269	0.203	0.112	0.000	0.023	9.76
0.236	0.114	0.212	0.081	0.269	0.215	0.112	0.000	0.021	9.82
0.424	0.121	0.237	0.067	0.295	0.249	0.121	0.000	0.025	9.91

(a) pH at test termination.

FIGURE 4. Comparison of Silicon and Boron Normalized Mass Releases from Redox-Adjusted Glasses (modified MCC-3 test, 90°C, deaerated DIW, 7-day)

bars represent experimental error of plus or minus two standard deviations. The standard deviations are based on the replicate tests as performed at the same time and do not include the time-related component of variability. The differences in boron and silicon releases among the glasses tested are small. The similarity of the silicon and boron releases suggests that the glasses have similar chemical durability and that redox state has negligible effect on chemical durability. Statistical analysis of variance confirms the negligible effect of redox state on boron and silicon releases.

The final pH of the leachate appears to increase with increasing $\text{Fe}^{2+}/\text{Fe}^{3+}$ of the glass leached. This increase could have been caused by the oxidation of Fe^{2+} in the leachate. As Fe^{2+} goes into solution, it is oxidized by dissolved O_2 in the following reaction:

This reaction consumes H^+ , 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^+ consumption support this theory.

Simulated Canister-Cooling Heat Treatments

Figure 5 graphically represents boron and silicon releases for the heat-treated glasses. The error bars represent experimental error of plus or minus two standard deviations. The standard deviations are based on replicate tests as performed at the same time and do not include the time-related component of variability. The figure demonstrates that the heat treatments have a slight effect on the chemical durability of the glass. A maximum decrease of 15%, based on boron release, over that of the reference glass is shown. Furthermore, Figure 5 shows the average normalized mass releases of boron and silicon from the heat-treated samples and DG-WV11R and DG-WV14R. The DG-WV11R may be treated as a control glass as its redox state is fairly close to that of the heat-treated glasses. Statistical analyses of variance methods were used to compare the six heat-treated glasses (specimens HT-S-1 through HT-S-6) with each other and with DG-WV11R and DG-WV14R. The boron and silicon releases for the more quickly cooled specimens (HT-S-2, -3, and -4) differ significantly from the releases for the more slowly cooled specimens (HT-S-1, -5, and -6), but the releases within these two groups do not differ significantly.

The boron and silicon releases of DG-WV11R do not differ significantly from those for the quickly cooled glasses, indicating that this cooling does not affect chemical durability any more than slight glass reduction does. The boron releases of DG-WV14R and the more slowly cooled glasses are similar, which indicates that their chemical durabilities also are not significantly different.

FIGURE 5. Comparison of Silicon and Boron Normalized Mass Releases from Slowly Cooled Heat-Treated Glasses. (Ordering of heat-treated glasses is from fastest to slowest relative cooling rates. Modified MCC-3 test, 90°C, deaerated DIW, 7-day.)

Isothermal Heat Treatments

Figure 6 shows the boron release data for the isothermally heat-treated glasses plotted as a function of heat-treatment time and treatment temperature on a time-temperature-transformation diagram. The boron release values for each sample are shown, as well as the approximate locations of a series of constant leaching isopleths.

The appearance of this diagram is essentially identical to what would be expected if crystallinity were plotted instead of chemical durability. This similarity is not surprising because devitrification (growth of crystallinity in) of the glass causes the decrease in durability. A maximum decrease in durability of a factor of two was found for the isothermally heat-treated samples (500°C for 2 hr versus 600°C for 240 hr). This type of behavior for a similar glass, SRL-165, was found in another study (Jantzen et al. 1984).

FIGURE 6. Time-Temperature-Transformation Diagram for Boron Releases, g/m², from Isothermally Heat-Treated WVCN-50 Glass

In that study, the decrease in glass durability was attributed to the formation of acmite, NaFeSi₂O₆, as one of the devitrification products.

Groundwater Effects

A graphic representation of boron and silicon releases for glasses leached in groundwater is given in Figure 7. The error bars represent experimental error of plus or minus two standard deviations. The standard deviations are based on replicate tests as performed at the same time and do not include the time-related component of variability. The releases of OG-WV11R are included in the figure to provide a comparison of chemical durabilities of the glass in deionized water (DIW) versus groundwater. The tests were conducted under identical conditions except that the redox-adjusted glass was leached under CO₂-free conditions, while the groundwater-leached glass was leached in a standard air atmosphere.

FIGURE 7. Comparison of Boron and Silicon Normalized Mass Releases from WVCN-50 Glass in Different Groundwaters (modified MCC-3 test, 90°C, 7-day)

Figure 7 shows that groundwater type has a definite effect on the chemical durability of the glass and that the glass appears to be more chemically durable in the groundwaters tested than in deaerated DIW, under CO₂-free conditions. Specifically, Figure 7 demonstrates that the glass is most durable chemically in PBB1 and least in DIW. The difference in durability, based on boron release, is greater than in DIW by a factor of about 5 in PBB1, 4 in PBB3, 3 in J-13 well water, and 2 in GR-4.

That the brines, PBB1 and PBB3, caused the least leaching is consistent with a known decreased solubility of SiO₂-bearing solids in solutions of high ionic strength. The relative saturation fraction of silicic acid in the leachant plays an important role in determining the glass reactivity (Strachan et al. 1985), which explains why the glass is less durable in DIW than in the basalt and tuff groundwaters. These are silicate groundwaters

and become saturated with silicic acid during the glass dissolution more quickly than DIW. Leaching studies conducted in aqueous solutions (Strachan et al. 1985) demonstrate that glass dissolution occurs about equally in DIW and a synthetic groundwater (composition close to that of GR-4) and less in brine at 90°C. The glass was found to leach more readily in DIW than in the synthetic groundwater at 40°C. The results reported here also agree with this outcome.

Figure 7 demonstrates also that glass dissolution is greater in PBB3 than in PBB1 and that dissolution is greater in basalt groundwater than in tuff groundwater. The brine-caused durability difference agrees with results found in the literature. The major difference between the brine compositions is magnesium concentration, which is higher in PBB3. Early leaching studies conducted in brine solutions (Braithwaite 1980) concluded that glass dissolution increases with increasing magnesium content of brine. This effect was attributed to magnesium causing a decrease in pH and substituting for divalent oxides like CaO and SrO in the glass matrix. However, other brine leaching studies (McGrail and Reimus 1987) have shown that the kinetics of dissolution of a defense waste glass were not affected by the difference in brine composition. The difference in durability observed between basalt and tuff groundwater is most probably caused by the higher initial pH of the basalt groundwater (10.18 versus 8.20) allowing for greater glass network attack.

CONCLUSIONS AND RECOMMENDATIONS

HANFORD WASTE VITRIFICATION PLANT

Based on the work reported herein, the following conclusions are made:

- Up to 5 wt% Na₂O can be removed from the HW-39 reference frit while maintaining a frit composition that can be processed. In turn, the potential addition of 0 to 20 wt% Na₂O in the waste would be possible. For the NCAW'84 waste, this would mean a Na₂O increase of from 11.1 to as high as 31.1 wt% in the waste. For NCAW'86 waste this would mean a Na₂O increase from 17.5 to ~33.5 wt%.

- The additional sodium allowable in the waste as the result of Na_2O removal from the frit could provide additional flexibility in the B-Plant specifications for washing efficiency.
- The existing flexibility of the reference glass composition can handle the normal fluctuation in the NCAW composition. The above modifications provide additional process flexibility for other waste being considered and for abnormal waste batched.
- Compositional ratios, the ratios of different glass components or the ratios of the sums of different glass components, can be used to estimate the T100P of glass melts based on composition. The ratios using the total weight percent alkali oxides over the sum of the weight percents of SiO_2 , Al_2O_3 , and ZrO_2 were found to predict the T100P well.
- Adding SiO_2 or sodium as partial replacement for frit will adjust the viscosity of abnormal waste batches or possibly other wastes to within operating specifications.

The following recommendations are made:

- The modification of the frit composition for processing adjustment should be reviewed after the NCAW'86 composition is refined early in FY 1988 to confirm the amount of Na_2O that can be removed from the frit.
- As additional glass viscosity data are generated, the relationship of glass compositional ratios to viscosity should be refined and quantified.
- Rheology and melter testing should be evaluated and the necessary testing performed to verify that the modified frit can be processed. Feeds modified with SiO_2 or sodium additions to bring glass viscosities within acceptable processing limits should also be tested.

WEST VALLEY DEMONSTRATION PROJECT

The results from the experiments conducted to date have led to the following conclusions:

- Leach test results indicate that adding 0.1 wt% total noble metal oxides does not significantly affect the reference glass durability.
- The linear mixture models developed may be used to predict how varying specific components affects the durability of the reference glasses (WVCM-47 and -50) within the defined composition region.
- The chemical durability of the target composition (WVCM-50 with 1 wt% less B_2O_3 and 1 wt% more K_2O) was not strongly affected by the variation of glass redox state over the Fe^{2+}/Fe^{3+} range of 0.07 to 0.42. The pH of the leachate increased with increasing Fe^{2+}/Fe^{3+} ratio; however, this rise is probably due to Fe^{2+} oxidation in the leachate.
- Certain isothermal heat treatments can cause up to a twofold decrease in the chemical durability of WVCM-50. However, heat treatments that simulate anticipated canister cooling conditions have no substantial effects on the chemical durability of this glass.
- The target composition is more durable in groundwater than in deionized water by up to a factor of 5 based on boron release.

REFERENCES

- Braithwaite, J. W. 1980. "Brine Chemistry Effects on the Durability of a Simulated Waste Glass." Sci. Basis Nuc. Waste Manag. 2:199, Plenum Press, New York.
- Chick, L. A., et al. 1984. West Valley High-Level Nuclear Waste Glass Development: A Statistically Designed Mixture Study. PNL-4992, Pacific Northwest Laboratory, Richland, Washington.
- Cornell, J. A. 1981. Experiments With Mixtures: Designs, Models, and the Analysis of Mixture Data. John Wiley and Sons, New York, New York.

