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LFCM Vitrification Technology

**Quarterly Progress Report
January-March 1985**

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

December 1985

**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
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LFCM VITRIFICATION TECHNOLOGY

PNL--5470-2

QUARTERLY PROGRESS REPORT

DE86 005796

January-March 1985

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

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MASTER

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ABSTRACT

This report is the second in a series of quarterly reports compiled by the Nuclear Waste Treatment Program at Pacific Northwest Laboratory (PNL) to document progress on liquid-fed ceramic melter (LFCM) vitrification technology. Progress in the following technical subject areas from January 1 through March 31, 1985, is discussed: pretreatment systems, melting process chemistry and glass development, feed preparation and transfer systems, melter systems, canister filling and handling systems, off-gas systems, and process/product modeling and control. For the first time, LFCM vitrification-related work funded through the Hanford Waste Vitrification Program is also included in this document. Thus, all PNL LFCM vitrification work is now included within the scope of this document.

SUMMARY

This technical quarterly 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 second quarter of FY 1985 are summarized below:

Pretreatment Systems - A reference supernatant treatment process was developed for West Valley Tank 8D-2 high-level waste (HLW). The alkaline supernatant will be treated with IONSIV IE-96 ion exchanger to recover the cesium. A pilot-scale ion-exchange column was used to determine the hydraulic properties of IE-96. The sludge in Tank 8D-2 was simulated, and investigations were completed to prepare formated and nitrated feeds for vitrification.

Melting Process Chemistry and Glass Development - Efforts to develop a glass composition for West Valley waste included testing West Valley and Savannah River Laboratory (SRL) glasses under MCC-1 and MCC-3 conditions. Based on these tests, a new glass composition (WV205) was developed that appears to be an excellent compromise between durability and processability. Twenty-four laboratory batches of melter feeds were prepared from the simulated HWVP reference feed to evaluate the effects of formic acid addition, sugar addition, type of glass-forming chemicals used, and final melter feed concentration on the rheological properties and melting characteristics of the slurries.

Feed Preparation and Transfer Systems - Long-term testing of the air displacement slurry (ADS) pump was completed after 3696 h of operation. The pump was disassembled, and the critical parts were inspected for wear and corrosion. The measured wear was not significant enough to affect pump operation, and the pump life is projected to be well beyond 4000 h.

Melter Systems - Operation of the radioactive liquid-fed ceramic melter (RLFCM) was limited to mostly idling during this quarter. The process control recovery from a reboil-type foaming incident was successfully executed by the automatic resistive feedback electrode voltage control system. Nonradioactive melter test analyses were completed for experimental- and pilot-scale melter experiments. Experimental-scale ceramic melter (ECM) testing verified the

processability of a simulated melter feed containing high concentrations of cesium and strontium. Data from an FY 1984 pilot-scale ceramic melter (PSCM) test on the processability of a candidate West Valley melter feed composition was evaluated.

Canister Filling and Handling Systems - Canister filling and handling systems have been developed for both the West Valley Demonstration Project (WVDP) and the radioactive liquid-fed ceramic melter (RLFCM) operation. These systems have been fabricated, tested, and placed in service.

Off-Gas Systems - ECM testing of the Federal Republic of Germany (FRG) feed formulation was conducted. No significant melter feed processing problems were noted.

Process/Product Modeling and Control - Initial work on process control algorithms included examination of the extensive PSCM data to determine if and how existing process instrumentation can be correlated with observed phenomena in the melter, including cold cap coverage and foaming. Discriminant analysis, a statistical technique that may be used when observations are to be classified into two or more groups, has been applied. The first phase of a major computer modeling effort on canister temperatures was completed; the radioactive FRG glass cooling history in a B-Cell environment was simulated using the TEMPEST computer code. Nonradioactive canisters of FRG glass were filled during PSCM runs to test the product quality, particularly with respect to cracking.

CONTENTS

ABSTRACT	iii
SUMMARY	v
INTRODUCTION	1
PRETREATMENT SYSTEMS	5
MELTING PROCESS CHEMISTRY AND GLASS DEVELOPMENT	21
FEED PREPARATION AND TRANSFER SYSTEMS	45
MELTER SYSTEMS	53
CANISTER FILLING AND HANDLING SYSTEMS	69
OFF-GAS SYSTEMS	79
PROCESS/PRODUCT MODELING AND CONTROL	81
APPENDIX - ACRONYMS AND ABBREVIATIONS	A.1

FIGURES

PRETREATMENT SYSTEMS

1	Cold Cap Burnoff Times for Formated and Nitrated Feeds	15

MELTING PROCESS CHEMISTRY AND GLASS DEVELOPMENT

1	Laboratory and ECM Melting Rate Comparison	28
2	Effect of Fluxes on Melting Nitrated and Reduced Feeds with Zeolite	29
3	Initial Simulated HWVP Reference Feed Viscosity as a Function of Formic Acid Additions	34

FEED PREPARATION AND TRANSFER SYSTEMS

1	Prototype Air Displacement Slurry Pump	47
2	ADS Pump Two-Way Valve After Testing	49
3	ADS Pump Lower Valve Seating Surface After Testing	49
4	ADS Pump Rocker Arm After Testing	50
5	Pivot Pins from ADS Pump After Testing	51

MELTER SYSTEMS

1	Melter Tank Time Distribution Curves for Li Oxide Concentration	67
2	Melter Tank Time Distribution Curves for Ba Oxide Concentration	67

CANISTER FILLING AND HANDLING SYSTEMS

1	Level 1 System Response to Two Consecutive Melter Glass Transfers	71
2	Counting Rate Reproducibility for Levels 1 through 4	72
3	Counting Rate Reproducibility for Levels 5 through 8	73
4	Counting Rate Reproducibility for Levels 9 through 11	74

5	Source Positional Counting Rate Data for Levels 1 through 6	75
6	Source Positional Counting Rate for Levels 7 through 11	76

PROCESS/PRODUCT MODELING AND CONTROL

1	Insulation Thickness Versus Radial Temperature Difference for Middle First Batch of PSCM Glass ($\phi W/L$)	89
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TABLES

PRETREATMENT SYSTEMS

1	West Valley Alkaline Sludge and Supernatant Composition	11
2	Acidification of West Valley Sludge Used to Prepare 1 L of West Valley Vitrification Feed	12
3	Addition of Glass-Forming Chemicals to West Valley Sludge or HNO ₃ -Treated Sludge to Prepare 1 L of WV183 Vitrification Feed	13
4	Rheological Data for Vitrification Feeds Prepared Using Nitrated Sludge Versus WV183	13
5	West Valley Sludge Used to Prepare 1 L of Formated Vitrification Feed	16
6	Rheological Data for Vitrification Feeds Prepared Using Formated Sludge Versus WV183	17

MELTING PROCESS CHEMISTRY AND GLASS DEVELOPMENT

1	Target Compositions of West Valley and SRL Glasses	24
2	MCC-1 Test Data for West Valley and Savannah River Glasses	25
3	MCC-3 Test Data for West Valley and Savannah River Glasses	26
4	Partial Glass Compositions	27
5	Composition of HWVP Reference Feed Simulations Used in Laboratory Screening Tests	32
6	Summary of Rheology, Melting Rate, and Melt Chemistry Properties of Melter Feed Batches Prepared with HWVP Reference Waste Simulations	36
7	Chemical Compounds Used to Make Up Various Types of Glass Formers for the HWVP Reference Feed Treatment Screening Tests	38
8	Non-Newtonian Flow Models	40
9	Calculated Parameters for Yield-Pseudoplastic Model of HWVP Melter Feeds	41
10	Effects of Rheological Model Identification on Predicted Values of Yield Stress	42

11	Effects of Rheological Model Identification on Calculated Values of Apparent Viscosity	43
----	--	----

FEED PREPARATION AND TRANSFER SYSTEMS

1	Weight and Dimensional Changes in ADS Pump Components Following 3696 h of Use in Simulated Melter Feed	48
---	--	----

MELTER SYSTEMS

1	Flush Glass Oxide Composition	56
2	Concentrated Slurry Composition	57
3	Nonzeolite Slurry Composition	58
4	Zeolite Slurry Composition	59
5	Operating Summary of ECM-85-4 and ECM-85-5	60
6	Boron and Cesium Decontamination Factors	60
7	Feed Analytical Results	61
8	Glass Analytical Results	61
9	Simulated West Valley Melter Feed Composition	63

OFF-GAS SYSTEMS

1	Boron and Cesium Decontamination Factors	80
---	--	----

PROCESS/PRODUCT MODELING AND CONTROL

1	Comparison of Calculated Radial Temperature Differences in FRG Glasses Between the Onset of Hardening and Steady State at Various Glass Levels	87
2	Radial Temperature Differences for Various Insulation Thicknesses of Nonradioactive Glass, Cooling Through the Hardening Zone	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 (DOE-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.

- 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 the various user groups: 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.

Beginning with this quarterly report, the results of applicable technical work performed by PNL in direct support of the HWVP is included. 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 reported in this quarterly report series to complement NWTP-supported activities. The PNL 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; lead authors are identified:

- Pretreatment Systems - L. A. Bray
- Melting Process Chemistry and Glass Development - D. S. Goldman and L. A. Chick

- Feed Preparation and Transfer Systems - H. T. Blair
- Melter Systems - R. D. Dierks and J. M. Perez, Jr.
- Canister Filling and Handling Systems - D. H. Siemens
- Off-Gas Systems - R. W. Goles
- Process/Product Modeling and Control - W. L. Kuhn.

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.

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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.

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PRETREATMENT SYSTEMS

L. A. Bray, D. S. Goldman, and B. M. Wise

SUMMARY

A reference supernatant treatment process has been developed for West Valley Tank 8D-2 high-level waste (HLW). The alkaline supernatant will be treated with IONSIV IE-96^(a) ion exchanger to recover the cesium. A pilot-scale ion-exchange column was used to determine the hydraulic properties of IE-96. The sludge in Tank 8D-2 was simulated, and investigations were completed to prepare formated and nitrated feeds for vitrification.

INTRODUCTION

Pacific Northwest Laboratory (PNL) has the responsibility to aid West Valley Nuclear Services (WVNS) in the selection and design of the West Valley Demonstration Project (WVDP) supernatant treatment system. In FY 1983, several processes were evaluated by PNL (Bray et al. 1982). In FY 1984, a reference supernatant process (inorganic zeolite ion exchange) was chosen by West Valley. The process is designed to treat the alkaline supernatant (pH 10) stored in the West Valley HLW storage Tank 8D-2. The process is designed to recover the cesium activity, thus converting the alkaline sodium waste liquid (6 to 7 M) to a radioactive low-level waste (LLW) for onsite disposal. The HLW solids remaining in Tank 8D-2 along with the cesium-loaded zeolite and a small volume of Thorex acid waste will then be mixed and used as melter feed for vitrification.

The selected pretreatment option for Tank 8D-2 alkaline supernatant consists of an ion-exchange system using a series of columns, providing a cesium decontamination factor (DF) of 10^3 to 10^4 . If 100% of the zeolite is utilized, about 80,000 kg of zeolite will be required to treat 2×10^6 L of waste.

(a) Registered trademark of Union Carbide Corporation, Tarrytown, New York.

The sludge phase remaining in Tank 8D-2 after removal of the alkaline supernatant will be blended with a small volume of Thorex acid waste from Tank 8D-4 and the cesium-loaded zeolite for vitrification. Additional nitric acid or formic acid may be required prior to vitrification to aid in rheological and redox behavior.

TECHNICAL PROGRESS

A number of investigations were conducted this quarter in support of the West Valley reference pretreatment system. These investigations included:

- testing a pilot-scale ion-exchange column
- simulating nitrated and formated feeds for the West Valley vitrification system.

ENGINEERING-SCALE ION-EXCHANGE COLUMN TESTS

The current reference process for decontaminating Tank 8D-2 supernatant involves ion-exchange columns that will be installed in process tanks at West Valley. The purpose of the engineering-scale ion-exchange column study was to obtain the data needed to complete the final design of the West Valley supernatant treatment system and to verify the proposed column design. This general objective was divided into the following components:

- determine the bed utilization efficiency of the test column - This information was needed to complete material balances for the front-end system and to predict system performance. A resin that changed colors was used in a series of column loadings to determine the shape of the interface between loaded and unloaded exchanger, thus giving column efficiency and suggesting column design changes that would improve efficiency.
- determine the hydraulic properties of the zeolite in the column - Test data will be used to determine necessary flow rates and pressures and to size pumps for the actual system. Upflow bed expansion and downflow pressure drop versus flow rate were investigated.

- evaluate the zeolite changeout efficiency for the column - The proposed design for the columns at West Valley includes a sluice outlet on the bottom of the column. This configuration was tested to determine a workable sluicing procedure and to determine the actual changeout efficiency and potential operating difficulties.
- determine the behavior of zeolite fines - Zeolite fines may be generated during the transfer of zeolite to the ion-exchange columns at West Valley. A test was performed to determine if fines would cause operating difficulties in the test system. A downflow pressure drop test was included to simulate the column loading procedure.
- identify potential operating difficulties with the test system - This objective was met by observing the tests and noting any difficulties.
- recommend system design changes to improve system performance - These recommendations were based on the problems identified during the tests.

The test column installation, calibration, and initial shakedown were completed last quarter. The column is similar in design to the column proposed by West Valley, but it is smaller (diameter of 2 ft versus 3 ft; cylindrical section height of 10 ft versus 10.5 ft). The cylindrical section of the column is fabricated from Plexiglas^(a) so that the exchange bed can be observed. The top and bottom of the column are fabricated from ASME dished heads. The vessel distribution/collector system consists of a series of Johnson screens^(b) with internal piping for the backwash distributor/service collector and inlet distributor and Johnson screens without internal piping for the backwash collector.

The significant findings of this work include:

- As tested, the column bed utilization is greater than 90% at 50% breakthrough. Unutilized volume included all the exchanger under the service collector and some of the exchanger above the distributor.

(a) Registered trademark of Rohm and Haas Company, Philadelphia, Pennsylvania.
 (b) Manufactured by Johnson Division-UPO, Inc., St. Paul, Minnesota.

The unutilized volume above the distributor could be attributed to column wall effects and distributor inefficiencies.

- Downflow pressure drop tests showed that at flow rates of interest the bed pressure drop was negligible. It was not possible to determine the pressure drop accurately with the test system due to the small pressure differences. Previous work has indicated that the pressure drop will be in the range of 2 to 10 in. H₂O/ft bed during column loading.
- When added at 6 wt%, zeolite fines increased the downflow bed pressure drop beyond the 5 psi allowable in the test system due to structural constraints. Backwashing the bed, however, lowered the pressure drop to allowable levels.
- It was possible to sluice all but a very small amount of zeolite (several grams) from the column. The following procedure worked quite well. The bed was backwashed to expand it and then the bottom valve was opened. The backwash water was left on during sluicing. After the bulk of the zeolite and water were removed from the column, water spray from the backwash distributor was used to rinse out the remaining zeolite.

REVIEW OF NITRATED AND FORMATED FEEDS

During the vitrification stage of the WVDP, WVNS will remove the Purex sludge from Tank 8D-2, blend it with Thorex waste from Tank 8D-4 and the zeolite generated by decontaminating the Tank 8D-2 supernatant, add glass-forming chemicals and acid, and then vitrify the resulting feed in a ceramic melter. In the current reference process, the melter feed is a nitrated slurry, obtained by blending the hydroxide Purex sludge, acidic Thorex waste, and other melter feed components with excess nitric acid. This process is not the only option, however; and several alternatives were the subject of the work described below:

- determine the optimum process conditions for making nitrated melter feeds - This work involved preparing simulated Purex (Tank 8D-2) sludge and simulated Thorex (Tank 8D-4) acid wastes, digesting them in acid, and preparing melter feeds from them. The optimum nitric acid addition was determined by comparing the rheological properties of the digested wastes and the resultant melter feed. The properties investigated included viscosity and percent settled solids. Observations were made of the feed-making process, including the concentration step.
- determine the optimum process conditions for making formatted melter feeds - This work was performed in the same manner as the nitric work. Formic acid was chosen due to the extensive experience at Savannah River Laboratory (SRL) and PNL with the formic acid flowsheet.
- verify the rheology of melter feeds made directly - Nitrated feeds for PNL melter runs are made with nitrate chemicals instead of nitrating the metal hydroxides found in the West Valley wastes. Comparisons were made between the rheology of the feeds prepared for this study and feeds prepared for current PNL melter experiments to determine if the simulated melter feeds are representative. Laboratory crucible melt tests were also performed to compare the melting behavior of the feeds.
- determine the flowsheet impacts of formatted versus nitrated melter feeds - Mass balances for nitrated and formatted flowsheets were completed. Expected quantities of nitrates, carbon, and water were compared in the balances. Results of the laboratory melting studies on formatted and nitrated feeds were used to determine possible impacts on melter performance.

