LFCM Vitrification Technology

Quarterly Progress Report July - September 1985

**H. C. Burkholder, J. H. Jarrett,
and J. E. Minor, Compilers**

May 1986

**Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830**

**Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
by Battelle Memorial Institute**

PNL-5470-4

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PNL-5470-4
UC-70

MASTER

LFCM VITRIFICATION TECHNOLOGY

PNL--5470-4

QUARTERLY PROGRESS REPORT

DE86 013076

July-September 1985

H. C. Burkholder, J. H. Jarrett,
and J. E. Minor, Compilers

Contributing Authors

C. M. Anderson	G. D. Maupin
S. O. Bates	R. K. Nakaoka
H. T. Blair	J. M. Perez, Jr.
L. R. Bunnell	M. E. Peterson
R. D. Dierks	B. A. Pulsipher
M. R. Elmore	N. L. Scharnhorst
L. J. Ethridge	K. J. Schneider
D. W. Faletti	G. J. Seigny
R. K. Farnsworth	D. H. Siemens
R. W. Goles	J. H. Westsik, Jr.
W. L. Kuhn	B. M. Wise

May 1986

Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Richland, Washington 99352

ABSTRACT

This report is compiled by the Nuclear Waste Treatment Program and the Hanford Waste Vitrification Program at Pacific Northwest Laboratory to document progress on liquid-fed ceramic melter (LFCM) vitrification technology. Progress in the following technical subject areas during the fourth quarter of FY 1985 is discussed: melting process chemistry and glass development, feed preparation and transfer systems, melter systems, canister filling and handling systems, off-gas systems, process/product modeling and control, and supporting studies.

SUMMARY

This report is compiled by the Nuclear Waste Treatment Program (NWTP) and the Hanford Waste Vittrification Program (HWVP) to describe the progress in developing, testing, applying, and documenting liquid-fed ceramic melter (LFCM) vitrification technology. Activities in the fourth quarter of FY 1985 are summarized below:

Melting Process Chemistry and Glass Development - Two simulated HWVP melter feeds (HW39 glass) with 0.5 and 1.0 wt% SO_3 , respectively, were used to produce glass samples that were adjusted to redox states corresponding to ferrous/ferric ratios ranging from less than 0.001 to 2.5. SO_3 concentrations within these glasses were determined. A chromium variability study was completed to evaluate the effects of Cr_2O_3 concentration on the physical properties and glass durability of the HW39 glass. Screening tests were performed to evaluate the effect of the amount of formic acid added on the rheological properties of HWVP reference feed simulation HWS4 that was concentrated to 190 g of waste oxides/L. Another study was conducted to determine if the process developed for the preparation of Defense Waste Processing Facility melter feed could be applied to HWVP melter feed with satisfactory rheological results.

Feed Preparation and Transfer Systems - The air displacement slurry (ADS) pump was used to charge both the radioactive LFCM during a 125-h run and the nonradioactive pilot-scale ceramic melter (PSCM) during an 18-day run. Overall, the melter feed systems using the ADS pumps performed adequately over a range of feed rates between 10 L/h and 65 L/h.

Melter Systems - A tank mixing study was completed that developed mathematical models, analytical techniques, and scale-up methods that can be used to estimate the significance of compositional, geometric, and kinematic changes on the degree of mixing in full-scale melter feed processing tanks. A Purex C-sampler was fabricated and tested in a remote test stand to determine how well it withstood vibrations caused by an impact wrench.

Canister Filling and Handling Systems - Canister filling and handling systems have been, or are being developed for the West Valley Demonstration Project (WVDP), HWVP, and the RLFCM operation. Several of these systems have been fabricated, tested, and placed in service.

Off-Gas Systems - Data on the effluent emissions and off-gas performance of the pilot-scale ceramic melter system were gathered during a melter experiment conducted this quarter. Analyses of the data began and the results will be reported next quarter.

Process/Product Modeling and Control - The work on process control instrumentation and process control algorithms continued. A review waste form qualification modeling pertaining to canister heat transfer and to a transient mass balance over a melter is also reviewed. A glass thermowell, pneumatic level detection system (bubbler), and an infrared camera were also tested during a melter experiment conducted this quarter.

Supporting Studies - As part of the effort to discover and evaluate viable second-generation high-level waste (HLW) forms, glasses with processing temperatures higher than the 1100 to 1200°C used for borosilicate glasses are being examined. Glasses processed at 1400°C have the potential for about an order-of-magnitude decrease in leach rates. Many of these compositions have been evaluated using three separate approaches: one based on high-temperature analogs to known waste glasses; one based on substitution of alkaline earths for boron and some alkali in a known waste glass; and one based on a statistically designed empirical mixture study. To date, the second approach has been the most successful; leaching rates about a factor of eight lower than those of the SRL-165 glass have been obtained for some elements. The third approach has resulted in a factor-of-six lower leaching rates. The first approach was abandoned because leaching rate decreases were minor.

CONTENTS

ABSTRACT	iii
SUMMARY	v
INTRODUCTION	1
MELTING PROCESS CHEMISTRY AND GLASS DEVELOPMENT	5
FEED PREPARATION AND TRANSFER SYSTEMS	31
MELTER SYSTEMS	45
CANISTER FILLING AND HANDLING SYSTEMS	61
OFF-GAS SYSTEMS	65
PROCESS/PRODUCT MODELING AND CONTROL	67
SUPPORTING STUDIES	83
APPENDIX - ACRONYMS AND ABBREVIATIONS	A.1

FIGURES

MELTING PROCESS CHEMISTRY AND GLASS DEVELOPMENT

1	Ferrous/Ferric Ratio and SO_3 Concentration of Glasses Produced from 0.5 wt% SO_3 Feed Versus the Amount of Reductant Added	11
2	SO_3 Concentration Versus Ferrous/Ferric Ratio in Glasses Produced from 0.5 wt% SO_3 Feed	11
3	Ferrous/Ferric Ratio and SO_3 Concentration of Glasses Produced from 1 wt% SO_3 Feed Versus the Amount of Reductant Added	13
4	SO_3 Concentration Versus Ferrous/Ferric Ratio in Glasses Produced from 1 wt% SO_3 Feed	13
5	Viscosity Versus Cr_2O_3 Content in HW39 Glass	16
6	Temperature at 100-poise Melt Viscosity Versus Cr_2O_3 Content for HW39 Glass	16
7	Electrical Conductivity Versus Cr_2O_3 Content for HW39 Glass	17
8	Electrical Conductivity at 1150°C Versus Cr_2O_3 Content for HW39 Glass	17
9	Effects of Formic Acid Addition on Rheological Properties of HWS4 Concentrate	20

FEED PREPARATION AND TRANSFER SYSTEMS

1	Air Displacement Slurry Pump Control System	34
2	Bench-Scale Impeller Arrangements	37
3	Bench-Scale Mixing System	39
4	Purex C-Sampler in Place on the Test Stand for Functional Testing of the Bottle Holder Mechanism	42

MELTER SYSTEMS

1	Pilot-Scale Ceramic Melter	47
2	Average Feed Rates During the PSCM-22 Experiment	52
3	Resistive Feedback Electrode Power Control and Its Effect on Melter Operating Parameters	56

CANISTER FILLING AND HANDLING SYSTEMS

1	HWVP Canister Glass Cooling Curves	63
---	--	----

SUPPORTING STUDIES

1	Results from MCC-3 Leach Testing for SRL-165 Glass and Two Analogs	86
2	Results from 7-day MCC-3 Leach Tests for Glasses in the Substitution Study	87
3	Ternary Diagram Showing Glass Composition	89
4	Silicon Release Rates Predicted by Computer Modeling for Mixture Study Compositions	89
5	Measured and Predicted Elemental Release the "Optimum" Glass for Best Glasses in the Mixture Study	90

TABLES

MELTING PROCESS CHEMISTRY AND GLASS DEVELOPMENT

1	HWVP Nominal NCAW/CRW Waste and Glass Composition for HW39.....	10
2	Results from Chromium Variability Study for HW39 Glass with Varying Cr_2O_3 Content.....	14
3	Summary of Properties of HWVP Reference Feed Simulation HWS4 Concentrated to 190 g WO/L.....	19
4	Specifications for DWPF Melter Feed Properties.....	22
5	Matrix of Melter Feed Treatment Combinations Evaluated.....	23
6	Properties of HWVP Melter Feed Test Batches Compared with DWPF Requirements.....	26

FEED PREPARATION AND TRANSFER SYSTEMS

1	Physical Properties of HWVP and West Valley Simulated Melter Feeds.....	38
2	Power Estimated to Achieve a Bulk Velocity of 50 ft/min in Selected Large-Scale Mixing Systems.....	41

MELTER SYSTEMS

1	Composition of Simulated Melter Feed Slurry.....	50
2	Summary of PSCM-22 Experiment.....	51
3	RLFCM-5 Slurry Composition.....	54

PROCESS/PRODUCT MODELING AND CONTROL

1	Least-Squares Fit of Residence Time.....	79
---	--	----

SUPPORTING STUDIES

1	Composition of Typical High-Temperature Glasses.....	85
2	Compositions of Waste Glasses Used in the Statistically Designed Empirical Mixture Study.....	88

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 (HLW), transuranic waste (TRUW), and other related wastes. 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 waste glass formulations and vitrification equipment for HLW; 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 heat and radiation sources to the Federal Republic of Germany (FRG) Asse Mine Test; developing and testing TRUW and second-generation HLW treatment technology; and providing processing technology and vitrification process equipment for treating West Valley wastes. These activities support the longer term goals of completing system design and operations documentation and production specifications for HLW treatment (vitrification) by 1992, for TRUW treatment by 1996, and for second-generation HLW treatment by 2000.

The NWTP is multifunded with base program funds from DOE-Nuclear Energy (NE) and user funding supplied by DOE-NE-West Valley (DOE-NE-WV), DOE-Defense Programs-Richland (DOE-DP-RL), FRG, and Japan. The NWTP is managed by H. C. Burkholder and J. H. Jarrett. The program is divided into the following tasks:

(a) Operated for DOE by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

- Technology Development - W. A. Ross
- Technology Testing - R. A. Brouns
- RLFCM Operations - W. J. Bjorklund
- A-Cell Facility Preparation - G. H. Bryan
- West Valley Support - J. R. Carrell.

Progress in all program elements is reported through informal monthly status reports, formal annual reports (McElroy and Burkholder 1984; Burkholder and Rusin 1985), and formal topical reports. Recognizing both the magnitude of the first-generation HLW 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 various potential user groups such as the West Valley Demonstration Project (WVDP), the Hanford Waste Vitrification Program (HWVP), and the Defense Waste Processing Facility (DWPF) Project. Quarterly reports will be established for other program elements as the need arises.

The results of applicable technical work performed by PNL in direct support of the HWVP under separate funding are also included in this report. The HWVP is being conducted by Rockwell Hanford Operations (RHO) for DOE; DOE and RHO have assigned to PNL the responsibility for development of vitrification system technology for application to the HWVP. The HWVP facility, one of three major U.S. vitrification facilities for defense HLW and TRUW, will use PNL-developed vitrification technology. This technology will also be used for the DWPF and the WVDP. 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 J. E. Minor.

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
- Feed Preparation and Transfer Systems - H. T. Blair
- Melter Systems - J. M. Perez, Jr., and R. D. Dierks
- Canister Filling and Handling Systems - D. H. Siemens
- Off-Gas Systems - R. W. Goles

- Process/Product Modeling and Control - W. L. Kuhn
- Supporting Studies - K. J. Schneider.

Each section contains summary, introduction, and technical progress subsections. The reports are compiled by H. C. Burkholder, J. H. Jarrett, and J. E. Minor and edited by S. K. Edler.

REFERENCES

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 and H. T. Blair

SUMMARY

The solubility of SO_3 in borosilicate glasses is known to be affected by changes in the redox state of the glass. Ferrous/ferric ratios were varied in HW39 glasses produced from two simulated Hanford Waste Vitrification Program (HWVP) melter feeds with 0.5 and 1.0 oxide wt% SO_3 , respectively. In glasses made from both feeds, the solubility changed little when the ferrous/ferric ratio was less than 0.3; however, the solubility decreased strongly when the ferrous/ferric ratio was above 0.3. There was no significant change in solubility for ferrous/ferric ratios from 0.001 to 0.3, the range recommended for melter operation. The solubility limit in HW39 glass was approximately 0.9 oxide wt% SO_3 (3.6 oxide wt% in the waste assuming a 25 oxide wt% waste loading) in the ferrous/ferric range currently recommended for melter operation. This concentration is the maximum allowable level in the glass and should not be exceeded. To allow for possible temperature and redox excursions during melter operation, a flowsheet goal of 0.5 wt% SO_3 in the glass (2.0 oxide wt% in the waste assuming a 25 oxide wt% glass waste loading) is recommended. Pretreatment process variabilities should also be determined before a final flowsheet goal for SO_3 is set.

The Cr_2O_3 concentration in HW39 glass was varied from 0 to 2.0 wt%; the resulting effects on the viscosity, electrical conductivity, crystallinity, and chemical durability of the glass were determined. Varying the amount of Cr_2O_3 within the HW39 glass affected the viscosity and the electrical conductivity, but these changes were not large enough to make the processability of the glass unacceptable. The glass durability (leaching) was not affected by changes in Cr_2O_3 content. An increase in crystalline material was also observed with increasing Cr_2O_3 content. Although the Cr_2O_3 concentration did not adversely affect the physical or leaching properties of the glass within the limits

tested, increased crystalline content could potentially cause processing problems within the melter if settling and sludge formation occurred.

Laboratory scoping tests were performed to determine if simulated HWVP reference feed could be concentrated to 190 g waste oxides/liter (WO/L) and still retain acceptable rheological properties. The test results showed that the waste could be concentrated to the desired level and still meet slurry specifications if 1.25 times the stoichiometric amount of formic acid were added before boiling began.

A statistically designed matrix study was performed to determine if the application of the Defense Waste Processing Facility (DWPF) melter feed preparation process to HWVP melter feed produced a slurry with acceptable rheological properties at a concentration of 400 g total oxides/liter (TO/L). The maximum concentration at which HWVP melter feed with acceptable rheological properties could be prepared was studied by varying the amount of formic acid added and the size of the frit particles used. The results showed that HWVP melter feed could not be prepared at a concentration of 400 g TO/L using the DWPF process and still meet the DWPF rheological requirements. Feeds prepared at 500 to 550 g TO/L did meet the requirements. HWVP melter feed may be prepared at concentrations as high as 600 g TO/L and have acceptable rheological requirements. However, the melting behavior of melter feeds at these concentrations must be evaluated before they can be considered for use in the waste vitrification process.

INTRODUCTION

The objectives of this work are to develop glass 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. For the West Valley Demonstration Project (WVDP), the feed includes simulated high-level waste (HLW), glass-forming chemicals, and (in some cases) ion-exchange material. Glass-forming chemicals and other chemicals used for redox control are selected to maximize melting performance and minimize problems due to foaming, metal precipitation, and other adverse phase

separation. The resulting glass composition is designed to have a viscosity of 100 poise and an electrical conductivity between 0.18 and $0.5 \text{ (ohm-cm)}^{-1}$ in the temperature region between 1070°C and 1150°C . In addition, the glass is designed to minimize the tendency to form crystals above 900°C or other secondary phases on the melt surface.

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

The technical approach involves a close interaction among feed formulation, glass composition, and waste processing work being conducted at Pacific Northwest Laboratory (PNL). 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 or hydroxide chemicals representing the waste fraction and glass-forming chemicals are made into a slurry in the laboratory. The redox state of the glass is then optimized using a reducing agent in the slurry until the ferrous/ferric ratio in the melted glass is between 0.1 and 0.3 . Then, the melting rate of this feed is determined using the bottom-heated crucible test in the laboratory, which measures the rate at which the cold cap formed from this feed 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 small-scale testing in the experimental-scale ceramic melter (ECM). The ECM test is used to corroborate the laboratory findings and to determine if melting problems occur over a longer time frame in a more continuous melting environment. If problems occur, additional laboratory glass composition or feed formulation work is conducted. A successful ECM test leads to the development of an extended test in the pilot-scale ceramic melter (PSCM).

Applicable technology developed in the HWVP is also presented in this section. The HWVP is dedicated to the vitrification of the liquid high-level and

transuranic defense wastes produced and stored at the Hanford Site, near Richland, Washington. The objectives of the HWVP are to:

- Develop a reference glass formulation incorporating neutralized current acid waste/cladding removal waste (NCAW/CRW). This glass composition 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.
- Prepare a simulation of the HWVP reference feeds that represent the true chemical and physical properties of the waste, with the exception of radiation and heat generation, and creates no artificial difficulties.
- Determine whether the glass-forming materials that are added to the waste can be added as a ground frit or whether some of the materials must be added as unreacted chemical compounds.
- Determine how the waste and glass-forming chemical blend can be processed before it is charged to the melter to achieve maximum melting rates, minimum foaming, and minimum phase separation in the melter.
- Determine ways to modify the rheology of the melter feed to improve homogeneity and minimize transport difficulties.
- Identify the critical rheological properties of the feeds and develop methods for evaluating these properties.
- Evaluate the maximum melter feed oxide concentration that exhibits acceptable rheological properties.

TECHNICAL PROGRESS

Technical progress in determining the effects of SO_3 solubility, the Cr_2O_3 concentration, waste concentration on rheological properties, and applying DWPF preparation techniques to HWVP feed preparation are presented in this section.