- Dill, J. A., et al. 1985. An Evaluation of the Stability of Synthetic Groundwater Formulations GR-3 and GR-4. SD-BWI-TD-013, Rev. 0, Rockwell Hanford Operations, Richland, Washington.
- Ilham, A., and P. Hrma. 1987. "A Review of Estimation Methods for Viscosity of Silicate Melts and Their Applicability to Nuclear Waste Glasses." Paper presented at the 89th Annual Meeting of the American Ceramic Society, April 26-30, 1987, Pittsburgh, Pennsylvania.
- Jantzen, C. M., D. F. Bickford, and D. G. Karraker. 1984. "Time-Temperature-Transformation Kinetics in SRL Waste Glass." Proceedings of the Second International Symposium on Ceramics in Nuclear Waste Management, Chicago, Illinois, April 24-27, 1983, Vol. 8, p. 30, American Ceramic Society.
- Materials Characterization Center. 1986. Test Methods Submitted for Nuclear Waste Materials Handbook. PNL-3990, Pacific Northwest Laboratory, Richland, Washington.
- McGrail, B. P., and M. A. Reimus. 1987. Salt Repository Project - Glass Studies Program: FY 1986 Annual Report. PNL/SRP-6389, Pacific Northwest Laboratory, Richland, Washington.
- Nakaoka, R. K., J. M. Perez, Jr., W. C. Buchmiller, R. W. Goles, and S. O. Bates. 1986. Nonradioactive LFCM Testing Results in FY 1986 Under the Hanford Waste Vitrification Program. RHD-RE-CR-17P/HWVP-86-HLVID, Pacific Northwest Laboratory, Richland, Washington.
- Oversby, V. M. 1985. The Reaction of Topopah Spring Tuff with J-13 Water at 150°C - Samples from Drill Cores USW G-1, USW GU-3, USW G-4, and UE-25h#1. UCRL-53629, Lawrence Livermore National Laboratory, Livermore, California.
- Piepel, G. F. 1982. "Measuring Component Effects in Constrained Mixture Experiments." Technometrics 24:29-39.
- Piepel, G. F. 1988. "Programs for Generating Extreme Vertices and Centroids of Linearly Constrained Experimental Regions." Journal of Quality Technology, Vol. 20.
- Reimus, M. A. H., G. F. Piepel, and G. B. Mellinger. 1988. "West Valley Glass Product Qualification Durability Studies: Effects of Composition, Redox State, Heat Treatment, and Groundwater." Waste Management '88, R. G. Post, ed., University of Arizona, Tucson, Arizona.
- Snee, R. D. 1985. "Computer-Aided Design of Experiments - Some Practical Experiences." Journal of Quality Technology 17:222-236.
- Strachan, D. M., L. R. Pederson, and R. O. Lokken. 1985. Results from the Long-Term Interaction and Modeling of SRL-131 Glass with Aqueous Solutions. PNL-5654, Pacific Northwest Laboratory, Richland, Washington.

FEED PREPARATION AND TRANSFER SYSTEMS

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SUMMARY

An experimental study was completed to qualify and quantify the off gases released during formic acid addition to Hanford Waste Vitrification Plant (HWVP) feed simulant. An experimental study was completed to establish the heat-transfer characteristics of a simulated HWVP feed in a bench-scale system. The effect of feed composition and formic acid addition on glass redox state has been investigated and reported on. The results from these three studies are summarized here.

A statistical feed process variability study using nonradioactive feeds has been designed and a test plan issued.

INTRODUCTION

Feed preparation and transfer systems consist of the equipment used to contain and process 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 PROCESS OFF GASES RELEASED DURING THE FORMATING OF A NEUTRALIZED HWVP FEED SIMULANT

The experimental study was completed for qualifying and quantifying the off gases released while formic acid is added to an HWVP feed simulant. The technical report Evaluation of Process Off Gases Released During the

Formating of a Neutralized Feed Simulant was issued. The experimental study and the results are summarized below.

In preparing HWVP feed, formic acid is added to adjust both the redox state and the rheology of the feed. Characterization of the gases released during feed formating is necessary for the design of the process off-gas vessel vent system. This system must be designed to handle and treat any potentially toxic, flammable or explosive levels of gases. Data also are required in order to characterize the solution kinetics during feed formating for process operation and control.

This study was performed primarily to characterize the gases released during feed formating and to relate these data to the solution kinetics. The rate and the quantity of gases released were measured as a function of time. Factors contributing to this release, including the feed chemistry, physical properties of the feed, and system operating parameters, were identified. A secondary objective, critical to the results of this study, was the development of a simulant that would more adequately represent chemically and physically the neutralized current acid waste (NCAW).

Seven test runs were performed using a simulated NCAW'86 feed composition. During the test runs formic acid was added at three different stoichiometric amounts and at three different rates. Samples of the released gases were collected as a function of time. Gas composition and amount, along with the elemental composition of feed, were determined for the respective samples. The physical and rheological properties of this simulated feed were measured to compare with the properties of previous simulants.

Maximum gas concentrations observed during feed formating were 85 mole% CO_2 , 1.4 mole% N_2O , 0.12 mole% NO_x , and 0.16 mole% H_2 . Unreacted formic acid was not detected in the off gas downstream from the condenser, which was operated at 15°C. Maximum gas releases were observed in the feed with a pH range of 5 to 7, a range in which the redox potential for Fe^{3+} to Fe^{2+} and NO_3^- to N_2O are extremely pH-dependent. The presence of NO_2^- in the feed in place of NO_3^- is not expected to alter the amount of NO_x released but may decrease the formic acid required for the reduction processes. The rate of gas released and the feed behavior (foaming) were dependent upon the degree

of mechanical agitation. During full-scale operation the gaseous species observed are not expected to differ from those observed in this study. The rate and amount of gas released during full-scale operation would depend on operating parameters such as the degree of agitation and the rate of purge of cover gas.

The NCAW'86 simulated feed was prepared for this study by neutralizing nitrate salts with sodium hydroxide. The precipitated solids of the major components were washed individually. The final feed was prepared by blending together the feed components. The procedure for precipitation and washing preparation more closely represented that for the NCAW than previous simulations did. Therefore more confidence can be placed in the off-gas results than if hydroxide salts were simply blended. The chemical composition of the feed prepared following this procedure was within 10% of the target concentration for the major components.

The most significant difference between the physical properties of the resultant feed simulant and those of previous simulants was in rheological behavior. The yield stress and the apparent viscosity of the feed increased with the addition of formic acid, whereas prior experience has shown these properties to decrease. In addition, the yield stress and apparent viscosity are higher by a factor of 7 and 4, respectively, than with previous PNL simulants. These results are significant if indeed this simulant is more representative of the NCAW. Further characterization of the radioactive waste and further development of simulant are required to verify the rheological behavior of the feed and to ensure that correct rheological properties are used in designing equipment for the feed preparation system.

EVALUATION OF HWVP FEED HEAT-TRANSFER CHARACTERISTICS IN AN AGITATED VESSEL

The experimental study to establish the heat-transfer characteristics of a simulated HWVP feed in a bench-scale system was completed. The technical report Evaluation of HWVP Feed Heat-Transfer Characteristics in an Agitated Vessel was issued. The experimental study and the results are summarized below.

The initial waste stream to be processed at the HWVP, pretreated NCAW, will require concentration before it is vitrified. The design of the HWVP

concentration system has been adopted from the Defense Waste Processing Facility (DWPF). Full-scale testing of feed preparation equipment is being conducted at the Savannah River Laboratory to establish DWPF process performance and time cycle requirements. Because the composition of the feed slurries and the process requirements of the DWPF differ from those of the HWVP, a technical evaluation of full-scale test data will be performed to determine the adaptability of DWPF technology to the HWVP process. Based on this evaluation, additional full-scale testing may be needed to assure that HWVP process requirements can be met with the DWPF concentration system.

The HWVP, pretreated NCAW, will be received and stored at the plant in the receipt and lag storage tank. The HWVP feed in this tank will have a nominal solids concentration of 2 wt%. Prior to adding formic acid during melter feed preparation, the feed will be concentrated to a solids loading of 12 wt%. Based on the current flowsheet, a total of 38,160 gal of HWVP feed (2 wt% feed) will be concentrated to 6000 gal of 12 wt% feed and, in the process, will generate 32,160 gal of process condensate during each melter feed preparation cycle.

The purpose of the work reported here was to establish a relationship between simulated HWVP feed characteristics and heat-transfer rates using a bench-scale test apparatus (Figure 1). The linear dimensions of the bench-scale concentration/mixing system were scaled down from the current design of the HWVP slurry receipt and adjustment tank (SRAT). The bench-scale SRAT was 1/10th scale based on linear dimensions and 1/750th scale on a volumetric basis. The dimensions of the full-scale and bench-scale mixing systems and heat transfer coils are compared in Tables 1 and 2, respectively. The study was designed to establish convective and boiling heat-transfer rates during operation of the bench-scale SRAT. In the first segment of the study, a series of tests was conducted to establish the effects of steam pressure on heat-transfer rates. The objective of the second segment of the investigation was to determine the effects of increased solids loading on concentration rate.

The results of this investigation demonstrated that the bench-scale system was not capable of generating the required heat-transfer data necessary for the design of full-scale feed preparation equipment. The large

FIGURE 1. Bench-Scale Test Apparatus

TABLE 1. Dimensions of the Full- and Bench-Scale Concentration/Mixing Systems

	<u>Full-Scale</u>	<u>Bench-Scale</u>
Tank Diameter	12.0 ft	15.3 in.
Tank Height	14.6 ft	19.0 in.
Impeller Diameter	3.0 ft	3.8 in.
Impeller Spacing	3.7 ft	4.6 in.
Liquid Height		
Full	10.6 ft	15.3 in.
Concentrated	7.1 ft	9.0 in.
Tank Volume		
Full	9000 gal	12.1 gal
Concentrated	6000 gal	7.1 gal
Impeller Diameter/ Tank Diameter	0.25	0.25
Liquid Level/ Tank Diameter		
Full	0.88	1.00
Concentrated	0.59	0.59
Impeller Spacing/ Impeller Diameter	1.23	1.23

pressure drop associated with the bench-scale coil bundle did not permit an overall convective heat-transfer coefficient to be determined during the heat-up segment of the tests. Moreover, the system's physical limitations prevented bench-scale operation at steam pressures in the range proposed for the full-scale SRAT. The maximum boiling heat flux obtained during the bench-scale tests was $6.7 \times 10^3 \text{ Btu/hr}\cdot\text{ft}^2$, which is less than half the current HWVP requirement of $1.4 \times 10^4 \text{ Btu/hr}\cdot\text{ft}^2$.