Nitrated Feeds

Simulated wastes are currently prepared for vitrification studies at PNL by combining metal nitrates, phosphates, and oxides. In the case of West Valley, ground zeolite, glass-forming chemicals, and sucrose are then blended

into the waste mixture to form the vitrification feed. Laboratory rheology, pumping, and redox control studies have each relied on this form of preparation.

To verify this feed approach, simulated West Valley Purex acid waste was prepared based on analysis of the West Valley Tank 8D-2 contents (Table 1). To prepare Tank 8D-2 sludge, the acid waste was adjusted with NaOH, Na_2CO_3 , and NaNO_2 and digested for 100 h at 95°C (to simulate years of in-tank heating and digestion). The resulting solids were separated by centrifugation and then washed with water. The sludge was washed four times (24 h each time) using 180 mL of H_2O /cycle/initial liter of sludge plus supernatant. The water wash step may be used at West Valley to lower the Na_2SO_4 and NaNO_3 content of the West Valley sludge prior to vitrification.

To determine the effect of nitric acid acidification of sludge, four sludge samples were prepared using the above procedure. To prepare 1 L of West Valley feed for vitrification, washed sludge (resulting from 3.3 L of sludge and supernatant) and synthetic Thorex acid waste were combined with varying volumes of nitric acid. These mixtures were then digested at 95°C and analyzed for free acid and total nitrate (Table 2). No acid was added to Sample 1; and 0.56, 1.14, and 2 moles of HNO_3 were added to Samples 2, 3, and 4, respectively. The values of 0.56 and 1.14 moles of HNO_3 per liter were chosen because they represent approximately 50% and 100% of the theoretical amount of nitric acid required to nitrate the basic sludge. The volume of centrifuged solids after digestion varied with final OH^- or H^+ ion concentration. The initial sludge volume was reduced from 227 mL when no acid was added to 4.25 mL when the sludge was neutralized with 1.14 moles of HNO_3 (Sample 3). As the sludge became acidic, a new precipitate formed (Sample 4) that was composed of iron and rare-earth phosphates.

To prepare 1 L of West Valley vitrification feed, the washed and nitrated sludges were combined with ground zeolite (IE-96) and glass-forming chemicals to an equivalent of approximately 300 g of oxide/L (Table 3). The resulting nitrated feeds were used to determine melting properties and feed rheology.

TABLE 1. West Valley Alkaline Sludge and Supernatant Composition

<u>Acid Feed Component</u>	<u>M/L Final</u>	<u>Final Composition</u>	
		<u>Component</u>	<u>M/L</u>
NaCl	0.04	Cl ⁻	0.04
NaNO ₃	2.37	NO ₃ ⁻	3.45
Al(NO ₃) ₃ • 9H ₂ O	0.017	Al	0.017
Ni(NO ₃) ₂ • 6H ₂ O	0.011	Ni	0.011
Cr(NO ₃) ₃ • 9H ₂ O	0.027	Cr	0.027
KNO ₃	0.19	K	0.19
Fe(NO ₃) ₃ • 9H ₂ O	0.226	Fe	0.306
CsNO ₃	0.00138	Cs	0.00138
Sr(NO ₃) ₂	0.00056	Sr	0.00056
RbNO ₃	0.00037	Rb	0.00037
Ba(NO ₃) ₂	0.0006	Ba	0.0006
Zr(NO ₃) ₄	0.0023	Zr	0.0023
Sm(NO ₃) ₃	0.008	Sm	0.008
Mn(NO ₃) ₂	0.012	Mn	0.012
HF	0.0013	F ⁻	0.0013
H ₂ SO ₄	0.25	P	0.1
H ₃ PO ₄	0.02	Na	6.6
		SO ₄ ⁼	0.25
		Mo	0.0015
		NO ₂ ⁻	2.09
		CO ₃ ⁼	0.345

Added During Neutralization

FePO ₄ • 2H ₂ O	0.08
NaOH	pH 10
Na ₂ MoO ₄	0.0015
NaNO ₂	2.09
Na ₂ CO ₃	0.345

TABLE 2. Acidification of West Valley Sludge Used to Prepare
1 L of West Valley Vitrification Feed

	<u>Sample 1</u>	<u>Sample 2</u>	<u>Sample 3</u>	<u>Sample 4</u>
Centrifuged sludge weight, g	274	304	280	286
Sludge volume, mL	227	227	227	227
Thorex addition, mL	56	56	56	56
HNO ₃ addition, mol	0	0.56	1.14	2
Solids volume after HNO ₃ digestion, mL	227	33.3	4.25	18.3
Solids weight after digestion, g	274	39	4.3	20.7
H ⁺ analysis, <u>M</u>	Basic	Basic	Neutral	0.14
NO ₃ ⁻ analysis, <u>M</u>	0.41	1.17	1.76	2.16

Samples of nitrated sludge prepared for vitrification (Table 3) were tested to determine viscosity (centipoise) and yield stress point (Pascal) as a function of nitration. The four nitrated feed samples (Table 2) were also compared with current vitrification feed (WV183) prepared by combining metal nitrates, phosphates, and oxides.

Rheological results (Table 4) show that all feeds prepared by simulating actual West Valley sludge have higher viscosity and yield stress point values than WV183 melter feed. Sludge-prepared feed that was not nitrated compared more closely with WV183 feed. As nitric acid was added to the sludge, the viscosity at 120 s⁻¹ shear rate and the initial yield stress point increased by more than 10-fold as the vitrification feed became acidic (see Sample 4 in Table 4). In all cases, the sludge-prepared feeds suspended the ground zeolite for more than 24 h. The WV183 feed dropped the zeolite/silica out of solution in a short period of time.

Melting rate tests were performed with Samples 2 and 4 and with the current WV183 melter feed to determine the effect of acid content on melting rate and to verify the validity of the current method for making feed for melter trials. A clay crucible with 40 g of a standard glass composition (PSCM-16)

TABLE 3. Addition of Glass-Forming Chemicals to West Valley Sludge or HNO_3 -Treated Sludge to Prepare 1 L of WV183 Vitrification Feed

<u>Chemicals Added to Table 2 Solution</u>	<u>Amount, g</u>
SiO_2 (-325 mesh)	130
$\text{Na}_2\text{B}_4\text{O}_7$	146
Na_2SO_4	6
Zeolite(a)	39.7
$\text{Ca}(\text{NO}_3)_2$	5.8
$\text{Na}_2\text{C}_2\text{O}_4$	44.3
Sucrose	25

(a) Ground zeolite, -200 +325 mesh (16.8 wt%);
-325 mesh (22.5 wt%); balance, >200 mesh.

TABLE 4. Rheological Data for Vitrification Feeds Prepared Using Nitrated Sludge Versus WV183

	<u>Sample 1</u>	<u>Sample 2</u>	<u>Sample 3</u>	<u>Sample 4</u>	<u>WV183</u>
Viscosity as a function of shear rate, cP					
120 s^{-1} shear rate	17	39	65	107	9
200 s^{-1} shear rate	13	29	45	71	7
400 s^{-1} shear rate	9	21	28	40	6
Initial yield stress point, Pa	1.2	2.0	5.3	11.0	0.6
Final yield stress point, Pa	0.4	1.4	3.2	7.4	0.3
HNO_3 added/L of vitrified feed, mol	0	0.56	1.14	2	--
H^+ analysis, <u>M</u>	Basic	Basic	Neutral	0.14	--
NO_3^- analysis, <u>M</u>	0.41	1.17	1.76	2.16	2.2

was placed in the top of a vertical tube furnace. After a temperature stabilization period, the melt temperature at the surface was $1030^\circ\text{C} \pm 10^\circ\text{C}$. Next, 15 mL of feed was poured into the crucible; after 2 min, an additional

15 mL of feed was poured into the crucible. The crucible was removed from the furnace about 2 to 7 min after the last feed addition. The cooled crucible was sectioned vertically along a diameter. A photographic enlargement was then made, an acetate sheet was placed over the photograph, and the cold cap was traced and cut from the acetate sheet. This cutout was then weighed. This process was repeated, and the results were plotted as a function of time to obtain a melting rate trend for that particular feed.

The redox potential of the feed was adjusted using sugar prior to the melting rate test to produce a ferrous/ferric ratio in the resulting glass of between 0.1 and 0.4. Ratios in this range minimize the potential for melt foaming and metal formation. The procedure used to determine the redox information was similar to that used to determine the melting rate, except that the feed was sequentially added to an empty crucible in the furnace at 10-min intervals until about 18 g of glass was produced. The melt was left in the furnace for 30 min after the last feed addition. The resulting glass was ground into powder; and, in some cases, it was analyzed to determine the ferrous/ferric ratio using a colorimetric wet-chemical procedure. Otherwise, the color of the glass powder was used to indicate the ratio. West Valley glass powder with a ferrous/ferric ratio of 0 has a light brown color. The color of the powder changes to charcoal as the ferrous/ferric ratio becomes positive, although the magnitude of the ratio is not readily discernible. Thus, this charcoal-colored sample was chemically analyzed to determine the ferrous/ferric ratio, and existing correlations were used to optimize the sugar concentration for the subsequent melting rate test.

Nitrate anion-ion chromatograph analyses of Samples 2 and 4 indicate 1.17 M and 2.16 M of NO_3^- , respectively. Consistent with these values, it was determined that these feeds required 25 g/L (0.88 M C) and 60 g/L (2.10 M C) of sugar, respectively, to produce acceptable ferrous/ferric ratios. Inductively coupled plasma (ICP) analyses indicated that these feeds were formulated close to the target WV183 composition (generally within 1 wt%). The amount of feed available for melting rate evaluation precluded duplicate testing. Sample 4, the fully nitrated feed, exhibited excellent melting behavior with slopes near -40 and cold cap burnoff times between 4 and 5 min (Figure 1). That slope is

similar to the standard WV183 formulation made from commercial nitrate chemicals. Sample 2, the partially nitrated feed, exhibited slower melting. However, since the carbon-to-nitrate ratio was low (0.88/1.17 mol ratio), this work should be repeated. For comparison, PSCM-16 feed (a standard glass feed) had a slope near -20, a cold cap burnoff time near 7 min, and a processing rate of about 44 L/h in the PSCM.

Formatted Feeds

The study of formatted feeds presented below covers experimental procedures, rheology of the samples, melting rates, and behavior of the prepared feeds. Three West Valley sludges were prepared that were similar to those prepared for the nitrated studies. The washed sludges were used to prepare

FIGURE 1. Cold Cap Burnoff Times for Formated and Nitrated Feeds

formatted West Valley vitrification waste (Table 5). The formic acid was added to a water solution of sludge, glass formers, Thorex waste, and zeolite at 80 to 90°C. The initial test was based on forming all of the mono- and divalent ions in the feed. Approximately 50 to 80 mL of formic acid (HCOOH) was added to the waste mixture and digested. The resulting waste was evaporated to a volume of 1 L.

A sample of formatted feed prepared for vitrification using sludge was tested to determine viscosity and yield stress point values as compared with current vitrification feed prepared by combining metal nitrates, phosphates, and oxides (WV183). Melting rate tests were performed with Sample 6 as described in the previous section.

The rheological results (Table 6) show that the formatted feed has higher viscosity and yield stress point values than WV183 but that it is similar to the Sample 1 feed with no HNO₃ added to the sludge (Table 4). The rheological

TABLE 5. West Valley Sludge Used to Prepare 1 L of Formated Vitrification Feed

	<u>Amount</u>
Centrifuged sludge weight	300 g
Centrifuged sludge volume	220 mL
Thorex waste volume	112 or 56 mL
SiO ₂ (-325 mesh)	130 g
Na ₂ B ₄ O ₇	146 g
Na ₂ SO ₄	6 g
Na ₂ CO ₃	35 g
Zeolite(a)	39.7 g
Ca(NO ₃) ₂	5.84 g
Approximate amount of H ₂ O	500 mL

(a) Ground zeolite, -200 +325 mesh (16.8 wt%); -325 mesh (22.5 wt%); balance, >200 mesh.

TABLE 6. Rheological Data for Vitrification Feeds Prepared Using Formated Sludge Versus WV183

	<u>Sample 6</u>	<u>WV183</u>
Viscosity as a function of shear rate, cP		
120 s ⁻¹ shear rate	16	9
200 s ⁻¹ shear rate	12	7
400 s ⁻¹ shear rate	8	6
Initial yield stress point, Pa	1.0	0.6
Final yield stress point, Pa	1.0	0.3
NO ₃ ⁻ analysis, <u>M</u>	0.52	2.2

data for the formated feed shows the same shear stress with increasing or decreasing shear rate and is the only feed tested that shows a Bingham flow.

Melting studies with the formated feed show that 10 g/L of sugar was required to bring the redox level to the desired range, which is consistent with the much smaller amount of nitrate in the feed and the increased caron due to the formate. Melting tests indicated that the formated feed melted at the same rate and had similar characteristics as fully nitrated feed made from sludge or from metal nitrate (see Figure 1).

Computer Mass Balances for Nitrated and Formated Flowsheets

The mass balances for nitrated and formated flowsheets revealed several significant differences. The formated flowsheet balance indicated a reduced amount of NO_x (approximately 31%) leaving the process due to a smaller nitrate input. The formated balance also showed small quantities of combustibles (CO and H₂) exiting the melter. These quantities would increase significantly in the balance if more of the feed were formated instead of nitrated. These combustibles may not exist in actual melter operation due to the increased nitrate levels, and thus oxidizing potential, of the West Valley feed. No data are currently available to support this speculation, however. It should be noted that the formated feed is inherently more complex because it contains hydroxides, formates, nitrates, sugar, and oxalate. Redox control of this feed is potentially more difficult because of the complexity of the feed.

In the formatted flowsheet, the assumptions concerning the operation of the submerged bed scrubber (SBS) are quite important because they determine the total quantity of formate and nitrate in the feed. The more effectively the SBS operates, the more HNO_3 is recycled until there are no mono- and divalent hydroxides left to react with the formic acid addition. In the formatted flowsheet, there is some incentive to operate the SBS in a manner that does not capture HNO_3 effectively. In the nitrate flowsheet, however, operating the SBS to recover HNO_3 as effectively as possible is desired because less makeup HNO_3 is required and less total NO_x must exit the vitrification process.

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions and recommendations result from the work conducted this quarter:

- No operating difficulties were found while testing the pilot-scale ion-exchange column. The basic design is quite sound and should be adequate for use at West Valley with minor modifications. The screened laterals appeared to work well; no plugging by zeolite fines was observed.
- The settled solids content of simulated West Valley nitrated sludges made from hydroxide sludges is a function of nitric acid addition. The total settled solids is at a minimum when the acid is added at the stoichiometric requirement for complete nitration of the waste. Further nitric acid addition increases the solids content of the waste.
- The rheology of feeds prepared from simulated sludges is considerably different than that of feeds prepared from metal nitrate chemicals for current melter trials. The feeds prepared from sludges have higher viscosities (2 to 10 times) and smaller volumes of settled solids.
- The rheology of formatted feeds is very similar to that of feeds prepared from hydroxide sludges with no nitric acid addition. These

feeds have relatively high viscosities, have a small volume of settled solids, and are easily resuspended.

- In crucible melting rate tests, the fully nitrated feeds prepared for this study melted at the same rate as those prepared for current melter trials in spite of the rheological differences of the feeds. Partially nitrated feeds melted at reduced but still acceptable rates. The formatted feeds melted at approximately the same rate as the fully nitrated feeds. These results should be considered preliminary because no attempts were made to optimize melting behavior.
- Comparison of the preliminary mass balances for the fully nitrated and formatted vitrification feed processes indicated that the formatted feed offers a significant reduction (approximately 69%) in NO_x levels exiting the vitrification process. Total carbon levels were also reduced with the formatted flowsheet. The water balance is very close to that of the nitrated feed, however. The mass balance also shows that production of combustibles (CO , H_2) in the melter may pose a safety hazard in the formatted flowsheet. Further study may show, however, that these combustibles do not form due to the increased nitrate level in the West Valley feed compared with SRL feeds.
- From a flowsheet standpoint, a partially nitrated feed appears to be the most desirable. A partially nitrated feed, utilizing HNO_3 recovered from the off gas to adjust the feed, would have the advantages of minimum total NO_x output from the process and would not have the complexities and safety problems inherent in the formatted flowsheet.

