LFCM Vitrification Technology

Quarterly Progress Report January - March 1987

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

May 1988

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

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PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE MEMORIAL INSTITUTE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC06-76RLO 1830

Printed in the United States of America
Available from
National Technical Information Service
United States Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161

NTIS Price Codes
Microfiche A01

Printed Copy

Pages	Price Codes
001-025	A02
026-050	A03
051-075	A04
076-100	A05
101-125	A06
126-150	A07
151-175	A08
176-200	A09
201-225	A010
226-250	A011
251-275	A012
276-300	A013

LFCM VITRIFICATION TECHNOLOGY

QUARTERLY PROGRESS REPORT JANUARY-MARCH 1987

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

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May 1988

Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RL0 1830

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SUMMARY

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

Melting Process Chemistry and Glass Development - A composition update of the neutralized current acid waste (NCAW) to be processed in the Hanford Waste Vittrification Plant (HWVP) has been generated. NCAW'86 and its resulting glasses were evaluated to learn what changes to expect in glass and melt properties because of variations in waste composition between it and the reference NCAW'84. Results will provide current input for design and be used for planning studies of glass properties and processing and for identifying potential problems.

An initial evaluation of NCAW'86 was conducted using computer models developed during previous HWVP variability testing to estimate melt viscosity and electrical conductivity for various glass compositions calculated from NCAW'86. Laboratory testing of the simulated waste glasses produced from NCAW'86 was used to confirm computer-based predictions of viscosity and electrical conductivity and to evaluate glass properties not included in the computer models: phase behavior (crystallinity and devitrification), chemical durability, glass transition temperature, and thermal expansion. The NCAW'86 composition produced with the HW-39 reference frit yields acceptable glasses that would be processable within the HWVP.

Feed Preparation and Transfer Systems - The experimental study to evaluate the rheological and physical properties of NCAW simulants was completed and the technical report issued. The study indicated that the updated composition NCAW'86 shows little change (over NCAW'84) in physical properties but shows improved rheology that may allow for processing feeds with higher oxide

concentrations. The test plan for the Evaluation of the Effect of Compositional Variability on the Redox State of HWVP melter feed was approved and testing started. Nine different melter feeds are to be tested in a three-stage experiment.

Melter Systems: Radioactive Testing - The removal of the glass plug in the inner discharge tube between the radioactive liquid-fed ceramic melter (RLFCM) discharge section and the receiving canisters below the melter was completed. Final modifications were completed on the discharge section temporary silicon carbide heaters. The second and third ten-canister campaigns (RLFCM-8 and 9) were completed for the Federal Republic of Germany (FRG). Two FRG canisters for the FRG thermal fracturing tests were fitted with temperature and acoustic-emission sensing devices, transferred to B-Cell, and filled with glass. Operation of the RLFCM was terminated 950 days after radioactive operation began. Design verification testing of the remelt furnace to be used in the FRG thermal fracturing tests was initiated and resulted in minor modifications.

Canister Filling and Handling Systems - During the recent canister-filling campaign PNL conducted for the FRG, stainless steel coupons were installed on certain canisters and later analyzed to provide information on canister contamination during filling. Little contamination occurred when the turntable was vented during pouring. Canister contamination was found to be higher with higher glass temperature. Some contaminated coupons taken from the FRG canisters were later used to demonstrate the Ce(IV) decontamination method being developed for use by the West Valley Demonstration Project. Preliminary results indicate that the Ce(IV) technique will decontaminate canisters sufficiently to meet the waste acceptance standards. Tests with the contaminated coupons are continuing.

Reference conceptual design of the HWVP is nearing completion. PNL recently conducted a preliminary failure mode evaluation of the melter/turntable based on current conceptual design. Potential failures were postulated, and impacts on operations were assessed. This study will provide input into a formal Failure Modes and Effects Analysis.

Process/Product Modeling and Control - A process simulation model (PSM) is being developed based on the vitrification system and control strategy of the West Valley Demonstration Project. Emphasis during the report period was placed on obtaining understanding of how West Valley plans to operate their system and on translating this into a control logic in the simulation. In developing the PSM, previous work on simulating a liquid-fed ceramic melter vitrification system has been reformulated to simplify programming changes.

The failed electrodes of the pilot-scale ceramic melter (PSCM) and their corrosion products have been analyzed. The resulting evaluation suggests the need for design modifications that minimize contact between the glass and the Inconel components at the melt line.

The techniques currently available for melter scale-up were evaluated in terms of melter processing rates. The goal is to provide insight for future designers of glass melters. By comparing rate data from five different melters from laboratory-scale to pilot-scale, with three glass formulations, it was determined that the nominal melt rate can be reasonably correlated to the melter glass surface area.

The topical report Development of a Continuous Liquid-Fed Laboratory-Scale Mini-Melter for Nuclear Glass Development was published.

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INTRODUCTION

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

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

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

Progress in all program elements is reported through informal monthly status reports, formal annual reports (McElroy and Burkholder 1984;

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

Burkholder and Rusin 1985; Burkholder and Jarrett 1986; Burkholder and Brouns 1987), and formal topical reports. Because of both the magnitude of the first-generation high-level waste program element and the large number of applications currently under way, this quarterly report series was begun in FY 1985 to facilitate the transfer of LFCM vitrification technology between and among the central source (PNL) and the various user groups: the West Valley Demonstration Project, the Hanford Waste Vitrification Program, and the Defense Waste Processing Facility Project.

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

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

- Melting Process Chemistry and Glass Development - S. O. Bates
- Feed Preparation and Transfer Systems - M. E. Peterson
- Melter Systems: Radioactive Testing - R. D. Dierks
- Canister Filling and Handling Systems - M. R. Elmore
- Process/Product Modeling and Control - W. L. Kuhn.

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

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MELTING PROCESS CHEMISTRY AND GLASS DEVELOPMENT

S. O. Bates

SUMMARY

A composition update of the neutralized current acid waste (NCAW) to be processed in the Hanford Waste Vitrification Plant (HWVP) has been generated, based on limited analyses of actual waste and on updated flowsheet projections. NCAW'86 and its resulting glasses were evaluated to learn what changes might be expected in glass and melt properties because of variations in waste composition between it and the reference NCAW'84. The results of this evaluation will provide current input for design. These results will be used also for planning future studies of glass properties and processing and identifying potential problems. This work was a limited evaluation of the update of the NCAW composition and not a redefinition of the reference glass composition.

An initial evaluation of NCAW'86 was conducted using computer models developed during previous HWVP variability testing to estimate melt viscosity and electrical conductivity for various glass compositions calculated from NCAW'86. Laboratory testing of the simulated waste glasses produced from NCAW'86 was used to confirm computer-based predictions of viscosity and electrical conductivity and to evaluate glass properties not included in the computer models. These properties included phase behavior (crystallinity and devitrification), chemical durability, glass transition temperature (T_g), and thermal expansion.

The NCAW'86 composition produced with the HW-39 reference frit yields acceptable glasses that would be processable within the HWVP. It would produce a waste form with durability and other properties similar to those of the HWVP reference glass. The NCAW'86 composition would present no significant difficulties in redefining an acceptable HWVP reference glass. If the trend in compositional changes indicated in the updated NCAW composition is

confirmed, frit composition should be adjusted so that viscosity and electrical conductivity of the melt are nearer the center of the HWVP operating ranges. This would give more flexibility in processing to compensate for compositional variability.

INTRODUCTION

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

A key product property is chemical durability. Specifications for chemical durability of waste glass as determined by laboratory tests have not been defined. Existing regulations pertain to radionuclide release from the controlled zone of the repository. Thus a prudent development strategy is to assume that the chemical durability, as measured by laboratory tests, should be as high as possible within the other processing constraints.