Testing during the first segment of the study did, however, establish a relationship between steam pressure and boiling heat flux for the bench-scale SRAT. Results of these tests showed that the boiling heat flux increased as the operating steam pressure increased from 20 psig to 30 psig. As steam pressure was increased from 30 psig to 45 psig, no appreciable increase in boiling heat flux was observed. This finding suggests that operation of the

TABLE 2. Dimensions of the Full- and Bench-Scale Steam Coil Bundles

	<u>Full-Scale</u>	<u>Bench-Scale</u>
Coil Height	5.5 ft	6.9 in.
Coil Diameters	3.9 ft	4.9 in.
	4.4 ft	5.5 in.
	4.9 ft	6.2 in.
Tube Diameter	2.4 in.	0.25 in.
Tube Spacing	3.5 in.	0.63 in.
Heat Transfer Area		
Heating	344.8 ft ²	3.2 ft ²
Cooling	151.4 ft ²	3.2 ft ²
Coil Height/ Liquid Height		
Full	0.52	0.45
Concentrated	0.78	0.47
Coil Diameter/ Impeller Diameter		
	1.30	1.31
	1.47	1.47
	1.63	1.65
Tube Spacing/ Tube Diameter	1.46	2.52

bench-scale SRAT at steam pressures above 30 psig would be unwarranted because no increase in boiling heat flux would be gained. If a similar relationship exists on a full scale, operation of the SRAT at a steam pressure lower than the current reference of 150 psig could lower costs associated with steam generation.

Data generated during this segment revealed also that operating the bench-scale process condensate collection system resulted in heat losses during heat-up and concentration of ~15%. The pressure in the bench-scale SRAT was maintained at a nominal value of -1/2 in. water column to remove vapors generated during testing. The negative pressure in the tank induced a flow of air through the concentration/mixing tank. While this sweep of air did not cause significant entrainment of solids, it did contribute to the overall heat losses of the system. It was also observed that significant

increases in vacuum were needed to prevent the tank from being pressurized once boiling began.

During the second segment of the investigation, the solids loading of simulated HWVP feed was increased from 2.7 wt% solids to 10.4 wt% solids using the bench-scale SRAT and a batch concentration sequence. Results of this test showed that the convective and boiling heat-transfer rates were unaffected by the increased concentration over the range tested. Inspection of the tank internals after the test showed that solids had collected on the tank walls. The outer surface of the steam coil, which remained submerged during the concentration sequence, did not accumulate solids.

Data generated for this study showed that the heat capacity of simulated NCAW feed depends on solids concentration and temperature. For a specific temperature, the heat capacity of the feed decreases as solids loading increases, as shown in Figure 2. For a specific solids concentration, the

FIGURE 2. Feed Heat Capacity Versus Solids Concentration at 66°C

heat capacity of the feed decreases as temperature increases. The data also suggest that an exothermic reaction is occurring at $\sim 74^{\circ}\text{C}$ for solids concentrations above 11.1 wt%.

This investigation completes the bench-scale evaluation of HWVP feed preparation equipment. Due to limitations imposed by the size of the bench-scale equipment, the information generated cannot be used to predict performance of the full-scale HWVP SRAT. Issues concerning successful operation of the equipment will require larger-scale test data. Information from bench-scale testing can be used as a guideline for designing full-scale tests if it is found that additional testing is required.

EFFECT OF FEED COMPOSITION AND FORMIC ACID ADDITION ON GLASS REDOX STATE

The technical report The Effect of Feed Composition and Formic Acid Addition on Glass Redox State was issued. The experimental study and the results are summarized below.

The HWVP will concentrate and chemically adjust a neutralized current acid waste to ensure acceptably efficient glass production. The modified waste will be blended with glass frit and pumped to a ceramic melter, where it will be converted to a molten borosilicate glass. The molten glass will then be poured into stainless steel canisters.

Previous studies have shown that carbon compounds, in the form of formic acid or sugar, can effectively adjust the rheology and melt characteristics of the waste. Specifically, formic acid can reduce the yield stress and viscosity of the feed, while formic acid or sugar can prevent reboil of the glass during melting by acting as a reducing agent to change the oxidation (or redox) state of the glass. However, the use of formic acid or sugar as a redox state modifier has some constraints. Too little formic acid or sugar will not adequately prevent the glass from foaming during melting. Foaming will decrease glass processing rates in the melter. Too much formic acid or sugar will cause certain metal oxides to reduce to their metallic state and settle out of the glass. This could create an electrically conductive path in the melter bottom that could short out electrodes and thus shorten the melter's service life.

This study examined the effect of HWVP feed composition and the addition of formic acid on the redox state and rheology of several melter feeds.(a) The compositional ranges selected (Table 3) for this study bracketed the range of HWVP feed compositions previously determined to provide an acceptable borosilicate glass for the HWVP.

The study was also intended to establish whether formic acid alone is sufficient to achieve an acceptable redox state without adversely affecting the melter feed's physical and rheological properties. The study examined the redox state and rheology of nine HWVP feed compositions, each with three to five different levels of formic acid addition. Seven of the nine compositions encompassed the compositional ranges (based on glass acceptability) that were defined for the four major components in the NCAW'84 low chromium feed (iron, aluminum, sodium, and zirconium).

The two additional feeds were the NCAW'84 low chromium and the NCAW'86 compositions. After formic acid was added, the HWVP feed samples were then combined with glass frit and the resultant melter feed was subjected to physical, rheological and redox state characterization. Each melter feed was characterized at a concentration of 500 g total oxides/L.

The study showed that the redox state and rheology of the nine compositions were acceptable upon adding 25 to 30 mL of 90 wt% formic acid to each

TABLE 3. Range of Major Component Concentrations Tested, NCAW

Component Oxide	Concentration, wt% Total Oxides	
	Minimum	Maximum
Fe_2O_3	12.0	60.0
Al_2O_3	1.6	26.0
Na_2O	4.5	22.0
ZrO_2	4.2	40.0

-
- (a) "Melter feed" is used here to refer to the slurry after frit addition. "HWVP feed," "HWVP waste," "NCAW feed," or "feed" refer to the slurry before frit is added.

liter of HWVP feed (at 150 g waste oxides per liter). The effect of formic acid addition on the redox state of the glass is shown in Figure 3. Its effect on viscosity and yield stress is shown in Figures 4 and 5, respectively. Provided that the compositions tested prove to represent the extremes of NCAW compositional variability, sugar will not need to be added to further modify the HWVP waste. The study showed also that redox state and rheology could be better controlled if the exact composition of the HWVP feed was known before formic acid was added.

The study results confirmed that the redox state of HWVP glass is controlled primarily by the melter feed's composition and the amount of reducing agent present. The results also showed that the near-linear relationship between redox state and formic acid amount was not altered by the acid-base reactions that occur between hydroxides and the formic acid when it is added. The effect of composition on the redox state of the glass

FIGURE 3. Effect of Formic Acid Addition (90 wt%) on the Redox State of Various Feed Compositions

FIGURE 4. Effect of Formic Acid Addition (90 wt%) on Apparent Viscosity of Various Feed Compositions

may relate to the Gibbs free-energy potential of each melter feed component and to the extent to which the components are reduced while in the melter cold cap prior to melting. Changes in feed composition will change the amount of organic material required before the oxides start to significantly reduce to their metallic form. Lowered amounts of components that readily reduce before the ferric ion is reduced will increase the reducing agent available to the ferric ion, thus increasing ferrous-to-ferric ratios (an indicator of glass redox state).

FIGURE 5. Effect of Formic Acid Addition (90 wt%) on Yield Stress of Various Feed Compositions

Higher ferrous-to-ferric ratios were achieved in the glass by increasing the zirconium or sodium concentration, or by decreasing the aluminum concentration in the HWVP feed. The effect of changing sodium and zirconium concentrations on glass redox state can be explained in terms of the Gibbs free-energy potentials for the reduction reactions in the melter cold cap. Increasing the concentration of zirconium or sodium in the feed decreases the amount of multivalent components that reduce before ferric ion reduction. However, an explanation for the opposite effect, seen by changing the aluminum concentration, is not readily apparent.

The influence of HWVP feed composition and formic acid addition on melter feed rheology was also examined. The results show composition to be the primary variable affecting melter feed rheology. In particular, increased concentrations of iron hydroxide in the HWVP feed will increase the yield stress and apparent viscosity of the melter feed. Any effect of the pH or formic acid reaction on feed rheology is less significant than that of iron hydroxide concentration.

These study results can be used to improve processing by basing the amount of formic acid added to the waste on the Gibbs free-energy potential and reduction reaction equilibria of each component and on feed composition. Sufficient control of formic acid addition will minimize impacts on glass production from factors such as metal reduction or foaming in the melter.

STATISTICAL HWVP FEED PROCESS VARIABILITY STUDY

The technical report Test Plan for the Statistical Feed Process Variability Study was issued.

Successful design and operation of the HWVP requires that process parameters for the feed preparation system be well defined and the technical data base established. Scoping and limited multivariable studies have been performed to provide design data and define the significant process and compositional variables for the first feed, pretreated NCAW. Overall knowledge of the interactions of the process and compositional variables will be required for the system.

A statistical feed process variability study will be performed to 1) identify any individual or interactive effects on the physical or rheological properties caused by varying compositional or process variables and 2) estimate the precision in determining the physical and rheological properties. For the compositional variables, the concentration of aluminum, iron, sodium, and zirconium will be varied. The process variables will include the amount of formic acid, the concentration at forming, waste loading, final melter feed concentration, and total organic carbon concentration. The results from this study will establish a statistically valid feed processing data base for the HWVP.

The test plan identifies the basic methodology required to accomplish the objectives. The statistical experimental design involves two experimental matrices: a compositional variability experimental matrix and a process variability experimental matrix. The final experimental design combines the two experiments. About 250 to 300 laboratory tests are required to determine the major individual and interactive effects among the process and compositional variables and to quantify the precision of the laboratory measurements.

The test plan describes the statistical variability testing using simulated (nonradioactive) feeds. The planned radioactive waste characterization and evaluation must be conducted in cooperation with this statistical study. This will ensure that the nonradioactive test matrix fully encompasses the expected waste variability range and that the HWVP feed simulations are accurate. It is important also that laboratory measurements and procedures be consistent to maximize the technical data obtained.

CONCLUSIONS AND RECOMMENDATIONS

The conclusions from the feed forming process off-gas study are summarized as follows:

- Carbon dioxide, nitrous oxide, nitrogen oxides, and hydrogen gases are released from the feed slurry during the forming process. Maximum gas concentrations detected were 85 mole% CO₂, 1.4 mole% N₂O, 0.02 mole% NO, and 0.62 mole% H₂.