REFERENCES

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MELTING PROCESS CHEMISTRY AND GLASS DEVELOPMENT

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SUMMARY

Efforts to develop a glass composition for West Valley waste included testing West Valley and Savannah River Laboratory (SRL) glasses under MCC-1 and MCC-3 conditions. Based on these tests, a new glass composition (WV205) was developed. The WV205 glass is patterned after the Interim SRL glass but with West Valley waste.

Laboratory tests were conducted to 1) optimize feed formulations for redox potential to eliminate foaming in the molten glass and 2) compare the melting rates for the compositions. WV205 appears to be an excellent compromise between durability and processability.

Laboratory samples and surface samples from experimental-scale ceramic melter (ECM) tests were investigated to better understand the surface layer (scum) formation problem.

Twenty-four laboratory batches of melter feeds were prepared from the simulated Hanford Waste Vitrification Program (HWVP) reference feed to evaluate the effects of formic acid addition, sugar addition, type of glass-forming chemicals used, and final melter feed concentration on the rheological properties and melting characteristics of the slurries. The HWVP melter feeds were determined to be non-Newtonian yield-pseudoplastic fluids.

INTRODUCTION

The objectives of this work are to design a feed formulation that can be processed in the liquid-fed ceramic melter (LFCM) at an acceptable rate and a glass composition that will produce a glass product having acceptable chemical durability. For West Valley, feed includes simulated high-level waste (HLW), glass-forming chemicals, and 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 0.1 and 0.5 (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). Hence, a glass composition is being developed to provide the appropriate high-temperature properties (viscosity, electrical conductivity) and low-temperature properties (elemental release rate, amount of crystallization). Nitrate or hydroxide chemicals representing the waste fraction and glass former 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 ECM. The ECM test was used to corroborate laboratory findings and evaluate if melting problems occur over a longer time frame in a more continuous melting environment. If problems occur, the work is

returned to the laboratory for further glass composition or feed formulation work. A successful ECM test would lead to the development of an extended test in the pilot-scale ceramic melter (PSCM).

Starting with this quarterly report, the applicable technology developed in the HWVP will also be presented. The HWVP is dedicated to the vitrification of 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 NCAW/CRW. This glass composition should have the required physical properties for processing LFCMs (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 all be added as a ground frit or whether some 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 to 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

During this quarter, efforts involved developing a glass composition for West Valley waste having acceptable durability and a feed formulation having acceptable processing properties and minimal potential to form a residual surface phase. Work was also completed on waste simulation and melter feed formulation with emphasis on rheological properties in support of the HWVP.

GLASS COMPOSITION DEVELOPMENT

Target compositions for West Valley and SRL glasses are shown in Table 1. Glasses labeled WV199 through WV203 contain simulated West Valley waste. Glasses labeled SRL TDS-165 and Interim SRL contain simulated Savannah River

TABLE 1. Target Compositions of West Valley and SRL Glasses

Oxide	West Valley Glasses, wt%					SRL Glasses, wt%	
	WV199 High B No Li	WV200 High B + Li	WV201 Low B No Li	WV202 Low B + Li	WV203 Working Glass Analog (131S)	SRL TDS-165	Interim with K ₂ O
SiO ₂	45.2	48.8	47.7	52.7	47.0	51.4	46.4
B ₂ O ₃	15.6	15.6	7.6	7.6	9.1	7.1	10.2
Na ₂ O	14.2	7.4	19.7	10.2	15.1	11.0	11.3
Li ₂ O	--	3.3	--	4.6	3.9	5.0	3.1
K ₂ O	0.1	0.1	0.1	0.1	0.1	0.1	3.6
MgO	0.2	0.2	0.2	0.2	0.2	0.8	1.4
TiO ₂	--	--	--	--	--	--	1.0
Other	24.7	24.6	24.7	24.6	24.6	24.6	23.0
100 poise temperature, °C	1125	1120	1115	1120	1020	1080	1020
Electrical con- ductivity at 1150°C, (ohm-cm) ⁻¹	0.27	0.22	0.40	0.34	0.48	--	--

waste for comparison. These glasses were prepared in the laboratory from reagent-grade powders and were used in several leaching tests to determine chemical durability.

The 28-day MCC-1 test data are summarized in Table 2. Boron release data indicate that the WV200, WV202, SRL TDS-165, and Interim SRL glasses have similar leaching behavior and are more durable in this test by a factor of about two compared with WV199, WV201, and WV203.

The 28-day MCC-3 test data are summarized in Table 3. These data indicate the WV202, SRL TDS-165, and Interim SRL glasses have similar durabilities and the lowest release rates of the samples tested. They are better by a factor of about three in comparison with WV199, WV200, and WV201 and are better by over an order of magnitude than WV203 (the high alkali initial working glass). An important result of this comparison is that similar release rates were observed for WV202 and SRL TDS-165, which contain nearly identical glass-forming oxides

TABLE 2. MCC-1 Test Data for West Valley and Savannah River Glasses^(a)

<u>Element</u>	<u>WV199</u>	<u>WV200</u>	<u>WV201</u>	<u>WV202</u>	<u>WV203</u>	<u>SRL TDS-165</u>	<u>Interim SRL</u>
Si	21	14	23	14	23	14	14
B	27	16	31	17	28	17	18
Li	NP ^(b)	16	NP	17	28	17	17
Na	26	16	29	17	28	17	17
Cs	31	23	30	25	36	NP	31
Al	16	13	19	14	21	12	10
Fe	0.12	0.085	0.13	0.16	0.11	0.28	0.076
Final pH	9.3	9.1	9.9	9.7	10.1	10.0	9.5

- (a) Values are an average of three samples in units of normalized mass release (g/m^2). Test conditions: MCC-1; 90°C ; deionized water; 28 days; surface area/volume ratio = 10 m^{-1} .
 (b) NP - not present in glass.

TABLE 3. MCC-3 Test Data for West Valley and Savannah River Glasses^(a)

Element	WV199	WV200	WV201	WV202	WV203	SRL TDS-165	Interim SRL
Si	0.61	0.67	1.2	0.66	2.9	0.62	0.50
B	3.8	2.8	3.7	1.1	15	1.1	1.1
Li	NP ^(b)	2.1	NP	1.1	11	1.2	0.99
Na	2.6	1.7	3.1	0.95	11	1.1	0.99
Cs	0.25	0.68	0.51	0.18	1.5	NP	0.40
Al	0.068	0.091	0.063	0.31	0.030	0.23	0.19
Fe	0.003	0.004	0.003	0.061	0.0004	0.001	0.001
Final pH	9.5	9.5	10.8	10.2	11.4	10.6	10.8

(a) Values are an average of three samples in units of normalized mass release (g/m^2). Test conditions: MCC-3; 90°C; deionized water; 28 days; surface area/volume = 635 m^{-1} ; 18 Å filter.

(b) NP - not present in glass.

but different simulated wastes (West Valley and Savannah River, respectively). The 28-day MCC-3 test data are considered to better simulate repository conditions in comparison to the MCC-1 test data due to the more saturated conditions.

These results led to the development of WV205, a glass that was patterned after the Interim SRL glass but with West Valley waste. The Interim SRL glass is apparently still under development at Savannah River to incorporate potassium from their waste; hence, it will probably not be their final composition. Nevertheless, its lower viscosity, higher alkali and boron contents, and comparatively good durability make it an attractive candidate for West Valley waste. Therefore, further durability and melting studies will be conducted on WV205. MCC-1 and MCC-3 tests are currently being conducted on WV205, which is expected to exhibit durability similar to the Interim SRL glass based on the WV202/SRL TDS-165 comparison described above. A summary of these and other compositions are presented in Table 4.

TABLE 4. Partial Glass Compositions

Glass	Concentration, wt%								Notes
	SiO ₂	B ₂ O ₃	Na ₂ O	Li ₂ O	CaO	Cr ₂ O ₃	RE ₂ O ₃	P ₂ O ₅	
131S	44.7	8.8	10.6	3.5	--	1.1	0.8	5.0	Working glass; PSCM-9, -15, -16; no zeolite
WV177	44.6	3.0	15.0	--	12.7	0.7	3.2	2.7	High Ca, low B for durability
WV182	44.5	12.7	15.0	--	3.0	0.7	3.2	2.7	PSCM-19, high B, Ca-P scum
WV183	44.6	15.5	14.7	--	0.7	0.7	2.0	2.6	ECM, minimum Ca, produced rare-earth phosphate scum
WV192	44.7	15.6	14.7	--	0.6	0.7	0.1	2.6	ECM, rare-earth elements minimized, Zr substituted for U + Th
WV199	45.2	15.6	15.2	--	0.6	0.2	0.1	2.5	ECM, high B, no Li, new waste with lower Cr
WV200	48.8	15.6	7.4	3.3	0.6	0.2	0.1	2.5	High B, some Li
WV201	47.7	7.6	19.7	--	0.6	0.2	0.1	2.5	Low B, no Li
WV202	52.7	7.6	19.2	4.6	0.6	0.2	0.1	2.5	ECM, low B, some Li, SRL TDS-165 analog
WV203	47.0	9.1	15.1	3.9	0.6	0.2	0.1	2.5	ECM, low temperature at 100 poise, 131S analog
WV204	49.5	7.5	12.5	4.0	0.6	0.2	0.1	2.5	ECM, intermediate temperature at 100 poise, between WV202 and WV203
WV205	45.2	10.0	11.0	3.1	0.6	0.2	0.1	2.5	ECM, interim SRL analog
SRL TDS-165	51.4	7.1	11.0	5.0	1.0	0.1	1.7	0.03	Past SRL reference glass
Interim SRL	46.4	10.2	11.3	3.1	1.0	0.1	0.6	0.04	3.6 wt% K ₂ O from new SRL waste

MELTING BEHAVIOR STUDIES

Efforts continued to develop a feed formulation with acceptable melting behavior, minimal melt foaming, and reduced potential for secondary phase formation (such as calcium phosphate). Laboratory tests were used to 1) optimize the feeds for redox potential to eliminate foaming in the molten glass and 2) compare melting rates for the compositions. The effects on melting rate of formating or fully or partially nitrating the feeds were explored. A reasonably good correlation exists between the slope (normalized to PSCM-16 feed) of the melting rate trend measured in the rapid laboratory test and the feed rate measured in the ECM (Figure 1). The results suggest that zeolite does not adversely affect melting based on Federal Republic of Germany (FRG) tests with and without IE-96 zeolite (+Z and -Z, respectively) and the similar

FIGURE 1. Laboratory and ECM Melting Rate Comparison (+Z = with zeolite; -Z = without zeolite; F = formated feed; N = fully nitrated feed; n = partially nitrated feed)

melting rate of WV203. No significant differences in melting rate were observed between formatted (F) and nitrated WV202 feed. Melting rates improved slightly when WV199 was modified from a partially (n) to a fully (N) nitrated feed formulation.

Melting rates measured in the ECM improved when boron and alkali contents in the glass were increased (Figure 2). The mole percent values were determined by substituting the boron and additional alkali oxides on a mole percent basis for sodium. The decrease in melt viscosity from WV202 and WV199 to WV205 and finally to WV203 is also correlated with the improvement in melting rate. Although WV203 is superior in terms of its melting performance, it is significantly less durable than the other glasses based on MCC-3 data, which adversely

FIGURE 2. Effect of Fluxes on Melting Nitrated and Reduced Feeds with Zeolite

impacts its selection as the reference glass composition. WV205 appears to be an excellent compromise between durability and processability. It processed acceptably at 3 L/h in the ECM, left only minor residual phases on the melt surface after the test, and compared well with the best glasses tested with MCC-3 in terms of durability. For these reasons, WV205 will be tested in the 10-day PSCM-21 test (June 1985).

SURFACE LAYER FORMATION

The surface layer (scum) formation problem is now better understood due to a variety of tests of laboratory samples and analyses of surface samples from the ECM tests. At higher calcium concentrations of 3% CaO in WV182 (PSCM-19), a liquid immiscible calcium phosphate phase formed, invaded the cold cap, and surrounded silica grains. This, in effect, chemically insulated the remaining silica grains and adversely affected the processing rate. Reducing the calcium concentration to 0.7% eliminated the calcium phosphate in WV183 and WV192 in the ECM. WV183 formed a scum that was enriched in a rare-earth phosphate crystalline phase after completion of the ECM test. This phase was eliminated by using Zr rather than La and Nd as substitutes for U and Th in laboratory tests. The results were confirmed in a subsequent ECM test using WV192. Laboratory tests evaluating radioactive WV183 and WV202 glasses melted from feed containing U and Th revealed no evidence of phosphate phases.

Other laboratory tests showed that the use of reductants (sugar, oxalate) to control melt foaming tended to strongly intensify the formation of the Fe-Cr phases. These phases appear to form metastably in the cooler surfaces and then change as the oxidation state changes (e.g., chromite spinel to hematite) or dissolve at higher temperatures. Little evidence of Fe-Cr phases was observed in glasses sampled from the PSCM-19 melter cavity. In contrast, sections of glass melted from PSCM-19 feed in the laboratory exhibited extensive Fe-Cr phase formation.

Glass compositions having greater alkali contents, such as WV205 and WV203, tended to minimize phosphate phase separation in laboratory tests. These compositions left the least amount of residual surface phases in the ECM. However, even at 0.7% CaO, it was still possible to form some calcium

phosphate, as evidenced by sampling the ECM melt surface after running WV205. In this case, the phosphate phase was a minor component of the scum. The dominant phase in WV202n, WV203n, and WV205n was zirconium oxide with some spinel. The zirconium phase appeared only after the supply of the usual starting material (zirconyl nitrate) was depleted and zirconium oxide was used as a replacement. The presence of the zirconium scum may have impacted the melting rate as well as the formation of the minor phosphate phase. Faster processing rates may sufficiently limit phosphate formation time.

WASTE SIMULATION AND FEED RHEOLOGY STUDIES

Simulations of HWVP reference feed were prepared and treated with formic acid as specified in the Defense Waste Processing Facility (DWPF) flowsheet. The same beneficial effects on the rheological properties were obtained for the HWVP melter feed as with the DWPF melter feed. Twenty-four laboratory batches of melter feeds were prepared from the simulated HWVP reference feed to evaluate the effects of formic acid addition, sugar addition, type of glass-forming chemicals used, and final melter feed concentration on the rheological properties and the melting characteristics of the slurries. The HWVP melter feeds were determined to be non-Newtonian yield-pseudoplastic fluids.

Waste Simulation

The HWVP reference feed is a blend of pretreated neutralized current acid waste (NCAW) from the Purex Plant operations and cladding removal waste (CRW). Maximum and minimum concentrations as well as a nominal value for each component in the pretreated waste blend have been projected. Simulations of this waste were prepared based on the nominal composition for use in laboratory-scale screening tests to evaluate both the chemical and physical properties of the melter feed. The compositions of the simulations used for these screening tests are presented in Table 5. The more rigorous simulation incorporates fluorides from the rare-earth strike of the CRW in the pretreatment process. This simulation also includes more of the metals and minor rare-earth components in the form of hydroxides rather than as carbonates or nitrates as was done in the initial simulation.

TABLE 5. Composition of HWVP Reference Feed Simulations Used in Laboratory Screening Tests

Initial Simulation		More Rigorous Simulation	
Compound Used	g/L (a)	Compound Used	g/L (a)
Al(OH) ₃	5.0	Al(OH) ₃	5.0
Fe(OH) ₃	11.3	Fe(OH) ₃	11.3
SiO ₂	0.56	SiO ₂	0.57
Cr(OH) ₃	1.38	Cr(OH) ₃	1.37
Ni(OH) ₂	0.56	Ni(OH) ₂	0.57
Zr(OH) ₄	0.58	Zr(OH) ₄	0.59
Mg(OH) ₂	0.1	Mg(OH) ₂	0.08
CaF ₂	0.08	CaF ₂	0.08
CuSO ₄	0.23	Cu(OH) ₂	0.14
Mn(NO ₃) ₂ • 4H ₂ O	0.38	Mn(OH) ₂	0.14
Na ₂ MoO ₄ • 2H ₂ O	0.38	Na ₂ MoO ₄ • 2H ₂ O	0.38
Sr(NO ₃) ₂	0.11	Sr(OH) ₂	0.09
Y(OH) ₃	0.052	Y(OH) ₃	0.05
CsOH	0.19	CsOH	0.20
BaSO ₄	0.11	BaSO ₄	0.12
		Ce(OH) ₃	0.15
Didymium ^(b) carbonate	1.71	Pr(OH) ₃	0.09
		Sm(OH) ₃	0.04
La(NO ₃) ₃ • 6H ₂ O	0.28	La(OH) ₃	0.09
		LaF ₃	0.41
Nd(NO ₃) ₃ • 6H ₂ O	0.27	Nd(OH) ₃	0.09
		NdF ₃	0.11
NaF	0.40	NaF	0.35
Na ₂ SO ₄	0.21	Na ₂ SO ₄	0.44
NaNO ₃	1.79	NaNO ₃	2.55
Na ₂ C ₂ O ₄	0.63	Na ₂ C ₂ O ₄	0.64
NaOH	0.29	NaOH	0.68

(a) Waste concentration = 19 g total oxides/L.