SULFATE/REDOX RELATIONSHIP IN HWVP GLASS

If the solubility limit of SO_3 in a glass melt is exceeded, an undesirable molten sulfate layer will form on the melt surface. This molten layer will readily incorporate radionuclides, principally cesium, that could volatilize and enter the off-gas system of the melter. If the molten sulfate is entrained in the molten glass and transported through the melter, a highly soluble cesium-enriched sulfate phase could be deposited in the canister. To reduce the possibility of a sulfate layer, the SO_3 concentration in the waste should be such that the solubility limit of SO_3 in the waste glass is not exceeded.

The solubility of SO_3 (and the amount of washing required in the waste treatment process to remove the sulfate) in borosilicate glasses depends on the oxidation state of the glass. Furthermore, the solubility first decreases as the glass becomes more reduced and then increases under strongly reducing conditions.

Using a bottom-heated crucible furnace, two simulated HWVP melter feeds (HW39 glass, see Table 1) with 0.5 and 1.0 wt% SO_3 were used to produce glass samples that were adjusted to redox states corresponding to ferrous/ferric ratios ranging from less than 0.001 to 2.5. Sulfate concentrations within these glasses were determined using a LECO CS244 sulfur analyzer.

In glass samples made from the 0.5 wt% SO_3 feed, the SO_3 content in the glass decreased as the ferrous/ferric ratio increased. No sulfate layer was observed on the top of the glass surface after the crucible was removed from the furnace. Figure 1 shows the increase in ferrous/ferric ratios and the decrease in SO_3 concentration as the amount of reductant (sugar) was increased. The change in SO_3 concentration versus ferrous/ferric ratio is shown in Figure 2. In the expected range of ferrous/ferric ratios considered

TABLE 1. HWVP Nominal NCAW/CRW Waste and Glass Composition for HW39

Oxide	Waste, wt%	Nominal Glass-Forming Oxide, wt%	Glass, wt%(a)
SiO ₂	3.0	67.25	51.2
Na ₂ O	10.7	10.25	10.4
B ₂ O ₃	0.0	12.75	9.6
Li ₂ O	0.0	5	3.8
CaO	0.3	3.75	2.9
MgO	0.3	1	0.8
Fe ₂ O ₃	44.4		11.1
Al ₂ O ₃	17.2		4.3
FP _{0.1.25} ^(b)	5.7		1.4
Cr ₂ O ₃	5.3		1.3
NiO	2.4		0.6
ZrO ₂	2.4		0.6
La ₂ O ₃	2.2		0.6
Nd ₂ O ₃	2.1		0.5
SO ₄	1.8		0.4
F	1.2		0.3
Cs ₂ O	1.0		0.2
Total	100.0	100.0	100.0

(a) At 25 wt% oxide waste loading.

(b) Fission products and trace oxides.

appropriate for melter operation (0.001 to 0.3), little or no change in the SO₃ concentration was observed. As the ferrous/ferric ratio was increased beyond 0.4, the SO₃ concentration decreased by more than a factor of two to a minimum SO₃ solubility of approximately 0.15. Each cut glass sample had a uniform texture, a shiny surface, and no visible metals on any of the exposed surfaces.

All glass samples produced from the 1 wt% SO₃ feed had a yellow layer on the glass surface when removed from the furnace. When a positive ferrous/ferric ratio was achieved, the surface layer changed from yellow to white.

FIGURE 1. Ferrous/Ferric Ratio and SO₃ Concentration of Glasses Produced from 0.5 wt% SO₃ Feed Versus the Amount of Reductant Added

FIGURE 2. SO₃ Concentration Versus Ferrous/Ferric Ratio in Glasses Produced from 0.5 wt% SO₃ Feed

These surface layers were water soluble and disappeared during the wet cutting procedure. Analysis of the water-soluble surface layers using inductively coupled plasma/atomic emission spectroscopy (ICP/AES) indicated a high concentration of sulfur. It was assumed that these layers contained sulfate.

The presence of a sulfate layer on the surface of the glass indicated that the sulfur solubility of the glass was exceeded. Thus, the amount of SO_3 measured in the glass at or near oxidizing conditions was the maximum solubility of SO_3 in the HW39 glass. Figure 3 shows the increase in ferrous/ferric ratios and the decrease in SO_3 concentration as the amount of reductant (sugar) was increased. The SO_3 concentration at oxidizing or low ferrous/ferric ratios was approximately 0.9 wt% in the glass (3.6 oxide wt% in the waste assuming a 25 oxide wt% waste loading). This level is the maximum allowable concentration in the glass. The design guideline for SO_3 in the waste should be low enough to provide for possible variations in the SO_3 concentration. To allow for possible temperature and redox excursions during melter operation, a flowsheet goal of 0.5 wt% SO_3 in the glass (2.0 oxide wt% in the waste assuming a 25 oxide wt% glass waste loading) is recommended. Pretreatment process variability should also be determined before a final flowsheet goal for SO_3 is set.

The glasses produced from the 1 wt% and the 0.5 wt% SO_3 feed exhibited much the same behavior when the ferrous/ferric ratio was increased (see Figures 3 and 4). At ferrous/ferric ratios of 0.0 to 0.4, the SO_3 concentration remained relatively unchanged. As the ferrous/ferric ratio increased beyond 0.4, the corresponding level of SO_3 decreased by more than a factor of two. Each cut glass sample had a uniform texture, shiny surface, and no visible metals on any of the exposed surfaces.

For glasses produced from both feeds, the decrease in SO_3 solubility was relatively slow at ferrous/ferric ratios below 0.3. If ferrous/ferric ratios are maintained within the currently recommended range for melter operation (0.001 to 0.3), there will be little change in the solubility of SO_3 in the glass.

FIGURE 3. Ferrous/Ferric Ratio and SO₃ Concentration of Glasses Produced from 1 wt% SO₃ Feed Versus the Amount of Reductant Added

FIGURE 4. SO₃ Concentration Versus Ferrous/Ferric Ratio in Glasses Produced from 1 wt% SO₃ Feed

CHROMIUM VARIABILITY

A chromium variability study was completed to evaluate the effects of Cr_2O_3 concentration on the physical properties and glass durability of the HWVP initial reference glass, HW39 (see Table 1). Five HW39 glass compositions were tested with Cr_2O_3 concentrations in the glass of 0.0, 0.5, 1.0, 1.34, and 2.0 wt%. The nominal Cr_2O_3 concentration in HW39 glass is 1.34 wt%. Rockwell Hanford Operations (RHO) has indicated that 2.0 wt% Cr_2O_3 in the glass (8 wt% in NCAW/CRW) is the maximum concentration expected. The physical properties considered were viscosity, electrical conductivity, and crystallinity. The durability of the glasses was also determined. The redox state of the tested glasses was adjusted to a level corresponding to a ferrous/ferric ratio of 0.1.

The results obtained from the chromium variability study are summarized in Table 2. Variations in Cr_2O_3 concentration affected the viscosity, electrical

TABLE 2. Results from Chromium Variability Study for HW39 Glass with Varying Cr_2O_3 Content^(a)

Element	Normalized Elemental Release, g/m ²				
	0 wt% Cr_2O_3	0.5 wt% Cr_2O_3	1 wt% Cr_2O_3	1.34 wt% Cr_2O_3	2 wt% Cr_2O_3
Si	12	12	12	12	11
B	14	15	15	14	14
Li	15	16	15	15	14
Na	15	15	15	15	14
Cs	20	21	18	17	17
Ca	6.9	6.6	6.8	7.1	6.8
Sr	5.9	5.5	5.7	6.2	5.9
Al	9.0	9.2	9.2	9.2	8.6
Fe	0.4	0.4	0.2	0.5	0.2
Final pH	9.7	9.7	9.7	9.7	9.7
T100P, °C	1077	1088	1101	1097	1116
E1150, (ohm-cm) ⁻¹	0.35	0.29	0.26	0.27	0.27

(a) MCC-1 test conditions: 28 days, deionized water, 90°C, surface-area-to-volume ratio = 10 m⁻¹.

conductivity, and crystallinity of the glass. No significant effect was observed in the leachability of the glasses over the Cr_2O_3 range tested. ICP/AES analysis found all five glasses to be equivalent with the exception of the Cr_2O_3 concentration.

The viscosity curves of the five glasses are shown in Figure 5. As the Cr_2O_3 concentration increased in the glass, the viscosity increased slightly. A plot of the temperature at which the glass has a viscosity of 100 poise (T100P) versus Cr_2O_3 content is shown in Figure 6. The viscosities were stable with time for all glass compositions tested except for the 2.0 wt% Cr_2O_3 glass. At 950°C, the viscosity of the 2.0 wt% Cr_2O_3 glass increased slowly. The increase in T100P was roughly linear within the range of Cr_2O_3 concentrations tested. While the viscosities did vary, all the glasses tested were within the limits required for melter operation (T100P from 1070 to 1150°C).

The electrical conductivity of the HW39 glass was affected by variations in Cr_2O_3 content. Electrical conductivity curves for the five glasses are shown in Figure 7. A plot of the electrical conductivity at 1150°C (E1150) versus Cr_2O_3 content in the glasses is shown in Figure 8. The electrical conductivity of the glasses increased significantly when the Cr_2O_3 concentration was less than 0.5 wt%. This increase was not large enough to cause the electrical conductivity of the glass to exceed the limits for acceptable melter processing: 0.18 to 0.5 (ohm-cm)⁻¹ at 1150°C.

As found in previous work, the amount of crystalline material within the glass is directly related to the Cr_2O_3 concentration. No crystalline material was observed in the 0.0 wt% Cr_2O_3 glass. With Cr_2O_3 concentrations of 0.5 to 2.0 wt%, a significant amount of crystalline material was observed. The amount of crystalline material observed increased directly with the increase in Cr_2O_3 content in the glasses with 0.5 wt% Cr_2O_3 and above, indicating that the Cr_2O_3 solubility in HW39 glass was less than 0.5 wt%. This was also the case with other borosilicate waste glasses tested in earlier HWVP, DWPF, and WVDP work. The only crystalline phase observed in the test glasses with a Cr_2O_3 concentration of 1.0 wt% or greater was the cubic spinel, FeCr_2O_4 (about 5 μm in size). At 0.5 wt% Cr_2O_3 , hexagonal platelets of the sesquioxide $(\text{Fe,Cr})_2\text{O}_3$ (about 35 μm in size) were also present with the spinel in the glass.

FIGURE 5. Viscosity Versus Cr_2O_3 Content in HW39 Glass

FIGURE 6. Temperature at 100-poise Melt Viscosity (T100P) Versus Cr_2O_3 Content for HW39 Glass

FIGURE 7. Electrical Conductivity Versus Cr_2O_3 Content for HW39 Glass

FIGURE 8. Electrical Conductivity at 1150 $^{\circ}\text{C}$ (E1150) Versus Cr_2O_3 Content for HW39 Glass

The durability of the glasses was evaluated using a 28-day MCC-1 leaching test (Table 2). Each value listed in Table 2 is an average of three test samples. No significant difference in the normalized elemental release was observed in any of the test glasses. The durability of HW39 glass was unchanged with variations in the Cr_2O_3 concentration range of 0 to 2.0 wt%.

WASTE CONCENTRATION

In the current HWVP melter feed preparation process, two concentration steps are prescribed. The waste stream is first heated to near boiling so that formic acid may be added. After the acid is added, the relatively dilute (19 g W0/L) waste is boiled to complete the reaction and to increase the concentration of the waste. The concentrate is then cooled so that it can be sampled and transferred to the melter feed makeup tank where the glass-forming frit is added as an aqueous slurry. After the frit slurry and waste concentrate are combined, the mixture is again heated to boiling and further concentrated to the desired level for charging to the melter. The melter feed is then cooled to below 50°C for sampling, transferred to the melter feed tank, and charged to the melter. The slurry must be cooled between each concentration step because the sampling, transfer, and melter feed pumps cavitate if the slurry is hotter than 50°C. The possibility of eliminating some of these thermal cycles was considered worthy of investigation.

In the last quarterly report (Burkholder, Jarrett, and Minor 1986), it was shown that simulated HWVP reference feed could be concentrated in excess of 140 g W0/L when formic acid is added and still have acceptable viscosity and yield stress values of less than 40 cP and 150 dynes/cm², respectively. It was determined that if the waste could be concentrated to 190 g W0/L, then one part by weight of the 30 wt% frit slurry from the canister decontamination process and two parts by weight of the 60 wt% frit slurry from outside the process cell could be added to the concentrate to produce a melter feed at a concentration of 400 g T0/L without further boiling.

Screening tests were performed to evaluate the effect of the amount of formic acid added on the rheological properties of HWVP reference feed simulation HWS4 that was concentrated to 190 g W0/L. Three aliquots of HWS4 were

concentrated to between 190 and 196 g W0/L and were treated with formic acid. One aliquot received the stoichiometric amount of 0.092 g HCOOH/L. The second received 1.5 times this amount, and the third received double the stoichiometric amount. The results are summarized in Table 3 and Figure 9.

The addition of formic acid reduces the apparent viscosity and yield stress of the simulated HWVP feed. However, the effect begins to diminish beyond the addition of 1.5 times the stoichiometric amount. The stoichiometric amount of formic acid is sufficient to bring the yield stress into the specified range. However, it appears that about 1.25 times the stoichiometric amount will be required to reduce the apparent viscosity to below the maximum allowable value of 40 cP. The apparent high dependence of the measured viscosity of the untreated simulation on the shear rate should be further studied. Researchers at Savannah River Laboratory (SRL) reported a relationship between agitator tip speed and slurry feed rheological properties.

TABLE 3. Summary of Properties of HWVP Reference Feed Simulation
HWS4 Concentrated to 190 g W0/L

Variables	Batch Numbers			
	3	8	9	10
Concentration, g W0/L	190	196	194	183
Boiled, h	120	122	122	122
Batch size, mL	250	250	250	250
g HCOOH/g W0	0	0.092	0.14	0.184
<u>Properties</u>				
Density, g/mL	1.11	1.17	1.16	1.13
pH	11.4	5.4	3.8	3.2
Viscosity, cP				
at 183 s ⁻¹	114	65	28	23
at 608 s ⁻¹	37	58	24	20
at 824 s ⁻¹	28	52	23	19
Yield stress, dyne/cm ²	194	76	52 to 67	56

FIGURE 9. Effects of Formic Acid Addition on Rheological Properties of HWS4 Concentrate

The HWVP reference feed may be sufficiently concentrated during the formic acid treatment so that additional concentration steps might not be required after the slurry of glass-forming frit is added to the concentrate, thus saving significant time and energy costs in the melter feed processing operations. However, achieving that concentration in a single tank could also lead to rather complex operational control requirements that must be evaluated.

MELTER FEED CONCENTRATION

The HWVP scoping studies performed during the first half of FY 1985 used melter feeds concentrated to 400 g T0/L,^(a) and the feeds used for all HWVP melter runs in FY 1985 were less than or at this concentration. This concentration was used because previous experience with melter feeds made with simulated NCAW showed that feeds could not be concentrated much beyond 400 g T0/L and remain fluid.

The concentration of the DWPF melter feed was believed to be 435 g T0/L (E. I. duPont de Nemours & Company, Inc. 1983). However, experience with the simulated HWVP melter feeds treated with formic acid showed they could be more concentrated than 400 g T0/L and still have acceptable physical and chemical properties. Therefore, a study was conducted to determine two things:

- whether the application of the process developed for the preparation of DWPF melter feed to HWVP melter feed preparation resulted in an HWVP melter feed with satisfactory rheological properties at concentrations exceeding 400 g T0/L
- the maximum concentration of HWVP melter feed with acceptable rheological properties that can be achieved by controlling the amount of formic acid added and the size of the frit used.

The scope of this study did not include evaluating the effects of increased concentration on the melting behavior of the feed. These effects must also be evaluated before any recommendations about melter feed property specifications or processing changes are made.

After the test was designed and sample preparation had begun, a new revision of the DWPF basic data report (E. I. duPont de Nemours & Company, Inc. 1985) indicated that the DWPF melter feed concentration was 515.5 g T0/L. This information provided further incentive to determine whether HWVP melter feeds could be prepared at concentrations above 500 g T0/L and still retain acceptable rheological properties.

(a) T0 - total oxides, including 25 wt% waste oxides and 75 wt% glass-forming oxides.

The measure of acceptance of the rheological properties of the melter feeds for the study was the criteria established for the DWPF melter feed by SRL. These DWPF melter feed specifications are presented in Table 4. The apparent viscosity (consistency) and the yield stress (point) were determined from the rheograms generated by the viscometer using the analytical model parameters and the extrapolation procedure that PNL has determined are appropriate for a yield-pseudoplastic non-Newtonian fluid (Burkholder, Jarrett, and Minor 1986).

Another aspect of the preparation process for DWPF melter feed, which is to be applied to HWVP feed vitrification, is the use of the glass-forming frit to decontaminate the canisters after they are filled with the waste-bearing glass. This decontamination frit makes up one-third of the total glass-forming material that must be added to the waste to produce the vitrified product. To be effective in the grit-blasting process, the frit is sized at -80/+200 mesh. This frit size is relatively coarse for suspension in a slurry, and it is erosive to the processing equipment. Better rheological properties of the melter feed and better process equipment performance may be achieved by using a finer grind of frit to make up the additional two-thirds required. Consequently, the effects on slurry properties with the frit size of two-thirds of the glass-forming material were evaluated during this study.