The technical approach involves close interaction of feed formulation, glass composition, and waste processing work being conducted at Pacific Northwest Laboratory (PNL). Hence a glass composition is being developed to provide the appropriate high-temperature properties (viscosity, electrical conductivity) and low-temperature properties (elemental release rate, crystallization rate). Nitrate, oxide, and hydroxide chemicals representing the waste fraction and glass-forming chemicals or frit are made into slurries in the laboratory. The redox state of the glass is then optimized using a

reducing agent in the slurries until the ferrous/ferric ratio in the resultant glass is between 0.005 and 0.3.

The melting rates of the feeds are then determined using laboratory melting tests that measure the rate at which the cold cap formed from these feeds melts on molten glass. Several variations are examined, and the feed formulation with the best melting characteristics in this rapid, inexpensive test is recommended for short-term testing in an experimental-scale melter. If problems occur, additional laboratory glass composition or feed formulation work is conducted. A successful short-term test leads to development of an extended test in the pilot-scale ceramic melter or high-bay ceramic melter.

This work has focused on feed and glass developed for the HWVP, which is dedicated to vitrification of the liquid high-level and transuranic defense wastes produced and stored at the Hanford Site. HWVP objectives are to do the following:

- Develop reference glass formulations incorporating the different waste streams to be processed through the HWVP. These glass compositions should have the required physical properties for processing in an LFCM (viscosity, electrical conductivity, and phase behavior) and for 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 simulations of the HWVP reference feeds that represent the true chemical and physical properties of the waste, except for radiation and heat generation, while creating no artificial difficulties.
- Determine ways to modify the rheology of the melter feed to improve homogeneity and minimize transport difficulties.
- Conduct laboratory-scale adjustment studies of feed rheological properties to support testing of feed processing and composition variables, optimization of melter feed, and evaluation of feed processing analytical requirements.

- Document laboratory-scale testing of effects of process and waste composition variability on feed rheological and redox properties.
- Document engineering-scale testing of effects of process and waste composition variability on feed rheological and redox properties.

TECHNICAL PROGRESS

The HWVP will vitrify liquid high-level and transuranic Hanford defense waste to a solid waste form (borosilicate glass) suitable for final disposal in a geologic repository. A reference glass composition has been developed for one of these Hanford wastes, NCAW, to be processed through the HWVP. The current composition, NCAW'84, was issued to PNL by Rockwell Hanford Operations in October 1984.^(a) The NCAW'84 composition was based on flowsheet projections and has been used for 2 years for glass development, slurry feed rheology studies, and melter testing. An updated composition, designated HW-39, has been developed which meets currently established requirements for processing and product quality.

Actual NCAW waste is now available and has been subjected to limited analyses. An updated NCAW waste composition (referred to here as NCAW'86) was generated by Rockwell based on the limited analyses conducted on actual waste and on updated flowsheet projections (Wagner 1986). Its evaluation, including assessment of resulting glass formulations, will indicate potential difficulties in vitrification of the updated NCAW composition and will provide insight into difficulties that might be encountered in processing wastes of varying composition. It is stressed that this investigation was not intended as a redefinition of the reference glass, but as an evaluation of trends in glass and melt properties due to the compositional changes indicated by the updated waste composition.

The objective of this work was to evaluate the NCAW'86 composition and the resulting glasses to determine what changes might be expected in glass

(a) Shah, K. R., letter to J. E. Minor, October 18, 1984, "Recommended (NCAW/CRW Blend) Feed Stream Composition and Range for PNL FY 1985 HWVP Glass Formulation."

properties due to variations in waste composition. The results will provide a better understanding of the glass and melt properties in the final update of the NCAW composition and will identify potential problems.

TECHNICAL APPROACH

The technical approach for this work consisted of three parts: 1) the acquisition of the NCAW'86 composition and the calculation of a simulated waste composition for laboratory studies, 2) a computer evaluation of glasses produced for the NCAW'86 using models generated from previously conducted variability testing, and 3) laboratory confirmations and evaluations of important glass and melt properties.

Updated Waste Composition

The composition of the updated NCAW was received from Rockwell Hanford Operations in November 1986. Using this composition of the NCAW'86 waste, a substituted waste composition was calculated for laboratory glass development and slurry rheology studies (Table 1). Minor components (≤ 0.1 wt% in the waste) and technetium were deleted from the waste. Because no adequate substitute for technetium was identified, it was deleted rather than adding a nonrepresentative substitute. Deleted components total 0.91 wt% of the waste. Uranium was replaced on a molar basis with neodymium to avoid the difficulties of working with radioactive compositions. Waste variability scoping studies have indicated that the effects of U_3O_8 and rare earth oxides on glass viscosity and electrical conductivity are very similar (Bates and Bowen 1986). Neodymium was also used as a substitute for other minor rare earth oxides (except lanthanum) for simplicity. Magnesium was substituted for beryllium on a molar basis because of beryllium's toxicity. These substitutions have been used in previous HWVP glass variability studies.

Table 1 compares the NCAW'86 composition with the reference NCAW'84 composition, where their major differences are highlighted by underscoring. Compared to the NCAW'84 composition, the updated composition was higher in Na_2O and ZrO_2 , but lower in Fe_2O_3 , Al_2O_3 , and Cr_2O_3 . All other oxide concentration differences are too small to be significant in the glass. Table 2

TABLE 1. Updated NCAW Waste Composition, Glass Development Version (with noble metals). All values in oxide wt%.

Oxide	As-Received	NCAW'88 Normalized Waste	Substituted Normalized			Reference NCAW'84 Waste
			Waste	With TOC	No TOC	
Fe ₂ O ₃	28.0	28.0	28.0	28.4	29.0	44.4
Na ₂ O	17.5	17.5	17.5	17.7	18.1	10.7
ZrO ₂	15.0	15.0	15.0	15.2	15.5	2.4
Al ₂ O ₃	10.0	10.0	10.0	10.1	10.3	17.2
SiO ₂	9.00	9.01	9.01	9.12	9.31	2.9
NiO	2.30	2.30	2.30	2.33	2.38	2.3
La ₂ O ₃	2.00	2.00	2.00	2.03	2.07	2.2
TOC	2.00	2.00	2.00	2.03	-	0.6
Nd ₂ O ₃	1.90	1.90	2.21	2.24	2.28	1.7
SO ₃	1.80	1.80	1.80	1.82	1.86	1.8
F	1.20	1.20	1.20	1.22	1.24	1.2
MoO ₃	1.20	1.20	1.20	1.22	1.24	1.2
U ₃ O ₈	0.70	0.70	Sub Nd ^(a)	Sub Nd	Sub Nd	0.6
CaO ₂	0.60	0.60	0.60	0.61	0.62	0.6
Ca ₂ O	0.60	0.60	0.60	0.61	0.62	0.6
CuO	0.60	0.60	0.60	0.61	0.62	0.6
MnO ₂	0.60	0.60	0.60	0.61	0.62	0.6
RuO ₂	0.60	0.60	0.60	0.61	0.62	0.6
Cr ₂ O ₃	0.50	0.50	0.50	0.51	0.52	6.3
BaO	0.40	0.40	0.40	0.41	0.41	0.4
Pr ₆ O ₁₁	0.40	0.40	0.40	0.41	0.41	0.4
SrO	0.40	0.40	0.40	0.41	0.41	0.4
Tc ₂ O ₇	0.40	0.40	Del ^(a)	Del	Del	0.4
CaO	0.30	0.30	0.30	0.30	0.31	0.3
MgO	0.20	0.20	0.36	0.37	0.37	0.2
PdO	0.20	0.20	0.20	0.20	0.21	0.2
Rb ₂ O	0.20	0.20	0.20	0.20	0.21	0.2
Rh ₂ O ₃	0.20	0.20	0.20	0.20	0.21	0.2
Sr ₂ O ₃	0.20	0.20	0.20	0.20	0.21	0.2
Y ₂ O ₃	0.20	0.20	0.20	0.20	0.21	0.2
B ₂ O ₃	0.10	0.10	0.10	0.10	0.10	0.0
BeO	0.10	0.10	Sub Mg	Sub Mg	Sub Mg	0.1
NpO ₂	0.10	0.10	Del	Del	Del	0.1
TeO ₂	0.10	0.10	Del	Del	Del	0.1
K ₂ O	0.05	0.05	Del	Del	Del	-
PbO ₂	0.05	0.05	Del	Del	Del	-
SeO ₂	0.03	0.03	Del	Del	Del	0.03
Am ₂ O ₃	0.02	0.02	Del	Del	Del	0.02
CdO	0.02	0.02	Del	Del	Del	0.02
Eu ₂ O ₃	0.02	0.02	Sub Nd	Sub Nd	Sub Nd	0.02
P ₂ O ₅	0.02	0.02	Del	Del	Del	0.02
PuO ₂	0.02	0.02	Del	Del	Del	0.02
SnO ₂	0.02	0.02	Del	Del	Del	0.02
Ag ₂ O	0.01	0.01	Del	Del	Del	0.01
Gd ₂ O ₃	0.01	0.01	Del	Del	Del	0.01
Nb ₂ O ₅	0.01	0.01	Del	Del	Del	0.01
Pa ₂ O ₃	0.01	0.01	Sub Nd	Sub Nd	Sub Nd	0.01
Ta ₂ O ₅	0.01	0.01	Del	Del	Del	0.01
TiO ₂	0.01	0.01	Del	Del	Del	0.01
Li ₂ O	0.00	0.00	Del	Del	Del	0.00
	99.91	100.00	98.76	100.00	100.00	100.00