(b) Natural rare-earth mix with 96% of the Ce removed.

Melter Feed Processing

A decision was made early in FY 1985 to use applicable portions of the DWPF flowsheet for HWVP melter feed preparation. In that process, glass frit is used as an abrasive slurry to decontaminate the filled canisters and the decontamination frit is incorporated into the melter feed. Therefore, at least one-third by weight of the glass-forming chemicals in the melter feed would be present as -80/+200 mesh frit.

In the DWPF flowsheet, formic acid is added to the waste slurry. SRL reports that this treatment results in a melter feed that has the rheological characteristics of a Bingham fluid and stabilizes the suspension of the waste sludge and relatively large decontamination frit particles. They also report that this formic acid treatment results in a reducing condition in the melter, which minimizes melt foaming. Therefore, the effects of treating HWVP reference feed concentrate with formic acid were evaluated to see if the same beneficial results experienced with DWPF feed could be obtained for HWVP melter feeds.

HWVP reference feed is formed by heating the waste with continuous agitation to 85 to 95°C. A 90 wt% formic acid solution is slowly added to the waste through a delivery tube that extends below the surface of the waste. The acid must be slowly added to the heated slurry to prevent the forming reaction, which evolves CO_2 , from proceeding too vigorously. After the acid addition is completed, the waste is digested with full reflux for 1 to 2 h to ensure that the reaction is complete. The boiling temperature of the formed simulated HWVP reference waste concentrate is 102 to 104°C.

The initial simulated HWVP reference feed was formed at formic acid concentrations between 0 and 2.0 mol/L of waste concentrate. The waste simulations were prepared at 144 g of waste oxides/L or 7.6 times the concentration of the projected reference feed coming into the HWVP. The 100% stoichiometric concentration is 1.87 mol of formic acid/L of SRL waste; the stoichiometric quantity for the initial HWVP reference feed simulation is 0.43 mol/L of waste. These stoichiometric quantities are calculated based on the complete reaction of the mono- and divalent hydroxides and all the carbonates with formic acid. The difference between the SRL waste and the HWVP reference feed is that the

HWVP feed contains no calcium and much less nickel and manganese. The stoichiometric quantity of formic acid for the more rigorous HWVP reference feed simulation is only 0.29 mol/L of concentrate because there are no carbonates in this simulation.

Simulated HWVP waste apparent viscosity values as a function of heat and formic acid treatments are presented in Figure 3. Boiling the simulated waste for several hours may reduce its viscosity. Formic acid additions of up to 1.0 mol/L of waste concentrate reduce the apparent viscosity of the simulated waste. Beyond 1.0 mol/L, the only effect appears to be dilution.

Complete melter feed test batches were prepared using unformatted or stoichiometrically formatted simulated HWVP reference feeds. The total equivalent oxide loading was 400 g/L of melter feed. The waste equivalent oxide loading was 100 g/L (25 wt%), and the glass-forming chemicals equivalent oxide content was 300 g/L (75 wt%). In all the batches, at least one-third or 100 g of the glass-forming chemicals per liter was added as -80/+200 mesh frit, which represented the decontamination frit contribution to the melter feed.

FIGURE 3. Initial Simulated HWVP Reference Feed Viscosity as a Function of Formic Acid Additions

These test batches were prepared to evaluate the effects on melter feed physical properties and melting behavior when the feed was prepared using the DWPF flowsheet and various types of glass-forming chemicals and additives to produce a reducing condition in the melt. Twenty-four laboratory-scale batches of melter feed were prepared from one master batch of the initial HWVP reference feed simulation. Three additional batches were recently prepared using the more rigorous simulation (see Table 5).

The makeup of the melter feed batches and the results of their characterization are presented in Tables 6 and 7. Batch 12F represented the state-of-the-art melter feed preparation for the HWVP as it existed at the end of FY 1984. Batches 14F and 31F represent the DWPF flowsheet applied to the HWVP reference feed. These two batches were prepared more than a month apart; the data provide some measure of reproducibility. Batches 14F through 19F were made to investigate the effects of treating the initial simulation with stoichiometric amounts of formic acid or sugar and of adding the glass-forming chemicals as frit or as unreacted nitrates. Batches 20F and 23F were made to probe the limits of melter feed concentrations. Batches 24F through 27F were prepared to evaluate the effects on slurry rheology and redox of using formate and oxalate salts in place of nitrate salts as glass-forming chemicals. Batches 28F through 33F were prepared to learn whether the desired Fe^{+2} to Fe^{+3} ratio (0.1 to 0.3) could be achieved by adding excess formic acid to a melter feed made with all the glass formers present as frit.

These screening tests indicated that the viscosity and yield stress values of melter feeds decrease with increases in the amount of formic acid added to the feed. Adding 0.43 to 1.0 mol of formic acid/L of concentrated waste reduced the yield stress from 37 dynes/cm² to 20 to 25 dynes/cm². Further additions of formic acid (1.87 to 2.0 mol/L of concentrated waste) reduced yield stresses roughly 10 dynes/cm². This additional formic acid also brought the Fe^{+2} to Fe^{+3} ratio into the desired range. However, the melting behavior of the slurry that contained excess formic acid was not acceptable. A violent vapor release preceded melting as the feed was introduced into the laboratory-scale melting chamber. Large additions of sugar also decreased the viscosity and yield stress values, but 70 g sugar/L of feed made the melt too reducing.

TABLE 6. Summary of Rheology, Melting Rate, and Melt Chemistry Properties of Melter Feed Batches Prepared with HWVP Reference Waste Simulations

Batch No.	12F	13F	14F	15F	16F	17F	18F	19F	20F	21F	22F	23F	24F
Concentration, g total oxides/L	400	400	400	400	400	400	400	400	500	500	500	500	400
Formic acid added to waste concentrate, M/L	0	1.03	0.43	0	0	0.43	70 g/L sugar	70 g/L sugar	1.0	1.0	0.43	0.43	0.43
Coarse frit added, fraction of total glass formers ^(a)	0	1/3	1/3	1/3	1/3	1/3	1/3	1/3	1/3	1/3	1/3	1/3	1/3
Fine frit added, fraction of total glass formers ^(a)	0	2/3	2/3	2/3	0	0	0	2/3	2/3	0	2/3	0	0
Unreacted glass former added, fraction of total glass formers	1/1	0	0	0	2/3	2/3	2/3	0	0	2/3	0	2/3	2/3
Type of unreacted glass formers ^(b)	N	--	--	--	N	N	N	--	--	N	--	N	0
Heat treatment	No	Yes	Yes	No	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Density, g/mL	1.36	1.30	1.30	1.33	1.35	1.35	1.37	1.31	1.34	1.41	1.34	1.40	1.34
pH	7.73	4.18	6.56	10.81	7.62	7.75	7.60	10.25	4.40	4.64	6.47	6.61	7.93
Dissolved solids, wt%	17.8	6.3	3.9	3.4	11.2	14.9	15.3	7.9	8.2	20.9	4.7	17.0	12.1
Suspended solids, wt%	27.1	30.5	32.9	35.8	30.5	28.2	29.5	35.9	35.1	27.7	36.5	29.6	28.7
Total solids, wt%	44.9	36.8	36.8	39.2	41.8	43.2	44.8	43.8	43.3	48.7	41.2	46.5	40.8
Viscosity, cP													
at 183 s ⁻¹	76	18	18	63	33	26	17	18	27	27	36	47	59
at 608 s ⁻¹	32	9	8	28	15	13	9	8	12	13	16	23	23
at 824 s ⁻¹	26	8	7	23	13	10	8	6	10	11	14	16	18
Yield stress, dynes/cm ²	NA	NA	21	85	36	31	22	27	43	29	48	66	82
Supernatant, vol%	1.3	NA	NA	9.0	4.1	4.1	3.2	4.8	7.0	2.4	5.9	2.9	2.5
Sediment resuspendability	Poor	NA	Fair	NA	Good	Fair	Good	Bad	Fair	Fair	Fair	Fair	Bad

TABLE 6. (contd)

Batch No.	25F	26F	27F	28F	29F	30F	31F	32F	33F	35F	37F	1F	2F	3F
Concentration, g total oxides/L	400	400	400	400	400	400	400	400	400	400	400	400	400	400
Formic acid added to waste concentrate, M/L	0	0.43	0	0	1.0	0.6	0.43	1.87	2.00	0.43	0.43	0.29	0.29	0.29
Coarse frit added, fraction of total glass formers ^(a)	1/3	1/3	1/3	1/3	1/3	1/3	1/3	1/3	1/3	1/3	1/3	1/1	1/3	1/3
Fine frit added, fraction of total glass formers ^(a)	0	0	0	2/3	2/3	2/3	2/3	2/3	2/3	0	0	0	0	0
Unreacted glass former added, fraction of total glass formers	2/3	2/3	2/3	0	0	0	0	0	0	2/3	2/3	0	2/3	2/3
Type of unreacted glass formers ^(b)	0	F	F	---	---	---	---	---	---	AF	AF	---	AF	NF
Heat treatment	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	No	No	No
Density, g/mL	1.38	1.35	1.32	1.29	1.28	1.27	1.29	1.30	1.28	1.32	1.33	1.32	1.32	1.32
pH	8.56	7.41	8.02	10.05	4.74	5.07	8.85	3.3	3.26	7.57	7.72	5.08	8.01	8.04
Dissolved solids, wt%	11.6	13.4	11.4	2.9	4.3	3.8	3.8	5.3	5.1	12.5	12.6	2.8	10.8	12.4
Suspended solids, wt%	32.4	27.8	28.5	31.4	31.2	30.8	29.8	30.3	28.4	26.6	28.1	29.9	27.6	26.0
Total solids, wt%	44.0	41.2	39.9	34.4	35.5	34.6	33.6	35.6	33.5	39.1	40.7	32.7	38.4	38.4
Viscosity, cP														
at 183 s ⁻¹	59	25	33	23	20	18	19	7	15	70	33	11	22	22
at 608 s ⁻¹	27	11	14	10	8	8	8	4	7	27	15	5	10	10
at 824 s ⁻¹	22	9	11	8	7	6	7	3	5	21	12	4	9	9
Yield stress, dynes/cm ²	74	30	43	37	23	19	25	6	15	107	43	15	28	28
Supernatant, vol%	3.8	5.8	6.4	NA	13.2	13.6	NA	NA	NA	NA	NA	---	---	---
Sediment resuspend-ability	Fair	Good	Good	Fair	Fair	Fair	Fair	NA	Fair	Bad	Good	---	---	---

(a) Coarse frit is -80/+200 mesh; fine frit is -200 mesh.

(b) See Table 7.

TABLE 7. Chemical Compounds Used to Make Up Various Types of Glass Formers for the HWVP Reference Feed Treatment Screening Tests

Types of Glass Formers	Chemical Compounds Used					
HW39 frit	SiO ₂	B ₂ O ₃	Li ₂ O	Na ₂ O	MgO	CaO
Unreacted nitrates (N)	SiO ₂	Na ₂ B ₄ O ₇ • 10H ₂ O	LiNO ₃	NaNO ₃	Mg(NO ₃) ₂ • 6H ₂ O	Ca(NO ₃) ₂ • 4H ₂ O
Unreacted oxalates (O)	SiO ₂	Na ₂ B ₄ O ₇ • 10H ₂ O	LiNO ₃	Na ₂ C ₂ O ₄	Mg(NO ₃) ₂ • 6H ₂ O	CaC ₂ O ₄
Unreacted formates (F)	SiO ₂	Na ₂ B ₄ O ₇ • 10H ₂ O	LiNO ₃	NaHCO ₂	Mg(NO ₃) ₂ • 6H ₂ O	Ca(HCO ₂) ₂
All unreacted formates (AF)	SiO ₂	Na ₂ B ₄ O ₇ • 10H ₂ O	LiHCO ₂ • H ₂ O	NaHCO ₂	Mg(HCO ₂) ₂ • 2H ₂ O	Ca(HCO ₂) ₂
Unreacted nitrates and formates (NF)	SiO ₂	Na ₂ B ₄ O ₇ • 10H ₂ O	LiHCO ₂ • H ₂ O	NaHCO ₂	Mg(NO ₃) ₂ • 6H ₂ O	Ca(NO ₃) ₂ • 4H ₂ O

Batches 35F and 37F were prepared as an extension of the 24F through 27F series to investigate the effects on the Fe⁺² to Fe⁺³ ratio of using the reducing salts in the glass-forming chemical makeup (see Table 7). In these tests, the oxalate and all formate unreacted glass-forming chemicals resulted in feeds with yield stresses greater than 80 dyne/cm² (the DWPF criterion). All melter feed samples made with the blends of nitrates and oxalate or formate salts were too oxidizing. The sample prepared with all formate salts (35F) was too reducing.

The samples used to determine settling rates were covered and stored in graduated cylinders. These samples were later probed to determine whether there had been significant settling of the frit and other insolubles and to evaluate the resuspendibility of these solids. The results are reported in Table 6. Generally, while the feeds tested did separate into phases, the phase containing solids held the frit in suspension. There was no significant separate frit layer in any of the samples. The firmness of the phase containing solids varied but in only the following four cases had it become quite firm:

- Batch 12F - a 100% nitrate glass-forming chemical makeup that had not been heat-treated or formated
- Batch 19F - an all-frit feed containing 70 g sugar/L of feed
- Batch 24F - a feed made with oxalate salts in the glass formers

- Batch 35F - a feed made with one-third frit and two-thirds unreacted formate glass formers.

The last three batches in Table 6 (1F, 2F, and 3F) were prepared using a more rigorous waste simulation. Less formic acid was used because the waste simulation did not contain any carbonates. There was, however, still some gas release when the acid was added to the 95°C slurry. The hydrated manganese is suspected to be the source of this gas release. The nitrate and formate salts (Table 7) used to make up the unreacted glass-forming chemical were adjusted to obtain the desired reducing conditions in the melt. The three batches prepared with the more rigorous simulation have acceptable viscosity and yield stresses values according to the DWPF criteria.

Rheological Properties

SRL indicates that line velocities as low as 1 ft/s are sufficient to prevent solids deposition in the DWPF design melter feed line with the SRL melter feed slurry. Viscosity data for the HWVP melter feeds are reported in Table 6 at shear rates of 183, 608, and 824 s⁻¹, which represent the values anticipated in the HWVP melter feed line. These values are calculated based on a feed line inside diameter of 0.305 in. (3/8-in. tubing) and feed rates of 30, 100, and 135 L/h. These feed rates produce line velocities of 0.6, 1.9, and 2.6 ft/s, respectively. The minimum line velocity of 0.6 ft/s is less than the 1.0-ft/s minimum velocity established at SRL. The minimum acceptable velocity for HWVP feed has yet to be determined.

SRL has identified the yield stress of melter feed slurries as a significant design criterion for the slurry transport and handling systems at the DWPF. A design yield stress of 80 dynes/cm² has been established by SRL. The yield stress reported by SRL is determined by extrapolation of the "straight" portion of the plot of shear stress versus shear rate back to the shear stress axis at the shear rate of zero. The yield stress values for HWVP feed slurries (Table 6) were obtained using the reference SRL extrapolation procedure. In some instances, the shear stress determined by the procedure was less than the startup shear stress measured by the viscometer. In these instances, the startup shear stress may be more indicative of unfavorable rheology.

The procedure for determining the yield stress is based on the fact that the SRL melter feeds are treated as if they were Bingham plastic fluids. Laboratory evaluations were conducted to determine whether the Bingham plastic rheological model (and the resulting extrapolation procedure used to determine yield stress) should be applied to HWVP melter feed slurries. Many slurries can be characterized as pseudoplastic, Bingham plastic, or yield-pseudoplastic non-Newtonian fluids. The equations that identify these fluids are summarized in Table 8. The yield-pseudoplastic model reduces to the Bingham plastic model when the flow behavior index $n = 1$, to the pseudoplastic model when the yield stress $\tau_y = 0$, and to the Newtonian model when $n = 1$ and $\tau_y \neq 0$.