TABLE 4. Specifications for DWPF Melter Feed Properties

<u>Property</u>	<u>Acceptable Range</u>
Density, g/mL	1.29 to 1.46
pH	Less than 8
Concentration, wt% total solids (dried at 105°C)	40 to 50
Consistency, cP	10 to 40
Yield point, dynes/cm ²	
Range	25 to 150
Design value	80

A full 4 x 3 x 3 factorial experiment was designed to evaluate the effects of the DWPF melter feed treatment and the frit size on the rheological properties of HWVP melter feeds at concentrations exceeding 400 g T0/L. The design included 36 distinct test conditions. These conditions comprised all possible combinations of the four concentration levels, the three frit particle size distributions, and the three amounts of formic acid addition, as shown in the upper half of the matrix in Table 5.

TABLE 5. Matrix of Melter Feed Treatment Combinations Evaluated

Concentration, g T0/L	Frit Size(a)	Amount of Formic Acid Addition, g/g W0		
		0.092	0.184	0.276
400	1	24 ^(b)	17 and 44	39
	2	23	27	3
	3	37	1	8 and 35
450	1	7 and 10	29	31
	2	30	22	2 and 9
	3	14	43	34
500	1	13 and 42	15	18
	2	4	16	19
	3	40	11 and 26	41
550	1	45	21	5 and 20
	2	25	32 and 36	6
	3	12 and 33	38	28
600	1			48
	2			47
	3			46
650	1			53
	2			52
	3			54
675	1			49
	2			50
	3			51
750	1			56
	2			55
	3			57

- (a) Size 1 = 1 part by weight of -80/+200 mesh and 2 parts of -200 mesh.
Size 2 = All -80/+200 mesh.
Size 3 = 1 part by weight of -80/+200 mesh and 2 parts of -400 mesh.
(b) Batch number and order of preparation.

The four levels of total oxide concentration of most interest were 400, 450, 500, and 550 g T0/L. The three different frit sizes chosen for study were:

- Size 1 - 1 part by weight of -80/+200 mesh and 2 parts by weight of -200 mesh (the size distribution used in FY 1985 HWVP melter studies)
- Size 2 - all -80/+200 mesh (the DWPF reference)
- Size 3 - 1 part by weight of -80/+200 mesh and 2 parts by weight of -400 mesh.

The three levels of formic acid addition studied were:

- the stoichiometric amount (calculated to be 0.092 g HCOOH/g WO in the simulated HWVP reference feed)
- double the stoichiometric amount (0.184 g HCOOH/g WO)
- triple the stoichiometric amount (0.276 g HCOOH/g WO).

Nine combinations of these factors were run twice to estimate the experimental error variance. The nine combinations were selected by applying a computer-aided experimental design program so that they provided a replicate and added the maximum amount of useful information to the experiment. The experiment was designed to provide information on the main effect of each factor, all two-way interaction effects among the three factors, the three-way interaction effect, and the experimental error variance. A total of 45 experimental runs were conducted for this portion of the study. They were run in the random order shown by the batch numbers in Table 5.

The four oxide concentrations (600, 650, 675, and 750 g T0/L) were each combined with all three frit sizes and only the highest amount of formic acid addition. To determine the maximum HWVP melter feed concentration having acceptable rheological properties, the experimental design for this portion of the study was a full 4 x 3 factorial, which included all 12 of the possible combinations of the four concentrations and the three frits. There were no replicates in this portion of the study because the estimated experimental variance from the first portion of the study was used for hypothesis testing

and confidence interval estimation. It was assumed that the experimental error variance would be the same for all concentrations.

When the measured properties of the batches of HWVP melter feed prepared for this study were compared with the DWPF melter feed criteria presented in Table 2, eight combinations of the 48 tested met all the requirements. These eight combinations are shown in Table 6, where the makeup and properties of each are presented. Only two combinations (Batches 4 and 25) were prepared with the DWPF reference frit size and amount of formic acid. Batches 4 and 25 had total oxide concentrations of 500 g T0/L and 550 g T0/L, respectively. (The apparent viscosity of Batch 25 is so near the upper limit that its acceptance is uncertain.)

All the combinations prepared at concentrations of 400, 450, and 500 g T0/L, with the exception of Batch 40, were disqualified because the yield stress, the apparent viscosity, or both the yield stress and the apparent viscosity were below the minimum values of the prescribed ranges. Batch 40 (prepared at 500 g T0/L) and all the disqualified batches prepared at concentrations of 550 g T0/L were disqualified because the apparent viscosity at the 183 s^{-1} shear rate exceeded 40 cP. However, the maximum apparent viscosity at 183 s^{-1} for these disqualified batches was 69 cP (Batch 32). Batch 32 also had the maximum yield stress for the 550 g T0/L group (82 dynes/cm^2).

The measured apparent viscosity values for the 550 g T0/L group suggests that the HWVP melter feed at this concentration could be qualified by modifying the rheological properties. In fact, the yield stress and apparent viscosity values for the batches prepared at 600 g T0/L may also be qualified. The combinations prepared at concentrations above 600 g T0/L have apparent viscosities and, in some cases, yield stresses that exceed the maximum limit.

The densities of six batches (Batches 1, 3, 17, 23, 27 and 35) of melter feed prepared at 400 g T0/L fell below the minimum limit by 0.01 g/mL. All other batches prepared at concentrations from 400 to 650 g T0/L had densities within the specified range. The batches prepared at 675 g T0/L and 750 g T0/L had densities between 1.49 g/mL and 1.57 g/mL.

TABLE 6. Properties of HWVP Melter Feed Test Batches Compared with DWPF Requirements

Properties	DWPF Requirements	Batch Numbers							
		10	14	13, 42	4	11, 26	41	25	28
Target concentration g TO/L	515.5	450	450	500	500	500	500	550	550
HCOOH added, g/g WO	90% of stoichiometric	0.092	0.092	0.092	0.092	0.184	0.276	0.092	0.276
Frit size, mesh	All -80/+200	Two-thirds -200	Two-thirds -400	Two-thirds -200	All -80/+200	Two-thirds -400	Two-thirds -400	All -80/+200	Two-thirds -400
Yield stress, dynes/cm ²	25 to 150	31	34	46	38	26	26	48	45
Apparent viscosity, cP, at 183 s ⁻¹	10 to 40	27	29	36 to 39	33	28 to 30	28	40	39
608 s ⁻¹		13	14	18 to 19	14	14 to 15	14	24	20
824 s ⁻¹		11	12	16	12	12	12	22	17
Density, g/mL	1.29 to 1.46	1.33	1.32	1.34 to 1.35	1.35	1.33 to 1.35	1.35	1.37	1.40
pH	<8	4.8	5.2	4.8 to 4.9	4.6	3.9	3.5	6.9	5.2
Total solids, wt%	40 to 50	42.6	38.7	41 to 41.5	40.8	41.4 to 40.4	41.5	42.8	47.0
Total oxides, g TO/L	None	510	459	498 to 513	503	494 to 475	481	536	557

The pH values of all the batches (with the exception of Batches 12 and 33) met the DWPF melter feed requirement. Batches 12 and 33, which had the same makeup, had a higher pH because they were prepared with the smallest amount of formic acid added. They were made with the finest frit, which provided the greatest surface area for the leaching of alkalis from the glass to form hydroxides. They were also boiled for 5.5 to 6.5 h to achieve the desired concentration, which also promoted leaching. In fact, 10 of the 11 batches with a pH above 5 were made with fine frit, and 7 of the 12 batches that were boiled to the 550 g TO/L concentration had a pH above 5. This association of higher pH with the use of the fine frits (-200 and -400 mesh) must be taken into consideration when assessing the use of finer frits to improve melter feed rheological properties.

Boiling melter feed batches to concentrated oxide loadings above 500 g TO/L is an important factor to consider when interpreting the data collected during this study. Boiling mixtures of simulated waste and frit have been known to alter melter feed rheological properties. Had all the batches been boiled, whether boiling was required for concentration or not, it is possible that the values for pH, wt% dissolved, and suspended solids would be different. This boiling factor was not considered when the significance of the two-way interactions between the independent factors affecting the measured properties were interpreted. Therefore, the statistical analysis of the results of this study is inconclusive.

The specified range of concentration provided by SRL for the DWPF melter feed is defined in units of weight percent of total solids. These units are determined by dividing the weight of a feed sample into the weight of solids left after the sample is dried to constant weight at 105°C. At PNL, concentrations are often reported in terms of grams of total oxide/liter of feed because this unit directly relates melter feed rates (in L/h) to glass production rates (in kg oxides/h). The oxide concentration is determined by dividing the volume of a feed sample into the weight of the solids that are left after the sample is heated at 950°C for 2 h in air. Total oxides differ from total solids because solids include hydroxides, nitrates, formates, sulfates, and organics that do not decompose when heated to 105 to 110°C. The solids concentrations

determined at 105°C are the appropriate values to compare to the DWPF specification. All the combinations prepared with concentrations of 400 g T0/L and 450 g T0/L had solids contents below the minimum 40 wt% specified, but none of the values were below 32 wt%. Batches prepared at concentrations of 500 to 600 g T0/L had solids contents within the prescribed range. The more concentrated batches exceeded the maximum limit of 50 wt%, but only one batch exceeded 60 wt%.

These findings show the HWVP reference feed cannot be prepared to concurrently satisfy the following three requirements:

- a nominal total oxide concentration of 400 g T0/L
- adding 90 wt% of the stoichiometric amount of formic acid and all the glass-forming materials as -80/+200 mesh frit
- a yield stress between 25 dynes/cm² and 150 dynes/cm² and an apparent viscosity between 10 cP and 40 cP.

Difficulties in meeting these requirements are associated with minimum rather than maximum limits. HWVP melter feeds prepared at concentrations of 400 g T0/L have yield stresses below the 25-dynes/cm² limit and apparent viscosities below the 10-cP limit. The validity of these lower limits depends on the settling behavior of the slurries, which must be carefully evaluated before changing the limits.

HWVP melter feeds prepared at concentrations of 450 to 550 g T0/L meet the DWPF melter feed rheological requirements. The HWVP reference feed is rheologically similar to the DWPF washed sludge in the application of the DWPF melter feed preparation flowsheet because both produce melter feeds with similar rheological properties at the same concentrations.

CONCLUSIONS

The following conclusions are based on the work reported in this section:

- The maximum SO₃ solubility in HW39 glass was approximately 0.9 wt% under oxidizing or slightly reducing conditions corresponding to ferrous/ferric ratios of 0 to 0.3. This concentration is the maximum

allowable in the glass and should not be exceeded. The design guideline for SO_3 in the waste should be low enough to allow for the maximum possible pretreatment process variation in the SO_3 concentration without exceeding a concentration of 0.9 wt% in the glass. To allow for possible temperature and redox excursions during melter operation, a flowsheet goal of 0.5 wt% SO_3 in the glass (2.0 oxide wt% in the waste assuming a 25 oxide wt% glass waste loading) is recommended.

- At the ferrous/ferric ratios expected during melter operation (0.001 to 0.3), there was little effect on the sulfate solubility in the HW39 glass composition.
- As the ferrous/ferric ratio of the glass increased above 0.3, the solubility of SO_3 decreased to values as low as 0.15 oxide wt%.
- Although the variation of Cr_2O_3 content within HW39 glass affected the viscosity and electrical conductivity, the changes in physical properties were not large enough to affect the processability of the glass within the melter.
- The glass durability was not affected due to changes in Cr_2O_3 content.
- While the increase in crystalline material with increasing Cr_2O_3 content did not adversely affect the physical or leaching properties of the glass, the increased crystal content could cause processing problems within the melter if settling and sludge formation occurred.
- HWVP reference feed may be concentrated to 190 g WO/L during the formic acid addition treatment and have rheological properties that meet the DWPF slurry specifications if 1.25 times the stoichiometric amount of acid is added.
- Melter feed cannot be prepared with the HWVP reference feed simulation and concurrently satisfy the following three requirements:

- 1) HWVP melter feed shall be prepared using the DWPF flowsheet.
 - 2) HWVP melter feed shall have the rheological properties specified to meet the DWPF equipment requirements.
 - 3) HWVP melter feed nominal total oxide concentration shall be 400 g TO/L.
- HWVP melter feed can be prepared using the DWPF process at concentrations of 500 to 550 g TO/L and meet the DWPF melter feed rheological property requirements. Whether or not such melter feeds meet the processing requirements of the melter was not evaluated.
 - HWVP melter feeds prepared at 400 and 450 g TO/L did not meet the minimum DWPF requirements for yield stress, apparent viscosity (consistency), and concentration in terms of wt% solids content.
 - HWVP melter feeds cannot be prepared at concentrations of 600 g TO/L or greater using the frit sizes and amounts of formic acid studied and meet the DWPF melter feed rheological requirements. However, HWVP melter feed can be prepared at 600 g TO/L, which would meet all the rheological requirements except that the apparent viscosity would be greater than 49 cP but less than 70 cP.

REFERENCES

Burkholder, H. C., J. H. Jarrett, and J. E. Minor. 1986. LFCM Vitrification Technology Quarterly Progress Report, April-June 1985. PNL-5470-3, Pacific Northwest Laboratory, Richland, Washington.

E. I. duPont de Nemours & Company, Inc. April 1983. Basic Data Report, Defense Waste Processing Facility Sludge Plant, 200S Area. DPWP-80-1033, Vol. 2 (Material Balance Tables, Sludge Only Feed), Savannah River, South Carolina.

E. I. duPont de Nemours & Company, Inc. April 1985. Basic Data Report, Defense Waste Processing Facility, Sludge Plant, Savannah River Plant, 200S Area. DPSP-80-1033, Vol. 2, Savannah River, South Carolina.

FEED PREPARATION AND TRANSFER SYSTEMS

H. T. Blair, M. R. Elmore, R. K. Nakaoka,
M. E. Peterson, and N. L. Scharnhorst

SUMMARY

The air displacement slurry (ADS) pump was used to charge both the radioactive liquid-fed ceramic melter (RLFCM) during a 125-h run and the nonradioactive pilot-scale ceramic melter (PSCM) during an 18-day run. Overall, the melter feed systems using the ADS pumps performed adequately over a range of feed rates between 10 L/h and 65 L/h. A fully remote full-scale ADS pump is now being tested at West Valley, New York.

A tank mixing study was completed that developed mathematical models, analytical techniques, and scale-up methods that can be used to estimate the significance of compositional, geometric, and kinematic changes on the degree of mixing in full-scale melter feed processing tanks.

A Purex C-sampler was fabricated and tested in a remote test stand to determine how well it withstood vibrations caused by an impact wrench. Modifications were then made to the assembly to obtain satisfactory performance.

INTRODUCTION

Feed preparation and transfer systems consist of the equipment used to contain and process liquid high-level waste (HLW) between the point of entry into a 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 liquid HLW.

Activities and results of the work being performed at Pacific Northwest Laboratory (PNL) to support the development, design, selection, and operation

of the feed preparation and transfer systems are discussed. During FY 1985, specific activities concerning feed preparation and transfer systems included:

- long-term demonstration of the ADS pump designed by PNL for charging slurry to melters
- radioactive demonstration of melter feed transfer equipment in support of the radioactive demonstration of the LFCM
- design of a fully remote ADS pump and a slurry sampler for the West Valley Demonstration Project (WVDP)
- development of a melter feed tank design including the agitator and heat transfer system
- demonstration of a slurry level and specific gravity measuring system that will work in concentrated slurries and high radiation fields
- evaluation of remote liquid sampling devices for concentrated slurries.

TECHNICAL PROGRESS

Technical progress in the use of the ADS pump, in the development of tank designs for slurry processing, and in the testing of a remote sampler are discussed in this section.

AIR DISPLACEMENT SLURRY PUMP

RLFCM-5, conducted during August 1985, was the first RLFCM run to extend beyond 100 h and use the ADS pump in B-Cell with the constant pressure control system instead of syringes. Feed was processed for 125 h 16 min at an average feed rate of 16 L/h. About 1990 L of feed was processed through the melter.

Four periods of extended downtime occurred during RLFCM-5; three of which were attributed to the ADS pump. In these three instances, the pump was allowed to pump down to the minimum tank level. Slurry was then transferred into the tank before melter feeding was resumed. A total of 11 h 7 min of downtime was accrued during the feed transfer operations.

The ADS pump with the constant pressure control system operated at higher and more constant feed rates than previously experienced. Feed rates to the melter were more than 10 L/h for 26.9% of the time and between 17.5 L/h and 20 L/h for 16.9% of the time. Feed rates were below 17.5 L/h for the remaining 56.2% of the time.

The RLFCM-5 run was terminated when the in-cell ADS pump solenoid failed. The nature of the problem was both electrical and mechanical. The electrical problem involved a fuse on the solenoid power supply that burned out each time the pump was started and had to be replaced several times. The mechanical problem was a leak in the in-cell solenoid. Water and air came through the normally closed entry port and the normally open exit port simultaneously.

Originally it was believed that a dead short existed in the electrical lead that ran between the gallery and the solenoid. A new lead and connector were fabricated and tested outside the cell; no shorts occurred. When installed and connected to the in-cell solenoid power lead, however, a dead short was again detected, indicating that the short existed in the other half of the in-cell connector, in the junction box on the solenoid cover, or in the solenoid coil itself.

When the solenoid was brought into the air lock, the mechanical operation of the two valves and the electrical characteristics were investigated. The solenoid was disassembled; the upper valve disk and upper valve seat were both worn. Greater wear was evident on the upper valve disk; and one side of the disk showed more wear, probably resulting from its misalignment. Both parts are fabricated from Type 303 stainless steel. A new seat and disk were installed, and no further instances of air leakage were detected during a functional check performed in the air lock.

A new electrical lead was run into the air lock to determine the cause of the electrical failure. While in the air lock, no electrical problems were detected; and the solenoid operated as intended. The only change from the previous test, when a dead short had been indicated, was that the in-cell connector had been cleaned. It is believed that water had fallen onto the solenoid connector and prevented the two connectors from making good contact. Once the connector was cleaned, the solenoid operated as intended.