- Gas release continues after heat treatment.
- Formic acid is not detectable in the off-gas downstream from the condenser which is operated at 15°C.
- The amount of CO_2 and H_2 released is dependent upon both the amount of formic acid added and the rate at which it was added.
- The procedure for preparing the simulated feed using neutralization and washing steps successfully produced a feed which was within 10% of the target composition for the major components.
- The rheological properties of the feed simulant prepared for this study are significantly higher than with previous feed simulants. The higher viscosity measurements strongly suggest that the attractive forces between the particles are higher. The yield stress of the feed used in the present study ranged from 50 to 150 dynes/cm². The design range for the DWPF is 25 to 150 dynes/cm². The HWVP design range may require expansion above 150 dynes/cm² to provide some design margin.
- The level of agitation is very important for process control during forming. Insufficient agitation results in foaming and sudden gas releases. Improved agitation minimized foaming and provided a more controlled release of gas from the feed slurry.

Based on the evaluation of the feed heat-transfer characteristics, the following conclusions were drawn:

- Operating the bench-scale SRAT at steam pressures greater than 30 psig did not increase boiling heat flux.
- An overall heat-transfer coefficient for the heat-up segment could not be measured accurately on a 1/10th linear-scale system using existing heat-transfer models because of the excessive pressure drop through the heating coils.
- Air leakage, generated by operation of the process condensate collection system, contributed significantly to the overall heat losses of the bench-scale SRAT concentration process.

- Increasing the solids concentration of simulated NCAW from 2.7 wt% to 10.4 wt% did not affect bench-scale heat-transfer rates.
- Solids accumulated on exposed internal components of the bench-scale SRAT during batch-transfer feed concentration. However, no accumulations were observed on the submerged coils.

Based on the results of the study of effects of feed composition and formic acid addition on glass redox state, the following conclusions were drawn:

- Adding formic acid to the HWVP feed can sufficiently modify its rheology and redox state over the compositional ranges tested, and thus sugar can be eliminated.
- Adding 25 to 30 mL of formic acid/L of feed effectively adjusted the glass redox state and melter feed rheology of all nine feed compositions tested. It kept the ferrous-to-ferric ratios between 0.005 and 0.3, and the yield stresses below 86 dyne/cm^2 , for all nine feeds tested.
- Basing the formic acid addition on feed composition improves the control of the HWVP feed's redox state and rheology.
- Of the nine feed compositions tested, only one (low iron) did not exhibit a yield stress within the 10 to 70 dyne/cm^2 range specified for the DWPF melter feeds. Yield stresses for melter feed samples from the low iron composition were all below 3 dyne/cm^2 . Previous studies, however, have shown that the DWPF range is unnecessarily limiting when used as design criteria for the HWVP melter feeds.
- The glass redox state of a given HWVP melter feed simulant is a function of the extent to which the reducing reactions have occurred, as determined by the Gibbs free-energy potential for each component reaction, and the amount of reducing agent added to the feed.
- The ferrous-to-ferric ratio of the glass, at equivalent levels of formic acid addition, increases when the concentration of zirconium or sodium (relative to other components) is increased in the feed.

Increasing this concentration decreases the amount of multivalent components that reduce before ferric ion reduction. This makes more reducing agent available to reduce the ferric ion, thereby increasing the ferrous-to-ferric ratios.

- The ferrous-to-ferric ratio was seen to increase when the relative concentration of aluminum was decreased. However, the Gibbs free-energy potentials show that aluminum is not reduced before the ferric ion. Reasons for these contrasting effects on redox state between the aluminum and the sodium and zirconium concentrations are not evident.
- Feed composition variability was found to significantly affect the glass redox state of the HWVP feed simulants. The results showed that the high zirconium and NCAW'86 feeds exhibit the highest ferrous-to-ferric ratios; the high aluminum and high iron feeds exhibit the lowest.
- Formic acid "stoichiometry" (based on the acid/base reactions that occur between the formic acid and selected feed components during feed preparation) did not alter the near-linear relationship between redox state and formic acid concentration that existed for the nine HWVP feed simulants.
- Formic acid stoichiometry alters the linear relationship between formic acid addition and the glass redox state for DWPF feed simulants, however. This alteration is caused by carbon dioxide release from the formic acid reactions that involve nitrites, carbonates, and manganese oxide, which are currently not included in the HWVP feed simulants. Future HWVP feed simulants need to include these components if their concentrations are found to be significant.
- Formic acid stoichiometry affects the pH of each feed composition. The pH of the waste may be used to monitor and control the rate of the formic acid reaction that occurs during processing.

- Feed rheology is affected primarily by the concentration of iron in the feed. Rheological results show that the high iron and low aluminum feeds exhibit the highest yield stresses and apparent viscosities; the low iron feed exhibits the lowest yield stresses and apparent viscosities.

CANISTER FILLING AND HANDLING SYSTEMS

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SUMMARY

During filling of the canisters with radioactive waste, semivolatile radioactive components will contaminate canister exteriors. A simple, effective decontamination method is being developed for West Valley Nuclear Services Co., Inc. The method employs a reduction/oxidation system [Ce(IV)/Ce(III)] in nitric acid solution to chemically mill a thin layer from the canister surface, removing surface contamination as canister surface dissolves. Several other methods had been evaluated previously by West Valley staff. Potential advantages of the Ce(IV)/nitric acid process over other methods include: more effective canister surface decontamination, simpler equipment requirements, fewer support service requirements, single-use throwaway solution, process-compatible waste stream, and compatible time-cycle requirements.

As part of a bilateral agreement between the Federal Ministry for Research and Technology (FRG) and the U.S. Department of Energy (DOE), the Nuclear Waste Treatment Program (NWTP) at the Pacific Northwest Laboratory (PNL) is preparing 30 radioactive canisters containing borosilicate glass for use by the 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. Preliminary tests of the system were conducted earlier to gain information on operating characteristics and develop operating parameters. During this reporting period, the final ten tests of the series were performed. In these tests, the operating parameters were further refined in preparation for electropolishing the FRG canisters filled with radioactive borosilicate glass. The thermal fracturing

tests for the FRG were also completed on an additional two instrumented canisters, the data from them were transmitted to the sponsor, and the test facility was dismantled.

INTRODUCTION

At the West Valley Nuclear Services Company, Inc., in West Valley, New York, high-level radioactive waste will be vitrified into a borosilicate glass form. The molten glass will then be poured into large stainless steel (304L) canisters. During the filling, volatile radioactive components, chiefly ^{137}Cs , will contaminate canister exteriors. The smearable contamination on the surface of the canisters must be removed before they are ultimately shipped to a repository for disposal.

West Valley staff had previously evaluated several canister decontamination methods, including electropolishing, liquid abrasive blast, high-pressure water wash, and ultrasonic cleaning. An alternative technique was identified that employed a cerium ion-based reduction/oxidation system [Ce(IV)/Ce(III)] in nitric acid to chemically mill the surface of a canister submerged in the solution. Additional laboratory investigation of this process has since been conducted at PNL (Bray 1987; Bray and Thomas 1987) to assess the important parameters of the Ce(IV) process and to simplify the process as initially conceived.

The Department of Energy has a project agreement with the Federal Ministry for Research and Technology in the FRG to provide 30 canisters of radioactive waste for the German repository testing program. PNL is providing the vitrified waste, containing specified amounts of ^{137}Cs and ^{90}Sr , in sealed stainless steel canisters. The filled canisters are being inspected and decontaminated at PNL: the smearable surface radionuclides will not exceed 2200 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.

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 has been necessary to verify the performance of engineered design features. The system requires extensive non-radioactive testing before installation in A-Cell.

As part of the bilateral agreement and in collaboration with the Karlsruhe Nuclear Research Center and the Institute for Underground Storage, PNL is also performing thermal fracturing tests on two additional canisters filled with waste glass. These canisters were specially instrumented with temperature and acoustic emission sensors and filled with a diluted formulation of the same highly radioactive glass so that each contained about 1 kW of decay heat.

TECHNICAL PROGRESS

CERIUM(IV) CANISTER DECONTAMINATION

Small-scale nonradioactive laboratory tests of the Ce(IV)/HNO₃ decontamination process were initially conducted with stainless steel coupons. Stainless steel dissolution (chemical milling) rates were determined by weight loss from the coupons as a function of initial Ce(IV) concentration [0.0025M to 0.1M Ce(IV)], temperature (25 to 78°C), and contact time (1 to 12 hr). The ratio of coupon surface area to solution volume was held constant at ~53 ft² (the surface area of the West Valley canister) to 175 gal of decontamination solution. Weight loss from the coupons increased with increasing temperature, time, and initial Ce(IV) concentration. Weight loss approached the value expected from the theoretical Ce(IV):Fe mole ratio of

3:1 with increasing contact time. This ratio is based on the following reaction:

Extrapolated to the canister surface, about 0.06 to 0.13 moles of Ce(IV) will remove a layer of stainless steel ~ 1.5 to $3 \mu\text{m}$ thick per 1 ft^2 .

Tests were also conducted using radioactively contaminated coupons to verify results from the nonradioactive tests. Stainless steel coupons had previously been installed on the outside of canisters that were filled with radioactive glass while inside a turntable similar to that to be used at West Valley. Some of the coupons were later analyzed for the characteristics and extent of the radioactive contamination (Thomas and Bray 1987). Other coupons were used to evaluate the effectiveness of the Ce(IV) decontamination technique. Various coupon decontamination schemes were applied, and test parameters were varied. The coupons were then reanalyzed to determine the decontamination factors that resulted from the various combinations. After decontamination, each coupon was smeared in a manner that simulated canister smear testing. This was done to determine whether they would comply with applicable federal specifications for smearable surface contamination of decontaminated canisters.

Results of the nonradioactive coupon tests indicated that the process performed very closely to theoretical expectations for dissolution of the stainless steel. Results of the radioactive tests showed that removal of $\sim 1.5 \mu\text{m}$ of the stainless steel surface was not sufficient for samples to meet the smearable contamination limits. When $\sim 3 \mu\text{m}$ of surface was removed, specimens were decontaminated to acceptable levels. Nitric acid solution cleaning alone did not meet the requirements for surface contamination removal. Contact times of 3 to 6 hr at temperatures above 45°C appear adequate for the process and are compatible with expected overall vitrification process time cycles.

Based on the outcome of the laboratory tests, it was estimated that the process as originally conceived can be greatly simplified. The original concept included electrolytic regeneration of the cerium solution, requiring

additional complex support equipment. Following evaluation of test results, it is expected that the solution would be used once and discarded. The nitric acid-based solution would then allow the waste stream to be recycled to the vitrification process.