(a) Sub = substitute. Del = delete.

TABLE 2. Comparison of HW-43 and HW-39 Glass Compositions

Oxide	Substituted NCAW '86	Frit	wt% Oxide	
			HW-43	HW-39
SiO ₂	9.31	67.26	52.77	51.3
Na ₂ O	18.10	10.26	12.21	10.4
B ₂ O ₃	0.10	12.75	9.59	9.8
Li ₂ O	Del	5.00	3.75	3.8
CaO	0.31	3.75	2.89	2.9
MgO	0.37	1.00	0.84	0.8
Fe ₂ O ₃	28.96		7.24	11.1
ZrO ₂	15.52		9.88	0.8
Al ₂ O ₃	10.34		2.59	4.3
NiO	2.38		0.59	0.8
La ₂ O ₃	2.07		0.52	0.6
Nd ₂ O ₃	2.28		0.67	0.6
SO ₃	1.88		0.47	0.3
F	1.24		0.31	0.3
MoO ₃	1.24		0.31	0.3
U ₃ O ₈	Sub Nd		-	-
CeO ₂	0.62		0.16	0.2
Co ₂ O	0.62		0.16	0.2
CuO	0.62		0.16	0.1
MnO ₂	0.62		0.16	0.2
RuO ₂	0.62		0.16	0.1
Cr ₂ O ₃	0.62		0.13	1.3
BaO	0.41		0.10	0.1
Pr ₆ O ₁₁	0.41		0.10	0.1
SrO	0.41		0.10	0.1
Tc ₂ O ₇	Del		-	-
PdO	0.21		0.05	0.05
Rb ₂ O	0.21		0.05	0.05
Rh ₂ O ₃	0.21		0.05	0.05
Sa ₂ O ₃	0.21		0.05	0.05
Y ₂ O ₃	0.21		0.05	0.05
BeO	Sub Mg		-	-
NpO ₂	Del		-	-
TeO ₂	Del		-	-
K ₂ O	Del		-	-
PbO ₂	Del		-	-
SeO ₂	Del		-	-
Am ₂ O ₃	Del		-	-
CdO	Del		-	-
Eu ₂ O ₃	Sub Nd		-	-
P ₂ O ₅	Del		-	-
PuO ₂	Del		-	-
SnO ₂	Del		-	-
Ag ₂ O	Del		-	-
Od ₂ O ₃	Del		-	-
Nb ₂ O ₅	Del		-	-
Pm ₂ O ₃	Sub Nd		-	-
Ta ₂ O ₅	Del		-	-
TiO ₂	Del		-	-
Total	100	100	100	100

compares the HWVP glass composition, HW-39, with HW-43 glass, which resulted from using the NCAW'86 waste but the same waste loading and frit composition.

Computer Evaluation

For the initial evaluation of NCAW'86, computer models developed during HWVP variability testing were used to estimate the 100-poise temperature (T100P) and the electrical conductivity at 1150°C (E1150) for various glass compositions calculated from NCAW'86. The models used to obtain these estimates were a combination of three models obtained from the Cr_2O_3 , ZrO_2 , and multiple-component variability tests. Because these models were not obtained from a single test, the predictions were viewed as preliminary until validated in the laboratory.

Two approaches were taken in this evaluation. First, the frit composition was modified to produce a glass as close as possible in composition to HW-39, while still maintaining the predicted T100P and E1150 values from the models within the required constraints. Second, the updated waste was mixed with HW-39 frit to produce a glass for characterization and comparison to the HW-39. The model predictions indicated that modification of the frit was not advisable as the major differences in the two wastes were in nonfrit components except for Na_2O . The models predicted also that compositional variations between NCAW'84 and NCAW'86 would negate each other and result in no significant net change in T100P or E1150. The higher T100P due to increased ZrO_2 and decreased Fe_2O_3 appeared to offset the lower T100P due to the increased Na_2O and the decreased Al_2O_3 .

For the second half of the evaluation, a glass composition consisting of a 25 wt% waste loading of NCAW'86 waste and 75 wt% reference frit was calculated and was identified as HW-43. The T100P of the HW-43 glass was estimated to be nearly the same as for the HW-39 glass, 1123°C and 1124°C, respectively. The electrical conductivity of HW-43 was estimated to be slightly higher than that of HW-39, at $0.32 \text{ (ohm-cm)}^{-1}$ compared to $0.28 \text{ (ohm-cm)}^{-1}$.

Laboratory Evaluation

The laboratory testing of the updated waste glasses was used to confirm computer-based predictions of T100P and E1150 and to evaluate other glass properties not included in the computer models. The properties that were evaluated included viscosity, electrical conductivity, crystallinity and devitrification, chemical durability, glass transition temperature (T_g), and thermal expansion.

Because of the lower total concentrations of transition metals in the composition of NCAW'86 compared to NCAW'84, particularly Cr_2O_3 , it was felt that the NCAW'86 waste loading could be increased significantly. The transition metals are the common sources of significant dense phase formation in waste glass melts. The Cr_2O_3 concentration was reduced to 0.5 wt% in NCAW'86 compared to 5.3 wt% in NCAW'84, and the Fe_2O_3 concentration was reduced to 28 wt% compared to 44 wt%. Any increase in the waste loading of the glass would have significant beneficial economic effects by reducing the number of canisters required to contain the vitrified waste. For example, an increase in the waste loading from 25 to 30 wt% would reduce the number of canisters by 17%. In the evaluation of the NCAW'86 waste, waste loadings of 25, 30, and 35 wt% were evaluated. The compositions of these three glasses (HW-43, HW-44, and HW-45, respectively) are shown in Table 3.

Viscosity

Melt viscosity curves were determined for the NCAW'86 glasses and are presented in Figure 1, along with the viscosity curve of an HW-39 glass that was low in Cr_2O_3 (0.13 wt%) for comparison. Viscosity measurements indicated that the T100Ps for the 25, 30, and 35 wt% waste loading were 1086°C, 1078°C, and 1074°C, respectively (see Table 4). This compares well with the 1081°C T100P for the HW-39 with 0.13 wt% Cr_2O_3 present, but is ~40°C lower than HW-39 with the NCAW'84 reference Cr_2O_3 level (1.34 wt% in the glass). The slightly negative effect on T100P with increasing waste loadings of NCAW'86 contrasts with the slightly positive effect of waste loading with NCAW'84 (Schreiber et al. 1986). This is due to the increased alkali and reduced Cr_2O_3 in NCAW'86.