The ADS pump was used for 367 h during an 18-day melter test performed for the Hanford Waste Vittrification Program (HWVP) in the PSCM (PSCM-22). The melter feed system using the ADS pump performed adequately at feed rates ranging between 25 L/h and 65 L/h. The pump flow rate controller (Figure 1) had to be adjusted frequently to maintain a constant feed rate throughout the run. When the input air pressure to the pump was held constant, the output of the feed system declined over time. A water flush or an increase in air pressure usually cleared the system and restored the desired flow rate. On several occasions, however, the water flush was not sufficient to restore the

FIGURE 1. Air Displacement Slurry Pump Control System

desired output. Increasing the air pressure maintained the desired output rate until the plug worked through the feed line. This behavior made it difficult to maintain a constant feed rate for an extended period of time.

The feed line was changed from 1/4- to 3/8-in.-dia tubing to try to improve the constancy of the flow rate. However, a 1-psig increase in the air pressure resulted in a 23-L/h increase in feed rate because the larger diameter feed line did not provide adequate back pressure for good flow rate control in the desired operating range.

Twice during the run the feed system ceased to deliver slurry to the melter. These incidents could not be corrected by flushing or increased air pressure. The stoppages are believed to be caused by the accumulation of solids in the feed line or in the pump chamber. After the first stoppage, the ADS pump was disassembled and inspected, but no solids deposits were found. The feed system worked after the pump was reinstalled. After the second stoppage, a plug of solids was located in the tubing between the pump and the flow meter.

PNL provided assistance in the startup of the fully remote ADS pump at West Valley. The pump was controlled using the microprocessor/controller built by PNL. The pump was installed in the concentrator/melter feed tank in the component test stand (CTS) facility and was started up in a recirculation loop pumping a slurry of frit and water. PNL also provided training in operating the ADS pump for West Valley personnel. The pump was used to feed the West Valley melter for about 1/2 h and operated for 28 h in a recirculation loop; no startup problems were encountered. West Valley is planning to operate the pump in a recirculation loop to obtain calibration data.

TANK DESIGN FOR SLURRY PROCESSING

The ability of the feed preparation system to produce and maintain a homogeneous melter feed within compositional tolerances strongly affects process control and quality control for the LFCM. A mixing evaluation was conducted to provide a quantitative description of the performance of a feed mixing system in terms of measurable process variables. The specific objectives of the

evaluation were to 1) examine the effects of impeller design, impeller diameter, impeller rotational speed, and the presence of baffles and heating/cooling coils on the distribution of solids in the mixing tank and 2) prepare a set of fabrication drawings for the construction of a large-scale mixing tank during FY 1986.

An extensive literature review was conducted to develop a basis for the selection of the variables that would most likely affect the mixing of melter feed slurries. The literature review focused on current industrial practices for the mixing of slurries and on the mixing tank designs for the slurry mix evaporator (SME) in the Defense Waste Processing Facility (DWPF) and the West Valley concentrator/melter feed tank. Six independent variables were selected for testing: the type of upper impeller, impeller diameter, impeller rotational speed, use/absence of wall baffles, use/absence of internal heat transfer coils, and the type of melter feed slurry used.

Impellers

Two upper impeller designs were evaluated: a 45° pitch four-blade turbine impeller and a three-blade high-efficiency impeller. The lower impeller was a four-blade flat turbine that acts as a sweeper to keep solids from depositing on the tank bottom.

Since the impeller diameter has a large effect on the mixing in the tank, three impeller diameters (Figure 2) were selected for testing: 3.74 in., 4.5 in., and 7.5 in. These diameters yield impeller diameter-to-tank diameter ratios that are commonly used in slurry applications.

The rotational speed of the impeller is the most critical parameter in the scale-up of bench-scale data. Therefore, four equally spaced rotational speeds were selected to bracket the well-mixed and the not-mixed conditions.

Baffles and Heating/Cooling Coils

Wall baffles are commonly used in mixing to eliminate vortexing and to direct the flow. Tests were conducted with and without wall baffles to determine their effect on the solids distribution in the tank.

FIGURE 2. Bench-Scale Impeller Arrangements

The use/absence of heating/cooling coils may affect the distribution of solids in the mixing tank. The coil design evaluated was the bayonet assembly used in the DWPF SME tank. The coils were evaluated with only the 3.75-in.-dia and 4.5-in.-dia impellers. Coils designed for the 7.5-in.-dia impeller would not fit into the bench-scale tank.

Melter Feed

Two slurries with different rheological and chemical properties were selected for evaluation.

Bench-Scale Experiment

An important step in the testing was to evaluate the physical and rheological properties of the simulated melter feed slurries. The slurries were tailored to simulate the physical and chemical properties of the melter feeds expected at the HWVP and West Valley facilities. The HWVP slurry is a formatted

waste with glass formers added as a one-third glass frit and two-thirds unreacted glass-forming chemicals. The West Valley slurry is a combination of waste, ion-exchange material, and glass-forming chemicals. The chemical, physical, and rheological properties of the simulated HWVP and West Valley melter feed slurries were evaluated in the laboratory. Some significant physical properties of these slurries at 20°C are listed in Table 1.

The rheological properties displayed by the simulated HWVP and West Valley slurries allowed them to be classified as yield-pseudoplastic non-Newtonian fluids. Mathematical models that have been developed to model this fluid behavior were applied to actual laboratory and bench-scale data and used to predict the level of turbulence that was present in the bench-scale mixing tank during each run. The level of turbulence was correlated with the degree of mixing achieved.

A statistical experimental design approach was used to assess the effects of impeller diameter, impeller type, impeller rotational speed, use of baffles, use of bayonet coils, and type of slurry on the distribution of solids in the mixing tank. The bench-scale mixing system (Figure 3) was designed to be geometrically and kinematically similar to large-scale mixing tanks frequently used in solids suspension mixing applications.

The dependent variable in this evaluation was the distribution of solids in the mixing tank. Samples were withdrawn from six locations in the mixing tank during each run. The total solids content of these samples was evaluated and compared with the total solids content of a homogeneously mixed batch of slurry.

TABLE 1. Physical Properties of HWVP and West Valley Simulated Melter Feeds

<u>Slurry</u>	<u>Density, g/cm³</u>	<u>pH</u>	<u>Dissolved Solids, wt%</u>	<u>Suspended Solids, wt%</u>	<u>Total Solids, wt%</u>	<u>Settling Rate, cm/h</u>
HWVP	1.29	8.3	20.9	20.8	41.7	0.45
West Valley	1.26	7.4	14.8	21.7	36.5	0.60

FIGURE 3. Bench-Scale Mixing System

The following overall trends were revealed by the bench-scale experiments:

- The distribution of solids in the mixing tank became more uniform as the rotational speed of the agitator (N) increased.
- HWVP melter feed slurry was easier to mix than West Valley slurry at low values of N .
- A proprietary impeller design (Lightnin A310) and a standard 45° pitched blade turbine achieved very similar mixing results.
- Impeller diameter was only significant at low values of N .
- Baffles improved mixing at low values of N but had little effect at higher rotational speeds.
- Bayonet coils reduced the degree of mixing achieved at low values of N .

Predictive equations were developed to quantify the magnitude of these trends. These predictive equations were extrapolated to predict the performance in a large-scale mixing system.

Large-Scale Mixing System Design

Large-scale mixing system designs similar to those installed at Savannah River Laboratory (SRL), West Valley, and mixing and metallurgical industrial sites were evaluated. This evaluation included an assessment of the level of power needed to maintain solids in a uniform suspension and an estimate of the power required to resuspend solids once they had settled.

The mixing system designs used a mixing tank shell that was a vertical cylinder with a flat bottom. The tank shell diameter was 9 ft and the design slurry depth was 9 ft. A power level of less than 1 hp (which induces a bulk fluid velocity of 5 to 15 ft/min) will be sufficient to maintain HWVP and West Valley solids in a uniform suspension ($\pm 1\%$ of the mean value of total solids). This unusually low power requirement (and bulk velocity) is due to the very slow settling rates exhibited by the simulated HWVP and West Valley slurries (0.45 and 0.60 cm/h, respectively). Yield stresses exhibited by the slurries substantially reduced the solids settling velocity in the slurry.

The large-scale mixer must be able to resuspend solids if they settle as a result of a power outage or other disturbance. The amount of agitation necessary to resuspend solids is higher than that needed to maintain solids in suspension. Historically, bulk fluid velocities of approximately 50 ft/min have been specified for solids suspension mixing applications where a uniform suspension of solids is required. The power that must be applied to HWVP and West Valley slurries for large-scale mixing systems estimated to achieve a bulk velocity of 50 ft/min is summarized in Table 2.

The motor used to operate the mixer will have a power rating higher than those listed in Table 2. This motor must overcome energy losses that occur in the motor and the gearbox. It must also possess a startup torque that can overcome the yield stress of the slurry in the tank. The yield stress increases over the length of time the slurry remains motionless in the tank.

TABLE 2. Power Estimated to Achieve a Bulk Velocity of 50 ft/min in Selected Large-Scale Mixing Systems

Mixing System Design	Impeller Diameter, ft	Upper Impeller Design	Design Impeller Rotational Speed, rpm	Shaft Power, hp	
				HWVP	West Valley
SRL	2.25	Lightnin A310 ^(a)	190	5.5	5.1
West Valley	2.70	Lightnin A310	100	7.6	8.2
Industry A	4.5	45° pitched blade turbine	20	8.1	7.9
Industry B	2.70	45° pitched blade turbine	100	9.4	9.3

(a) Mixing Equipment Company, Rochester, New York.

The effect of time on the yield stress value was not evaluated. This evaluation should be performed before the motor size is specified. This startup torque requirement will probably be the critical factor that will determine the size of the motor needed for melter feed slurry mixing applications.

The large-scale impeller diameter and rotational speed can be specified once the need for and design of internal heating/cooling coils has been established. If bayonet coils are not required, the West Valley, Industry A, or Industry B designs could be specified. The West Valley or Industry B designs are preferred since standard variable-speed drive units can be used. These units should be specified for each large-scale melter feed slurry application since the degree of agitation required will vary with time.

Summary

The HWVP and West Valley melter feed slurries have been tailored to produce an acceptable glass product based on site-specific HLW chemical and physical properties. The reference composition of the slurries may change in the future. The data acquisition, data analysis, and mixing scale-up methods developed in this study can be used to obtain estimates of the significance of compositional or other geometric or kinematic changes on the degree of mixing that can be achieved in full-scale melter feed mixing tanks. These methods

provide a low-cost and rapid means of obtaining information that can be used to formulate efficient and cost-effective designs for a wide variety of mixing systems.

REMOTE SLURRY SAMPLER

The Purex C-Sampler was fabricated; and testing was initiated according to the approved test procedures, "Functional Test of Remote C-Sampler Sample Bottle Holder," Rev. 1. The purpose of the test was to evaluate the ability of the C-Sampler bottle holder to function as intended (i.e., to hold the sample bottle in proper position for sampling) during sampler installation under full impact from a 500 ft-lb impact wrench.

A PNL-fabricated adapter was used to mount the sampler on a simulated tank lid. The sampler was then installed on the adapter with a crane. Figure 4 shows the sampler in place on the test stand. The Purex connector was tightened

FIGURE 4. Purex C-Sampler in Place on the Test Stand for Functional Testing of the Bottle Holder Mechanism

with an impact wrench until there was no more rotation. The condition of the sample bottle and holder was noted. The connector was then loosened and the sampler was lifted off the adapter with the crane. This procedure was repeated several times.

For most cycles, no problems occurred; however, during two of the test cycles, the vibration from the impact wrench caused the handle of the toggle clamp to fall down and the bottle was released from the stopper. The toggle clamp is designed to hold the bottle against the stopper during installation and removal when the handle is fully raised. When the handle was raised, it did not go far enough past center to function properly under severe vibration.

This problem was corrected by grinding the back plate of the clamp, allowing the handle to go farther past center when raised. The sampler was then retested through several cycles of tightening and loosening of the Purex connector. The handle on the toggle clamp functioned properly during the retesting. Once testing was completed, the sampler was packaged and shipped to West Valley for additional functional testing.

CONCLUSIONS

The following conclusions are based on the work described in the preceding sections:

- The ADS pump with the constant pressure control system supplied larger and more constant feed rates in the radioactive tests.
- Frequent adjustment of the ADS pump controller was required to maintain a constant feed rate during an 18-day run in the PSCM. Frequent flushing with water and increased air pressure were required to keep the feed system unplugged.
- Mixing tank studies showed: 1) the distribution of solids in an agitated tank became more uniform as the rotational speed of the agitator increased; 2) HWVP melter feed was easier to mix than West Valley melter feed at low rotational speeds; 3) a proprietary impeller design and a standard 45° turbine produced similar mixing results;

- 4) impeller diameter was significant only at low rotational speeds;
 - 5) baffles improved mixing only at low rotational speeds; and
 - 6) bayonet coils reduced the degree of mixing at low rotational speeds.
- Predictive equations can be used to quantify the magnitude of the trends presented and these predictions can be applied to large-scale tank systems to produce valid results.
 - The Purex C-Sampler design will retain the sample bottle during the vibration caused by an impact wrench.

MELTER SYSTEMS

J. M. Perez, Jr., R. D. Dierks, B. M. Wise,
M. E. Peterson, and R. K. Nakaoka

SUMMARY

A long-term pilot-scale ceramic melter (PSCM) experiment was conducted in support of the Hanford Waste Vittrification Program (HWVP). The PSCM-22 test included 427 h of melter operation during which over 17,000 L of feed was processed.

The RLFCM-5 experiment was also completed; the melter was operated for approximately 175 h with an on-stream efficiency of approximately 80%. Approximately 75,000 Ci of activity was immobilized during the experiment. The completion of this work allows specific preparations to be initiated for the production of the first 10 isotopic heat and radiation sources for the Federal Republic of Germany (FRG). The FRG canister storage racks were installed. These racks are needed for temporary storage of the FRG canisters in B-Cell while A-Cell cleanout and equipment installation is completed. Individual racks with versatile placement possibilities were designed.

INTRODUCTION

The objective of this work is to demonstrate laboratory-developed melter concepts--first with simulated radioactive feeds in the engineering-scale ceramic melters, then in the nonradioactive PSCM (Figure 1), and finally with radioactive feed compositions in the pilot-scale radioactive liquid-fed ceramic melter (RLFCM). The laboratory-developed concepts include feed formulation modifications that affect melter performance (foaming, slag formation, free metal precipitation, and secondary phase formation) or the final glass characteristics (crack formation, leachability, and devitrification).

FIGURE 1. Pilot-Scale Ceramic Melter

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

TECHNICAL PROGRESS

Progress on nonradioactive and radioactive melter testing conducted this quarter is discussed below.

NONRADIOACTIVE MELTER TESTING

The major objective designated by the HWVP for the PSCM-22 experiment was to evaluate the processing characteristics of the current HWVP melter feed during long-term PSCM operation. The current melter feed, identified at the beginning of FY 1985, consists of reference feed (HWVP-RF) and glass-forming chemicals.

Two options for the addition of glass-forming chemicals to the current HWVP melter feed were evaluated during HWVP-11/HBCM-85-1 (completed in April 1985) (Burkholder, Jarrett, and Minor 1986). This test showed that a melter feed having glass-forming materials added solely as premade frit (100% frit feed) processed better during actual melter conditions than a feed consisting of glass-forming chemicals added as one-third frit and two-thirds unreacted bulk chemicals.

PSCM-22 consisted of 427 h of melter operation and was completed on August 2, 1985. During operation, approximately 17,100 L of feed was converted to 6,800 kg of glass. The 18-day melter experiment was only the second test that used the current HWVP melter feed. Glass-forming chemicals were added as premade frit (100% frit feed) based on the results of HWVP-11.

The joule-heated PSCM has an exposed glass surface of 0.73 m^2 (7.85 ft^2). During normal operating conditions, the glass volume is maintained at approximately 270 L.

The following major objectives in support of the HWVP were completed during PSCM-22:

- The processability of HWVP melter feed (100% frit) under long-term pilot-scale conditions was evaluated.
- The effects of the melt redox on the processing characteristics of the current feed were investigated.
- The settling potential for spinel crystals formed in the current glass (high Cr concentration) was evaluated.
- Additional data to be used in continuing efforts to correlate the results of laboratory-scale melting behavior with the results from PSCM tests were generated.
- The performance of the off-gas equipment was characterized.
- Preliminary information on the compatibility of the proposed HWVP melter/turntable design with the HWVP reference canister was collected.

The following objectives in support of the Nuclear Waste Treatment Program (NWTP) were also completed during PSCM-22:

- A 24-in.-dia instrumented canister was filled to obtain additional glass temperature profiles to be used in verification of a canister-cooling predictive computer code.
- The constant glass temperature feedback control algorithm was evaluated.
- Tracers were added to the melter feed in an effort to generate additional data for use in verification of process mass balance models.

Finally, 10 half-scale test canisters were filled in support of the Transportation Technology Center (TTC), Sandia National Laboratory (SNL), under a Materials Characterization Center (MCC) task. Six of these canisters will be used in impact testing of shipping casks to be done during the first quarter of FY 1986 at SNL. The remaining four canisters will be used in future testing at PNL.