DECONTAMINATION OF FRG CANISTERS BY ELECTROPOLISHING

Functional testing of the canister electropolisher system was performed in the high-bay extension of 324 Building. Experiments began in April 1987 and continued through this reporting period, with a total of 20 nonradioactive tests performed. During the third quarter of FY 1987, ten tests were conducted to functionally test the equipment and to develop operating parameters for the system (see PNL-6320-3). FRG canisters were used that were filled with sand or nonradioactive glass to determine the handling characteristics. An oxidized FRG canister was electropolished, and removal of 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.

During this reporting period, the second ten tests (experiments 11 through 20) were conducted, following the repair of the malfunctioning anode grapple. These tests were performed to refine the operating parameters before electropolishing the 30 FRG canisters filled with radioactive borosilicate glass.

Experiments 11-20

In experiment 11, an unoxidized test canister was electropolished to try to obtain a highly polished surface and then to matte it by operating the electropolisher in an etching mode. The canister was first electropolished at a current density of 70 A/dm^2 for 3 min and then at 104 A/dm^2 for 3 min. This resulted in a very shiny finish on the canister wall. To matte the surface, the electropolisher was then operated at 7 A/dm^2 for 10 min, which dulled the surface.

A test canister was electropolished in experiment 12 to determine the optimum current density with which to process the canister lid. As the canister used had been oxidized with a torch, it was pitted and rough after electropolishing.

In experiment 13, the lid and sides of an oxidized canister were electropolished. It was determined that the optimum operating current density to electropolish the lid is 70 A/dm^2 . This removed all the oxide layer from the lid and left the lid highly polished and shiny. The sides of the canister were electropolished by starting with a 6-in. band at the lower end of the canister. Then the canister was lowered in 6-in. increments until it was entirely electropolished. Electropolishing from the canister bottom to the top is opposite the operation used in experiment 10, which was from top to bottom. After electropolishing this canister, the rings that were observed in experiment 10 were not observed on this canister. This confirmed that raising the canister from the electrolyte as in experiment 10 did cause the rings. The canister did, however, have an uneven appearance, with the lower wall having more of a matte finish than the upper walls (Figure 1).

The canister electropolished in experiment 14 had been filled with glass in the pilot-scale ceramic melter (PSCM). Its surface oxidation is believed to be typical of what canisters produced in the radioactive liquid-fed ceramic melter will have. Previous tests had indicated that the most effective method was to first electropolish canister walls from top to bottom at 35 A/dm^2 and then do the reverse, electropolishing from bottom to top but offsetting the position of the canister by 3 in. to obtain a more evenly polished surface. Each 6-in. interval was electropolished at 35 A/dm^2 for 5 min. Then the surface was etched by operating at a current density of 7 A/dm^2 . Using this method, the canister surface appeared polished but uneven after the first pass through the cathode ring as the canister was raised through the ring electropolishing from top to bottom. The surface polish became very even, however, after the second pass through the cathode ring as the canister was electropolished from bottom to top but offset 3 in. from the first electropolishing pass. Etching by electropolishing from bottom to top at 7 A/dm^2 for 15 min at each 6-in. interval as the canister

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FIGURE 1. Electropolished Canister with Rings Removed
but with Finish Still Uneven

was incrementally lowered through the cathode ring produced a matte finish with a measured emissivity of >0.4 .

In experiment 15 the electropolisher was operated for more than 35 hr with a simulated FRG canister. This was done to accumulate operational hours

on the system and to determine whether any stray electropolishing of the tank was taking place.

In experiment 16, a canister was used which had been filled with glass in the same PSCM run as in experiment 14. The objective of this experiment was to electropolish this canister using exactly the same procedure as used earlier and observe whether any changes in results would occur because of the large increase in metal ions after the prolonged operation in experiment 15. After experiment 16, the electropolisher was down-loaded, and there was no indication that unwanted electropolishing of the electropolisher tank was occurring.

Experiment 17 focused on developing the optimum operating parameters for electropolishing the bottom of canisters. The bottom of an oxidized test canister was electropolished at 500 A for 10 min positioned 2 in. above the lower electrode of the cathode cage. The result was that although the bottom was polished, the dimple centered in the bottom was not polished.

The PSCM-filled canister from experiment 16 was used to determine operating parameters for electropolishing the canister bottom. The canister was positioned 4 in. off the lower electrode and operated at current settings of 500, 1000, and 1500 A. Although the canister bottom was polished, the area of the dimple was still not satisfactory. There were still areas of oxide left in it and on the remainder of the bottom.

The objective of experiment 19 was to remove from the sides of the same canister the rings which were observed after experiment 16. The acid in the electropolisher was new and had no dissolved metal ions. The canister was electropolished for 1 min at a current density of 35 A/dm^2 in 6-in. increments from bottom to top on the canister sides. The rings all disappeared, and the finish was dull (Figure 2) and had a measured spectral emissivity of >0.4 .

In the final test of the series, the PSCM-filled canister from experiment 14 was used. The bottom was electropolished at positions of 4 and 6 in. above the lower electrode on the cathode cage at a current density of 70 A/dm^2 . The best results were obtained when electropolishing the canister

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FIGURE 2. Oxidized Canister Before and After Electropolishing

bottom at a position of 6 in. off the bottom electrode and at a current setting of 1000 A.

Operating Procedures Established

As a result of the 20 tests to determine and refine operating parameters for electropolishing the FRG canisters, the following procedures were established.

The canister lid is electropolished first at 1000 A for 10 min. The electrical contact to the canister is through the lower electrode, on which the canister is sitting. The lid is located in the center of the cathode ring when the canister is in this position.

Next the bottom of the canister is electropolished. First the anode grapple is connected to the canister, which is now sitting on the lower electrode of the cathode cage. The canister is then raised to 6 in. above the lower electrode and electropolished for 10 min at 1000 A. The level of the canister is determined by reading the calibration on the side of the anode grapple, which directly corresponds to the spacing between the bottom of the canister and the lower electrode.

Lastly the canister walls are electropolished in two stages, first at a high current density and secondly at a low current density. In the first stage the power supply is operated at 500 A, and the actual decontamination takes place with the removal of ~1 mil of the canister's surface metal. The canister wall is electropolished by sequentially first raising and then lowering the canister through the cathode ring in 6-in. increments. Before the canister is lowered, it is offset by 3 in. to obtain a more uniform finish. In the second stage, with the power supply set at 100 A, the canister surface is etched to dull it and enhance its emissivity. An emissivity of greater than 0.4 is specified to provide for adequate heat transfer in the canister shipping cask.

THERMAL FRACTURING TESTS

During the report period the last four of 14 controlled cooling experiments were completed with two instrumented canisters to evaluate the effects of radionuclide self-heating on the cracking of large glass castings. Experiments 11, 12, 13, and 14 are listed in Table 1 together with the overall schedule of the tests. The last four cooling experiments proceeded without difficulty, and no changes in procedure were required.

With the completion of the last experiment, copies of all thermal and acoustic emission data taken during the thermal fracture tests were transmitted to the sponsor for analysis.

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 7/07/87	5 5/07/87	6 5/25/87
					13 7/17/87	9 6/12/87
	14 7/24/87	--	2 4/29/87	4 5/05/87	8 6/02/87	10 6/22/87
13 (lined)						12 7/10/87

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

The control systems for the two heating zones of the remelt furnace controlled the temperature of the canisters in the vicinity of the system feedback temperature sensors with superlative accuracy. It is believed, however, that the primary intent of the control system, to provide a controllable isothermal environment within the remelt furnace, was not realized. This point was clearly seen: mid-level skin temperatures of the canisters were consistently higher during the heating-up and equilibrating portions of the programmed temperature cycling, and then the controlled cooling periods consistently showed higher temperatures on both the canister mid-level and top-level sensors than on the bottom-level sensor. Also, a dark spot on the canister wall, where furnace cooling air was injected, indicated nonisothermal conditions on the canister surfaces at this point during controlled cooling. With thermocouples located at only three levels in the canisters, the actual deviation from isothermal conditions could not be measured.

Furthermore, less power was consistently required to maintain the upper heating zone at the same temperature as the lower heating zone. This fact, coupled with the nonuniform skin temperatures, suggested that the upper zone was being heated convectively from the lower zone and that the mid-level of the canister was being heated from both zones. These differences resulted in

complex temperature gradients in both the upper and lower halves of the canisters.

CONCLUSIONS

Ce(IV) DECONTAMINATION PROCESS

Results of the nonradioactive coupon tests indicated that the process performed very close to theoretical expectations for dissolution of the stainless steel. Results of the radioactive tests showed that removal of $\sim 1.5 \mu\text{m}$ of the stainless steel surface was sufficient for some samples to meet the smearable contamination limits. When $\sim 3 \mu\text{m}$ of surface were removed from two coupons, both specimens were decontaminated to acceptable levels. Nitric acid solution cleaning alone did not meet the requirements for surface contamination removal. Contact times of 3 to 6 hr at temperatures above 45°C appear to be adequate for the process and are compatible with expected overall vitrification process time cycles.

Based on the outcome of the laboratory tests, it was estimated that the process as originally conceived can be greatly simplified. Following evaluation of test results, it is expected that the cerium solution would be used once and discarded. The nitric acid-based solution would then allow the waste stream to be recycled to the vitrification process.

Engineering-scale design of the decontamination system is being completed for West Valley Nuclear Services in FY 1988.

TESTING OF THE ELECTROPOLISHING SYSTEM

Preparatory to decontamination of the 30 FRG canisters of radioactive glass, the electropolishing system has been tested extensively and optimum operating parameters defined. The equipment will be installed in A-Cell, where the canisters will be electropolished.

THERMAL FRACTURING TESTS

To obtain more nearly isothermal furnace conditions, the following changes are recommended if a similar test facility is assembled for future tests:

- Increase the length of the furnace to about 150% of the length of the canister, and position the canister so that there is the same free space above and below the canister to expose the canister surface to approximately the same heat source from the center of the canister to the two ends.
- Decrease the clearance between the furnace walls and the canister walls to minimize convection in the furnace air space.
- Increase the number of controlled heating zones to at least six, one each for the space above and below the canister and four for the length of the canister.
- Insulate the furnace heavily above and below the level of the top and bottom of the canister to minimize "end effect" heat losses.
- Minimize furnace wall insulation from the level of the top of the canister to the bottom of the canister to provide a means of heat loss from the canister for controlled cooling periods. Do not sparge the furnace with cooling air to cool the canister within the furnace. This merely overheats the canister downstream of the injection of the cooling air.