Rheograms (plots of shear stress versus rate of shear) were prepared using a Haake Rotovisco^(a) viscometer for HWVP Batches 26F, 31F, 33F, and 37F (Table 6) and were fit to the yield-pseudoplastic rheological model. The melter feed samples fit the model very well. The calculated values of τ_y , n ,

TABLE 8. Non-Newtonian Flow Models

Fluid Type	Equations for Mathematical Model	Definitions
Newtonian	$\tau = \mu \left(\frac{dV}{dr} \right)$	τ = shear stress μ = viscosity $\frac{dV}{dr}$ = rate of shear
Pseudoplastic	$\tau = k \left(\frac{dV}{dr} \right)^n$	k = consistency index n = flow behavior index
Yield-pseudoplastic	$\tau = \tau_y + k \left(\frac{dV}{dr} \right)^n$	τ_y = yield stress
Bingham plastic	$\tau = \tau_y + \eta \left(\frac{dV}{dr} \right); \tau > \tau_y$ $0 = \left(\frac{dV}{dr} \right); \tau < \tau_y$	η = plastic viscosity

(a) Haake Buchler Instruments, Inc., Saddle Brook, New Jersey.

and k for each sample are listed in Table 9. The calculated values of the flow behavior index for the melter feed samples evaluated were usually much less than 1.0, indicating that the simulated HWVP melter feeds were not Bingham plastics.

The yield stress values for these feeds determined by the Bingham plastic extrapolation model used by SRL are listed in Table 10. These values differ greatly from the values of yield stress calculated using the parameters in Table 9. The Bingham plastic extrapolation method for determining yield stress results in substantially higher yield stress values for the HWVP melter feeds than the values calculated based on the yield-pseudoplastic rheological model that fits ($R = 0.99$) the rheograms of HWVP melter feed samples. Thus, the simulated HWVP melter feed is a yield-pseudoplastic material, while the SRL-prepared simulated DWPF melter feed is treated as a Bingham plastic fluid.

The question that remains to be resolved is whether the SRL design yield stress value of 80 dynes/cm^2 for DWPF melter feeds should be utilized as the

TABLE 9. Calculated Parameters for Yield-Pseudoplastic Model of HWVP Melter Feeds(a)

Sample	τ_0	K	n	F	R^2	SD of Regression
26F-U	1.585	0.2770	0.452	3,516	0.9990	0.0313
26F-D	1.803	0.0199	0.877	5,545	0.9994	0.0313
31F-U	2.070	0.0599	0.610	224	0.9846	0.0818
31F-D	1.673	0.0084	0.969	338	0.9898	0.0968
33F-U	0.127	0.4916	0.322	7,438	0.9995	0.0141
33F-D	0.698	0.0505	0.661	593	0.9941	0.0597
37F-U	1.358	0.4596	0.443	17,000	0.9998	0.0222
37F-D	2.534	0.0259	0.887	18,760	0.9998	0.0237

(a) The -U and -D sample designations refer to the values of the flow curves from the "up" and "down" cycles, respectively, of the applied shear rate. The F value is a measure of the significance of the fit. The R^2 value reflects the total variation that is explained by the fitted function. The SD (standard deviation) of regression is an estimate of the standard deviation of the data about the fitted line.

TABLE 10. Effects of Rheological Model Identification on Predicted Values of Yield Stress

Sample	Yield Stress, dynes/cm ²		(BP - YP)/BP, %
	Yield-Pseudoplastic (YP) Model	Bingham Plastic (BP) Extrapolation	
26F-U	16	30	47
26F-D	18	23	22
31F-U	20	25	20
31F-D	17	19	11
33F-U	1	15	93
33F-D	7	11	37
37F-U	14	43	67
37F-D	25	29	14

design parameter for HWVP melter feeds. It is believed that this question can be resolved only by further testing with simulated HWVP melter feed in a pump-pipe transfer system as was done at SRL.

The values of apparent viscosity in Table 6 were calculated based on the pseudoplastic rheological model. These values are compared in Table 11 with apparent viscosities based on the yield-pseudoplastic parameters from Table 9. The model selected does not appear to significantly affect the calculated values of apparent viscosity for the melter feed samples evaluated.

CONCLUSIONS

The following conclusions can be drawn from the work conducted this quarter:

- A glass composition (WV205) has been developed to incorporate West Valley waste and is expected to have durability comparable to the SRL TDS-165 glass based on MCC tests.
- A partially nitrated feed formulation of WV205 glass has been developed. This feed exhibited good melting performance in laboratory and ECM (3 L/h) melting tests, which is attributed to its lower melt viscosity and greater alkali and boron contents.

TABLE 11. Effects of Rheological Model Identification on Calculated Values of Apparent Viscosity (cP)

Sample	183 s ⁻¹ Shear Rate		608 s ⁻¹ Shear Rate		824 s ⁻¹ Shear Rate	
	YP Model ^(a)	P Model ^(b)	YP Model	P Model	YP Model	P Model
26F-U	25	25	11	11	9	9
26F-D	20	21	12	11	11	10
31F-U	19	19	8	8	7	7
31F-D	16	16	10	9	9	8
33F-U	15	15	7	7	5	5
33F-D	13	12	7	7	6	6
37F-U	33	33	15	15	18	12
37F-D	28	29	17	16	15	13

(a) YP - yield-pseudoplastic model.

(b) P - pseudoplastic model.

- The occurrence of residual phosphate surface phases has been minimized in WV205. A surface layer enriched in zirconium oxide can be corrected with the proper choice of zirconium starting materials.
- U and Th phosphate phases were not observed in glasses prepared from WV202 and WV183 feeds in the laboratory.
- A reasonably good correlation exists between the melting rates measured in laboratory crucible and ECM tests.
- Melting rate evaluations suggest that 1) zeolite does not adversely affect melting, 2) fully formatted and nitrated feeds melt similarly, 3) melting improves as the feed becomes more fully nitrated, and 4) melting improves with greater alkali and boron content and lower melt viscosities.
- A chemically correct simulation of the HWVP reference feed can be made by using rare-earth fluorides and hydroxides to reproduce the precipitates formed when CRW is treated with a rare-earth strike prior to blending with NCAW to form the HWVP feed.

- Treating the PNL simulation of HWVP reference feed with formic acid and heat reduces the consistency and yield stress of the melter feed, but it does not make the melt sufficiently reducing to eliminate the need to add sugar or some other reducing agent to the melter feed to achieve the desired Fe^{+2} to Fe^{+3} ratio.
- Melter feeds that appear to have acceptable rheological properties can be prepared from simulated waste treated with stoichiometric amounts of formic acid to concentrations of 400 g total oxides/L. The glass-forming chemicals in these melter feeds can be totally in the form of a frit or two-thirds by weight can be added as unreacted nitrate and formate salts.
- Melter feeds prepared by blending HW39 glass-forming chemicals with the PNL simulation of HWVP reference feed treated with formic acid and concentrated to a total oxide loading of 400 g/L are most correctly classified as yield-pseudoplastic fluids. Therefore, it is not certain that the melter feed rheological property specifications developed for the DWPF melter feed, which is treated as a Bingham plastic fluid, are valid for the HWVP melter feed.

FEED PREPARATION AND TRANSFER SYSTEMS

H. T. Blair

SUMMARY

Long-term testing of the air displacement slurry (ADS) pump was completed after 3696 h of operation. The pump was disassembled, and the critical parts were inspected for wear and corrosion. The measured wear was not significant enough to affect pump operation, and the pump life is projected to be well beyond 4000 h.

INTRODUCTION

Feed preparation and transfer systems consist of the equipment used to contain and process the 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 the 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 in this quarterly report. During FY 1985, specific activities concerning feed preparation and transfer systems include:

- 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 radioactive demonstration of the liquid-fed ceramic melter (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.
- Evaluation of remote liquid sampling devices when applied to concentrated slurries.

TECHNICAL PROGRESS

Long-term testing of the prototype ADS pump was completed. The pump was operated in a test loop for a total of 3696 h using primarily a simulated neutralized defense waste mixed with unreacted glass-forming chemicals. The pump was operated for about 250 h with a simulated West Valley melter feed containing ground zeolite. Both slurries contained -325 mesh silica as the major particulate.

Following the test, the pump, which is shown in Figure 1, was disassembled and inspected for areas of wear that would limit its service life. Weight and dimensional measurements were made; the deviations from previous measurements are shown in Table 1. In general, the pump components were in good condition. The pump was designed anticipating the areas of high wear. Although wear had been expected due to the number of hours of operation, the resulting wear was not significant enough to affect pump operation.

The two-way valve (Figure 2) was worn on the seating surfaces and where contact was made with the guides. A flashing on the lower seat of the valve, corresponded with the increased width of the seat in the mating surface (Figure 3) and probably resulted from the wear that occurred on the rocker arm that drives the valve and adjusts the position of the seat. This seating surface was centered, indicating proper mating. The width of the upper seat on the valve had increased. It appeared that the valve was contacting the upper seat at a slightly off-center position and then sliding into position. The areas where contact was made with the guides were discolored, and some small

FIGURE 1. Prototype Air Displacement Slurry Pump

TABLE 1. Weight and Dimensional Changes in ADS Pump Components
Following 3696 h of Use in Simulated Melter Feed

Pump Component	Weight Loss, g	Dimensional Change After 3696 h, in.	Dimensional Change Extrapolated to 1 yr of Operation, in./yr
Lower valve seat:	No change		
Lower valve seat width	--	0.013	0.031
Upper valve seat:			
Upper valve seat diameter	--	0.023	0.054
Two-way valve:	No change		
Upper seat width		0.016	0.038
Upper guide surface diameter		0.002	0.005
Lower guide surface diameter		0.001	0.002
Rocker arm mating surface		0.011	0.026
Pump chamber inlet diameter	--	(1) 0.003 (2) 0.005	(1) 0.007 (2) 0.012
Initial feed line inside diameter	--	0.002	0.005
Valve lower guide diameter	--	No change	--
Valve upper guide diameter	No change	0.005	0.012
Rocker arm:	0.3	--	
Valve contact	--	(1) No change (2) 0.002 (3) 0.002	(1) -- (2) 0.005 (3) 0.005
Wear at contact points	--		
Change in length of wear	--	0.12	0.28
Change in width of wear	--	0.009	0.02
Pivot pins	--	0.001	0.002
Pivot pin openings	--	0.001	0.002
Screen assembly	0.1	--	
Drive rod diameter change due to guides	--	0.004 ^(a) 0.008 ^(a)	0.009 0.019

(a) Changes since the initial testing.

FIGURE 2. ADS Pump Two-Way Valve After Testing

FIGURE 3. ADS Pump Lower Valve Seating Surface After Testing

longitudinal grooves were noted. These grooves appeared to be caused when large particles became wedged between the valve and the guide, producing the grooves as the valve was driven up and down.

The rocker arm (Figure 4) had a worn area located where contact was made with the valve stem. The size of this area had increased as a result of this testing. The mating area on the valve stem was also worn slightly. The pivot pins used for the drive rod/rocker arm mechanism showed a very small amount of wear (Figure 5).

The drive rod had a worn area approximately 1 in. long at the location of the two drive rod guides. The majority of this wear was noted during the initial 500 h of operation. However, no measurements were made. This drive rod was fabricated from thick-walled tubing so that even with projected wear for 1 year of operation, the drive rod would not be worn through.

The maximum amount of wear was found on the upper valve seat. Proper seating of the upper seat is highly desirable from an efficiency standpoint, but it is not critical for pump operation.

FIGURE 4. ADS Pump Rocker Arm After Testing

FIGURE 5. Pivot Pins from ADS Pump After Testing

CONCLUSIONS

The ADS pumps can be operated for more than 4000 h without failure due to erosion or corrosion of the wetted parts made with the prototype materials.

MELTER SYSTEMS

R. D. Dierks and J. M. Perez, Jr.

SUMMARY

Operation of the radioactive liquid-fed ceramic melter (RLFCM) was limited to mostly idling during this quarter. The process control recovery from a reboil-type foaming incident was successfully executed by the automatic resistive feedback electrode voltage control system.

Nonradioactive melter test analyses were completed for experimental- and pilot-scale melter experiments. Experimental-scale ceramic melter (ECM) testing verified the processability of a simulated melter feed containing high concentrations of cesium and strontium. The testing was done in support of future RLFCM operation to process a radioactive waste containing high cesium and strontium loadings. The pilot-scale ceramic melter (PSCM) testing evaluated the processability of a candidate West Valley melter feed composition. The 320-h experiment demonstrated the ability to maintain the glass melt in a reduced state by using carbon reductants. Several vitrification system components were tested: feed systems, melter instrumentation, and off-gas treatment systems.

INTRODUCTION

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

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 radioactive and nonradioactive testing conducted this quarter is discussed below.

RADIOACTIVE TESTING

The operation of the RLFCM was limited to mostly idling this quarter. Approximately 60 kg of glass was generated during the startup procedure for the second radioactive experiment, and approximately 90 kg of glass was subsequently discharged from the melter into the receiving canister to minimize the probability of a glass discharge from the melter due to an inadvertent off-gas system pressure balance fluctuation.

Foaming characteristics were noted shortly after the feed was started into the melter during the short (25.7-h) startup procedure for the second radioactive experiment. The initial foaming indications were similar to those reported last quarter for the first three melter experiments: a relatively sharp drop in the glass specific gravity indication; a relatively sharp increase in the melter tank electrical resistance; and a steady increase in the average glass temperature by about 55°C.

In previous experiments, a manual technique was used to control the reboil-type foaming activity. The electrode voltage control was quickly shifted from an AUTOMATIC to a MANUAL operating mode, and the electrode voltage was decreased to its minimum value. As the glass temperatures and the melter tank electrode resistance values began to return to normal, the electrode voltage was slowly increased. When the temperature and the melter tank resistance values returned to normal, the electrode voltage control was shifted back

to AUTOMATIC. While this procedure is relatively simple, it did require a considerable amount of operator attention and judgment.

For this short startup procedure, the electrode voltage control was left in an AUTOMATIC operating mode throughout the entire foaming occurrence. The foaming characteristics were much the same as during previous experiments. The average glass temperatures increased by about 50°C to a maximum of about 1190°C before the foam collapsed, dropping the melter tank resistance value sufficiently below the set point to cause the electrode voltage to drop to its minimum value, exactly as had been done with the MANUAL operation. As the influence of the foam on the melter tank resistance value decreased, the AUTOMATIC process control system readjusted the electrode voltage values until the glass temperature values returned to their normal range. Thus, in its AUTOMATIC operating mode, the recovery of the control system was achieved without operator intervention in one overshoot/undershoot cycle (the cycle period was about 2 h long).

NONRADIOACTIVE TESTING

ECM Testing

Nonradioactive process development work involving the LFCM continued during the second quarter of FY 1985. ECM experiments were performed to evaluate the processability of a high Cs- and Sr-containing waste and glass former melter feed simulations. The ECM is a small test melter used to perform preliminary scoping studies to evaluate slurry and glass processing characteristics (Burkholder and Jarrett 1985). The ECM testing was conducted to provide preliminary information on operating procedures and flowsheet processability prior to the PSCM experiment scheduled for the third quarter of FY 1985. The PSCM experiment will verify the processability of a high cesium and strontium glass prior to use in the RLFCM. The PSCM test will identify equipment operating parameters to be followed to optimize the performance of the RLFCM and produce the highest quality glass/canister product.

ECM testing consisted of the evaluation of a melter tank flush procedure and the evaluation of two slurry compositions. An objective of the nonradioactive testing was to demonstrate a procedure to conserve the amount of Cs and Sr required to bring the melt tank contents to the target concentrations. The melter was initially flushed with a chemical batch composition (Table 1). The composition was designed to have acceptable glass physical properties while in the melter alone and when mixed with a composition containing a high concentration of the Cs and Sr waste streams. Physical properties include viscosity, electrical conductivity, and meltability. With this procedure, the RLFCM melt tank glass inventory could be brought up to the target Cs and Sr concentrations without having to consume Cs and Sr during repetitive flushings.