At this time, HWVP-RF is a simulation of a neutralized current acid waste (NCAW) and cladding removal waste (CRW) blend. The target composition of the reference feed is shown in Table 1. The concentrations of the bulk chemicals used in feed makeup and the assumed oxide concentrations in the glass are also listed in Table 1. The basis for the feed simulation is 400 g of total oxides per liter (TO/L) of melter feed with the reference feed supplying 25% of the total oxide. The remaining oxides in the melter feed are provided by the glass-forming chemicals in the form of a premelted glass frit (see Table 1). The oxide loading value (400 g/L) is based on laboratory evaluations of melter feed rheological properties performed during FY 1984 and FY 1985. Because of the envisioned neutralized waste stream, most reference feed components are added as hydroxides, although a very few nitrates are present.

Preparation of the HWVP melter feed involved the treatment of reference feed at 90 to 95°C with formic acid. Formic acid reacts with the monovalent and divalent waste metals to form formate salts. This step, which is part of the Defense Waste Processing Facility (DWPF) flowsheet, improves the rheology of the slurry and provides additional total organic carbon (TOC). The acid addition rate is controlled to prevent excessive reaction, which can lead to foaming of the reference feed. Following acid addition, the reference feed was heated to around 100°C and held there for 2 h. This step was done to insure that all reactions occurring in the slurry had gone to completion and to correlate more closely with the DWPF flowsheet.

To provide the necessary amount of melter feed for PSCM-22, five 2300-L batches of reference feed were prepared in the manner described above. The five batches were combined in a 12,500-L holding tank and homogenized for 12 h. A total of 11,200 L of reference feed was prepared before the beginning of the experiment. During the test, melter feed was prepared in a secondary tank by combining reference feed from the holding tank with frit, water, and any additional constituents. The melter feed was then transferred into a 2000-L PSCM feed tank.

The higher-than-expected feed rates during the experiment and the losses incurred in transferring the reference feed from tank to tank created the need for additional reference feed. An additional 1500-L batch of melter feed was

TABLE 1. Composition of Simulated Melter Feed Slurry^(a)

Compound ^(b)	Concentration, g/L	Assumed Oxide	Concentration, g/L	Glass, wt%
Fe(OH) ₃	59.5	Fe ₂ O ₃	44.4	11.10
Al(OH) ₃	26.3	Al ₂ O ₃	17.2	4.30
NaNO ₃	13.4	Na ₂ O	10.7	2.68
Cr(OH) ₃	7.21	Cr ₂ O ₃	5.3	1.33
NaOH	3.58	ZrO ₂	2.4	0.60
Na ₂ C ₂ O ₄ ^(c)	3.37	SiO ₂	3.0	0.75
Zr(OH) ₄	3.11	NiO	2.4	0.60
SiO ₂	3.00	SO ₃	1.5	0.38
Ni(OH) ₂	3.00	La ₂ O ₃	2.2	0.55
Na ₂ SO ₄	2.32	MoO ₃	1.2	0.30
LaF ₃	2.16	Nd ₂ O ₃	2.1	0.53
Na ₂ MoO ₄ · 2H ₂ O	2.00	Cs ₂ O	1.0	0.25
Nd(OH) ₃	1.84	CeO ₂	0.7	0.18
CsOH	1.05	CuO	0.6	0.15
Ce(OH) ₃	0.79	MnO ₂	0.7	0.18
Cu(OH) ₂	0.74	BaO	0.4	0.10
Mn(OH) ₂	0.74	F ⁻	1.2	0.30
BaSO ₄	0.63	SrO	0.4	0.10
NdF ₃	0.58	Pr ₆ O ₁₁	0.4	0.10
Sr(OH) ₂	0.47	MgO	0.3	0.08
Pr(OH) ₃	0.47	CaO	0.3	0.08
La(OH) ₃	0.47	Y ₂ O ₃	0.2	0.05
NaF	0.47	Sm ₂ O ₃	0.2	0.05
Mg(OH) ₂	0.42	TOC	0.6	0.15
CaF ₂	0.42	I ⁻	0.04	0.01
Y(OH) ₃	0.26			
Sm(OH) ₃	0.21			
NaI	0.05			
Subtotal	138.56		99.4	24.9
HW39 frit ^(d)	300.0	SiO ₂	201.8	50.44
		B ₂ O ₃	38.2	9.56
		Na ₂ O	30.8	7.69
		Li ₂ O	15.0	3.75
		CaO	11.2	2.81
			3.0	0.75
Subtotal	300.0		300.0	75.0
Total	438.5		400.0	100

Reductants: 9.2 g/L formic acid, 3.5 to 0 g/L sugar

(a) Basis: 400 g oxide/L slurry, 25 wt% waste oxide loading.

(b) Prior to reaction with formic acid.

(c) TOC substitute.

(d) HW39 frit size distribution as follows: 1/3 to be -80/+200 mesh;
2/3 to be -200 mesh.

prepared. Because of differences in bulk chemicals, this feed is referred to as the auxiliary feed and is treated as a separate segment of the experiment (see Table 2).

To gain additional information on the effect of feed and glass redox on processing characteristics, 3.5 g/L of sugar was added as additional reductant to the melter feed for the first eight days of the experiment. The target ferrous/ferric ratio for this segment of the test was 0.1/0.2. For the next 10 days, no sugar was added to the feed in the hopes of generating a slightly oxidizing glass.

The melting performance of the two feeds processed during the first 16.5 days was not significantly different. A plot of feed rates (6-h average values) versus time is shown in Figure 2. Both feeds generated thin, flexible cold caps and numerous active vents. The melt surface coverage ranged from 50% to 100% during the first two segments of the run. Because of the thinness of

TABLE 2. Summary of PSCM-22 Experiment^(a)

	Test Segments		
	Sugar Added to Feed	No Sugar Added	Auxiliary Feed
Duration, h	186	198	30.5
Total feed, L	6737	9213	1123
Nominal feed rate, L/h	36.9	44.5	39.5 ^(b)
Maximum feed rate, L/h	40.1	52.9	
Feed redox	0.104	0.002	0.42 ^(c)
Glass redox	0.160	0.015	0.147 ^(d)

(a) Scheduled downtime = 7.5 h; unscheduled downtime = 5.0 h; feed rate values are averaged rates.

(b) Due to the short duration of the auxiliary segment, no distinction was made between nominal and maximum feed rates.

(c) The initial batch of auxiliary feed had a ferrous/ferric ratio of 1.2. Addition of NaNO_3 lowered the value to 0.028 for the remainder of the segment.

(d) Due to the high redox level in the initial batch of auxiliary feed, the glass ferrous/ferric ratio never reached equilibrium.

FIGURE 2. Average Feed Rates During the PSCM-22 Experiment

the cold cap, the plenum temperature, which is used to gauge overfeeding, remained within the acceptable range even though the cold cap seemed excessive at times.

The absence of sugar in the melter feed during the second segment of the test did not generate an oxidizing feed. The forming process used in the preparation of the reference feed introduced sufficient TOC to keep the average feed redox slightly above zero. Because of the feed redox, the glass remained reducing during this segment of the run and no incidents of unstable melt conditions were observed. The redox state of this feed did, however, lead to higher processing rates than those of the added-sugar feed; similar results were obtained in PSCM-21 (Burkholder, Jarrett, and Minor 1986).

Feed rates observed during the auxiliary portion of the run were lower than expected for the first 13 h of the segment because of a thick, unyielding cold cap. The lower feed rates were attributed to the excessively high redox level of the melter feed. The ferric hydroxide $[\text{Fe}(\text{OH})_3]$ used in the preparation of the reference feed was contaminated with chlorine and caused the high redox state (ferrous/ferric ratio of approximately 1.2 in the feed). Sodium nitrate (NaNO_3) was added to the melter feed in an effort to oxidize the ferric chloride (FeCl_3) in the feed and thus lower the redox level. Feed rates did increase over the final 18 h of the test.

RADIOACTIVE MELTER TESTING

The RLFCM-5 experiment completed the radioactive shakedown testing with the West Valley feed composition. The two major objectives of this experiment were to operate the melter for a minimum of 100 h and to realize an on-line efficiency of at least 80%. The run lasted for 174 h 41 min and had an overall efficiency of 78.8%. Four periods of extended downtime were experienced during the run. Three periods were attributed to the air displacement slurry (ADS) pump. In all three instances, the pump was allowed to pump down to its minimum level (approximately 315 L), and slurry had to be transferred from another tank before feeding could be resumed. A total of 11 h 7 min of downtime was accrued during the feed transfer operations. A total of 1990.5 L of feed was processed during the run and 75,000 Ci of activity was immobilized in over 300 kg of glass. The feed composition for this experiment is shown in Table 3.

TABLE 3. RLFCM-5 Slurry Composition

Waste/Glass Compounds	Waste, g/L	Cold Chemicals, g/L	Combined Total, g/L	Assumed Oxide Compound	Oxide, g/L	Waste Glass, wt%
Al(NO ₃) ₃ ·9H ₂ O	27.80	62.33	51.97	Al ₂ O ₃	7.06	2.18
Ba(NO ₃) ₂	2.24	0.00	0.67	BaO	0.40	0.12
Ca(NO ₃) ₂	12.32	3.39	6.07	CaO	2.07	0.64
Ce(NO ₃) ₃ ·9H ₂ O	3.85	0.55	1.54	Ce ₂ O ₃	0.52	0.16
Cr(NO ₃) ₃ ·9H ₂ O	5.31	3.57	4.09	Cr ₂ O ₃	0.78	0.24
CsNO ₃	0.08	0.67	0.49	Cs ₂ O	0.36	0.11
Eu ₂ O ₃	0.00	0.00	0.00	Eu ₂ O ₃	0.00	0.00
Fe(NO ₃) ₃ ·9H ₂ O	125.90	236.92	203.61	Fe ₂ O ₃	40.24	12.42
FePO ₃ ·2H ₂ O	0.00	0.00	0.00	P ₂ O ₅	0.00	0.00
H ₃ BO ₃	0.74	0.00	0.22	B ₂ O ₃	53.23	16.43
H ₃ PO ₄	0.00	0.00	0.00			
KNO ₃	1.60	0.01	0.49	K ₂ O	0.23	0.07
La(NO ₃) ₃ ·6H ₂ O	2.49	0.00	0.75	La ₂ O ₃	0.28	0.09
LiNO ₃	10.61	0.00	3.18	Li ₂ O	0.69	0.21
Mg(NO ₃) ₂ ·6H ₂ O	7.59	1.75	3.50	MgO	0.55	0.17
Mn(NO ₃) ₂ ·4H ₂ O	10.46	13.69	12.72	MnO ₂	4.41	1.36
Na ₂ B ₄ O ₇ ·10H ₂ O	0.00	206.32	144.43			
Na ₂ C ₂ O ₄	0.00	59.25	41.48			
Na ₂ MOO ₃ ·2H ₂ O	4.44	0.00	1.33	MoO ₃	0.79	0.24
NaNO ₃	62.11	0.00	18.63	Na ₂ O	50.48	15.58
Na ₃ PO ₄ ·12H ₂ O	0.00	0.00	0.00			
Na ₂ SiO ₃ ·5H ₂ O	0.00	3.32	2.33			
Na ₂ SO ₄	0.00	1.16	0.81	Na ₂ SO ₄	0.81	0.25
Nd(NO ₃) ₃ ·6H ₂ O	4.98	0.00	1.49	Nd ₂ O ₃	0.57	0.18
Ni(NO ₃) ₂ ·6H ₂ O	7.98	1.81	3.66	NiO	0.94	0.29
PbNO ₃	0.00	0.00	0.00	PbO	0.00	0.00
Pr ₂ O ₃	0.00	0.00	0.00	Pr ₂ O ₃	0.00	0.00
RE(NO ₃) ₃	0.00	1.14	0.80	RE ₂ O ₃	0.42	0.13
RuO ₂	1.33	0.00	0.40	RuO ₂	0.40	0.12
Sb ₂ O ₃	0.00	0.00	0.00	Sb ₂ O ₃	0.00	0.00
SeO ₂	0.00	0.00	0.00	SeO ₂	0.00	0.00
SiO ₂	2.78	215.25	151.51	SiO ₂	152.51	47.07
Sr(NO ₃) ₂	0.94	0.00	0.28	SrO	0.14	0.04
TeO ₂	0.30	0.00	0.09	TeO ₂	0.09	0.03
Th(NO ₃) ₄ ·4H ₂ O	0.00	9.10	6.37	ThO ₂	3.05	0.94
TiO ₂	1.32	2.40	2.07	TiO ₂	2.07	0.64
UO ₂	0.00	0.69	0.49	UO ₂	0.49	0.15
Y ₂ O ₃	0.00	0.00	0.00	Y ₂ O ₃	0.00	0.00
ZrO(NO ₃) ₂ ·2H ₂ O	0.00	1.81	1.26	ZrO ₂	0.58	0.18
Sugar	0.00	0.00	0.00			
Total	297.20	825.12	666.75		324.15	100.05

Some of the more significant operating parameters of the RLFCM-5 experiment are depicted in Figure 3. Some insight into improved melter operating techniques can be derived from this figure.

The run plan for this experiment specified that the average glass temperature would be maintained at $1150^{\circ}\text{C} \pm 25^{\circ}\text{C}$ and that the power delivered to the melter electrodes would be controlled to maintain a constant melter tank electrical resistance, based on the assumption that the melter tank resistance would be a constant inverse function of the average melter tank temperature.

Figure 3 is a set of plots relating the use of the electrode power control system and the subsequent effects of this use on the melter operating parameters. Figure 3A is a record of the power control system set point and operational mode changes that were used to achieve the specified glass temperature conditions, and Figure 3B shows the response of the control system to these changes. Figure 3C shows the power delivered to the melter electrodes during the experiment. The two horizontal lines at 35 kW and 40 kW indicate the idling power requirements at approximately 1100°C and 1130°C and are useful in identifying the periods of feed transfer into the melter, the approximate feed transfer rates, and cold cap burnoff periods. Figure 3E is useful in identifying the onset of glass foaming conditions in the melter. Figure 3D shows the average glass temperature during the experiment, with the target glass temperature and range indicated by horizontal solid and dashed lines.

Two observations are apparent from Figure 3:

- The operating glass temperature should be established well before an experiment. Any necessary set point changes should be limited to 0.3 ohm/4 h or less to avoid foaming.
- Because of the long lag time in the response of the melter to process changes, automatic electrode power control techniques are preferable to manual electrode power control.

The first usable glass samples from the RLFCM melter were successfully obtained from the glass stream falling from the melter discharge trough lip during glass transfers to the receiving canister. The samples were obtained by

FIGURE 3. Resistive Feedback Electrode Power Control and Its Effect on Melter Operating Parameters

extending a graphite sample boat into the falling glass stream using the extension of a pneumatic cylinder piston. While the piston-operated sampler was simply a modification of a previous manually extended model that operated in basically the same manner, the piston-operated sampler was much easier to handle with manipulators. In addition, the extension and retraction of the piston-operated samples was controlled electrically by the operator with an easily controlled momentary contact switch located beside the manipulator window. Modifications to this initial piston-operated sampler have been completed making it even easier to handle with the manipulator, easier to replace the sample boat in-cell should it become damaged, and less prone to lose its very fluid glass sample as the boat is retracted from the glass stream.

CONCLUSIONS

The major results and conclusions from the PSCM-22 experiment are listed below:

- The HWVP melter feed exhibited excellent processing characteristics.
- The forming process used in feed preparation added sufficient TOC to the melter feed to maintain a reducing feed without the addition of sugar.
- Feed rates for the segment of the test where sugar was added to the feed matched predicted rates from HWVP-11.
- A feed without added sugar (lower redox level) processed at higher rates than feed with added sugar.
- Chlorine contamination in $\text{Fe}(\text{OH})_3$ stocks substantially increased the ferrous/ferric ratio of the auxiliary feed.
- Sodium nitrate was used successfully to lower the redox level of the auxiliary feed.
- The constant temperature control algorithm was not effective in controlling wide variations in glass temperature.
- The ADS feed pump operated with only minor problems.

- Laboratory predictions of feed redox levels closely matched the actual levels in the PSCM.
- Concentrations of certain components in feed samples were consistent throughout the run while other components varied. This variation indicated preferential segregation of solids, presumably in the reference feed holding tank.
- The PSCM pour stream was stable; half-scale canisters with 6.4-cm (2.5-in.) inside neck openings were filled. This procedure also demonstrated the compatibility of the PSCM overflow design with the HWVP canister opening of 11.5 cm (4.5 in.).

Data obtained during PSCM-22 in support of NWTP objectives will be analyzed during the first quarter of FY 1986. The evaluation of spinel crystal settling and off-gas equipment performance will also be concluded during the first quarter of FY 1986. The results of these experiments will be reported in the final draft of the PSCM-22 run summary.

The major results and conclusions from the RLFCM-5 experiment are listed below:

- As in-cell mechanical problems with the ADS pump were slowly resolved, the normal operating characteristics of the pump became apparent and the reliability of this pumping system improved.
- The flexibility of the resistive feedback melter electrode voltage control system was very effective in maintaining a relatively constant average glass temperature during RLFCM-5, despite feed rate adjustments and startup or shutdown procedures.
- Further refinement of the resistive feedback control system would minimize glass temperature fluctuations as the melter tank electrical resistance responds to glass level changes as the glass is batch discharged from the melter.

REFERENCES

Burkholder, H. C., J. H. Jarrett, and J. E. Minor. 1986. LFCM Vitrification Technology Quarterly Progress Report, April-June 1985. PNL-5470-3, Pacific Northwest Laboratory, Richland, Washington.