REFERENCES

- Bray, L. A. September 1987. Development of a Chemical Process Using Nitric Acid-Cerium (IV) for Decontamination of High-Level Waste Canisters. WVST 87/263A. Pacific Northwest Laboratory, Richland, Washington.
- Bray, L. A., and N. M. Thomas. 1987. "Decontamination of Stainless Steel Canisters That Contain High-Level Waste." Transactions, vol. 55, TANSO 55 1-760, ISSN:0003-018X, American Nuclear Society, Inc., La Grange Park, Illinois. Presented at the 1987 Winter Meeting, Los Angeles, California.
- Thomas, N. M. and L. A. Bray. September 1987. Summary of RLFCM Canister Contamination Testing. PNL-6567, Pacific Northwest Laboratory, Richland, Washington.

PROCESS/PRODUCT MODELING AND CONTROL

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SUMMARY

A simulation model has been developed and tested preliminarily by applying it to approximate operation of the West Valley Demonstration Project (WVDP) vitrification system. A control logic for the WVDP process was approximated and cast in the form of an input file as required by the simulation model. Multivariate statistical techniques have been identified and described that can be applied to analyze large sets of process measurements.

The TEMPEST heat-transfer computer code was used to simulate thermal behavior of nuclear waste glass in canisters of varying dimensions. The experimental data obtained provided a sufficiently accurate basis for validation of this code.

INTRODUCTION

The main objective of this work is to demonstrate and document a technical approach to waste-form qualification. However, special attention is being given to the technical approach's applicability to the WVDP. A technical approach has been developed that calls for developing product and process models as means for relating product quality to process measurements. Because the Nuclear Waste Technology Program (NWTP) is not responsible for qualifying a specific vitrification process, its contribution is chiefly to provide and demonstrate waste-form qualification methodology in a manner that will assist waste-form producers to develop their waste-form qualification reports.

The process models consist of a mass balance model predicting the glass composition and a thermal model predicting the temperature history in glass poured into a canister. Work on product models is limited to integrating

into the process model the general relationships between the composition and the durability of a glass and between the extent of devitrification and the temperature history of a glass. Work on process and product models is described below.

TECHNICAL PROGRESS

VITRIFICATION PROCESS SIMULATION

A principal objective of the NWTP is to establish relationships between vitrification process control and glass product quality.

An important goal during testing of a vitrification system is to show that departures significant enough to affect product quality can also be detected in time to prevent an unacceptable canister from being produced, while also showing that departures too insignificant to be detected will not significantly decrease the quality of the product. That both of these hold is a practical definition of a successful strategy for sampling, data analysis, and process control. Simulation of the process allows this definition to be tested early in the development of a process, based on whatever hypothetical departures from ideal process behavior can be identified and included in the simulation.

The NWTP approach to waste-form qualification thus includes:

- simulating the process
- introducing departures from ideal behavior
- analyzing the data as though it were real data in order to determine:
 - the effectiveness of statistical methods to monitor and control the process when departures from ideal behavior occur
 - what impact detectable departures from ideal behavior have on the quality of the product.

Implementation of the approach is not yet complete; two important steps, however, have been added. First, a simulation model has been developed and

tested preliminarily by applying it to approximate the operation of the WVDP vitrification system. A control logic for the WVDP process was approximated and cast in the form of an input file as required by the simulation model. The model includes the capability to simulate random errors in measurement and control, systematic errors, and departures from ideal mixing behavior. This provides for generating large sets of simulated process measurements that reflect the existence or absence of systematic errors or departures from ideality. These sets can be investigated using trial data analysis techniques to determine whether such errors or departures can be detected during operation of a real process.

Secondly, multivariate statistical techniques have been identified and described that can be applied to analyze large sets of process measurements. Their use in controlling a process through process control charting is also described. The techniques involve collecting information on the composition of a number of the chemical components in the feed and glass, for batches in each of the tanks (including the melter), and for each repetition of the batching cycle of the vitrification system. This information over components, tanks, and time is then combined to create a single statistic through which all the information can be used at once to determine whether the process has departed from normal operation. Process control charting is used to examine the statistic and to make decisions about the need for changes in the process.

Simulation Model

In an ideal process there would be ideal mixing in tanks, and, aside from measurement and control errors, the composition of the feed and glass could be predicted from simple mass balances. Plausible departures from such ideality that could affect the validity of an assumed mass balance model would be sedimentation and resuspension of part of a slurry in tanks. Sedimentation and resuspension of solids in a slurry are addressed in the process simulation. Caking of all the slurry on the sides of tanks and return of cake to the slurry are also included. Other phenomena can be included as desired.

A vitrification process was simulated by defining the following:

- tanks (which might not be process tanks) for which transient mass balances are solved by integration time derivatives of masses in the tanks
- phases within tanks that allow water, dissolved solids, undissolved (suspended) solids, and sediment and caked material to be treated separately in the calculations
- streams connecting tanks to each other
- events described in terms of volumes of liquid in tanks or of elapsed time, which when detected interrupt the normal integration over time and cause various actions that modify the process (for example, streams are turned on or off).

Each tank in the process is described in terms of the distribution of each incoming chemical component among phases 1 through 3 (only water resides in phase 1) and the density of each of the phases in that tank. The tanks have no prescribed volume; the volume is manifest only in control actions, where the volumes at which liquid transfers begin or end are specified. To allow simulation of the disposition of chemical species upon entering tanks, leaving tanks, and while in tanks, five phases are defined to exist in each tank. They are 1) water, 2) dissolved solids, 3) suspended, undissolved solids, 4) undissolved solids settled on the bottom of a tank, and 5) dissolved and undissolved solids caked on the sides of a tank above the liquid level. Each stream in the process is described by its inlet and outlet tanks, and the simulation continuously determines whether it is flowing at any given time. The distribution of mass from a tank into a stream is described in terms of the fraction of the volumes of each of phases 1 through 3 in the tank that contributes to the volumetric flow rate of the stream.

Control of the process is defined in terms of events; these are either that a volume reaches some specified value or time reaches some specified value. Whenever an event occurs, some predetermined control action is taken. Examples of actions are turning a stream on or off, defining that some condition is true or false (for use in future control decisions), taking a sample from a tank, etc. Once an event occurs, any number of control actions might

occur, including secondary reactions to actions. However, the entire series of actions always begins when an event is detected. The process is simulated as being stochastic by introducing uncertainty into the simulation of certain measurements and actions as follows:

- The act of sampling is treated as though collecting suspended solids from the liquid is a random process characterized by a normal distribution centered on equal access to liquid and suspended solids by the sampler (this is discussed further below) with a specified standard deviation.
- Chemical analysis of samples is treated as though the reported individual weight fractions were random, uncorrelated, and described by a normal distribution centered on the true weight fractions with a specified relative standard deviation.
- Detection of events by comparing volumes in tanks to specified values is treated as though measurement of the volume is random and described by a normal distribution centered on the actual volume with a specified relative standard deviation.
- Addition of chemical components is treated as being random and described by a normal distribution centered on the calculated masses to be added and with a specified relative standard deviation.

A process control strategy is implemented in a simulation by defining a set of "cases." Each case is described in terms of a set of tests followed by a set of actions. The tests for a case are evaluated using "and" logic. That is, all tests must be satisfied before the case actions are executed. The tests that are included are for a specified liquid volume occurring in a tank, for a stream flowing or not, and for a flag set true or false.

There are currently seven kinds of actions that might be taken, separately or in combination, if a case's tests are met and the case is executed. They are: change stream flow, set flag, delay, sample, test contents, add chemicals, and reset tank.

To evaluate the ability of the methods described above to simulate a vitrification process, they were applied to the case of a system patterned

roughly after the West Valley Demonstration Project at West Valley, New York (see Figure 1). The simulation is not of this process exactly, since parts of the West Valley process and control strategy are still being determined. Rather, some of the essential features of the process have been included as well as plausible values for the simulation parameters in order to test the simulation methods.

A strategy for controlling the WVDP vitrification process was constructed that is thought to simulate roughly the actual process. We have not attempted to simulate the WVDP control strategy faithfully; rather, we assume the construction is close enough to reality to provide a realistic test of our simulation model. Probably the most significant departure from our understanding of the WVDP strategy is that we have included an additional sampling step.

The salient features of the control strategy simulation are as follows:

1. Liquid is sent from the submerged bed scrubber (SBS) to the concentrator feed makeup tank (CFMT) if the measured liquid volume in the SBS has exceeded a specified level.

FIGURE 1. Schematic of LFCM Vitrification System Patterned Generally After the West Valley System

2. Waste is transferred from the waste tanks to the CFMT whenever the measured liquid volume in the CFMT is low enough and provided that any need to send liquid from the SBS has been satisfied.
3. After the CFMT receives liquid from the SBS and then is filled from the waste tanks, the contents are sampled, the amount of volume to be removed by evaporation is computed, and evaporation begins.
4. When the evaporation is complete as determined by measuring the volume in the CFMT, chemicals are added to create a feed that will become glass of the target composition, with enough water being added to achieve a desired solids loading in the feed. The chemicals and water are assumed to be added in the form of a slurry; if the solids loading of the slurry would exceed a specified limit, part of the contents of the tank are sent back to the waste tank, and the chemicals to be added are computed again.
5. After the addition of chemicals is completed, a sample is taken. This is believed to be a departure from current WVDP plans, but was included to simplify (in the simulation) recording the contents of the CFMT after the chemicals are added.
6. The chemical addition cycle in the CFMT is completed and the liquid in the melter feed tank (MFT) is decreased to a specified volume. Then feed is transferred from the CFMT to the MFT until either the liquid in the CFMT has decreased to a specified volume or in the MFT it has increased to a specified volume.
7. The contents of the MFT are sampled. If allowed (see below), feed is sent to the melter. Once the MFT sample results are available, they are checked to see if the contents are acceptable. If not, melter feeding is stopped, the contents are rejected to the waste tank, and the MFT awaits a replacement batch from the next CFMT cycle.
8. Feeding the melter is disallowed if the liquid volume in the SBS exceeds a specified level, if melting is disallowed (see below), or if feed is not available from the MFT.

9. Melting is disallowed if the volume of glass in the melter is too high and a canister is not in place.
10. Glass pours from the melter to the canister by overflow whenever the glass volume exceeds a pouring threshold.
11. When the volume of glass in the canister reaches a specified level, glass is airlifted from the melter to the canister for a specified period. When the airlift is complete, a new canister is installed.