Following the flushing of the ECM melt tank, the tank volume was lowered to 67% capacity. A slurry of the composition shown in Table 2 was then metered to the melter. The slurry contained approximately three times the Cs and Sr waste fractions that would normally exist. The concentrated slurry was fed to the melter over a 6.5-h period

Two slurry compositions were then fed to the ECM in two separate experiments (Tables 3 and 4). The compositions differed only in that zeolite ion-exchange material was present in one slurry to study the effect that zeolite would have on the processability of the slurry. The nonzeolite slurry contained additional unreacted chemicals so that the overall compositions remained identical. Sugar was added to all three feed slurries as a reductant to maintain the glass melt redox within a prescribed range as determined by the ferrous/ferric ion ratio. A ferrous/ferric ratio of 0.1 to 0.3 was attempted. Off-gas sampling was conducted during the experiments to measure particulate and volatility losses.

TABLE 1. Flush Glass Oxide Composition

<u>Oxide</u>	<u>wt%</u>
SiO ₂	53.2
B ₂ O ₃	22.0
Na ₂ O	10.8
Fe ₂ O ₃	14.0

TABLE 2. Concentrated Slurry Composition

Compound	g/L	Assumed Oxide	
		Compound	g/L
$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	176.67	Al_2O_3	24.01
$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	38.25	Fe_2O_3	7.56
NaNO_3	199.42	Na_2O	74.06
		B_2O_3	6.58
H_3BO_3	12.88		
$\text{Ba}(\text{NO}_3)_2$	20.52	BaO	12.04
$\text{Ca}(\text{NO}_3)_2$	29.77	CaO	7.07
$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	27.39	MgO	4.31
CsNO_3	83.93	Cs_2O	57.78
$\text{Sr}(\text{NO}_3)_2$	39.24	SrO	19.22
$\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	21.49	MnO_2	7.20
$\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	1.44	ZrO_2	0.66
$\text{Pb}(\text{NO}_3)_2$	10.28	PbO	6.93
$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	36.86	Cr_2O_3	7.00
$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	11.72	NiO	3.01
$\text{Re}(\text{NO}_3)_3$	19.18	CeO_2	2.94
$\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	25.71	Nd_2O_3	10.68
$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	28.44	La_2O_3	12.00
		Pr_6O_{11}	0.31
SiO_2	85.58	SiO_2	85.58
Na_2SO_4	3.10	SO_3	1.75
Sugar	80.00		
		Total	351.19

These experiments are summarized in Table 5. All three slurry compositions melted well. No differences were noted in processing the nonzeolite versus the zeolite slurries. The cold cap was rigid but thin and melted readily. In all cases, the cold cap disappeared in less than 5 min, and within 1 h the glass surface was clean of any residue.

Off-gas decontamination factors (DFs) for boron and cesium are shown in Table 6. The boron DFs were similar to previous test data on boron volatility.

TABLE 3. Nonzeolite Slurry Composition

Compound	g/L	Assumed Oxide	
		Compound	g/L
$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	61.81	Al_2O_3	8.40
$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	178.51	Fe_2O_3	35.28
NaNO_3	71.13	Na_2O	42.00
$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	90.54	B_2O_3	52.50
H_3BO_3	36.26		
$\text{Ba}(\text{NO}_3)_2$	7.75	BaO	4.55
$\text{Ca}(\text{NO}_3)_2$	11.94	CaO	2.84
$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	11.80	MgO	1.86
CsNO_3	29.38	Cs_2O	20.23
$\text{Sr}(\text{NO}_3)_2$	13.72	SrO	6.72
$\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	7.52	MnO_2	2.70
$\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	0.53	ZrO_2	0.24
$\text{Pb}(\text{NO}_3)_2$	3.58	PbO	2.42
$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	12.90	Cr_2O_3	2.45
$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	4.09	NiO	1.05
$\text{Re}(\text{NO}_3)_3$	6.62	CeO_2	1.02
$\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	9.75	Nd_2O_3	3.74
$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	9.91	La_2O_3	4.20
		Pr_6O_{11}	0.11
SiO_2	157.50	SiO_2	157.50
Na_2SO_4	3.10	SO_3	1.75
Sugar	85.00		
		Total	351.56

The cesium DFs were higher than expected. As a result of these findings, boron and cesium concentrations will be increased above ECM levels during the upcoming PSCM experiment to account for volatility losses.

Feed and glass analytical results are shown in Tables 7 and 8, respectively. The feed density ranged from 1.37 to 1.45 g/mL; and total nitrates ranged from 200 to 400 g/L, with the Cs spike having the highest values. A glass sample from the first glass poured after the Cs spike addition indicated

TABLE 4. Zeolite Slurry Composition

Compound	g/L	Assumed Oxide	
		Compound	g/L
$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	15.45	Al_2O_3	2.10
$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	189.49	Fe_2O_3	33.88
NaNO_3	57.60	Na_2O	39.20
$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	90.75	B_2O_3	52.50
H_3BO_3	32.55		
$\text{Ba}(\text{NO}_3)_2$	8.35	BaO	4.20
$\text{Ca}(\text{NO}_3)_2$	11.79	CaO	2.49
$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	13.36	MgO	1.51
CsNO_3	29.38	Cs_2O	20.23
$\text{Sr}(\text{NO}_3)_2$	13.72	SrO	6.72
$\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	7.52	MnO_2	2.70
$\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	0.53	ZrO_2	0.24
$\text{Pb}(\text{NO}_3)_2$	3.58	PbO	2.42
$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	12.90	Cr_2O_3	2.45
$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	4.09	NiO	1.05
$\text{Re}(\text{NO}_3)_3$	6.62	CeO_2	1.02
$\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	9.75	Nd_2O_3	3.74
$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	9.91	La_2O_3	4.20
		Pr_6O_{11}	0.11
SiO	129.85	SiO_2	133.35
Zeolite IE-96	35.70	Na_2O	2.80
		SiO_2	24.15
		CaO	0.35
		Al_2O_3	6.30
		Fe_2O_3	1.40
		BaO	0.35
		MgO	0.35
Na_2SO_4	3.10	SO_3	1.75
Sugar	70.00		
		Total	351.56

TABLE 5. Operating Summary of ECM-85-4 and ECM-85-5

	ECM-85-4		ECM-85-5
	Cs Spike	Nonzeolite	Zeolite
Total liters	25	140	94
Time, h	6.5	40.3	27.8
% on time	100	100	100
Average feed rate, L/L	3.9	3.4	3.5
Average cold cap coverage, %	70	60	70
Glass production calculation, kg	--	49	32.9
Glass temperature, °C	1115 to 1133	1113 to 1195	1126 to 1190
Power, kW	5.8 to 7.2	5.8 to 7.1	5.8 to 7.2
Resistance, ohms	0.61 to 0.73	0.49 to 0.75	0.61 to 0.91
Off-gas temperature, °C	210 to 290	185 to 330	195 to 295

TABLE 6. Boron and Cesium Decontamination Factors

Feed Type	Boron Decontamination Factor	Cesium Decontamination Factor
Cs spike	8	32
Cs spike	12	66
Average	10	49
Nonzeolite	56	160
Nonzeolite	47	100
Nonzeolite	22	170
Nonzeolite	21	150
Average	37	145
Zeolite	39	260
Zeolite	38	330
Zeolite	38	190
Average	38	260

that the melt tank had not mixed completely. Two hours had been allowed for mixing prior to the start of feeding the nonzeolite slurry. During the PSCM experiment, a longer mixing period will be allowed and the glass homogeneity will be confirmed prior to feeding. Analysis of glass samples after the ECM experiment showed that none of the samples had a ferrous/ferric ratio greater than 0.001. Despite the under-reduced conditions of the melt, no foaming occurred. No crystals were present in polished sections of the glass.

TABLE 7. Feed Analytical Results

	Al_2O_3	B_2O_3	BaO	CaO	CaO_2	Cr_2O_3	Dy_2O_3	Fe_2O_3	La_2O_3	Li_2O	MgO	MnO_2	Na_2O	Nd_2O_3	NiO	PbO	SiO_2	SrO_2	TiO_2	ZrO_2	Co_2O	CuO
Initial Cs spike feed	7.21	2.16	2.89	2.29	0.96	1.99	0.02	2.14	3.46	0.04	1.28	2.93	20.51	2.52	0.85	1.82	24.91	5.35	0.01	0.13	16.53	---
Final Cs spike feed	7.62	2.22	3.01	2.42	1.02	2.11	0.02	2.28	3.67	0.03	1.35	3.11	21.54	2.67	0.91	1.92	21.06	5.68	0.01	0.14	17.21	---
Initial nonzeolite feed	2.61	14.57	1.26	0.95	0.33	0.68	0.01	9.79	1.25	0.03	0.54	1.09	11.68	0.91	0.29	0.65	45.37	1.91	0.01	0.07	5.99	---
Intermediate nonzeolite feed	2.86	14.72	1.36	1.05	0.36	0.75	0.01	10.76	1.37	0.03	0.59	1.20	12.99	1.01	0.32	0.72	40.77	2.09	0.01	0.08	6.40	---
Final nonzeolite feed	3.20	10.31	1.52	1.18	0.41	0.84	0.01	12.10	1.54	0.03	0.67	1.34	14.63	1.13	0.35	0.80	38.19	2.35	0.01	0.09	7.43	---
Initial zeolite feed	2.75	15.07	1.18	0.88	0.32	0.67	0.01	9.77	1.24	0.01	0.50	1.07	11.77	0.90	0.29	0.66	45.30	1.99	0.04	0.07	5.67	0.01
Final zeolite feed	2.61	15.42	1.21	0.90	0.32	0.70	0.01	9.90	1.28	0.02	0.50	1.10	12.25	0.93	0.30	0.67	44.29	2.04	0.03	0.06	5.44	0.01

TABLE 8. Glass Analytical Results

	Al_2O_3	B_2O_3	BaO	CaO	CaO_2	Cr_2O_3	Fe_2O_3	La_2O_3	Li_2O	MgO	MnO_2	Na_2O	Nd_2O_3	NiO	PbO	SiO_2	SrO_2	TiO_2	ZnO	ZrO_2	Cs_2O
Chemical flush composition	0.2	0.04	0.08	0.04	---	---	15.7	0.37	0.24	0.15	---	11.2	---	---	---	51.0	0.01	0.013	---	0.01	---
3rd to last pour flush glass	1.1	19.2	0.12	0.27	0.11	0.51	14.2	1.02	0.14	0.33	0.33	14.9	0.27	0.21	0.17	45.6	0.52	0.04	---	0.22	1.50
1st pour after feeding	2.45	16.37	0.74	0.68	0.26	0.61	12.64	1.18	0.13	0.40	0.87	14.40	0.72	0.37	0.50	42.57	1.53	0.02	0.04	0.13	3.62
1st pour of nonzeolite	2.69	15.34	0.92	0.81	0.30	0.65	11.55	1.18	0.12	0.42	1.01	14.39	0.85	0.40	0.59	41.70	1.80	0.03	---	0.12	5.15
4th pour of nonzeolite	2.69	15.19	0.98	0.85	0.30	0.76	11.16	1.24	0.07	0.50	1.02	13.74	0.85	0.36	0.60	42.58	1.79	0.02	---	0.11	5.27
10th pour of nonzeolite	2.73	14.80	1.16	0.978	0.30	0.79	10.66	1.25	0.047	0.47	1.09	13.25	0.90	0.34	0.63	43.06	1.90	0.02	---	0.09	5.48
15th pour of nonzeolite	2.72	14.75	1.20	0.952	0.30	0.74	10.38	1.24	0.05	0.46	1.08	12.67	0.915	0.33	0.65	43.72	1.91	0.01	---	0.09	5.82
Last pour of nonzeolite	2.70	14.66	1.20	0.93	0.29	0.73	10.43	---	---	---	1.07	12.70	0.90	0.31	0.63	44.30	1.90	0.02	---	0.09	5.37
1st pour of zeolite	2.76	14.50	1.22	0.95	0.30	0.74	10.46	1.26	0.04	0.48	1.09	12.64	0.91	0.32	0.64	43.93	1.93	0.02	---	0.09	5.70
5th pour of zeolite	2.86	14.28	1.17	0.90	0.27	0.68	10.12	1.22	0.04	0.44	1.06	12.21	0.87	0.32	0.63	45.01	1.91	0.03	---	0.08	5.90
Last pour of zeolite	2.77	14.11	1.22	0.90	0.26	0.88	9.89	1.20	0.05	0.41	1.03	12.55	0.86	0.29	0.62	44.81	1.99	0.03	---	0.09	6.01

PSCM Testing

Evaluation of data generated during a PSCM experiment in the last quarter of FY 1984 was completed this quarter. The experiment was conducted within the West Valley Support task during August (PSCM-19) and September 1984 (PSCM-19E). The PSCM-19 test lasted 275 h; most of the test objectives were achieved. PSCM-19E was a 45-h test in which melter tank convection bubblers were tested to improve processing. A total of 8205 L of simulated West Valley slurry was processed in the PSCM during 320 h of testing. At the conclusion of PSCM-19, an extended period of off-gas sampling was performed to quantify emission rates under idling conditions.

The simulated slurry was composed of West Valley waste representing washed sludge, which was acidified with nitric acid, Thorex waste, zeolite ion exchanger (concentration was based on a ion-exchange loading efficiency of 30 column volumes), and glass formers composed of silica, sodium oxalate, sodium tetraborate, and calcium nitrate (Table 9). Other additions to the slurry batch were 0.5 mol/L of nitric acid and commercial sugar. The addition of the nitric acid at this particular concentration was based on an assessment of a logical quantity of acid remaining after acidification of the alkaline sludge. Carbon as oxalate and sugar were added to stabilize the oxidation state of the multivalent elements in the glass melt and thus prevent glass melt foaming or reboiling. Previous laboratory and ECM tests have shown that carbon in these forms can provide a more stable glass batch that is less sensitive to fluctuations in temperature, cold cap coverage, and electrode power.

The major objectives of the PSCM-19/19E experiment were to demonstrate acceptable melting characteristics and to confirm that stable processing conditions could be maintained by controlling the glass melt redox through the use of carbon reductant. Additional objectives of this test were to:

- characterize stable processing conditions of the reference flowsheet
- evaluate the ability of new melter instrumentation to improve melter control and operation
- evaluate off-gas equipment performance and control
- evaluate convection cell stabilization bubblers

TABLE 9. Simulated West Valley Melter Feed Composition

Substituted Waste		Assumed Oxide		Final Glass		
Compound	g/L	Compound	g/L	Oxide	g/L	wt%
Fe(NO ₃) ₃ · 9H ₂ O	158.0	Fe ₂ O ₃	41.51	SiO ₂	156.4	44.7
NaNO ₃	8.9	Na ₂ O	3.64	Na ₂ O	52.8	15.1
Al(NO ₃) ₃ · 9H ₂ O	14.7	Al ₂ O ₃	2.00	B ₂ O ₃	44.4	12.7
Cr(NO ₃) ₃ · 6H ₂ O	12.5	Cr ₂ O ₃	2.38	F ₂ O ₃	43.0	12.3
Ni(NO ₃) ₂ · 6H ₂ O	6.1	NiO	1.58	RE ₂ O ₃	10.2	2.9
Ce(NO ₃) ₃ · 9H ₂ O	14.6	RE ₂ O ₃	10.26	CeO ₂	0.6	0.17
Rare earth	1.7	CeO ₂	0.60	Al ₂ O ₃	8.4	2.4
KNO ₃	0.60	K ₂ O	0.28	CaO	10.5	3.0
CsNO ₃	0.48	Cs ₂ O	0.35	P ₂ O ₅	9.1	2.6
Mn(NO ₃) ₂ · 4H ₂ O	4.9	MnO ₂	1.68	Cr ₂ O ₃	2.38	0.68
ZrO(NO ₃) ₂ · 2H ₂ O	14.7	ZrO ₂	5.88	ZrO ₂	5.88	1.68
NaCl	0.34	--	--	MnO ₂	1.72	0.49
Ba(NO ₃) ₂	0.36	BaO	0.21	NiO	1.58	0.45
FePO ₄ · 2H ₂ O	24.1	P ₂ O ₅	9.14	Cs ₂ O	0.35	0.10
Na ₂ SO ₄	0.87	SO ₃	0.49	K ₂ O	0.60	0.17
RuO ₂	0.28	RuO ₂	0.28	BaO	0.35	0.10
Y ₂ O ₃	0.07	Y ₂ O ₃	0.07	SO ₃	0.70	0.20
Sr(NO ₃) ₂	0.22	SrO	0.11	RuO ₂	0.28	0.08
	263.4		30.5	Y ₂ O ₃	0.07	0.02
				SrO	0.10	0.03
				TiO ₂	0.10	0.03
				MgO	0.35	0.10
					349.9	100.0

Zeolite

Substituted Waste		Assumed Oxide	
Compound	g/L	Compound	g/L
SiO ₂	24.1	SiO ₂	24.1
Al ₂ O ₃	6.5	Al ₂ O ₃	6.5
Na ₂ O	1.3	Na ₂ O	1.3
Fe ₂ O ₃	1.4	Fe ₂ O ₃	1.4
CaO	1.5	CaO	1.5
SO ₃	0.2	SO ₃	0.2
K ₂ O	0.3	K ₂ O	0.3
BaO	0.1	BaO	0.1
MgO	0.4	MgO	0.4
TiO ₂	0.1	TiO ₂	0.1
H ₂ O	4.5		
	40.4		35.9

Glass Formers and Additives

Substituted Waste		Assumed Oxide	
Compound	g/L	Compound	g/L
SiO ₂	132.3	SiO ₂	132.3
Na ₂ B ₄ O ₇ · 10H ₂ O	128.2(a)	B ₂ O ₃	44.6(a)
Ca(NO ₃) ₂	26.3	CaO	9.0
Na ₂ C ₂ O ₂	56.0	Na ₂ O	47.7
Sugar	(b)	--	--
	342.8		233.6
TOTAL	646.6		350.0

(a) Assumes a 5% loss of boron due to volatility.