CANISTER FILLING AND HANDLING SYSTEMS

D. H. Siemens, G. J. Sevigny, and R. K. Farnsworth

SUMMARY

Canister filling and handling systems have been, or are being developed for the West Valley Demonstration Project (WVDP), the Hanford Waste Vitrification Program (HWVP), and the radioactive liquid-fed ceramic melter (RLFCM) operation. Several of these systems have been fabricated, tested, and placed in service. To determine the extent of crystalline growth in glass cooled in an open turntable, a computer simulation of the glass cooling rate was performed. The resulting cooling rates were then compared with laboratory melts with corresponding cooling rates. Based on these laboratory tests, glass cooled at the computer-simulated predicted rate had more crystals than rapidly cooled samples.

INTRODUCTION

The objectives of this work are to develop and demonstrate systems for positioning canisters under the ceramic melter overflow; sealing the canisters to the melter overflow, and monitoring the glass level in the canister during filling, sealing, and leak testing the filled canisters; and decontaminating the filled canisters. A turntable is used to position the canister under the melter. The turntable is enclosed in a tank that is sealed to the melter overflow, or the canister can be sealed directly to the melter overflow. Two methods (weight and gamma ray detection) are being developed to monitor the glass level in the canister during filling. Two canister handling systems have been fabricated and tested; both systems are installed in their respective locations where operational testing will be conducted.

TECHNICAL PROGRESS

The glass canister filled from an LFCM must allow the contained glass to cool at a minimum rate in the temperature range between 1000°C and 600°C to prevent glass devitrification. To determine the extent of crystalline growth in glass cooled in an open turntable, a computer simulation of the glass cooling rate was performed. The cooling rates were then compared with laboratory melts with corresponding cooling rates.

The modified TEMPEST computer code (Trent et al. 1983) was used to simulate the continuous filling and cooling of a 24-in.-dia HWVP canister in open air. The simulation was based on a canister fill height of 9 ft at a production rate of 60 kg/h. The glass properties were based on a Savannah River Laboratory (SRL) glass with a similar composition for which data are available. The simulation also used the following input:

Decay heat	0.93 W/kg (1.41 Btu/lb-h)
Canister glass weight	4400 lb
Canister emissivity	0.5
Surrounding temperature	38°C

The glass temperatures at the bottom centerline (BC), middle centerline (MC), middle glass/canister interface (MGI), and top centerline (TC) of the computer simulation are shown in Figure 1.

The centerline cooling curves for the open turntable were used in laboratory tests to prepare a nonradioactive glass (HW39) to determine the extent of crystallization that could be expected in an actual canister. The laboratory melt tests were performed using the HW39 composition with a rapid cooling rate ($>100^{\circ}\text{F}/\text{min}$) and a cooling rate that matched the predicted cooling rate. The amount of crystallization was determined by x-ray diffraction, which gives semiquantitative results with a minimum detection level of 5 wt%.

The crystallization observed in the rapidly cooled glass was near the detection limit of the equipment; the crystallization was estimated to be 5%. Laboratory tests showed the HW39 glass that was cooled at the predicted

FIGURE 1. HWVP Canister Glass Cooling Curves

centerline cooling rate of 40°F/h had approximately 10 wt% more crystals than a rapidly cooled sample. The majority of the crystals based on past x-ray diffraction patterns were spinels, which have not increased leach rates in other waste glasses. Therefore, the leach rates should meet the anticipated Waste Acceptance Committee's (WAC) recommended repository specifications (a leach rate of 1 g/day-m²) (September 1985).

The laboratory tests were also performed using HW39 glass without chromium. The glass was cooled at >100°F/min and at the predicted rate. The rapidly cooled glass had no detectable crystals, while the slow-cooled glass appeared to have acmite crystals. Acmite crystals (Na_xSi_xFe_xO_x) usually increase the leachability of the glass. The amount of crystals in the slow-cooled glass was less than 5 wt%; thus, the leach rate would be affected very little and the HW39 glass without chromium cooled in an open turntable should be acceptable for repository storage.

The WAC does not currently recommend a limit on the amount of crystals in waste glass. Since the HW39 glass samples were monolithic glass products, the HW39 glass cooled in an open turntable should be acceptable to a waste repository. Future repository acceptance criteria may affect the glass canister qualification, but they cannot be addressed at this time.

In summary, the HW39 glass cooled at the predicted cooling rate (approximately 40°F/h) had more crystals than a rapidly (>100°F/min) cooled sample, but the canisters of glass should still be acceptable to a repository. The HW39 glass without chromium had fewer crystals than the typical HW39 glass.

CONCLUSIONS

The following conclusions are based on the work reported in this quarterly:

- HW39 glass cooled in an open turntable will probably meet waste repository acceptance criteria.
- HW39 glass cooled at a rate of about 40°F/h has more crystals than a rapidly cooled glass.
- HW39 glass without chromium has fewer crystals than the reference HW39 glass when cooled at 40°F/h.

REFERENCES

Trent, D. S., et al. 1983. TEMPEST: A Three Dimensional Time Dependent Computer Program for Hydrothermal Analysis. PNL-4348, Vols. 1 and 2, Pacific Northwest Laboratory, Richland, Washington.

OFF-GAS SYSTEMS

R. W. Goles and C. M. Anderson

SUMMARY

Data on the effluent emissions and off-gas performance of the pilot-scale ceramic melter system were gathered during a melter experiment conducted this quarter. Analyses of the data began and the results will be reported next quarter.

INTRODUCTION

Effluent emission and off-gas performance characterization studies are being conducted to establish processing criteria that will satisfy all pertinent licensing regulations governing future LFCM operations. The scope of these studies is quite broad and includes:

- establishing the nature and extent of melter feed component losses
- characterizing the efficiencies of off-gas processing equipment
- correlating melter exhaust composition with LFCM processing conditions
- identifying and/or monitoring potentially hazardous off-gas situations.

65/66

PROCESS/PRODUCT MODELING AND CONTROL

W. L. Kuhn, L. J. Ethridge, D. W. Faletti,
R. K. Farnsworth, B. A. Pulsipher, and J. H. Westsik, Jr.

SUMMARY

The progress on process control instrumentation and process control algorithms is discussed in this report. The waste form qualification modeling pertaining to canister heat transfer and to a transient mass balance over a melter is also reviewed. A glass thermowell, pneumatic level detection system (bubbler), and an infrared camera were also tested during a melter experiment conducted this quarter.

A temperature control algorithm is being developed for the control of electrical power to the melter using glass temperatures as feedback to the controller. A cascade control scheme is used to achieve the desired control. A foam detection scheme was added to the algorithm. During foaming incidents, glass temperatures increase throughout the melter. Temperatures measured by thermocouples in the cold cap region increase as the foam level rises. The foam detection scheme looks for this temperature increase in the region of the cold cap.

INTRODUCTION

The purpose of this work is to develop correlations and models that can be used in the future to 1) adapt liquid-fed ceramic melter (LFCM) technology to new high-level waste (HLW) compositions and processing rates and 2) operate the adapted LFCM processes. During FY 1985, the focus is on process control. Procurement of developmental control instrumentation is included in this work; data from nonradioactive and radioactive testing conducted by PNL, Savannah River Laboratory (SRL), or West Valley will be used.

Correlations will be developed by applying statistical analyses to data, including consideration of the uncertainty of the data. Analysis of propagation of uncertainty will be made regarding the intended future use of the correlations to determine if the correlations are adequate. If they are not, additional data needs will be identified.

For certain aspects of LFCM performance, models will be formulated where a description of physicochemical phenomena that are hypothesized to control performance are converted to a mathematical model and tested statistically against available data. The model will be either statistically accepted or rejected. If the confidence level of the decision is not adequate, additional data will be identified and included in data collection requirements of future nonradioactive or radioactive tests.

TECHNICAL PROGRESS

Technical progress completed during this quarter is discussed in the following sections on process control instrumentation, process control algorithm, and waste form qualification modeling.

PROCESS CONTROL INSTRUMENTATION

The objective of this work is to develop instrumentation that will improve the control of an LFCM process. A glass thermowell, pneumatic level detection system (bubbler), and an infrared camera were tested this quarter during a melter experiment (PSCM-22). The time domain reflectometer level detection system and the acoustic monitor were not used during the run.

Glass Thermowell

The glass thermowell is used to monitor the glass temperatures within the melter. Seven Type K thermocouples were positioned 5.5, 8, 11, 14, 15, 16, and 17 in. above the melter floor in the 1-in.-dia and 0.25-in.-thick Inconel 690 thermowell. The thermowell was located in the south rectangular port on the melter, just south of the film cooler.

Data from the lowest three thermocouples were averaged to define the bulk glass temperature. This average temperature was displayed on the data acquisition system and was used by the temperature control algorithm (see Process Control Algorithm section). The upper four thermocouples were located in the region of the glass/cold cap interface as a possible method to detect foaming. No foaming occurred during the run, and the detection method was not tested.

Level Detection System

The pneumatic level detection system (level bubbler) determines the specific gravity and the level of glass in the melter and monitors the stability of the cold cap, including the occurrence of foaming. A new three-tube design was tested during the run because of severe corrosion that occurred along the air ports of the old one-rod probe. The probe was installed in the north rectangular port on the melter.

Detecting the level of the glass using the probe appeared to be affected by the pressure and flow rate of the air flowing into the probe. Detecting the occurrence of foaming was not evaluated because foam did not form in the glass.

Infrared Camera

Testing of the infrared camera was plagued with a number of problems. The camera was not installed until the final week of the PSCM-22 run. Before the run started, the nose piece protecting the lenses and mirrors extending into the melter plenum was found to have corroded through, and cooling to the lenses was lost. This loss necessitated the refabrication of several parts of the camera housing. Installation was further delayed by a short circuit in the electronics of the camera. A buildup of glass and corrosion products in the melter lid nozzle sleeve, through which the camera must slide to look into the melter, had to be removed before the camera could be installed. Picture quality was not as good as during previous melter runs. Changes in critical distances within the optical path caused by the refabrication of the camera housing may have been the cause of the reduced picture quality.

Acoustic Monitoring System

The acoustic monitoring system was not used during PSCM-22, but preliminary analysis of the data from the PSCM-21 test was completed. A large effect

on the measured acoustic activity within the melter was shown when melter power was turned off and on. Whether this measured activity is due to actual acoustic events or is the result of electrical noise is not clear. Regardless of the source, the signal density is large enough to mask the signals of interest--foaming, overfeeding, and feed stoppage. With the melter power at steady state, changes in the acoustic emission rate could be correlated with foaming and feed stoppage incidents. Overfeeding is a process that occurs slowly and does not show up in the acoustic rate data. Overfeeding might be reflected in the amplitude of the acoustic events if the power on/off signals would not dominate the amplitude data.

Time Domain Reflectometer (TDR)

Following difficulties with the electronics of the TDR observed during PSCM-21, the instrument was returned to the manufacturer for repairs. Sensitivity to humidity and an unusually long warmup time were identified as the causes of the problems. Repairs are being made by the manufacturer.

PROCESS CONTROL ALGORITHM

A temperature control algorithm is being developed to control electrical power to the melter using glass temperatures as feedback to the controller. A cascade control scheme is employed to achieve the desired control. The computer/data acquisition system serves as the primary control loop and calculates the power setpoint based upon the average glass temperatures and the glass temperature setpoint. A 0 to 10-volt signal is sent from the computer to the research-incorporated power controller which then provides proportional-integral-derivative PID control of the power at the specified setpoint.

For PSCM-22, a foam detection scheme was added to the control algorithm. During foaming incidents, glass temperatures increase throughout the melter and temperatures measured by thermocouples in the cold cap region increase as the foam level rises. The foam detection scheme looks for this increase in temperature in the region of the cold cap. If the glass temperatures at the 43-in. and 41-in. levels exceeded 1050°C and 1100°C, respectively, an alarm would sound and the power set point would be reduced to zero. These temperatures are higher than those measured during idling so that the alarm will not

sound when the cold cap has burned off or when the melter is idling. Foaming was not observed during the melter experiment so the foam detection scheme was not tested.

PSCM-22 was characterized by wild temperature fluctuations that made temperature and power control very difficult. For example, late in the run, glass temperatures dropped 100°C in a 5-min period. On another occasion, power levels greater than 90 kW did not force glass temperatures above 1120°C.

Several changes in the control parameters were made to try to improve the temperature and power control under these difficult conditions. While the changes were not successful in achieving control, additional information was gained regarding the response of the temperature control algorithm. The PID control mode appeared to work well during the initial startup of feeding to the melter. Power levels were adjusted appropriately by the controller to account for the increased load as the feed rate increased and the cold cap grew. Decreasing the effect of the digital filter used to smooth the average glass temperatures over time resulted in a quicker response to the temperature changes. The algorithm was designed to not make any power set point changes as long as the glass temperatures were within an acceptable range ($\pm 10^\circ\text{C}$) around that set point. Nor were power set point changes to be made on a frequency greater than 5 to 10 min (the acceptable temperature deviation and the frequency are selected by the operators). During PSCM-22, the algorithm was operated with no acceptable temperature deviation and at the 1-min scan rate of the computer data acquisition system. In this mode, the power changes were smooth and gradual as compared with the large step changes observed with former control parameters. Additional experience is needed to verify that these changes result in better control of glass temperatures and melter power.

WASTE FORM QUALIFICATION MODELING: CANISTER HEAT TRANSFER

A letter report entitled "Application of TEMPEST Computer Code to Canister Filling Heat Transfer Problems" was completed. This report summarizes the findings on the accuracy and facility of the TEMPEST computer code when applied to the task of computing thermal histories of the glass poured into canisters.

The LFCM is under intense study in this country and abroad as a promising method of processing material for the long-term immobilization of high-level radioactive wastes. The glass produced in an LFCM is subsequently poured into canisters ranging from 12 to 24 in. in diameter and from 4 to 10 ft in height. Among the factors used to determine the suitability of glass as a disposal material are the devitrification and the cracking of the glass in the waste canister. These factors are determined, to a large extent, by the cooling history of the glass. Therefore, a method to model the thermal history of canisters--from the time that filling of the canister begins until the canister has reached thermal equilibrium with the environment--produced by the LFCM process is needed.

Experimental Efforts

Five canisters were instrumented with thermocouples located at appropriate radial and axial locations to gather experimental data to compare to the TEMPEST (Trent et al. 1983) predictions. The variables studied included canister diameter (12, 13, and 24 in.), canister height (45, 56, and 85 in.), internal (0 to 1/2 in.) and external (0 to 3 in.) insulation thicknesses, and the use of both continuous- and batch-filling modes. In addition, one canister was filled within a "turntable simulant" (a group of shells having heat transfer resistances similar to that of an LFCM turntable) to determine the ability of the TEMPEST code to model heat transfer not only within a canister but also within a structure similar to a turntable on a heat transfer basis.

Computer Computations

The two adaptations of the TEMPEST code used in this study were called the batch-fill and the continuous-fill models. The batch-fill adaptation of TEMPEST was used to model the three 12-in. canisters that were filled in three pours of roughly equal size. The continuous-fill adaptation of TEMPEST was used to model the continuously filled 13-in.-dia canister and the batch-filled 24-in. canister. The 33 batch pours used to fill the 24-in. canister were modeled using the continuous-fill adaptation of TEMPEST because of the labor savings of the reduced input.

Comparison of Experimental with Predicted Results

The batch-adaptation of TEMPEST was sufficiently accurate to be useful for many LFCM applications. Temperature predictions near the centerline were accurate to the range of 50 to 125°C over most of the cooldown. However, during periods immediately following a pour, TEMPEST overpredicted temperatures by as much as 250°C. These deviations were caused by a large underprediction of the cooldown immediately following a pour and by another, but less severe, underprediction of the cooldown rate at times greater than 10 h after a pour.

Even though other causes cannot be eliminated at this time, the underprediction of the cooldown immediately following a pour was judged to be caused by two factors:

- an underprediction of the heat loss from the surface of the glass - This heat loss occurs because the batch model calls for the instantaneous placement of the glass from a pour into the canister, eliminating the radiant heat transfer of the constantly changing glass surface during filling.
- a greatly increased radial and axial heat transfer in the glass near the surface far in excess of that predicted by conduction used in the model - This fast heat transfer is either the result of glass mixing and convection or the result of using low values of thermal diffusivity.

The underprediction of the cooldown during later time periods is possibly a result of the canister insulation having a 25% higher conductivity than used by TEMPEST. Further analysis is necessary to confirm this hypothesis.

The continuous-pour adaptation of TEMPEST predicted temperatures more accurately than the batch-pour adaptation. Temperatures near the centerline were within 50°C or better over most of the cooldown. This was also true for temperatures further from the center and for periods far removed from the time the glass surface passed a given position.

The continuous-pour model produced significant deviations in time (late predictions) and temperature (up to 400°C) in the 1 or 2 h after the glass surface covered a thermocouple level. However, the cooldown underprediction of the continuous-pour adaptation was still better than that of the batch-pour adaptation. These deviations are believed to be caused by the fast heat transfer mechanism mentioned above.

The turntable simulant experiments demonstrated that:

- the unsymmetrical temperature field caused by the unsymmetrical turntable geometry can be adequately modeled by TEMPEST
- TEMPEST does an acceptable job of predicting the temperatures within a turntable simulant in spite of the code's limitations in computing simultaneous radiation and convective heat transfer and a considerable uncertainty in predicting the emissivities of stainless steel surfaces.

Recommendations for Future Work

The following recommendations are made:

- The adaptations of TEMPEST used in this study should be documented. Writing an addendum to the User's Manual, arranging proper long-term storage, and doing any necessary cleanup would be included in this documentation. Code development activities should be initiated as soon as funding permits to 1) make TEMPEST capable of concurrently computing radiation and convective heat transfer in a more rigorous manner, which would make the code considerably more accurate, particularly in conducting turntable computations; 2) develop models for TEMPEST that predict the high rates of heat transfer observed in the region just below a newly poured glass surface; and 3) make the code more user-friendly to reduce the time required to prepare input models and to reduce the user's dependency on the TEMPEST code developers.