TABLE 3. Compositions of NCAW'86 Glasses and HW-39 Low Cr₂O₃ Glass

Oxide	Substituted Normalized Waste (a)	Frit	HW-43 25 wt%	HW-44 30 wt%	HW-45 35 wt%	HW-39 25 wt%
SiO ₂	9.31	67.25	62.77	49.87	48.97	51.21
B ₂ O ₃	0.10	12.75	9.59	8.98	8.32	9.58
Na ₂ O	18.10	10.25	12.21	12.61	13.00	10.50
Li ₂ O	Del	5.00	3.75	3.50	3.25	3.75
CaO	0.31	3.75	2.89	2.72	2.55	2.89
MgO	0.37	1.00	0.84	0.81	0.78	0.85
Fe ₂ O ₃	28.96		7.24	8.69	10.14	11.77
ZrO ₂	15.52		3.88	4.68	5.43	6.62
Al ₂ O ₃	10.34		2.59	3.10	3.62	4.55
NiO	2.38		0.59	0.71	0.83	0.62
Nd ₂ O ₃	2.28		0.57	0.69	0.80	0.53
La ₂ O ₃	2.07		0.52	0.62	0.72	0.59
SO ₃	1.88		0.47	0.58	0.65	0.40
MoO	31.24		0.31	0.37	0.43	0.32
F	1.24		0.31	0.37	0.43	0.32
CeO	20.62		0.16	0.19	0.22	0.16
Ce ₂ O	0.62		0.16	0.19	0.22	0.16
CuO	0.62		0.16	0.19	0.22	0.16
MnO	20.62		0.16	0.19	0.22	0.16
RuO	20.62		0.16	0.19	0.22	0.16
Cr ₂ O ₃	0.52		0.13	0.16	0.18	0.13
Pr ₆ O ₁₁	0.41		0.10	0.12	0.14	0.11
SrO	0.41		0.10	0.12	0.14	0.11
BaO	0.41		0.10	0.12	0.14	0.11
PdO	0.21		0.06	0.08	0.07	0.06
Rh ₂ O ₃	0.21		0.06	0.08	0.07	0.06
Rb ₂ O	0.21		0.06	0.08	0.07	0.06
Y ₂ O ₃	0.21		0.06	0.08	0.07	0.06
Sm ₂ O ₃	0.21		0.06	0.08	0.07	0.06
Am ₂ O ₃	Del (b)					
P ₂ O ₅	Del					
U ₃ O ₈	Sub Nd (b)					
PuO ₂	Del					
NpO ₂	Del					
SnO ₂	Del					
K ₂ O	Del					
Ag ₂ O	Del					
SeO ₂	Del					
Gd ₂ O ₃	Del					
CdO	Del					
Nb ₂ O ₅	Del					
BeO	Sub Mg					
Pm ₂ O ₃	Sub Nd					
PbO ₂	Del					
Ta ₂ O ₅	Del					
Eu ₂ O ₃	Sub Nd					
Tc ₂ O ₇	Del					
TeO ₂	Del					
TiO ₂	Del					
Total	100	100	100	100	100	100

(a) No total organic carbon.

(b) Del = delete, Sub = substitute.

FIGURE 1. Viscosity Curves for NCAW'86 Glasses of Various Waste Loadings

TABLE 4. Summary of Glass and Melt Properties for NCAW'86 and HW-39 Low Cr_2O_3 Glasses

	HW-43	HW-44	HW-45	HW-39 (Low Cr_2O_3)
T100P, °C	1086	1078	1074	1081
E1150, $(\text{ohm-cm})^{-1}$	0.39	0.44	NA	0.35
Glass Transition, °C	495	487	490	490
Thermal Expansion/°C				
Below T_g (10^{-5})	1.08	1.11	1.07	1.07
Above T_g (10^{-4})	1.08	0.98	0.94	1.06

The computer model predictions for viscosity were lower than the observed values because the model was based on the stronger Fe_2O_3 - Cr_2O_3 interaction present in the reference glass due to the higher concentration of Cr_2O_3 .

If the final update of the NCAW composition also has a similar level of alkali, the increased alkali could easily be compensated for by the reduction of alkali in the frit. This would increase the T100P of the nominal glass composition nearer the center of the 1070 to 1150°C range required for HWVP processing and would allow for more flexibility in the melt viscosity due to composition variability.

A small amount of very fine-grained crystalline material was observed at all three waste loadings. Because the crystals were very small, they had no observable effect on the viscosity of the melt. The phase behavior of the glass compositions are discussed under the heading "Phase Behavior."

Electrical Conductivity

The electrical conductivity of the NCAW'86 glasses HW-43 and HW-44 was measured. The curves are presented in Figure 2 along with the electrical

FIGURE 2. Electrical Conductivity Curves for NCAW'86 Glasses of Various Waste Loadings

conductivity data for the HW-39 (low Cr_2O_3) glass for comparison. The electrical conductivity of HW-45 was not determined, as the glass sample was destroyed due to a furnace malfunction. The electrical conductivities at 1150°C (E1150) for the NCAW'86 glasses and the HW-39 (low Cr_2O_3) glass are shown in Table 4. Even without the HW-45 electrical conductivity measurement, the trend of increasing electrical conductivity with increased waste loading of NCAW'86 was apparent. The increased alkali content in the NCAW'86 was responsible for this increase in E1150 with waste loading. It is possible that, at 35 wt% waste loading (HW-45), the E1150 of the melt could be higher than the $0.5 \text{ (ohm-cm)}^{-1}$ limit set for HWVP processing. However, as stated earlier regarding viscosity, if the final update of the NCAW has higher levels of alkali, these could be compensated for easily by the reduction of alkali in the frit. This would reduce the E1150 of the nominal glass composition nearer to the center of the 0.18 to $0.5 \text{ (ohm-cm)}^{-1}$ range required for HWVP processing and could also allow for increased waste loadings.

Phase Behavior

The phase behavior of the NCAW'86 waste was evaluated in quenched and heat-treated glasses. Thin sections of the glasses were examined using transmitted and reflected light microscopy to first determine the presence of crystalline content. When crystals were observed, the thin sections were examined with scanning electron microscopy/energy-dispersive x-ray (SEM/EDX) for qualitative analysis. Powder portions of each glass were also submitted for x-ray diffraction (XRD) analysis.

Optical evaluation of the quenched NCAW'86 glasses revealed a small amount of very fine grain crystalline material at all three waste loadings. The large amounts of chromite spinel observed in the HW-39 reference glass were not present due to the reduced Cr_2O_3 level in the NCAW'86. The amounts of crystalline material observed were about the same in the HW-43 and an HW-39 low Cr_2O_3 glass, both of which had the same Cr_2O_3 level and waste loading (see Table 3). The amount of crystalline material increased slightly as the waste loading increased in HW-44 and HW-45. Analysis by SEM/EDX indicated that the crystalline phases were composed of ruthenium, rhodium, and palladium. Analysis by XRD could not detect these crystalline phases, indicating

that the amount of each was less than 5 wt%. This was typical of what had been observed in the HW-39 (low- Cr_2O_3) glass using the NCAW'84 waste composition. At melter operating temperatures ($\sim 1150^\circ\text{C}$), noble metals (ruthenium, rhodium, and palladium) are only slightly soluble in borosilicate glasses. Solubility of ruthenium has been observed to be less than 0.001 wt% in borosilicate melts (Schreiber et al. 1986). The ruthenium will usually exist as oxide crystals except under very reducing conditions when ruthenium metal can form. Rhodium and palladium typically remain alloyed in the metallic state. At the current noble metal concentration, it is not known whether the noble metal phases will pose a problem. However, work is currently under way in a separate study to evaluate the impact of noble metals on processing and glass properties.