(b) Sugar concentrations of 0, 42, 57, and 75 g/L were used.

- collect data for developing correlations that relate glass cracking and devitrification to the thermal history of the canister
- collect idling data on off-gas emissions.

One of the two major objectives--to demonstrate processing without melt foaming--was completed. The use of sugar and sodium oxalate as reductants at four carbon levels demonstrated that the redox of the glass could be adjusted to control foaming. In doing so, the glass was quite stable and no foaming incidents were recorded. However, the more reduced glasses appear to have increased the formation of the calcium/rare-earth/phosphate crystals. This crystal formation resulted in the development of an immiscible phase that concentrated at the glass/cold cap interface and severely constricted the fluxing rate of the feed. The maximum processing rate was approximately 20 L/h, which is at least two times lower than previous rates achieved with West Valley waste compositions. In addition, at the end of the test, a heavy layer of this immiscible phase remained on the melter surface and is still present. As a result of the melting problems, the main objective of the test was not satisfactorily achieved.

The major results and conclusions of PSCM-19/19E are listed below:

- The ability of both the air-lift pump and the air displacement slurry (ADS) pump to pump the zeolite-containing feed slurry was demonstrated. The air-lift pump operated at the lower end of its design range, resulting in a unstable flow. The ADS pump functioned well; but the operation was affected by tank head, a phenomena observed during long-term pump testing. Further refinement of the process controller can eliminate this problem.
- The use of sugar and sodium oxalate as reductants demonstrated that redox control of the glass melt will eliminate glass foaming.
- Processing the West Valley composition resulted in an immiscible glassy phase containing rare-earth/calcium/phosphate crystals that collected near the melting surface. These crystals impaired the fluxing of the cold cap and reduced feed rates by as much as 50%.

Some preliminary evidence suggests that crystal phase formation may be worsened by the reduced state of the glass.

- The presence of crystals in the melter outlet glass was not significant. At the maximum reductant level of 10 wt%, crystal formation increased.
- The average bulk glass temperatures were about 1175°C and remained within 40°C of the average to within two standard deviations during steady-state conditions. Manual adjustment of the electrode power was used to maintain this temperature control.
- Melter tank tracer studies indicated that the PSCM tank geometry promotes good mixing with minimal dead space and plug flow characteristics.
- The glass level detector probe performed well in indicating glass level, processing stability, glass specific density, and time to pour.
- Initial testing of the time domain reflectometer indicated that the instrument can distinguish the glass/cold cap interface. Further development is required to increase its reliability.
- The melter viewing system performed very well in maintaining a consistent field of view. The picture quality, however, was poor at reasonable to high cold cap coverage due to limited illumination in the plenum. Remote operation with this system is questionable. A viewing system based on light in the infrared regime may be more appropriate.
- Two convection cell stabilization bubblers were used during PSCM-19E. Melting rates during this test were 20% higher than during PSCM-19. The data are too limited to determine whether the higher rates can be solely attributed to the use of the bubblers.
- The film cooler was effective in preventing excessive solids accumulation in the off-gas jumper. The material that did collect was friable and easily removed.

- Melter vacuum stability was improved with the air injection control system compared to the previous control system based on a downstream, in-line diaphragm-operated valve.
- Backwashing the high-efficiency mist eliminator (HEME) with water effectively cleaned the element of soluble material in less than 10 min.
- The NO/NO_2 ratio in the LFCM exhaust appears to be useful as a real-time indicator of the redox condition of melter glass.
- Process conditions involving a HEME must be carefully controlled to insure operational performance.
- LFCM idling emissions do not produce an inordinate off-gas burden.

Melter Tank Characterization Tracer Study

To determine melter tank characteristics in the PSCM, a tracer study was performed during PSCM-19 using nonradioactive barium and lithium. The initial glass in the PSCM contained 4.6% Li_2O and very low levels of BaO ; the feed contained no lithium and initially contained no barium. On the third day of the test, the feed was spiked with 0.25% BaO . The glass exiting the melter was analyzed for Li_2O and BaO as the study progressed. The data were normalized to account for the variable feed rate during the experiment and transformed into a time distribution function, $F(t)$, for Li_2O and BaO . Time distribution curves are shown in Figures 1 and 2 for Li_2O and BaO , respectively, along with theoretical curves for an ideally mixed melter tank.

Data from the Li_2O test are inconclusive primarily due to the low level of the PSCM glass tank at the start of PSCM-19. The melter was fed for 18 h before the first pour was made, which made it difficult to determine a consistent set of initial conditions for the Li_2O experiment. The data presented in Figure 1, adjusted to account for the initially low glass level, indicate good agreement with the predicted curve for a perfectly mixed tank. However, due to the uncertainty in the initial glass level, it is felt that the barium data provide a more representative picture of the mixing characteristics in the PSCM. The BaO data are quite good because the melter was operated for some time under steady-state conditions before adding the Ba spike. Analysis of the

FIGURE 1. Melter Tank Time Distribution Curves for Li Oxide Concentration

FIGURE 2. Melter Tank Time Distribution Curves for Ba Oxide Concentration

BaO data indicates that the mean residence time in the PSCM during the melter trial was 3.02 days, which agrees very closely with the predicted value of 2.98 days calculated by dividing the melter tank size by the feed rate. The shape of the BaO curve relative to the ideal theoretical curve indicated that the PSCM undergoes some small degree of plug flow, causing the BaO output level to be lower than predicted at the beginning of the experiment and higher at the end of the experiment. The close agreement of the predicted and actual mean residence times indicate that the tank has very little dead volume. Very little volume is available then for crystal growth. The rectangular design of the PSCM appears to be quite adequate for good glass tank behavior.

CONCLUSIONS

Based on the work reported in this quarterly report, the resistive feedback electrode voltage process control system can maintain control of the melter glass temperatures, without operator intervention, during a reboil-type foaming occurrence incurring only a minor temperature excursion.

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CANISTER FILLING AND HANDLING SYSTEMS

D. H. Siemens and R. W. Goles

SUMMARY

The positioning reproducibility of the ^{60}Co gamma ray transmission source associated with the radioactive liquid-fed ceramic melter (RLFCM) level detection was found to be more than adequate to support detection and diagnosis of nonuniform canister glass filling conditions. Count rate variations associated with source positioning uncertainties were typically less than 2%, which is equivalent to the effect produced by a 1/16-in. thick glass absorber. For a 12-in. canister, this absorber thickness corresponds to 0.5% of the total canister cross-sectional fill.

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. The approach used to accomplish these objectives is the development of a canister turntable for canister positioning. The turntable is enclosed in a tank that is sealed to the melter overflow, thus providing the required canister-to-melter seal. Two methods (weight and gamma ray detection) are being developed to monitor the canister glass level during filling. Two canister handling systems have been fabricated and subjected to varying degrees of testing. Both systems are currently installed in their respective locations, where extensive operational testing will be conducted.

TECHNICAL PROGRESS

RLFCM CANISTER LEVEL DETECTION SYSTEM

The RLFCM glass level detection system is composed of a translatable in-cell gamma ray source, out-of-cell gamma ray detection/analysis equipment, and a microprocessor controller/interpreter. Functionally, the microprocessor sequentially positions the gamma ray transmission source adjacent to 11 fixed out-of-cell detectors with the melter canister interposed. At each detector elevation, a 1-min count is automatically initiated; the resulting counting rate is transferred to the microprocessor where the value is compared with a previously established background rate. This comparison serves to establish both the presence of the glass level and the extent of canister cross-sectional fill. Since out-of-cell detector response will be functionally dependent on source positioning as well as interposed glass, the diagnostic abilities of the level system will be limited by source positioning reproducibility. The operational characteristics of the system have been investigated and the results are discussed below.

Operational characteristics of the canister level detection system were tested during the RLFCM-2 test. The data generated by this system during 24 h of uninterrupted service have been partially evaluated. During this 24-h period of surveillance, two glass transfers were conducted, both of which influenced the counting data associated with the first (lowest) canister level. The response of the system to the glass level is summarized in Figure 1. The effective cross-sectional fill at Level 1 after each transfer was calculated on the basis of a glass density of 2.5 g/cm^3 and a canister inside diameter of 12 in.

The counting rate reproducibility associated with each of the 11 detectors was also evaluated over the 48-h test period. These data are shown in Figures 2, 3, and 4 for the 11 levels or detector positions as percent deviation from the mean. Mean values and associated variations were determined only from comparable data. The data associated with Detector 1 (Level 1) were calculated using three separate mean values while all others were based on a single value derived from approximately 260 separate observations. The reproducibility was

FIGURE 1. Level 1 System Response to Two Consecutive Melter Glass Transfers

generally excellent, with most detectors exhibiting count rate variations less than $\pm 2\%$. This variability is, however, much greater than the statistical variations inherent in counting data and, consequently, is a direct measure of positional reproducibility of the source stage.

Figures 5 and 6 characterize the functional relationship between counting rate and source positional displacement from the level reference point for each of the 11 level detectors. Although the data are limited, it is clear that for most detectors positional displacements as small as 0.1 in. have a dramatic effect on counting rate. As a result, the positional reproducibility of the source translator must be, on the average, significantly better than ± 0.1 in.

The larger-than-average variability associated with the data from Detector 2 can be totally accounted for on the basis of its corresponding response function in Figure 5. The reference position for this detector lies between two relative counting rate maxima. Consequently, the detector counting rate for this level would be expected to be much more sensitive to source

FIGURE 2. Counting Rate Reproducibility for Levels 1 through 4

FIGURE 3. Counting Rate Reproducibility for Levels 5 through 8

FIGURE 4. Counting Rate Reproducibility for Levels 9 through 11

FIGURE 5. Source Positional Counting Rate Data for Levels 1 through 6

FIGURE 6. Source Positional Counting Rate for Levels 7 through 11

positional uncertainties than would other levels. However, the variability in the counting rate of Detector 11 cannot be similarly explained on the basis of its positional response function (Figures 5 and 6). Its behavior seems to be linked to glass transfers; that is, the discontinuities associated with Detector 11 are similar to those exhibited by Detector 1 and are coincidental to the glass transfers that occurred during RLFCM-2. One interpretation that would explain the form of these plotted data involves the formation and buildup of glass in the throat of the receiving canister between air lifts, which is subsequently swept away during the glass transfer process. This effect will be investigated in future RLFCM tests.

CONCLUSIONS

The operational characteristics of the RLFCM canister glass level detection system were evaluated. Source positioning reproducibility was excellent and, in most cases, was better than ± 0.1 in. As a result, counting rate variations for most levels were less than 2%. Since a 2% variation in counting rate is equivalent to the effect of a 1/16-in. thick glass absorber, the accuracy of the RLFCM level detection system is more than adequate to detect and diagnose small nonuniformities in the canister glass fill.

OFF-GAS SYSTEMS

R. W. Goles, P. A. Scott, and C. M. Anderson

SUMMARY

Experimental-scale ceramic melter (ECM) testing of the Federal Republic of Germany (FRG) feed formulation was conducted. No significant melter feed processing problems were noted.

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 liquid-fed ceramic melter (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 associated with off-gas processing equipment
- correlating melter exhaust composition with LFCM processing conditions
- identifying and/or monitoring potentially hazardous off-gas situations.

TECHNICAL PROGRESS

Much of the activity this quarter was devoted to planning and evaluating melter tests using high cesium-loaded feeds. An ECM scoping test was used to characterize cesium and boron melter emission rates in preparation for the pilot-scale ceramic melter (PSCM) test to be performed next quarter. The results obtained from ECM testing are summarized in Table 1. During all phases of the testing, cesium loss rates were lower than predictions made prior to the

TABLE 1. Boron and Cesium Decontamination Factors

<u>Sample Period</u>	<u>Feed Type</u>	<u>Decontamination Factors</u>	
		<u>Boron</u>	<u>Cesium</u>
2/12 1600	Spike	8	32
2/12 1900	Spike	12	66
2/12 average	Spike	10	49
2/13 0100	Nonzeolite	56	160
2/13 0700	Nonzeolite	47	100
2/13 1700	Nonzeolite	22	170
2/14 0200	Nonzeolite	21	150
2/13-2/14 average	Nonzeolite	36	145
2/14 2100	Zeolite	39	260
2/15 0200	Zeolite	38	330
2/15 0640	Zeolite	38	190
2/14-2/15 average	Zeolite	38	260

test. Although major differences can exist between small- and large-scale melter tests, ECM cesium decontamination factor (DF) data indicate that most of the cesium will be incorporated in the glass during PSCM processing of the FRG feed formulation.

The ECM boron loss rates were also found to be quite reasonable and agreed with predictions based on previous melter testing. The boron DF data suggest that no special FRG feed preparation problems exist with regard to this glass-forming element.

Preparations for conducting parametric melter effluent emission studies were finalized this quarter. A series of small-scale ECM tests will be conducted to evaluate the effect of feed redox states on melter emission rates of cesium and ruthenium. This series of tests will be initiated during the coming quarter.

CONCLUSIONS

Based on ECM testing of the FRG feed formulation, no special off-gas emission or feed preparation problems should exist during the PSCM-20 melter experiment to be conducted next quarter.

PROCESS/PRODUCT MODELING AND CONTROL

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SUMMARY

Work this quarter included progress on process control algorithms, modeling of temperatures in a canister of glass, and simulation of cracking by experimentation with nonradioactive glass. Initial work on process control algorithms included examination of the extensive pilot-scale ceramic melter (PSCM) data to determine if and how existing process instrumentation can be correlated with observed phenomena in the melter, including cold cap coverage and foaming. Work is under way to apply statistical analyses to the data. Discriminant analysis, a statistical technique that may be used when observations are to be classified into two or more groups, has been applied.

The first phase of a major computer modeling effort on canister temperatures was completed this quarter. The radioactive Federal Republic of Germany (FRG) glass cooling history in a B-Cell environment was simulated using the TEMPEST computer code. A batch filling mode was used with various assumed pouring histories and external heat transfer coefficients (different amounts of insulation).

Nonradioactive canisters of FRG glass were filled during PSCM runs to test the product quality, particularly with respect to cracking. The pouring procedure and amount of insulation were varied during the tests, and each canister was instrumented with thermocouples to monitor the temperatures with time.

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 during this quarter is discussed in the following sections.

PROCESS CONTROL ALGORITHMS

Algorithms are being developed for LFCM process control based on available and developing process instrumentation; tests will be conducted to validate the algorithms. Initial activities included examination of the extensive PSCM run data to determine if and how existing process instrumentation can be correlated with observed phenomena in the melter, including cold cap coverage and foaming. Glass temperatures, measured with a seven-thermocouple thermowell, provide indications of foaming and glass transfers from the melter. Foaming is characterized by increases in temperatures at all levels in the glass melt.

Using glass temperatures to indicate foaming is difficult due to problems in discriminating changes from the normal temperature fluctuations associated

with convection currents in the glass. Therefore, an attempt was made to identify glass temperature profile characteristics that would provide a better indication of foaming. Since glass temperature profiles are roughly parabolic, a second-order polynomial was fitted to the profiles to determine if the coefficients of the polynomial could be used to indicate foaming. While the coefficients did indicate when foaming occurred, they reflected changes at the top and bottom thermocouples more than changes at the other thermocouple levels and as such are not any more valuable than observing only the temperatures. The intensity of the temperature fluctuations was examined to determine if there was any change associated with foaming; no trends were identified.