The simulation progressed with an average speed of 200 simulated hours per computer hour using a MicroVax® computer system.

Multivariate Statistical Process Control

Multivariate statistical methods intended for use as part of waste-form qualification have been developed in four parts as follows:

1. Models have been developed that describe the relationships of the concentrations of chemical components (expressed as oxides in the equivalent glass) in adjacent tanks as batches progress from tank to tank. The models have been formulated in matrix form to facilitate the development and description of a corresponding computational scheme. In the development the vitrification system has been approximated as a feed preparation tank, melter feed tank, and melter; for the WVDP, these would be the CFMT, melter feed tank, and melter. All tanks have been assumed to be perfectly mixed. The effect of any accumulation in the cold cap in the melter has been neglected.
2. Multivariate statistical methods have been used to develop equations for estimating the true oxide concentrations in tanks. The methods account for correlation between concentrations (for example, tank to tank and component to component) that would be expected in the data. This is particularly important when trying to sense whether the process is in statistical control or whether it is drifting--that is, fluctuations increasing or changing in character. One needs to evaluate not how a

® A registered tradename of Digital Equipment Corporation, Maynard, Massachusetts.

single variable fluctuates, but how several variables fluctuate together. For example, it may be normal--that is, typical of a stable process--for two measured variables to fluctuate independently of each other, but not for them to fluctuate in unison. Multivariate statistical methods have been applied to permit distinguishing between such cases for a large set of measured variables or to discover what relationships are normal among complicated combinations of measured variables.

3. Multivariate process control charts have been described that can be used for monitoring the oxide concentrations of the frit/waste slurry wherever it is sampled in the process. To control the process based on deviations from normal behavior as discerned from many measurements, at several locations, and over weeks of time requires a method for combining all such data into a single statistic. Data can be combined into a statistic distributed as "Hotelling's T^2 " statistic; its application to process control charting has been examined.
4. The extent of sampling required and the assumptions that have been made in the statistical analyses have been examined. It is important to determine what sampling is required to build covariance matrices from process measurements one wants to consider when monitoring and controlling the process.

MULTIVARIATE STATISTICAL ANALYSIS OF GLASS DURABILITY

In controlling a process it is desirable to limit the number of variables whose values are to be constrained. In the case of a waste vitrification system, one important quality characteristic of the glass to be achieved is adequate chemical durability. Plodinec, Jantzen, and Wicks (1984) and Grambow (1985) have related the durability of nuclear waste glasses to their composition by calculating a free energy of hydration for each glass and correlating it with the chemical durabilities.

It is also possible to reduce such data using purely statistical methods. Data accumulated by Plodinec, Jantzen, and Wicks^(a) and by Chick et al. (1984) were analyzed to examine the relationship between the logarithm of chemical durability and the composition of the glass. The release of boron into solution after 28 days in a static leach test was taken to be the measure of chemical durability.

The data were analyzed using the "partial least squares" (PLS) method (Wold 1982). This is an extension of the principal components method for extracting from a covariance matrix a set of variables that are each linear combinations of the original variables used to form the matrix. These new variables, called principal components, more clearly reveal the source of the covariances. Often the majority of the variance over the independent variables is explained by a few principal components; if so, it implies that some of the supposedly independent variables are in fact not statistically independent and should be reduced to a fewer number of variables (viz., principal components) before attempting correlations with a dependent variable.

The PLS method differs from the principal components method in that the principal components are "rotated" (thinking of the principal component in a vector in "space" where the "directions" are the different independent variables, e.g., weight fractions) to line up better with a "vector" representing the dependent variable, e.g., chemical durability. This results in forming a clearer picture of the contribution of the independent variables in predicting the values of the dependent variable. Specifically, the relative importance of the independent variables in predicting the dependent variable is established.

When used in correlating the chemical durability of a collection of nuclear waste glasses to their composition, the PLS method reveals the relative importance of different chemical elements to the correlation. The importance is revealed by examining the contribution of the weight fractions of the elements to the PLS components. These contributions are termed "loadings," and they describe how a PLS component is formed as a linear

(a) We are indebted to Dr. Carol Jantzen of Savannah River Laboratory for making this data available.

combination of the weight fractions. The magnitude of the loadings is not easily interpreted, but the relative magnitudes of the loadings describe the relative importance of the weight fractions to the chemical durability.

The result of applying a PLS analysis to the data of Plodinec, Jantzen, and Wicks and of Chick et al. (1984) is shown in Table 1. For the data examined, the " R^2 " value is 0.75, meaning that 75% of the variance of the dependent variable (chemical durability) can be explained by the nonrandom effect of the independent variables (weight fractions). Practically all of this variance is explained by only the first three of the PLS components. These components are as shown in Table 1; the values in the columns are the "loadings" that show how each of the three components depends linearly on the weight fractions of the chemical elements listed.

The first PLS component alone explains about 50% of the variance. A component constructed instead by "loading" in proportion to the free energies of hydration of the chemical elements (which is equivalent to applying the free energy of hydration correlation discussed above) explains about 40% of

TABLE 1. Results of Applying Partial Least Squares Analysis to Data on Nuclear Waste Glasses

Element	First PLS Component	Second PLS Component	Third PLS Component
Al	-0.32	-0.24	-0.08
Ca	-0.06	-0.34	-0.14
Fe	-0.02	-0.15	-0.45
Mg	-0.11	0.41	0.34
Mn	-0.10	0.19	-0.39
Na	0.53	0.04	0.06
Li	-0.03	0.37	-0.08
Ni	-0.06	0.06	-0.28
Si	-0.48	-0.17	0.08
Cr	0.13	-0.30	0.21
B	0.49	0.11	-0.08
Sr	0.06	-0.19	0.35
Zr	-0.08	0.05	0.27
Ti	-0.20	0.31	0.22
K	-0.14	0.26	0.10
Cs	-0.04	-0.20	0.14
P	0.15	-0.28	0.24
Nd	-0.08	-0.10	0.18

the variance. From a purely statistical viewpoint, the first PLS component does as well or better than the free energy of hydration in explaining the data. Therefore, it is worth examining the loadings to see what is implied.

The first PLS component depends most strongly on the aluminum, sodium, silicon and boron weight fractions. The signs of the loadings show that, to a rough first approximation, the chemical durability depends on the ratio of the weight fractions of sodium and boron to silicon and aluminum. The implications of this are that in trying to control a waste vitrification process to maintain acceptable chemical durability of the glass, controlling the ratio (for example) of sodium and boron to silicon and aluminum should be emphasized. This implication needs further confirmation, but if confirmed suggests that the fluctuation of some chemical components during processing may need to be closely controlled, while others may not be important enough to be included in process control criteria. For example, given the above results, it might be desirable to control independently the sodium, boron, silicon and aluminum weight fractions when adding chemicals to form the melter feed from the waste, while it may also be unnecessary to control other chemical species.

CANISTER THERMAL MODELING

The TEMPEST heat-transfer computer code^(a) was used to simulate thermal behavior of nuclear waste glass after it is poured into canisters for long-term storage. This work was done to determine the accuracy and applicability of the TEMPEST code when used to compute canister thermal histories.

The TEMPEST code was selected for use in this study for five primary reasons:

- TEMPEST can compute combined conduction and convection directly based on fundamental physical principles (the physical conservation laws) without having to use empirical convection-related heat transfer coefficients.

(a) Trent, D. S., L. L. Eyler, and M. J. Budden. 1983. TEMPEST - A Three-Dimensional Time-Dependent Computer Program for Hydrothermal Analysis. Volume I: Numerical Methods and Input Instructions. Pacific Northwest Laboratory, Richland, Washington.

- TEMPEST allows for three-dimensional solutions of transient thermo-fluid phenomena using temperature-dependent material properties that can be specified by the user. TEMPEST can model density-induced flows and the large changes in viscosity with temperature that are typical of glasses.
- TEMPEST is accurate and user-friendly. Significant verification and benchmarking experience with the code has been accumulated and documented.^(a)
- TEMPEST is portable; it is written in ANSI FORTRAN-77 and will run on virtually any machine. It is currently being used on CDC-7600 computers, as well as CRAY-1S, CRAY-XMP, DEC-VAX, and IBM machines.
- TEMPEST is available for continued code development and refinement, so that discrepancies in the comparison of any results with computer predictions can be rectified.

Despite its advantages, TEMPEST is not entirely without weaknesses when modeling the complex thermofluid phenomena associated with pouring waste glass into canisters and the following cooldown. The glass pouring and cooldown procedures result in relatively slow transients in which radiation is also a dominant mode of heat transfer. Inside the glass, conduction and, at high temperatures, convection are also important. The large temperature changes result in extremely wide ranges of viscosity that TEMPEST was not designed to handle.

Related to potential cracking and devitrification is the cooldown history of a canister when emplaced on a turntable with other canisters in various stages of fill/cooldown themselves. Modeling the cooldown history requires a nonconcentric cylindrical coordinate system, or even a multi-region coordinate system. TEMPEST does not currently have such a capability.

(a) Eyler, L. L., D. S. Trent, and M. J. Budden. 1983. TEMPEST - A Three-Dimensional Time-Dependent Computer Program for Hydrothermal Analysis. Volume II. Assessment and Verification Results. Pacific Northwest Laboratory, Richland, Washington.

Finally, TEMPEST, like most codes, is a fixed-grid code. Pouring glass into the canisters causes a moving boundary or interface between glass and air. For best accuracy, the moving glass/air interface must also be modeled.

For these reasons, the actual TEMPEST models described in this report contain simplifications and approximations, some of which are significant.

Experimental data were obtained to validate our application of the TEMPEST code. Five canisters of three different designs were used in the two pilot-scale ceramic melter (PSCM) experiments. All were made of 304L stainless steel. Their design features are compared in Table 2. Three canisters had 12-in. nominal diameters; the other two were 13 in. and 24 in. in diameter. Canister height varied from 45.4 in. to 85.4 in. The bottoms of the 12-in.-dia canisters were flat except for a 0.5-in. lip and a 3.5-in.-dia by 1.6-in.-high cylindrical bulge in their centers. The bottom of the 13-in.-dia canister was slightly rounded and supported by four bars located at 90° intervals beneath the canister. The 24-in.-dia canister's bottom was dished up 1.06 in. in the center, in a reversed-flange design. The radial variation of this design is shown in Table 2.