To evaluate devitrification behavior of NCAW'86 glasses, a heat treatment was conducted on each glass to simulate the canister cool-down conditions. Canister cooling curves (Figure 3) were derived from data generated from the TEMPEST computer code used to model the continuous filling and cooling of

FIGURE 3. Predicted Centerline Canister Cooling Rates of the Open and Closed Canister Turntable Designs

canisters in an open turntable and a closed one (Elmore 1986). The closed turntable curve was used to simulate the conservative case, as greater devitrification takes place with slower cooling rates.

To simulate the cool-down, a furnace was programmed to perform a series of linear cooling rate steps, very closely simulating the model cooling curve. A powdered sample of each glass placed in an alumina crucible was put in the furnace at 1150°C, allowed to melt for 1 hr, and then allowed to cool at the programmed cooling rate. The crucible was then halved vertically; a thin section of the glass was made from one half, and an XRD powder sample was taken from the other.

No significant devitrification was observed (optically or by XRD) in the heat-treated HW-43 or HW-39 (0.13 wt% Cr_2O_3) glass samples. A large amount of devitrification, however, was observed in the HW-44 and HW-45 glasses. The XRD analysis could detect no devitrification products in the HW-43 or HW-39 (0.13 wt% Cr_2O_3) glass samples, but indicated that between 5 and 10% devitrification occurred in HW-44 and HW-45. Analysis by SEM/EDX found two devitrification products. Iron-chromium-nickel spinel crystals were observed to have nucleated off the noble metal crystals. Iron-calcium silicate (pyroxene) crystals were observed to have both nucleated on the spinel crystals and to have homogeneously nucleated, resulting in their independent existence in the melt. The fact that the pyroxenes nucleated on spinel crystals indicates that the spinels formed first, followed by the pyroxenes at lower temperatures. As these devitrification products occur after the glass is in the canister, the observed devitrification presents no processing problems. However, the pyroxenes have been observed to affect the durability of the waste form (Bates and Reimus 1986). Once durability specifications are set, the level of pyroxenes that is acceptable will have to be assessed.

Chemical Durability

To provide a preliminary evaluation of the durability of glasses produced from the NCAW'86 waste, 28-day MCC-1 leaching tests were conducted (Materials Characterization Center 1983). All tests were performed with a surface area/volume of 10 m^{-1} in deionized water at 90°C using quenched and annealed glass samples. So that glasses of different composition can be compared, the

results are given in terms of normalized elemental mass release. This is calculated with use of the following equation:

$$NR_i = m_i / (F_i \times SA)$$

where NR_i = normalized mass release of element i (g/m^2)

m_i = mass of element i in leachate (g)

F_i = fraction of element i in glass (dimensionless)

SA = surface area of monolith (m^2).

Table 5 summarizes the 28-day MCC-1 leach testing results for the NCAW'86 glasses and also presents the results for the HWVP glass, HW-39, for comparison. Based on these test results, the glasses made from NCAW'86 are as durable as the HW-39 glass. The increased ZrO_2 was thought to be the major cause of increased durability, offsetting any decrease caused by the increase of Na_2O in the waste and glass. Any modifications to the frit to adjust the T100P or E1150 nearer the center of the HWVP operation ranges, most likely reduction of Na_2O , should improve glass durability.

TABLE 5. Normalized Elemental Mass Releases from 28-day MCC-1 Leaching Tests for NCAW'86 Glasses. Surface area/volume = $10\ m^{-1}$, $90^\circ C$, in deionized water.

Element	HW-43	HW-44	HW-45	HW-39
Si	11.66	9.97	9.21	12.18
B	16.24	13.51	13.22	14.49
Li	16.60	13.80	13.00	14.94
Na	15.47	13.59	13.05	14.62
Ca	4.48	3.47	2.48	7.13
Mo	15.96	14.99	12.90	NA
Sr	2.96	2.36	1.60	6.19
Al	7.24	7.04	7.04	9.16
Fe	0.30	0.15	0.10	0.46
Cs	16.97	12.24	12.73	17.13
Final pH	9.63	9.63	9.64	9.65

Thermal Properties

The Waste Acceptance Preliminary Specifications for the Defense Waste Processing Facility (U.S. DOE 1986) require that the glass transition temperature (T_g) be reported. Below the glass transition temperature, rearrangement of the glass structure is severely limited, so that the glass structure is essentially independent of time and temperature. Thermomechanical analysis was used to determine the glass transition temperature and the linear thermal expansion coefficient.

During thermomechanical analysis, a glass bar is placed in a furnace and heated at a predetermined rate while the change in sample length versus the temperature of the glass sample is measured. As an annealed glass is heated, some of its properties change sharply in a narrow temperature range. These properties include thermal expansion, electrical conductivity, and heat capacity. The temperature at which these properties change abruptly is the glass transition temperature. For this evaluation, glass bars $\sim 1 \text{ cm} \times 1 \text{ cm} \times 2 \text{ cm}$ were cut from a larger annealed glass bar and were heated at a rate of $20^\circ\text{C}/\text{min}$.

The glass transition temperatures for the NCAW'86 glasses were determined by extending the two linear rates of thermal expansion as shown in Figure 4, which is the thermomechanical analysis curve for HW-43. The intersection of extensions of the two linear rates defines the glass transition temperature. In Figure 4, the rate of the change in sample length with temperature begins to decrease at about 540°C , due to penetration of the probe into the sample, and not to a change in the rate of thermal expansion. The transition temperatures for all the NCAW'86 glasses are about 490°C , the same value as was measured for the HW-39 glass (see Table 4).

The thermal expansion coefficients for the NCAW'86 glasses are given in Table 4. The coefficient of linear thermal expansion is the fractional change of a linear dimension per unit increase in temperature: $(1/l_0)(\Delta l/\Delta t)$, where l_0 is the original length of the sample and Δl and Δt are the changes in the length and temperature, respectively. The low coefficient of linear thermal expansion describes the thermal expansion below T_g , and the high coefficient of linear thermal expansion describes thermal expansion above T_g .

FIGURE 4. Thermal Expansion Curve and Determination of the Glass Transition Temperature for HW-43 Glass Produced from NCAW'86 Waste

Both low and high coefficients of thermal expansion for the NCAW'86 glasses were about the same as for HW-39. Both glass transition temperature and thermal expansion were very insensitive to the composition changes in the NCAW update and present no problem to HWVP processing or product quality.

CONCLUSIONS AND RECOMMENDATIONS

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

- The NCAW'86 composition with the HW-39 reference frit would be processable within the HWVP and would produce a waste form with properties and durability similar to those of the HW-39 glass. This work found the NCAW'86 would present no significant difficulties in redefining the HWVP reference glass once a final update of the waste is obtained.