Work is under way to apply statistical analyses to the PSCM run data to help distinguish between foaming and nonfoaming periods during melter operation. Discriminant analysis is a statistical technique that may be applied when observations are to be classified into two or more groups. Data from the thermocouples (response variables) can be used to obtain a function that is the best discriminator between the foaming and nonfoaming occurrences. If there are many possible response variables, using only those variables that are significant contributors to the discriminatory ability of a function can be accomplished using stepwise discriminant analysis.

The PSCM-11 data were used in the stepwise discriminant analysis. First, erroneous data and data for variables that were directly affected (biased) by operator response to the foaming (power, current, voltage, and feed rate) were deleted. The analysis provided a derived discriminant function that can be used to classify the data as either foaming or nonfoaming.

Another discriminant function was obtained from PSCM-11 data using only those variables available in the PSCM-16 data set. Using this discriminant function, approximately 94% of the PSCM-11 data was correctly classified with respect to foaming. However, when applied to the PSCM-16 data, this function performed very poorly (less than 60% correct). Both data sets were then standardized so that all variables had an average of 0 and a standard deviation of 1. The classification results were similar to those for the unstandardized data.

Because the discriminant function derived from PSCM-11 data did a poor job of discriminating when applied to PSCM-16 data, there was concern about the ability of the function to discriminate well when parameters changed over time. To investigate this concern, the PSCM-11 data were split into two groups: one set contained observations from the first half of the run and the other set contained observations from the second half of the run. The PSCM-11 data were used because it had previously been shown that derivation of a good discriminating function for all of the PSCM-11 data was possible. A discriminant function derived from the first half of the run would be unsuited for parameter changes over time if it classified the first half well and the second half poorly. The discriminant function was derived from the first group and was used to classify both the first and second groups. For the first group, the classification was approximately 96% correct. However, for the second group, the classification was less than 65% correct.

This stepwise discriminant analysis has had only limited success in developing a function using existing process data to distinguish between foaming and nonfoaming in the PSCM. Statistical analyses of the data are continuing, particularly in support of the development of control algorithms.

COMPUTER MODELING AND FRACTURE INVESTIGATION

The first phase of a computer modeling effort was completed this quarter to predict the degree of cracking expected in actual FRG glass and to simulate the expected cracking with nonradioactive glass pours. A computer simulation of the radioactive (28 W/L) FRG glass cooling history in a B-Cell environment was completed; a number of computer simulations of the nonradioactive (0 W/L) cooling histories for FRG canisters over a range of insulation thicknesses were also completed. From this work, two insulation thicknesses were recommended for nonradioactive glass pours that would bracket the expected cooling rates in B-Cell. The nonradioactive PSCM run, scheduled for early next quarter, will use these insulation thicknesses. Several of the canisters are extensively instrumented with thermocouples to determine the actual cooling gradients in the glass. After the glass is cooled, the canisters will be cut open to determine the degree of cracking for the different cooling gradients.

In general, the planned work calls for modeling the change in centerline-to-wall radial temperature differences between the radioactive glass at steady state and the glass as it begins to go through the hardening point (glass wall temperature at 550°C). To physically model radioactive glass fracture using nonradioactive glasses, where the nonradioactive steady-state centerline-to-wall temperature difference is zero, the experiment is designed so that the temperature difference for the nonradioactive glass at the hardening point is equal to change in the temperature difference between hardening and steady-state for the radioactive glass. Previous studies (Peters and Slate 1981) have shown that defense waste glasses and nonradioactive glasses (with little or no decay heat) will not fracture appreciably if centerline-to-wall temperature differences are less than 70°C after the glass has hardened. Extending this idea to waste glasses with high loadings of decay heat, it is expected that the glass will not fracture appreciably if the change in centerline-to-wall temperature difference between the time that the glass starts to harden and the time that it reaches its steady-state temperature profile is less than 70°C. If the difference in centerline-to-wall temperature exceeds 70°C, it is assumed that more cracking will occur but that it will be primarily a function of the difference.

A preliminary computer simulation of the FRG canister in a B-Cell environment was completed and has been reviewed to determine its accuracy. Two major errors were found:

- The emissivities used for stainless steel (0.2 and 0.3) were too low because they did not account for the expected oxidation of stainless steel at the temperatures involved.
- Assuming no air gaps between the canister and the metal in the turntable to simulate the radiation transfer from one metal surface to another should not be used for cylindrical coordinates. Assuming no gaps caused the calculated area of the metal to be too small and falsely increased the calculated heat flux to the metal surface.

In addition, a design change called for a new liner to be placed between the canister overpack and the turntable liner of the B-Cell turntable.

Consequently, a new, larger noded model that includes the new liner, the use of emissivities of 0.5 to 0.7, and uncollapsed but highly conductive air gaps was created to better simulate the transient cooling history in B-Cell. The changes increased the complexity of the model and required a revision to the TEMPEST code (Trent et al. 1983) to increase maximum array size and to include the ability to automatically increase the time step taken by the implicit solution (in a manner that minimizes computational time while avoiding potential inaccuracies caused by radiation heat transfer).

The new computer simulation for the FRG canister using a three-batch filling scheme was run for the 33-h case in the B-Cell turntable (the time at which the canister must be pulled from the turntable). Three alternative versions were also run: the canister and overpack were pulled after 14 h (1 h after filling) and put into one of three insulation modes (uninsulated, 1-in. Durablanket^(a) insulation, and 3/16-in. Durablanket insulation). Throughout the run, temperatures at 14 points in the glass were calculated, representing the glass centerline and wall temperature at seven levels in the glass: the bottom, top, and middle of the first batch; and the top and middle of the second and third batches.

The results of these computer simulations are shown in Table 1. The canister was assumed to be filled with three batch pours of glass. Centerline-to-wall temperature differences are given for a number of locations. For example, "Top, First Batch" refers to a position one-third the distance from the bottom to the top of the glass column of a full canister; "Middle, Second Batch" is located at the center of the canister. Assuming that the canister is placed within an overpack with a minimum of 3/16 in. of insulation, relatively little cracking is expected because the change in the centerline-to-wall temperature difference once the glass hardens (see the third column of Table 1) never exceeds 70°C.

Initially it was planned to bracket the expected cracking in B-Cell in the PSCM run. Since the above-mentioned 70°C temperature difference should produce relatively crack-free glass, an amount of insulation that will give temperature

(a) Registered tradename of the Carborundum Company. Niagara Falls, New York.

TABLE 1. Comparison of Calculated Radial Temperature Differences in FRG Glasses Between the Onset of Hardening and Steady State at Various Glass Levels

Location	Centerline-to-Wall Radial Temperature Differences		Difference
	With Wall at 550°C	At Final Temperature	
Bottom, First Batch	117	66	51
Middle, First Batch	165	100	65
Top, First Batch:		106	
In B-Cell turntable	165		59
Removed, uninsulated	200		94
Removed, 1-in. insulation	--		--
Removed, 3/16-in. insulation	160		54
Middle, Second Batch:		107	
In B-Cell Turntable	162		55
Removed, uninsulated	223		116
Removed, 1-in. insulation	--		--
Removed, 3/16-in. insulation	160		53
Top, Second Batch:		106	
In B-Cell turntable	168		62
Removed, uninsulated	243		137
Removed, 1-in. insulation	--		--
Removed, 3/16-in. insulation	173		67
Middle, Third Batch:		101	
In B-Cell turntable	189		88
Removed, uninsulated	225		154
Removed, 1-in. insulation	--		--
Removed, 3/16-in. insulation	183		82
Top, Third Batch:		50	
In B-Cell turntable	81		31
Removed, uninsulated	82		32
Removed, 1-in. insulation	88		38
Removed, 3/16-in. insulation	82		32

differences in nonradioactive glass similar to those in the third column of Table 1 for the "low cracking case" was chosen. For the "high cracking case," an amount of insulation was chosen that would result in temperature differences similar to the first column of Table 1. In this case, cracking will be similar to that of the radioactive glass after it has fully decayed, assuming no stress relief by creep.

The results of TEMPEST transient cooling simulations of PSCM runs with 3-in., 2-in., 1-in., 1/2-in., and no insulation around the canister are shown in Table 2. Because of time constraints, the TEMPEST simulations were run only to the end of canister filling (13 h) and only the first four levels in the canister were reported. However, as shown in Table 1, the difference in radial temperature gradient was similar through all levels of the canister (ignoring effects at the bottom and top of the glass). As shown in Table 2, the low bracketed temperature difference would occur somewhere between the 2-in. and 3-in. insulation cases, while the high bracketed temperature difference would occur between the uninsulated and 1/2-in. insulation cases. For the low bracketed case, the 3-in. insulation was chosen due to time constraints. For the high bracketed case, a plot of the insulation thickness versus radial temperature difference was made for the middle of the first batch (see Figure 1). The results show that a 1/4-in. insulation thickness would give a radial temperature difference similar to the radioactive case of 165°C.

TABLE 2. Radial Temperature Differences for Various Insulation Thicknesses of Nonradioactive Glass, Cooling Through the Hardening Zone (550°C wall temperature, unless otherwise noted)

Location	Insulation Thickness					Desired Brackets
	3-in.	2-in.	1-in.	1/2-in.	None	
First Batch						
Bottom	109	127	142	163	224	
Middle	<53(a)	<59(b)	70	114	303	<65,165
Top	<63(c)	<76(d)	<97(e)	110	177	<54,160
Second Batch						
Middle	<61(f)	<81(g)	<111(h)	<143(i)	302	<53,160

(a) 616°C wall temperature.

(b) 593°C wall temperature.

(c) 725°C wall temperature.

(d) 699°C wall temperature.

(e) 628°C wall temperature.

(f) 795°C wall temperature.

(g) 769°C wall temperature.

(h) 695°C wall temperature.

(i) 617°C wall temperature.

FIGURE 1. Insulation Thickness Versus Radial Temperature Difference for Middle First Batch of PSCM Glass ($\phi W/L$)

Because of the slow cooling rates expected in B-Cell, the potential for increased devitrification in the glass has become a bigger concern than originally thought. To examine this potential, a somewhat conservative cooling rate simulation of the FRG glass in B-Cell was analyzed for devitrification. Actual PSCM glass melts will be reheated to melting and cooled at the rates given by the computer simulation. It is expected that 10% to 20% devitrification could occur in this glass.

The steady-state profile for radioactive glass could also be used to determine the potential cracking caused by significant temperature gradients that may occur when the canister is immersed in phosphoric acid for decontamination. Currently, plans call for a 150°C phosphoric acid batch to minimize thermal shock, although there are strong operational incentives to reduce this temperature to below 100°C. Steady-state canister wall profiles for the FRG canisters are 85 to 130°C on the bottom, 55 to 75°C at the top, and 54 to 175°C

on the side. Barring any problems caused by glass shock (which may be minimized with the 1/8-in. inner Fiberfrax^(a) insulation blanket), a radial temperature difference of 220°C should be possible without significant cracking in the glass, which may allow for reduction of the phosphoric acid batch temperature to below 100°C.

FRG CANISTER EXPERIMENTATION

The major objective for the FRG canisters filled in the RLFCM was to minimize glass cracking and voids in the canisters. The glass filling rate and canister insulation (glass thermal history) were controlled to define the proper experimental design. A nonradioactive melter experiment was conducted to test a variety of conditions.

The first experimental parameter chosen was the filling rate of the canisters. Continuous pouring of the glass was not an option because of the feed rate limitation for the RLFCM (20 L/h). Batch pouring would minimize the void areas in the canisters. The size of the glass tank in the RLFCM makes it impossible to fill the canisters in one batch pour. Therefore, two filling procedures were chosen to bracket the expected pouring procedure in the RLFCM; these procedures were tested during the nonradioactive run. Filling the canisters in three equal pours would be the largest amount of glass that could be poured by the RLFCM without major melter upset. Six batch pours was chosen as the lower limit of the batch sizes.

The second experimental condition that was varied during the nonradioactive test was the thermal history of the glass. The TEMPEST computer code was used to model the thermal behavior of the glass. To determine the conditions that should be tested during the PSCM experiment, several computer runs were made concerning the nonradioactive cases to determine insulation requirements. Thermal data were collected from thermocouples inside the canisters to support the code. The thermocouples were placed inside four of the canisters to determine temperature profiles at the following points of interest:

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- near the bottom where significant axial temperature gradients are expected
- near the pour interfaces to determine the amount of cooling after filling and the amount of reheating of the glass when the next batch is poured
- at the vertical midpoint of the pours, where possible.

Except for the thermocouples located at the bottom of the canister, all thermocouples were located either on the outer metal surface of the canisters or 1, 2, or 4.25 in. inside the canister wall.

The effect of the turntable on the glass cooling behavior is not well defined. A simulated turntable was constructed for use in the PSCM. The data from the thermocouples within the barriers of the turntable will be used to support the TEMPEST calculations of the turntable thermal behavior. Sixty thermocouples were used inside the simulated turntable and 30 thermocouples were attached to the outside surface of the two canisters filled within the simulated turntable to map the temperature field within the turntable and the surface of the canister.

CONCLUSIONS

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

- Stepwise discriminant analysis has had only limited success in developing a correlation for predicting foaming based on thermocouple data. Good results were obtained when the analysis was applied to data from a single PSCM run (94% of the data was correctly classified as foaming or nonfoaming). However, when the resulting discriminant function was applied to data from a different PSCM run, less than 60% of the data was correctly classified.
- A reduction of PSCM thermocouple data versus position in the molten glass was attempted by fitting the profiles as polynomials, but the results do not appear to be any more useful than the temperature at a given location for monitoring foaming.

- Two insulation thicknesses for experimental pours of simulated FRG canisters are recommended, based on computer simulations of canister temperatures.
- Based on computer simulations of canister temperatures, little or no cracking is expected in simulated FRG canisters, assuming that a 70°C center-to-wall temperature difference is the minimum difference required to cause cracking. This simplistic criterion should be useful for predicting the onset of additional cracking beyond some typical minimum.

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APPENDIX

ACRONYMS AND ABBREVIATIONS

APPENDIX

ACRONYMS AND ABBREVIATIONS

A - angstrom
ADS - air displacement slurry (pump)
Al - aluminum
B - boron
Ba - barium
C - carbon
°C - degree Celsius
Ca - calcium
Ce - cerium
Cl - chlorine
cm - centimeter
Co - cobalt
cP - centipoise
Cr - chromium
CRW - cladding removal waste
Cs - cesium
Cu - copper
DF - decontamination factor
DOE - U.S. Department of Energy
DWPF - Defense Waste Processing Facility
Dy - dysprosium
ECM - experimental-scale ceramic melter
EPA - Environmental Protection Agency
F - fluorine
Fe - iron
FRG - Federal Republic of Germany
ft - feet
FY - fiscal year
g - gram
h - hour
H - hydrogen
HEME - high-efficiency mist eliminator
HLW - high-level waste
HWVP - Hanford Waste Vitrification Program
ICP - inductively coupled plasma (spectroscopy)
in. - inches
K - potassium
kg - kilogram
km - kilometer
kW - kilowatt
L - liter
La - lanthanum
LFCM - liquid-fed ceramic melter
Li - lithium

LLW - low-level waste
 M - molar
 MCC - Materials Characterization Center
 mg - milligram
 Mg - magnesium
 min - minute
 mL - milliliter
 mm - millimeter
 Mn - manganese
 Mo - molybdenum
 MTU - metric ton uranium
 N - nitrogen
 Na - sodium
 NCAW - neutralized current acid waste
 Nd - neodymium
 Ni - nickel
 NRC - Nuclear Regulatory Commission
 NWTPO - Nuclear Waste Treatment Program Office
 O - oxygen
 P - phosphorus
 Pa - Pascal
 Pb - lead
 PNL - Pacific Northwest Laboratory, Richland, Washington
 Pr - praseodymium
 PSCM - pilot-scale ceramic melter
 psi - pounds per square inch
 Rb - rubidium
 RE - rare earth
 Re - rhenium
 Rh - rhodium
 RLFCM - radioactive liquid-fed ceramic melter
 s - second
 S - sulfur
 SA/V - surface area/volume
 SBS - submerged bed scrubber
 Si - silicon
 Sm - samarium
 Sr - strontium
 SRL - Savannah River Laboratory, Aiken, South Carolina
 Te - tellurium
 Th - thorium
 Ti - titanium
 TRUW - transuranic waste
 U - uranium
 wt% - weight percent
 WVDP - West Valley Demonstration Project
 WVNS - West Valley Nuclear Services
 Y - yttrium
 yr - year
 Zn - zinc
 Zr - zirconium

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