- Values of thermal diffusivity for the two glasses used in the canisters described in this study should be obtained for temperatures ranging up to 1150°C to determine if inaccurate thermal properties are the cause of the above-mentioned high heat transfer.
- Experimental and modeling activities should be conducted to develop a means for predicting the temperature of the glass stream impacting the glass surface.
- Studies should be conducted to develop methods to accurately predict the emissivity of stainless steel surfaces within an LFCM turntable because these surfaces are a major source of uncertainty, particularly for turntable computations.

WASTE FORM QUALIFICATION MODELING: MELTER MASS BALANCE

The NWTP has outlined a technical approach that calls for development of product and process models as the means for relating product quality to process measurements. The process model is a collection of correlations relating the product characteristics (e.g., composition of the glass) to the process variables (e.g., flow rates, temperatures). The model is provided through testing of the process, where varying product characteristics are correlated with varying process variables, or where acceptable values of product characteristics are translated into limits on process variables. Given the process model, and given that the process variables are quantitatively known, the mean and standard deviation of product characteristics or the probability that the product characteristics are in an acceptable range can be established.

The process model can be divided into a mass balance model and a thermal model of the canister as it fills with glass and cools. The mass balance is mathematically simple but must be validated considering all aspects, from sampling to sample analysis to a mass balance over the melter and off-gas systems. During this quarter, a letter report entitled "Report on Progress on Waste Form Qualification Mass Balance Modeling" was prepared exploring transient mass balance effects for an LFCM.

Transient Mass Balance for the Melter

At steady state, the outlet glass and inlet feed compositions will be the same, based on the nonvolatile species intended to form the glass. During actual operation, various fluctuations in the process can be expected; and, as a result, the glass composition in the melter would be fluctuating continuously about some mean value. If the melter is treated as a well-mixed tank, then the outlet composition for a given species is related to the inlet composition by the following mass balance:

$$M \frac{dC}{dt} = m'(C' - C) \quad (1)$$

where M = the mass of glass in the melter

C = the composition expressed as a mass fraction for the species of interest in the glass in the melter

m' = the mass rate at which glass passes through the melter

C' = the composition expressed as a mass fraction among nonvolatile species for the species of interest in the feed entering the melter.

If the cumulative amount of glass passing through the melter and the inlet composition are known explicitly as functions of time, and if M and m' can be considered constant, then $m = m't$, and the residence time can be defined as $T = M/m'$. Then, the outlet composition is given by:

$$C = e^{-t/T} \int_0^t e^{t'/T} C'(t') \frac{dt'}{T} \quad (2)$$

Damping of Fluctuations in Feed Composition

One likely source of fluctuation in the glass composition is fluctuation in the feed composition because of variations in the waste stream or the addition of glass-forming materials. Equation (2) is useful for exploring the effect that the residence time has on damping fluctuations in the composition as the glass mixes in the melter. Assume that the inlet composition is fluctuating sinusoidally about some mean value:

$$C' = C'' + A \sin (wt) \quad (3)$$

where A = a constant describing the magnitude of the fluctuation
 w = a constant describing its frequency = $2\pi/P$, where P is the period of the assumed cyclic fluctuation.

When this is substituted into Equation (2) and only the composition after long times is considered (the initial departure of C' from C'' is then irrelevant), the result is:

$$C - C'' = \frac{A}{[1 + (wT)^2]} [\sin (wt) - (wT) \cos (wt)] \quad (4)$$

If the square of this difference is averaged over one fluctuation cycle and then the square root is taken, the root mean square (RMS) of the departure of the damped outlet composition from the mean of the inlet composition is obtained. The result is:

$$\text{RMS}[C - C''] = \frac{A}{2^{1/2} [1 + (wT)^2]^{3/2}} \quad (5)$$

Similarly, the RMS of the departure of the inlet composition C' can be calculated. When it is divided into the result given by Equation (5), the ratio of the RMS of the fluctuation in the outlet composition relative to that of the fluctuation in the inlet composition is obtained; the ratio is:

$$\frac{\text{RMS}(C - C'')}{\text{RMS}(C' - C'')} = [1 + (2\pi T/P)^2]^{-3/2} \quad (6)$$

This ratio is evaluated as follows:

<u>P/T</u>	<u>Ratio of Fluctuations</u>
1	0.004
2	0.03
3	0.08
5	0.24
10	0.61

It can be concluded that the period of the fluctuation must be long (e.g., five times the residence time) in order for fluctuations in the inlet (feed) composition to propagate significantly to the outlet glass composition.

Error Caused by Uncertainty in Residence Time

Uncertainty in the feed composition will propagate mostly as an uncertainty in the mean composition, so a transient mass balance over the melter is not pertinent to this problem. However, there will also be an uncertainty in the melter residence time, T , due to measurement uncertainties in both the mass of glass in the melter and the mass flow rate through the melter. If there is a fluctuation of sufficient duration that its effect is important, the uncertainty in the calculated outlet composition due to the uncertainty in the residence time needs to be considered.

The error in predicting the outlet composition can be approximated using a one-term Taylor series if the error in the residence time is assumed to be short. If the period of the fluctuation is long, then the frequency constant w is small, and hence the product wT would be small. Then, the following expression can be approximated:

$$(\text{Error in } C) = -A \frac{w(\text{Error in } T)}{[1 + (wT)^2]^2} [(wt) \sin (wt) + \cos (wt)] \quad (7)$$

If the RMS value of this error is calculated and divided by the RMS value of the fluctuating part of the inlet concentration C' , the ratio is:

$$\frac{\text{RMS}(\text{Error in } C)}{\text{RMS}(C' - C'')} = \frac{w(\text{Error in } T)}{[1 + (wT)^2]^{3/2}} \quad (8)$$

As wT becomes smaller, the ratio becomes proportional to the product of w and the "Error in T ".

The residence time in the PSCM has been determined by a statistical fit of Equation (2) for the case of a step change, rather than a sinusoidal fluctuation, in the inlet composition. Given that the initial glass composition is known explicitly but that the final composition is not assumed to have been reached during the test, then there are two parameters to fit: the concentration difference and the residence time.

A nonlinear least-squares fit was applied to composition data taken during recent "step change" experiments on the PSCM. The results are shown in Table 1.

The calculated residence time is based on the maximum height of glass that can reside in the melter without overflowing. Since batch pouring was used for both of these runs, the mass of glass residing in the melter was kept below the overflow height. The mass may have been down about 10% of the maximum depth at the end of a batch pour. Hence, the residence time calculated based on the maximum possible mass of glass can be estimated to be too large by about 5% to 10% (see "standard error" in Table 1).

For the PSCM-21 run, there is reasonable agreement between the two fitted values of T , but significant disagreement between the fitted and calculated values. This assessment depends on the degree of overestimation of the resident mass. For the PSCM-22 run, there is good agreement between calculated and fitted values based on the barium tracer. For the PSCM-21 run, the calculated

TABLE 1. Least-Squares Fit of Residence Time

<u>PSCM-21 Run</u>	<u>Time, h</u>	<u>Standard Error, h</u>
Fitted based on barium tracer	53.7	± 6.6
Fitted based on cobalt tracer	49.1	± 3.3
Calculated from melter parameters	63.3	-5% to 10% ?
<u>PSCM-22 Run</u>		
Fitted based on barium tracer	48.1	± 6.7
Calculated from melter parameters	46.4	-5% to 10% ?

value was 23% greater than the average of the fitted values; thus, based on pilot-scale operations, an error of 10% to 15% in the calculated residence time during LFCM operations is plausible.

If in Equation (9) the product of the residence time T and the relative error in T is substituted for the absolute error in T , then

$$\frac{\text{RMS}(\text{Error in } C)}{\text{RMS}(C' - C'')} = \frac{wT}{[1 + (wT)^2]^{3/2}} (\text{Relative Error in } T) \quad (9)$$

The quotient term involving wT has a maximum value of 0.3849 at $wT = 0.7071$. If the fluctuations are "fast," their propagation is strongly damped (denominator large); if the fluctuations are slow, their propagation is not greatly affected by the residence time (numerator small). For the PSCM, the relative error in T would be up to 0.15; hence, the RMS error in C would be no larger than about 10% of the RMS of the fluctuating part of C' .

CONCLUSIONS

The following conclusions are based on the work conducted this quarter:

- Temperature is a critical indicator of the glass melting process. A quality product is produced and the melter equipment is in good operating condition at the proper temperature (or within the proper temperature range). Additional information about the operation of the melter including foaming, feeding, cold cap coverage, and glass transfers can be obtained from temperature data. As has been generally recognized, foaming is characterized by a temperature increase at all levels in the glass melt. The identification of this temperature increase amid all the random temperature fluctuations associated with the convection currents in the melter has yet to be resolved. Clustering thermocouples in the region of the cold cap could provide an early indication of the onset of foaming.
- Plenum temperatures indicate the cold cap coverage. Typically, the higher the plenum temperatures and the greater the separation in

temperature from top to bottom of the plenum thermowell, the smaller the cold cap. During overfeeding, the temperature profile apparently inverts with cooler temperatures closer to the cold cap. A quantitative relationship between cold cap coverage and plenum temperatures will be difficult to develop. Off-gas temperatures may provide some information on the melting process, but additional work is needed.

- A melter viewing system consisting of an infrared camera and associated electronics has provided clear pictures of the melter interior and cold cap surface during melter operation. Additional design work is needed to provide adequate cooling to critical components within the melter cavity and to provide pictures of the entire glass surface so that quantitative estimates of cold cap size can be made.
- The pneumatic level detection system functions well for measuring glass specific gravity and level in the melter. Additionally, the bubbler is designed to provide indications of overfeeding, bridging of the cold cap, and foaming. Corrosion is a potential problem with the bubbler as well as with all instrumentation within the molten glass and melter plenum. Additional development and evaluation is needed before the feasibility of the acoustic probe and the time domain reflectometer can be determined. The acoustic probe appears to respond to changes in the glass/cold cap region, but no strong correlations have been established. The TDR has been plagued by problems with the electronics of the system so the evaluation is incomplete.
- The turntable simulant experiments demonstrated that:
 - The unsymmetrical temperature field caused by the unsymmetrical turntable geometry can be adequately modeled by TEMPEST.
 - TEMPEST does an acceptable job of predicting the temperatures within a turntable simulant in spite of the code's limitations in computing simultaneous radiation and convective heat

transfer and a considerable uncertainty in predicting the emissivities of stainless steel surfaces.

- Code development activities should be initiated to make TEMPEST capable of concurrently computing radiation and convective heat transfer in a more rigorous manner, to predict the high rates of heat transfer observed in the region just below a newly poured glass surface, to make the code more user-friendly by reducing the large amount of time required to prepare input models, and to reduce the dependency of the user upon assistance from the TEMPEST code developers.
- The effect of the melter residence time on damping fluctuations in the composition as the glass mixes in the melter has been explored. The period of the fluctuation must be long (e.g., five times the residence time) in order for fluctuations in the inlet (feed) composition to propagate significantly to the outlet glass composition.
- A nonlinear least-squares fit was applied to composition data taken during recent "step change" experiments in the PSCM to estimate the melter residence time for these experiments. For the PSCM-21 run there appeared to be reasonable agreement between the two fitted values of T, but significant disagreement between the fitted and calculated values exists. This assessment depends on the degree of overestimation of the resident mass. For the PSCM-22 run, there is good agreement between calculated and fitted values based on the barium tracer. For the PSCM-21 run, the calculated value was 23% greater than the average of the fitted values. From the pilot-scale operations, an error of 10% to 15% in the calculated residence time during LFCM operations is plausible.

REFERENCES

Trent, D. S., et al. 1983. TEMPEST: A Three Dimensional Time Dependent Computer Program for Hydrothermal Analysis. PNL-4348, Vols. 1 and 2, Pacific Northwest Laboratory, Richland, Washington.

SUPPORTING STUDIES

K. J. Schneider, Compiler

L. R. Bunnell and G. D. Maupin

SUMMARY

As part of the effort to discover and evaluate viable second-generation high-level waste (HLW) forms, glasses with processing temperatures higher than the 1100 to 1200°C used for borosilicate glasses are being examined. Glasses processed at 1400°C have the potential for about an order-of-magnitude decrease in leach rates. Many of these compositions have been selected for evaluation using three separate approaches: one based on high-temperature analogs to known waste glasses; one based on substitution of alkaline earths for boron and some alkali in a known waste glass; and one based on a statistically designed empirical mixture study. To date, the second approach has been the most successful; leaching rates about a factor of eight lower than those of the SRL-165 glass have been obtained for some elements. The third approach has resulted in a factor-of-six lower leaching rates. The first approach was abandoned because leaching rate decreases were minor, indicating that the approach would probably not be as productive as the others.

INTRODUCTION

The objective of these supporting studies is to carry out technical analyses that provide input and guidance for development of vitrification technology. Studies are being performed that support various aspects of nuclear waste vitrification technology development. These studies include generic assessments of vitrified waste performance during subsequent waste management operations, development of requirements/criteria for vitrified waste, assessment of alternative waste forms, and documentation of vitrification technology and plans for specific applications.

TECHNICAL PROGRESS

Progress on one of the approaches being evaluated for second-generation nuclear waste forms is presented below. The purpose of this work is to examine the chemical durability of higher melting temperature waste glass compositions. High-temperature glasses generally exhibit chemical durability superior to low-temperature glasses but are more difficult and costly to process. Recent studies indicate that the liquid-fed ceramic melter (LFCM), which is currently operated at 1100 to 1200°C, could be modified to operate at 1400 to 1500°C (Burkholder, Jarrett, and Minor 1986). The increased cost of building and operating a high-temperature LFCM may be justified by a significant (perhaps an order of magnitude) improvement in the resulting chemical durability of the waste form.

Initial development and testing of glass compositions with viscosities of about 100 poise^(a) at 1400°C and incorporating 25 wt% simulated PW-4b waste have thus far identified glass compositions with chemical durabilities a factor of six to eight better than those of SRL-165 glass (based on 7-day MCC-3 tests). Further optimization of these glasses is expected to exceed the desired factor-of-ten improvement over the current reference glass. However, long-term MCC-3 testing must be done to determine if the advantage is significant in the long term.

Three experimental approaches--an analog study, an empirical mixture study, and a substitution study--were employed simultaneously in order to consider a large and varied number of glass compositions in a short period of time. All of the glasses considered were prepared from oxides, contained 25 wt% simulated PW-4b (see Table 1), and had viscosities near 100 poise at 1400°C. Silicon metal was used as a reductant to eliminate gross alkali-molybdate phase separation. Seven-day leach testing using the MCC-3 method was utilized for a quick indication of long-term chemical durability. The analog study also included 28-day leach tests. Unfortunately, comparison of the 7- and 28-day data suggests that the short-term MCC-3 tests may not always

(a) A viscosity of 100 poise is generally considered fluid enough for good melting behavior.

TABLE 1. Composition of Typical High-Temperature Glasses

Glass Constituents	Composition of Glasses, wt%							
	Reference	Analog		Substitution			Mixture	
	SRL-165	SRL-165	PNL 72-68	Ca	Mg	Mg and Ca	EMS 2	Optimum
SiO ₂	51.0	56.3	48.4	53.1	53.5	53.3	41.4	43.5
Al ₂ O ₃	4.9	5.5		7.1	7.1	7.0	18.6	16.7
B ₂ O ₃	7.1	4.2	5.2				7.5	9.4
Na ₂ O	10.8	6.2	2.0	1.2	1.0	1.0	3.9	3.9
Li ₂ O	5.1	2.9		1.0	1.0	1.0	1.9	1.8
CaO	1.0	0.7	0.8	12.7		6.3	0.7	0.8
MgO	0.8	0.5	0.8	0.3	12.7	6.5	0.5	0.5
ZnO (a)			13.3					
K ₂ O (a)			2.2					
BaO (a)			0.9					
SrO (a)			0.8					
Waste	19.3	23.8	25.7	24.7	24.7	24.9	25.4	23.4

(a) As frit in PNL 72-68.

represent long-term chemical durability trends. Some of the more promising glass compositions from the empirical and substitution studies are being subjected to 28-day MCC-3 tests. The reference glass was the SRL-165 composition that is comparable to current West Valley and Hanford waste glasses in terms of leach-test performance with the MCC-3 method. The reference data were collected in earlier studies under identical test conditions.

The analog study involved modification, via reduction of flux contents, of SRL-165 and PNL 72-68 glasses in order to incorporate 25 wt% PW-4b waste and also to exhibit a viscosity of 100 poise at 1400°C. The compositions are presented in Table 1, and MCC-3 leaching performances for these compositions are shown in Figure 1. By scanning the bar graphs in Figure 1 and paying particular attention to boron as a good indicator of leaching behavior, it can be seen that the durability of the SRL analog is generally about a factor of two better than SRL-165 and that the PNL 72-68 analog is generally less durable than the SRL-165 glass. In most cases, the amount of leaching changes little from 7 to 28 days; but the 72-68 analog is an exception, leaching at what appears to be a linear rate with time. In summary, the analog approach seems unlikely to produce the targeted order-of-magnitude increase in durability.