- Glasses produced from the NCAW'86 waste composition and the HW-39 reference frit composition have acceptable 100 poise temperatures (T100Ps) near the lower HWVP process limit (1070 to 1150°C). The T100Ps ranged from 1086 to 1074°C as the waste loading increased from 25 to 35 wt% oxides. Modification of the frit could easily adjust the T100P nearer the middle of the range.
- Increasing the waste loading of NCAW'86 in the glass from 25 to 35 wt% oxides lowered slightly the T100P of the melt. This contrasts with the slight increase using the reference NCAW'84. This was due to the increased alkali and reduced Cr_2O_3 contents in NCAW'86.
- The electrical conductivity of the melts increases as the waste loading increases, due to the increased alkali content of the NCAW'86. The electrical conductivities of glasses composed of NCAW'86 waste and the HW-39 reference frit are in the upper portion of the range required for processing in the HWVP if the waste loading is maintained below 35 wt%. If required, modification of the frit composition could easily adjust the electrical conductivity of the melt at 1150°C (E1150) nearer the center of the required processing range by compensating for the higher Na_2O levels in the waste.
- At a 25 wt% waste loading, the phase behavior of glass made with NCAW'86 was very similar to a low Cr_2O_3 version of the HW-39 glass. The amount of crystalline material in quenched glass samples was observed to increase slightly as the waste loading increased to 30 and 35 wt% due to the small increase in insoluble noble metals. This increase should present no problems in processing or product quality.
- At a 25 wt% waste loading, the devitrification behavior of glass made with NCAW'86 was very similar to a low Cr_2O_3 version of the HW-39 glass. At 30 and 35 wt% waste loadings, devitrification of the NCAW'86 glasses was significant at simulated closed-turntable canister cooling rates. Further evaluations of the devitrification characteristics and effects need to be conducted if waste loadings of 30 wt% or more are considered.

- Based on 28-day MCC-1 leaching data, the NCAW'86 glass waste form was as durable as, or possibly more durable than, the HWVP reference glass produced from the NCAW'84 composition. The durability of the glass increased very slightly with increased waste loadings. Any modifications to the frit to adjust the T100P or E1150 nearer the center of the HWVP operation ranges should improve glass durability.
- The glass transition temperatures and coefficients of linear thermal expansion were not affected significantly by the changed waste composition in the updated NCAW. Glass transition temperatures for all the tested glasses were $490 \pm 5^{\circ}\text{C}$.
- Because of the increased amount of alkali in the waste fraction of the glass, the processing (melting) rate for an NCAW'86 melter feed composition should be comparable to, or possibly faster than, the rate for the NCAW'84 melter feed.

Based on the work reported here, the following recommendations are made:

- If the trend in compositional changes indicated in the updated composition of the NCAW is confirmed, modification of the frit composition should be undertaken to shift the viscosity and electrical conductivity properties of the melt nearer to the center of the HWVP operating ranges. This would provide additional flexibility in processing to compensate for composition variability.
- Because of the similar effects of the NCAW'84 and NCAW'86 compositions on glass and melt properties, it is recommended that the current glass data base not be updated until further analysis of the actual NCAW is conducted.

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FEED PREPARATION AND TRANSFER SYSTEMS

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SUMMARY

The experimental study to evaluate the rheological and physical properties of neutralized current acid waste (NCAW) simulants was completed and the technical report issued. The study indicated that the updated composition NCAW'86 shows little change (over NCAW'84) in physical properties but shows improved rheology that may allow for processing feeds with higher oxide concentrations.

The test plan for the Evaluation of the Effect of Compositional Variability on the Redox State of Hanford Waste Vitrification Plant Melter Feed was approved and testing started. Nine different melter feeds are to be tested in a three-stage experiment that focuses on controlling redox, rheology and physical properties primarily by additions of formic acid.

NWTP bench-scale heating tank tests using an internal steam coil bundle and an external steam jacket as heat sources were completed. Analytical data will appear in subsequent quarterly reports.

INTRODUCTION

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

TECHNICAL PROGRESS

EVALUATION OF UPDATED HWVP FEED COMPOSITION

The experimental study to evaluate the rheological and physical properties of NCAW simulants was completed and the technical report issued. The first feed stream that will be processed at the Hanford Waste Vitrification Plant (HWVP) is pretreated NCAW. The HWVP will receive an NCAW slurry containing less than 10 wt% solids. This slurry will be concentrated, treated with chemicals that modify the rheological and melting characteristics of the feed, and then mixed with glass-forming frit before being fed to a ceramic melter for vitrification. The specific details of the procedure for feed preparation will depend on the rheological, physical and chemical properties of the feed.

The experimental study conducted in FY 1987 evaluated the physical and rheological properties of an updated composition (NCAW'86) feed simulant. The NCAW'86 composition, defined by Rockwell Hanford Operations late in FY 1986, is an updated version of the HWVP reference feed, which was defined early in FY 1985. During FY 1985 and FY 1986, the physical and rheological properties of the reference feed simulants were extensively evaluated. This work has formed the foundation of the feed-processing data base used for the HWVP design. Rockwell updated the reference composition to the NCAW'86 composition based on component concentration trends observed in FY 1986 characterization data for the aging waste tank and recent flowsheet analyses for NCAW pretreatment. Evaluating the effects of the composition change on basic rheological and physical properties was the basis for this study.

The specific objectives of the study were to 1) determine the rheological and physical properties of slurry simulants prepared according to the NCAW'86 composition, 2) identify the effects of the composition change on these properties, and 3) determine whether these properties are affected significantly, compromising the validity of the existing feed processing data base for the NCAW'86 composition. To meet these objectives, a simulated NCAW'86 feed (HWS9) was prepared and processed by sequential dilution, concentration, forming and further concentration. Rheological and physical

properties, including apparent viscosity, yield stress, pH, density, solids loading and oxide loading, were measured for HWS9 at various processing stages. These data were then compared to rheological and physical property data for an earlier simulant (HWS7), which was prepared based on the reference composition.

The HWS9 and HWS7 compositions are compared in Table 1. The composition change was found to have varied effects on the properties of HWVP feed simulants. The physical and rheological properties for HWS9 are shown in Table 2. The rheological properties of the slurries were significantly affected by the change in composition, whereas the physical properties were affected only slightly. A significant reduction in apparent viscosity and yield stress values was attributed to the changed composition. This effect was observed at all concentrations of both the unformatted and formatted NCAW'86 simulation. Yield stress values were lowest at the higher concentrations where values for the NCAW'86 lab simulation, HWS9, were an order of magnitude lower than values measured on HWS7. Apparent viscosity values followed the same trend: those measured for higher concentrations of HWS9, at a shear rate of 468 sec^{-1} , were as low as 8% of analogous measurements made on HWS7 samples. Figures 1 and 2 compare the rheological properties for the HWS9 and HWS7 compositions. Two factors are suspected of reducing rheological properties. HWS9 contained 33% less ferric hydroxide than did HWS7. Ferric hydroxide slurries are thick, yield-pseudoplastic fluids that are known to dominate the rheology of HWVP feed simulants. Water-soluble salts made up a larger fraction of the solids used to prepare HWS9. The resulting higher ratio of dissolved solids to total solids could account for some of the reduction in rheological property values. An increase in the ratio of fluids-dissolved solids to total solids, with total solids concentration remaining constant, can lead to a reduced yield stress and more Newtonian fluid behavior.