The inside surfaces of the 13-in.-dia canister were lined with 1/8-in.-thick Fiberfrax paper and a graphite mold release compound. Half of the bottom and a 180° arc of the side were lined with Fiberfrax; the remainder of the canister was coated with graphite mold release agent. This was done to compare the effects of Fiberfrax, which minimizes both shear and compressive stresses, to the mold release compound, which reduces only the shear stresses at the wall. This canister was insulated with the same total amount of combined internal and external insulation in both the graphite and the Fiberfrax sides, to keep radial temperature differences the same for both the graphite- and Fiberfrax-lined regions. Thus, in addition to the 1/4 in. of Durablanket placed over the entire surface, 1/8 in. of Fiberfrax paper was used on the outside of the graphite-coated region. The other canisters were covered with 0 in. to 3 in. of Durablanket insulation (Table 2).

The canisters were filled using the PSCM at PNL in either a continuous- or batch-filling mode. Typical results are shown in Figures 2 and 3. One of the canisters was also filled within a simulated turntable (a group of

TABLE 2. Canister Information

Design Features	Canister				
	12LI	12HI	12TTS	13	24
PSCM run	20	20	20	21	21
Height, in.	45.4	45.4	45.4	56.0	85.0
Outside diameter, in.	11.75	11.75	11.75	12.75	24.0
Inside diameter, in.	11.12	11.12	11.12	12.25	23.5
Wall thickness, in.	0.31	0.31	0.31	0.25	0.25
Liner					
Material	FF ^(a)	FF	FF	FF&gr ^(b)	Dura ^(c) &FF
Thickness, in.	1/8	1/8	1/8	1/8 ^(b)	1/4 sides 1/2 bottom
External insulation					
Material	Dura	Dura	Dura	Dura & FF ^(d)	None
Thickness, in.	1/4	3	--	1/4 & 3/8 ^(d)	--
Bottom design	Bulge	Bulge	Bulge	Rounded	Dished

(a) Fiberfrax[®] ceramic paper type 970J (12 lb/ft³ density).

(b) A 180° arc and half of the bottom of this canister were lined with 1/8 in. of Fiberfrax. The remainder of the canister was coated with a graphite mold release compound (Dylon Grade AE Mold Release Agent, Dylon Industries).

(c) Durablanket[®] (8 lb/ft³ density).

(d) A 180° arc and half of the canister bottom were externally insulated with 1/8 in. of Fiberfrax and 1/4 in. of Dura-blanket (graphite side, see [b]). The remainder of the canister was externally insulated with only 1/4 in. of Durablanket.

® Fiberfrax is a ceramic paper manufactured by Carborundum Resistant Materials Co., Insulation Division, Niagara Falls, New York.

® Durablanket is a ceramic fiber blanket manufactured by Carborundum Resistant Materials Co., Insulation Division.

FIGURE 2. Typical Experimental and Predicted Temperatures for a 12-in. Canister Filled in Three Batch Pours. The glass level did not reach the thermocouple (located 24.9 in. from the bottom) until the second pour.

cylindrical shells with heat-transfer resistances similar to those of an actual canister in a liquid-fed ceramic melter turntable). This was done to provide a basis for assessing the TEMPEST code's ability to also model heat transfer within a structure thermally similar to such a turntable.

After the data were obtained from the PSCM runs, two versions of TEMPEST--the batch-fill and the continuous-fill models--were used to simulate the experimental conditions. The thermal histories predicted by these TEMPEST versions were then compared to the experimentally measured data.

We found that the batch-fill model predicted canister centerline temperatures that agreed closely with experimental temperatures, varying from only 50 to 125°C over most of the canister cooldown period. However, during periods immediately following a glass pour, temperatures were overpredicted by as much as 250°C.

FIGURE 3. Typical Experimental and Predicted Temperatures for a 13-in. Canister with Thermocouples Located 26 in. from the Bottom. This canister was filled continuously.

The continuous-fill model was found to predict temperatures with more accuracy. Variation from experimentally measured temperatures was within 50°C or less over most of the cooldown. Close agreement was achieved also for temperatures at other radial positions away from the centerline and for periods long after the glass surface rose above a given elevation.

The experiment using the simulated turntable demonstrated that TEMPEST can adequately model the asymmetric temperature field caused by the turntable geometry. Further, TEMPEST can acceptably predict the temperatures within a turntable, despite code limitations in computing simultaneous radiation and convection heat transfer between shells, along with uncertainty in stainless-steel surface emissivities.

Based on the successful performance of the continuous-fill model, development was initiated to incorporate 1) full viscous glass convection, 2) a dynamically adaptive grid that automatically follows the glass/air interface throughout the transient, and 3) a full-enclosure radiation model to allow

radiation heat transfer to non-nearest neighbor cells. At the end of FY 1987, the first feature was fully incorporated and the second feature had been partially accomplished. A more advanced application of TEMPEST was attempted but could not be completed within available time and funding.

Details of the work described here are presented by Farnsworth, Faletti, and Budden (1988).

CONCLUSIONS

Conclusions from the process and product modeling reported here are as follows:

- For waste-form qualification, a practical definition of a successful system to monitor and control an inherently fluctuating waste vitrification process is the ability to detect departures from assumed ideal process behavior that are great enough to substantially affect product quality.
- The fluctuating behavior of compositions in a waste vitrification process can be simulated in terms of a set of cases, each consisting of a set of tests to be satisfied and a set of actions to then be taken. The tests should include at least tank volume, stream flow, and conditions signified by true/false flags. The actions should include at least: setting a flag, setting a flag after a specified delay, turning a stream on or off, evaporation, sampling tank contents, chemical addition, testing tank contents, and resetting tank masses to zero.
- Mass balances and separation of mass in a process can be simulated sufficiently to address waste-form qualification issues by considering the distribution of chemical components among phases upon entering a tank and in terms of the relative access of the phases to a stream exiting the tank.
- Multivariate statistical methods for analysis of variance and covariance can be combined with simplified mass balance equations

cast in matrix form to estimate compositions and their variance-covariance matrix for a vitrification process, where information from different tanks and different times is used simultaneously.

- The variance-covariance matrix for compositions can be combined into a single statistic approximately distributed as "Hotelling's T^2 " statistic to provide a reduced variable for process control charting. This will be sensitive simultaneously to composition data over all components, tanks, and previous sample times.
- Given a preliminary multivariate statistical analysis of glass leach data, it might be desirable to emphasize control of the sodium, boron, silicon and aluminum weight fractions when adding chemicals to form the melter feed from the waste. This approach, however, considers only the chemical durability of the glass.

Conclusions from the work testing TEMPEST code predictions against experimental data are as follows:

- The experimental data provided a sufficiently accurate basis to validate this application of the TEMPEST code and will continue to be valuable for any future code validation study of glass pour and cooldown phenomena.
- The TEMPEST batch-fill model was sufficiently accurate to be useful for many LFCM applications. However, during periods immediately following a pour, this TEMPEST model overpredicted temperatures by as much as 250°C.
- The underprediction of cooldown at times later than 10 hr after a pour is probably the result of the canister insulation having about a 25% higher effective thermal conductivity than that used by TEMPEST. Further analysis is necessary to confirm this hypothesis.
- The TEMPEST continuous-fill model did a better job of predicting temperatures than did the batch model. Temperatures predicted near the centerline were within 50°C or better over most of the cooldown.

- Experiments using a simulated turntable demonstrated the following:
 - The asymmetrical temperature profile caused by the asymmetrical turntable geometry can be modeled by TEMPEST.
 - TEMPEST produces reasonable predictions of the temperatures within a simulated turntable, despite the code's limitations in computing simultaneous radiation and convective heat transfer, and despite considerable uncertainty in the emissivities of the stainless-steel surfaces.
 - The best agreement between predicted and observed temperatures was found between the overpack to seal liner, the seal liner to thimble, and the thimble to turntable wall. Poorest agreement was observed between the canister wall to the overpack and the turntable wall to the ambient.

REFERENCES

- Chick, L. A., et al. 1984. West Valley High-Level Nuclear Waste Glass Development: A Statistically Designed Mixture Study. PNL-4992, Pacific Northwest Laboratory, Richland, Washington.
- Farnsworth, R. K., D. W. Faletti, and M. J. Budden. 1988. Application of the TEMPEST Computer Code to Canister-Filling Heat Transfer Problems. PNL-6474, Pacific Northwest Laboratory, Richland, Washington.
- Grambow, B. 1985. "A General Rate Equation for Nuclear Waste Glass Corrosion." In Scientific Basis for Nuclear Waste Management VII, ed. G. L. McVay, pp. 15-27, North Holland and New York.
- Plodinec, M. J., C. M. Jantzen, and G. G. Wicks. 1984. "Thermodynamic Approach to Prediction of the Stability of Proposed Radwaste Glasses." In Nuclear Waste Management. Advances in Ceramics, Vol 8., eds. G. G. Wicks and W. A. Ross, pp. 491-495, American Ceramic Society, Columbus, Ohio.
- Wold, H. 1982. In Systems Under Indirect Observation, Part II, eds. K. G. Jareskog and H. Wold, North Holland Publishing Co., Amsterdam, pp. 1-54.

APPENDIX

ACRONYMS AND ABBREVIATIONS

°C - degrees centigrade
Å - angstrom
CFMT - concentrator feed makeup tank
cm - centimeter
CUA - Catholic University of America
CVS - composition variability study
DG - doped glass
DIW - deionized water
DOE - Department of Energy
DWPF - Defense Waste Processing Facility
FRG - Federal Republic of Germany
g - gram
GR - Grande Ronde
HLW - high-level waste
HT-S - heat-treated sample
HW - Hanford waste
HWVP - Hanford Waste Vitrification Plant
ICP - inductively coupled argon plasma emission spectroscopy
kW - kilowatt
L - liter
LFCM - liquid-fed ceramic melter
μm - micrometer
m - meter
MCC - Materials Characterization Center
MFT - melter feed tank
min - minute
mL - milliliter
NCAW - neutralized current acid waste
NWTP - Nuclear Waste Treatment Program
PBB - Permian Basin Brines
PLS - partial least squares
PNL - Pacific Northwest Laboratory
PSCM - pilot-scale ceramic melter
redox - chemical reduction oxidation
RLFCM - radioactive liquid-fed ceramic melter
SBS - submerged-bed scrubber
SRAT - slurry receipt and adjustment tank
T100P - the temperature at which viscosity is 100 poise
TOC - total organic carbons
W - watts
wt% - weight percent
WVCM - West Valley ceramic melter
WVDP - West Valley Demonstration Project
WVNS - West Valley Nuclear Services Company, Inc.

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