FIGURE 1. Results from MCC-3 Leach Testing for SRL-165 Glass and Two Analogs

The substitution study basically involved trading alkaline earths for boron and some magnesium in SRL-165. The more promising compositions resulting from this study are shown in Table 1. Figure 2 indicates that the best durability was obtained in the case where calcium was substituted, followed closely by a composition that substituted equal amounts of calcium and magnesium. For elements such as molybdenum (another prime indicator of glass leaching performance used because not all compositions contain boron), a factor-of-eight improvement can be seen in Figure 2. For unknown reasons, the alkaline earth substitution produced a higher strontium leach rate than the SRL-165 glass. Currently, another empirical study including calcia, magnesia, and alumina substitution is being designed to take advantage of the leach rate improvements to date and to decrease the time required to find the optimum composition.

The empirical mixture study encompassed conventional alkali/borosilicate compositions but also considered some extreme compositions. The experiment was

FIGURE 2. Results from 7-day MCC-3 Leach Tests for Glasses in the Substitution Study

statistically designed by varying the molar ratios of the flux components alkali, boron, and alumina. The overall ternary and hexagonal compositional field is shown in Figure 3. All glass compositions contained nominally 25 wt% (alkali, boron, and alumina). The overall ternary and hexagonal compositional PW-4b calcine and 1 wt% alkaline earth (Table 2). The flux and silica concentrations were adjusted to obtain 100 poise viscosity at 1400°C. Data obtained from 7-day MCC-3 testing were used to construct empirical models representing elemental release as a function of flux composition.

The silicon release model is illustrated in Figure 4. Clearly, MCC-3 leaching performance is improved when the amount of alkali is minimized. The ideal alumina concentration appears to be 36 mol% regardless of whether diluted with alkali or boron. From this model, the predicted optimum flux composition

TABLE 2. Compositions of Waste Glasses Used in the Statistically Designed Empirical Mixture Study

Components	EMS 1		EMS 2		EMS 3		EMS 4		EMS 5	
	wt% of Total Glass	mol% of Flux	wt% of Total Glass	mol% of Flux	wt% of Total Glass	mol% of Flux	wt% of Total Glass	mol% of Flux	wt% of Total Glass	mol% of Flux
Na ₂ O	3.7	15.6	3.9	15.1	7.2	25.3	6.1	34.6	5.2	34.2
Li ₂ O	1.8	15.8	1.9	15.3	3.5	25.5	3.0	35.3	2.6	35.5
B ₂ O ₃	12.0	45.2	7.5	25.9	1.8	5.6	1.2	6.1	4.2	24.6
Al ₂ O ₃	9.1	23.4	18.6	43.7	20.4	43.6	7.0	24.1	1.4	5.6
SiO ₂	46.8		41.4		42.5		56.6		60.3	
Other (a)	26.7		26.6		24.6		26.1		26.2	

Components	EMS 6		EMS 7		EMS 8		EMS 9		Optimum	
	wt% of Total Glass	mol% of Flux	wt% of Total Glass	mol% of Flux	wt% of Total Glass	mol% of Flux	wt% of Total Glass	mol% of Flux	wt% of Total Glass	mol% of Flux
Na ₂ O	3.9	24.7	5.1	25.6	4.8	24.6	4.7	22.8	3.9	14.9
Li ₂ O	1.9	24.9	2.4	25.0	2.3	24.5	2.9	29.4	1.8	14.3
B ₂ O ₃	8.0	45.0	5.6	25.0	5.8	26.0	5.6	24.0	9.4	32.0
Al ₂ O ₃	1.4	5.4	8.0	24.4	8.1	24.9	8.1	23.8	16.7	38.8
SiO ₂	58.5		52.1		52.0		52.2		43.5	
Other (a)	26.4		26.9		27.0		26.4		24.7	

(a) Other is nominally 25% Pw-4b waste simulant, 0.5% CaO, and 0.5% MgO.

FIGURE 3. Ternary Diagram Showing Glass Composition (low silicon release rates between Compositions 1 and 2 prompted additional work shown by dotted line)

FIGURE 4. Silicon Release Rates Predicted by Computer Modeling for Mixture Study Compositions (see Figure 3)

is 30% alkali, 34% boron, and 36% aluminum and lies on the extreme edge of the hexagonal compositional field. To verify the model, a similar glass called "optimum glass" (actual composition varied somewhat from target; see Table 2) was prepared and evaluated in 7- and 28-day MCC-3 leach tests. As seen in Figure 5, the empirical models representing 7-day elemental release of Si, B, Mo, and Li appear to be useful (accurate to within 20%). Considering the boron release, the optimum glass exhibits about a factor of six improvement in chemical durability compared with SRL-165. This success has prompted expansion of the original compositional field (see dotted region in Figure 3); further gains in durability are expected next quarter.

FIGURE 5. Measured and Predicted Elemental Release for the "Optimum Glass" for Best Glasses in the Mixture Study

CONCLUSIONS

Development of glass compositions incorporating PW-4b, having viscosities of 100 poise at 1400°C, and producing MCC-3 7-day chemical durabilities a factor of 10 better than SRL-165 appears to be achievable. However, these glasses are unlikely to be similar to conventional well-understood alkali/borosilicates. The long-term chemical durability, electrical conductivity, and devitrification/phase separation behavior of these new compositions will all require evaluation.

REFERENCES

Burkholder, H. C., J. H. Jarrett, and J. E. Minor, compilers. 1986. LFCM Vitrification Technology Quarterly Progress Report, April to June 1985. PNL-5470-3, Pacific Northwest Laboratory, Richland, Washington.

APPENDIX

ACRONYMS AND ABBREVIATIONS

APPENDIX

ACRONYMS AND ABBREVIATIONS

Å - angstrom
ADS - air displacement slurry (pump)
Ag - silver
Al - aluminum
Am - americium
atm - atmosphere
B - boron
Ba - barium
Be - beryllium
C - carbon
°C - degree Celsius
Ca - calcium
Cd - cadmium
Ce - cerium
Cl - chlorine
Ci - curie
cm - centimeter
Co - cobalt
cP - centipoise
Cr - chromium
CRW - cladding removal waste
Cs - cesium
CTS - component test stand
Cu - copper
DF - decontamination factor
dia - diameter
DOE - U.S. Department of Energy
DOE-DP - DOE-Defense Programs
DOE-NE - DOE-Nuclear Energy
DWPF - Defense Waste Processing Facility
Dy - dysprosium
E1150 - electrical conductivity at 1150°C
ECM - experimental-scale ceramic melter
EDX - energy-dispersive x-ray
Eu - europium
EVS - ejector venturi scrubber
F - fluorine
Fe - iron
FRG - Federal Republic of Germany
ft - feet
FY - fiscal year
g - gram
gal - gallon

Gd - gadolinium
 h - hour
 H - hydrogen
 HBCM - high-bay ceramic melter
 HEME - high-efficiency mist eliminator
 HEPA - high-efficiency particulate air (filter)
 HLW - high-level waste
 hp - horsepower
 HWVP - Hanford Waste Vittrification Program
 IAEA - International Atomic Energy Agency, Vienna, Austria
 ICP/AES - inductively coupled plasma/atomic emission spectroscopy
 in. - inches
 K - degrees Kelvin
 K - potassium
 KEH - Kaiser Engineers Hanford Company, Richland, Washington
 kg - kilogram
 km - kilometer
 kW - kilowatt
 L - liter
 La - lanthanum
 lb - pound
 LFCM - liquid-fed ceramic melter
 Li - lithium
 LLW - low-level waste
 m - meter
 M - molar
 MCC - Materials Characterization Center, PNL
 MEVS - Mobile Encapsulation and Volume Reduction System
 mg - milligram
 Mg - magnesium
 min - minute
 mL - milliliter
 mm - millimeter
 Mn - manganese
 Mo - molybdenum
 MTU - metric ton uranium
 N - nitrogen
 Na - sodium
 Nb - niobium
 NCAW - neutralized current acid waste
 Nd - neodymium
 Ni - nickel
 Np - neptunium
 NRC - U.S. Nuclear Regulatory Commission
 NWTP - Nuclear Waste Treatment Program
 O - oxygen
 P - phosphorus
 P - poise
 Pa - Pascal
 Pb - lead
 Pd - palladium

DISTRIBUTION

No. of
Copies

No. of
Copies

OFFSITE

30 DOE Technical Information Center

5 Geologic Repository Division
DOE Office of Civilian
Radioactive Waste Management
Forrestal Building
Washington, DC 20585
ATTN: J. W. Bennett, RW-20
C. R. Cooley, RW-4
M. W. Frei
B. C. Rusche, RW-1
R. Stein, RW-23

3 DOE Office of Defense Waste &
Byproducts Management
GTN
Washington, DC 20545
ATTN: R. K. Heusser
J. E. Lytle, DP-12
R. D. Walton, Jr., DP-123

7 DOE Office of Terminal Waste
Disposal & Remedial Action
GTN
Washington, DC 20545
ATTN: J. E. Baublitz, NE-24
J. A. Coleman, NE-25
D. J. McGoff, NE-23
T. W. McIntosh, NE-25
W. R. Voigt, NE-20
H. F. Walter, NE-25
J. B. Zorn, NE-25

M. J. Bell
Division of Nuclear Materials
Safety & Safeguards
Mail Station 881-SS
Nuclear Regulatory Commission
Washington, DC 20555

A. T. Clark
Division of Fuel Material Safety
Nuclear Regulatory Commission
Washington, DC 20555

W. J. Dircks
Office of the Executive
Director for Operations
Mail Station 6209
Nuclear Regulatory Commission
Washington, DC 20555

2 Environmental Protection Agency
Office of Radiation Programs
401 M Street, S.W.
Washington, DC 20460
ATTN: D. Egan
G. L. Sjoblom

3 DOE Albuquerque Operations
Office
P.O. Box 5400
Albuquerque, NM 87185
ATTN: K. A. Carlson
M. H. McFadden
J. McGough

P. G. Hagan
Joint Integration Office
Bldg. 3, 2nd Floor
2201 San Pedro N.E.
Albuquerque, NM 87110

E. Maestas
DOE West Valley Operations
Office
P.O. Box 191
West Valley, NY 14171

No. of
Copies

- 3 DOE Idaho Operations Office
550 Second Street
Idaho Falls, ID 83401
ATTN: M. J. Barainca
J. D. Hamric
J. B. Whitsett
- F. T. Fong
DOE San Francisco Operations
1333 Broadway
San Francisco, CA 94612
- M. R. Jugan
DOE Oak Ridge Operations Office
P.O. Box E
Oak Ridge, TN 37830
- S. A. Mann
DOE Chicago Operations Office
9800 South Cass Avenue
Argonne, IL 60439
- J. O. Neff
DOE National Waste Program
Office
505 King Avenue
Columbus, OH 43201
- W. J. Brumley
DOE Savannah River Operations
Office
P.O. Box A
Aiken, SC 29801
- D. L. Vieth
DOE Nevada Operations Office
P.O. Box 14100
Las Vegas, NV 89114
- 2 Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439
ATTN: M. J. Steindler
L. E. Trevorrow

No. of
Copies

- C. S. Abrams
Argonne National Laboratory
P.O. Box 2528
Idaho Falls, ID 83401
- 2 Battelle Memorial Institute
Office of Crystalline Repository
Development
9800 South Cass Avenue
Argonne, IL 60439
ATTN: W. J. Madia
B. D. Shipp
- 3 Battelle Memorial Institute
Project Management Division
505 King Avenue
Columbus, OH 43201
ATTN: W. A. Carbeiner/
S. H. Basham
J. F. Kircher
B. Rawles
- F. Holzer
Lawrence Livermore National
Laboratory
University of California
P.O. Box 808
Livermore, CA 94550
- D. T. Oakley, MS 671
Los Alamos Scientific Laboratory
P.O. Box 1663
Los Alamos, NM 87544
- 5 Oak Ridge National Laboratory
P.O. Box Y
Oak Ridge, TN 37830
ATTN: J. O. Blomeke
W. D. Burch
R. T. Jubin
L. J. Mezga
T. H. Row

No. of
Copies

- 5 Sandia Laboratories
P.O. Box 5800
Albuquerque, NM 87185
ATTN: D. R. Anderson
J. F. Ney
R. W. Lynch
W. Weart
Technical Library
- J. R. Berreth
Westinghouse Idaho Nuclear
Co., Inc.
P.O. Box 4000
Idaho Falls, ID 83401
- 6 E. I. du Pont de Nemours
Company
Savannah River Laboratory
Aiken, SC 29801
ATTN: M. D. Boersma
J. G. Glasscock
E. J. Hennelly
J. R. Knight
M. J. Plodinec
C. T. Randall
- E. A. Jennrich
EG&G Idaho
P.O. Box 1625
Idaho Falls, ID 83415
- V. Ricks
EG&G
P.O. Box 1680
Idaho Falls, ID 83415
- G. W. Meyers
Atomics International Division
Rockwell International
8900 DeSoto Avenue
Canoga Park, CA 91304

No. of
Copies

- T. H. Pigford
Department of Nuclear
Engineering
University of California
Berkeley, CA 94720
- M. E. Spaeth
Science Applications, Inc.
2769 South Highland
Las Vegas, NV 89109
- J. F. Strahl
Weston
2301 Research Boulevard
Third Floor
Rockville, MD 20850
- R. Williams
Electric Power Research
Institute
3412 Hillview Avenue
P.O. Box 10412
Palo Alto, CA 94304
- 5 West Valley Nuclear Services
Company
P.O. Box 191
West Valley, NY 14171
ATTN: C. C. Chapman
J. C. Cwynar
J. L. Knabenschuh
J. E. Krauss
J. M. Pope
- J. W. Bartlett
The Analytic Sciences
Corporation
6 Jacob Way
Reading, MA 01867
- W. A. Freeby/J. L. Jardine
Bechtel National, Inc.
P.O. Box 3965
San Francisco, CA 94119

No. of
Copies

Librarian
Westinghouse Electric
Corporation
Technical Library
P.O. Box 2078
Carlsbad, NM 88220

L. L. Hensch
Department of Materials Science
& Engineering
University of Florida
Gainesville, FL 32611

J. L. Larocca, Chairman
Energy Research & Development
Authority
Empire State Plaza
Albany, NY 12223

R. G. Post
College of Engineering
University of Arizona
Tucson, AZ 85721

ONSITE

12 DOE Richland Operations Office

J. H. Anttonen
E. A. Bracken
G. J. Bracken
C. R. DeLannoy
R. D. Izatt
N. T. Karagianes
M. J. Plahuta
J. L. Rhoades
M. W. Shupe
J. J. Sutey
J. D. White
J.K.W. Wukelik

10 Rockwell Hanford Operations

R. N. Gurley
H. E. McGuire
J. W. Patterson
R. D. Prosser
I. E. Reep

No. of
Copies

R. J. Thompson
T. B. Venziano
D. D. Wodrich
R. D. Wojtasek
File Copy

UNC United Nuclear Industries

T. E. Dabrowski/W. J. Kyriazis

2 Westinghouse Hanford Company

R. E. Lerch
J. D. Watrous

66 Pacific Northwest Laboratory

R. P. Allen
S. O. Bates
H. T. Blair
W. F. Bonner
D. J. Bradley
L. A. Bray
R. A. Brouns
G. H. Bryan
H. C. Burkholder (10)
J. R. Carrell
D. B. Cearlock
R. D. Dierks
S. K. Edler
L. J. Ethridge
D. W. Faletti
R. K. Farnsworth
S. T. Treim
D. S. Goldman
R. W. Goles
H. A. Haerer
M. S. Hanson
L. K. Holton
J. H. Jarrett
S. S. Koegler
D. E. Knowlton
M. R. Kreiter
W. L. Kuhn
W. W. Laity
L. T. Lakey/K. M. Harmon
J. M. Latkovich
J. L. McElroy

Pm - promethium
 PNL - Pacific Northwest Laboratory, Richland, Washington
 Pr - praseodymium
 PSCM - pilot-scale ceramic melter
 psig - pounds per square inch gauge
 Pu - plutonium
 Ra - radium
 Rb - rubidium
 RE - rare earth
 Re - rhenium
 Rh - rhodium
 RHO - Rockwell Hanford Operations, Richland, Washington
 RLFCM - radioactive liquid-fed ceramic melter
 rpm - revolutions per minute
 Ru - ruthenium
 s - second
 S - sulfur
 SA/V - surface area/volume ratio
 Se - selenium
 SEM - scanning electron microscope
 Sn - tin
 Si - silicon
 Sm - samarium
 SME - slurry mix evaporator
 Sr - strontium
 SRL - Savannah River Laboratory, Aiken, South Carolina
 T100P - temperature at which the glass has a 100-poise viscosity
 Ta - tantalum
 Tc - technetium
 Te - tellurium
 TDR - time domain reflectometer
 Th - thorium
 Ti - titanium
 TOC - total organic carbon
 TO/L - total oxides/liter
 TRUW - transuranic waste
 U - uranium
 W - watt
 WAC - Waste Acceptance Committee
 WO/L - waste oxides/liter
 wt% - weight percent
 WVDP - West Valley Demonstration Project
 WVNS - West Valley Nuclear Services
 Y - yttrium
 yr - year
 Zn - zinc
 Zr - zirconium

No. of
Copies

No. of
Copies

• G. L. McVay
J. E. Mendel/M. D. Merz
G. B. Mellinger
J. E. Minor
D. R. Montgomery
L. G. Morgan
T. R. Myers
J. M. Perez, Jr.
R. D. Peters
M. E. Peterson
A. M. Platt/R. E. Nightingale

J.T.A. Roberts
J. V. Robinson
W. A. Ross
P. A. Scott
K. J. Schneider
G. J. Seigny
D. H. Siemens
J. H. Westsik, Jr.
B. M. Wise
Publishing Coordination (2)
Technical Information (5)