The physical properties of HWS9 were similar to those of HWS7. The ratio of dissolved solids to total solids was slightly higher for HWS9 slurries. The pH values for unformatted HWS9 slurries were similar to those measured on unformatted HWS7 slurries. The pH values for formatted HWS9 slurries appeared to be lower than those measured for formatted HWS7 slurry

TABLE 1. Compositions of Simulated HWVP Reference Feed Batch
HWS7 and NCAW'86 Feed Batch HWS9

Equivalent Oxide	Compound Used	HWS7		HWS9	
		g/L	Desired Oxide Content, wt%	g/L	Desired Oxide Content, wt%
Al ₂ O ₃	Al(OH) ₃	39.13	17.2	24.07	10.5
BaO	BaSO ₄	0.94	0.4	0.97	0.4
CaO	CaF ₂	0.63	0.3	0.65	0.3
CeO ₂	Ce(OH) ₃	1.17	0.7	1.04	0.6
Cr ₂ O ₃	Cr(OH) ₃	10.72	5.3	1.07	0.5
Cs ₂ O	CsOH	1.57	1.0	1.00	0.6
CuO	Cu(OH) ₂	1.10	0.6	1.15	0.6
Fe ₂ O ₃	Fe(OH) ₃	88.44	44.4	58.92	29.3
La ₂ O ₃	La(OH) ₃	0.70	2.2	1.51	2.1
--	LaF ₃	3.21	--	1.80	--
MgO	Mg(OH) ₂	0.63	0.3	0.83	0.4
MnO ₂	Mn(OH) ₂	1.10	0.7	0.96	0.6
MoO ₃	Na ₂ MoO ₄ •2H ₂ O	2.97	1.2	3.18	1.3
--	NaF	2.74	--	1.67	--
--	Na ₂ SO ₄	3.44	--	4.43	--
Na ₂ O	NaNO ₃	19.96	10.7	27.14	18.4
--	Na ₂ C ₂ O ₄	5.01	--	17.41	--
--	NaOH	5.32	--	7.23	--
Nd ₂ O ₃	Nd(OH) ₃	0.70	2.1	3.44	2.3
--	NdF ₃	0.86	--	0.60	--
NiO	Ni(OH) ₂	4.46	2.4	4.49	2.4
Pr ₆ O ₁₁	Pr(OH) ₃	0.70	0.4	0.72	0.4
SiO ₂	SiO ₂	4.46	3.0	14.15	9.4
Sm ₂ O ₃	Sm(OH) ₃	0.31	0.2	0.37	0.2
SrO	Sr(OH) ₂	0.70	0.4	0.75	0.4
ZrO ₂	Zr(OH) ₄	4.62	2.4	30.50	15.7
Y ₂ O ₃	Y(OH) ₃	0.39	0.2	0.39	0.2

TABLE 2. Rheological and Physical Properties Data for NCAW'86 Simulant HWS9

Feed (a)	Yield Stress, dyne/cm ²	Apparent Viscosity, cP			Waste Oxides, wt%	g WO/L	Total Solids, wt%	Dissolved Solids, wt%	Suspended Solids, wt%	Density, g/mL	pH
		183 s ⁻¹	323 s ⁻¹	468 s ⁻¹							
MUA	8.7	11.5	8.1	7.1	12.75	146.6	16.79	4.99	1.80	1.15	12.12
MUB	8.7	10.7	7.6	6.8	12.70	142.2	16.77	4.92	11.85	1.12	12.13
50UA	0.5	2.6	2.1	2.9	4.77	49.6	6.32	1.81	4.51	1.04	11.83
50UB	0.5	2.6	2.2	3.0	4.74	48.8	6.30	1.82	4.48	1.03	11.83
75UA	1.0	2.9	2.7	3.3	7.23	77.3	9.55	2.93	6.62	1.07	11.72
75UB	1.0	2.9	2.4	2.7	7.34	78.6	9.69	2.97	6.72	1.07	11.72
100UA	1.9	4.7	3.9	3.5	9.76	106.4	12.85	3.76	9.09	1.09	11.78
100UB	1.9	4.2	3.3	3.0	9.74	107.2	12.87	3.82	9.05	1.10	11.77
125UA	3.9	6.3	5.1	4.5	11.46	128.4	15.23	4.58	10.65	1.12	11.74
125UB	2.9	5.3	4.5	4.1	11.47	128.4	15.24	4.51	10.73	1.12	11.75
140UA	7.7	10.6	7.8	7.0	13.37	149.7	17.70	4.86	12.84	1.12	11.74
140UB	7.7	11.1	8.4	7.6	13.44	153.2	17.73	5.16	12.57	1.14	11.77
140FA	3.9	7.4	5.7	5.4	13.33	150.6	19.16	6.07	13.09	1.13	4.13
140FB	3.9	6.9	5.4	5.0	13.35	153.5	19.20	6.49	12.71	1.15	4.14
140FC	3.9	7.4	5.7	(b)	13.52	155.5	19.47	5.98	13.49	1.15	4.27
140FO	3.9	7.4	5.7	5.0	13.50	153.9	19.42	5.49	13.93	1.14	4.27
175FA	7.7	11.6	8.7	7.6	15.80	188.1	22.57	6.70	15.87	1.19	4.37
175FB	7.7	11.1	8.1	7.0	15.79	186.3	22.54	5.60	16.94	1.18	4.35
210FA	13.0	18.2	13.5	12.1	18.01	217.9	25.86	8.22	17.64	1.21	4.46
210FB	14.5	18.2	13.9	12.4	18.02	218.0	25.83	8.51	17.32	1.21	4.46
250FA	26.1	29.3	20.2	16.4	19.79	247.4	28.42	8.72	19.70	1.25	4.57
250FB	26.1	28.5	20.2	16.1	19.92	247.0	28.50	8.61	19.89	1.24	4.55
275FA	46.4	48.6	34.1	27.2	22.14	283.5	31.81	9.33	22.48	1.28	4.57
275FB	50.2	50.7	35.9	28.1	22.25	282.6	31.95	9.25	22.70	1.27	4.61
FC	405.7	300.9	194.4	142.4	30.04	426.5	42.93	11.75	31.18	1.42	4.76

(a) Identifying codes are as follows: MU = stock slurry as prepared; U = unformatted; F = formatted; numbers indicate the concentration (grams of waste oxide per liter); the final letter, A, B, indicates replicate subsamples; C and D indicate samples that were heat-treated for 2 hr and are for comparison with A and B, which were not heat-treated.

(b) Fluid reached turbulence in viscometer gap; data at this point is not accurate.

FIGURE 1. Yield Stress Values of HWVP Slurries Prepared from Laboratory Simulations HWS7 and HWS9 Versus Slurry Concentration

FIGURE 2. Apparent Viscosity Values, at 468 sec, of HWVP Feed Slurries Prepared from Laboratory Simulations HWS7 and HWS9 Versus Slurry Concentration

samples, but this difference was almost negligible. The density values for HWS9 samples also appeared to be slightly lower than those measured for HWS7 samples. The ratio of total solids to total oxides was slightly higher for HWS9 than for HWS7 samples, and the ratio experienced a greater increase upon forming for HWS9 samples.

The reduced rheological properties indicate that NCAW'86 slurry simulants have more favorable fluid processing characteristics than the reference feed slurry simulants. These improved properties may allow for processing of melter feeds with higher concentrations of oxide. Rheological data obtained during this study indicate that the existing data base of rheological information generated during FY 1985 and FY 1986 on reference feed simulants cannot be applied directly to NCAW'86 simulants. However, the existing data base will prove to be very conservative if utilized for designing HWVP equipment to process slurries with the same rheological properties as HWS9 and for this reason should be retained. The change in composition did not significantly affect the physical properties of HWVP feed simulants, and the existing feed-processing data base remains valid for the physical properties.

EVALUATION OF THE EFFECT OF COMPOSITIONAL VARIABILITY ON THE REDOX STATE OF HWVP MELTER FEED

The test plan for the Evaluation of the Effect of Compositional Variability on the Redox State of the HWVP Melter Feed was approved and testing initiated. The physical and chemical properties of the HWVP feed will require adjustments to satisfy the melter feed specifications and ensure processability in the feed preparation system equipment. These properties are adjusted by means of chemical additions and reactions in process vessels. The primary adjustments will be made to add glass-forming materials, to improve slurry rheology, to concentrate the slurry, and to control the slurry redox state. Laboratory studies will be required to study the feed's process and compositional parameters. These will be performed by measuring the redox state and the physical, chemical and rheological properties of the feed under varying feed compositions and process adjustments.

Proper redox control is essential for successful operation of the HWVP melter. If the redox state of the feed is oxidizing, the feed can release gases during melting that can cause foaming and destabilization of the melt. If the redox state of the feed is too reducing, metallic or secondary phases can form in the glass melter, which also destabilizes processing. The redox state of the melter feed is affected by the composition of the incoming waste and by adjustments made during feed processing. The current method used to control redox is to add formic acid as a chemical modifier. However, the addition of formic acid or any other chemical modifier may affect the feed rheology. The feed rheology must be evaluated along with redox to verify that the process equipment will operate safely and efficiently.

The objective of this study is to evaluate the effect of compositional variability on the redox state of the prepared melter feed. Compositional variations are expected in the HWVP feed because of difficulty in retrieving and sampling the waste from the double-shell tanks. Therefore, the process must be designed to operate within a range of feed compositions. Current feed compositional variability is based on the acceptability of the glass product. If the actual waste composition is outside the range of compositions set for an acceptable glass product, the composition of the glass-forming frit may have to be changed.

In this study, laboratory-scale experiments will be conducted using nine different melter feed compositions. These compositions represent the range of major component variabilities previously determined to produce acceptable glasses (Bates and Bowen 1986). The primary objective of the experiments is to determine how much chemical modifier must be added to each feed composition to obtain an acceptable redox state. The redox state is currently determined by the ferrous-to-ferric ratio of the feed, with a low value indicating an oxidizing feed and a high value indicating a reducing feed. Studies by Goldman (1985) have determined an acceptable range of ferrous-to-ferric ratios between 0.005 and 0.3 for all borosilicate glasses. Formic acid is the primary chemical modifier added for redox control, but if the formic acid is not sufficient, sugar will also be added. The amount of formic acid or sugar required to achieve an acceptable redox potential must

be determined for various compositional variabilities in the feed. Testing will first determine whether formic acid alone is sufficient to control redox in a particular feed. Then the amount of formic acid and/or sugar necessary to obtain an acceptable redox state will be determined for each feed composition. Adding formic acid and/or sugar to the feed will also affect the feed's rheology. Feed rheology, therefore, must be evaluated along with redox control to verify that the process equipment will operate safely and efficiently. The results of these tests will be used also to determine whether a sugar addition stream is needed in the HWVP feed processing system.

This test is one in a series to evaluate the effect of compositional variability on feed and melter processing. Previous studies have examined the range of compositional variabilities allowed for HWVP glasses (Bates and Bowen 1986) as well as the effect of compositional variability on feed rheology and melting behavior (Farnsworth et al. 1986; Nakaoka et al. 1986).

Feed Compositions to be Tested

The major-component variabilities acceptable for HWVP glasses have been determined by Bates and Bowen (1986) for the glass designated HW-39. Resultant major-component variabilities for the feed were also established based on this work, and Table 3 shows the range. A feed component is determined to be a major one if its concentration is expected to exceed 5%, based on the NCAW'86 feed.^(a) However, a concentration of about 10% of silica in the NCAW'86 feed is not considered significant enough to warrant evaluation.

TABLE 3. Major-Component Variabilities for FY 1986 Reference Feed, Based on Acceptable Glass Component Variability

<u>Oxide</u>	<u>Component Range, %</u>
Fe ₂ O ₃	12.0 - 60.0
Al ₂ O ₃	1.6 - 26.0
Na ₂ O	4.5 - 22.0
ZrO ₂	0.0 - 40.0

(a) Wagner, R. N. 1986. Review of Hanford Waste Vitrification Plant Feed Specification for NCAW Feed. Letter No. 65652-86-062, Rockwell Hanford Operations, Richland, Washington.

As part of this redox control study, nine melter feeds with compositions that encompass the range of major-component variabilities listed above will be prepared at an approximate concentration of 150 grams waste oxides per liter. Eight of these feeds are to be based on the reference feed composition for HW-39 glass, while one feed will be based on the NCAW'86 feed update. The nine melter feeds that are to be prepared are:

1. the nominal reference composition
2. the reference feed composition with a low iron concentration
3. the reference feed composition with a high iron concentration
4. the reference feed composition with a low aluminum concentration
5. the reference feed composition with a high aluminum concentration
6. the reference feed composition with a low sodium concentration
7. the reference feed composition with a high sodium concentration
8. the reference feed composition with a high zirconium concentration
9. the nominal composition for the NCAW'86 feed.

The eight feeds based on the reference composition for HW-39 glass will be prepared with a chromium concentration an order of magnitude lower than that originally given for the HW-39 glass variability study. This decrease is based on the NCAW'86 feed, which gives a reduced chromium concentration (Cr_2O_3 : 0.5 wt%) about 10% of the former level. This decreased concentration in the waste eliminates chromium as a major feed component. The absence of an HW-39 reference feed batch with low zirconium concentrations is also based on the NCAW'86 feed update, which shows zirconium levels about six times higher than previously thought.

Preparation of feeds for this study included proportioning the nitrate content of each feed to the relative concentration of soluble ions (Al^{+3} , Na^+ , Cs^+ , MoO_4^- , F^- , SO_3 and NO_3) also present. The ratio of soluble ions to nitrate ions that was used for all feeds is about 9.86. This ratio was originally determined based on information supplied in the NCAW'86 feed update, which gave a nitrate level of 7.11 g per 100 g waste oxides and a soluble ion level of 70.1 g per 100 g waste oxides.

Because of the compositional variabilities encountered in this study, the use of NaNO_3 as the sole source of nitrates in the feeds (as in the previous test batches) will not be sufficient for some batches. Other nitrate compounds that can be substituted without changing the ratio of soluble-to-insoluble solids are:

- $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ for $\text{Al}(\text{OH})_3$
- CsNO_3 for CsOH .

For these redox control studies, CsNO_3 will be used in place of CsOH . This will afford better control over batch preparation, since the CsNO_3 does not hydrate like CsOH . The remaining nitrates are to be put in as NaNO_3 , provided that the sodium levels are not exceeded. For the reference low sodium batch composition, hydrated aluminum nitrates will be used where too little sodium and cesium is present to allow the nitrates to be put in as NaNO_3 and CsNO_3 .

The compositions for the above nine feeds will also include noble metal oxides (RuO_2 , PdO and Rh_2O_3). These are necessary to evaluate their effect on controlling the redox state of each feed and will also provide information on their effect on feed rheology. Previous laboratory batches have excluded these oxides because of their significant costs. However, with the relatively low masses of noble metals required in this study, their actual cost will be small.

Because of the normalizing process used in setting up the various batch compositions, some of the major component concentrations were somewhat outside the ranges established for HW-39 glass, shown in Table 3. This was noted particularly for the aluminum oxide concentration in the low-iron batch reference. However, the range established for aluminum oxides in the feed is based only on changing aluminum oxide concentration relative to the other components. The difference between the high aluminum oxide concentration in the low iron batch and its applicable range (see Table 3) is seen as too small to require modification.

Feed Preparation and Evaluation

In preparing the feed simulants for vitrification, chemical modifiers such as formic acid and sugar are used to ensure efficient operation. The

feed is modified to 1) achieve an acceptable redox state that prevents metals reduction or excessive off-gas release and foaming in the melter during vitrification and 2) ensure an acceptable rheology for pump mixing and concentrating. Increasing the levels of organic carbon in the feed results in a more reduced state of the melter feed. The rheology of the melter feed is affected by its pH: slurries with low pHs have reduced yield stresses and apparent viscosities.

Experience at PNL has shown that the use of formic acid (HCOOH) as a chemical modifier can reduce the pH of the feed, improving rheology. Adding enough formic acid also provides an acceptable redox state (Farnsworth et al. 1986). However, only the nominal composition of the HWVP reference feed (HW-39 glass composition) has been tested to date.

The laboratory evaluations are divided into three stages. In the first stage, samples of each composition will be processed and characterized after formic acid is added to a pH of 4. Following characterization, those batches found to exhibit acceptable redox states and rheologies will be sampled again. The new samples will be processed and characterized after undergoing formic acid addition to a pH of 6. The level of formic acid addition required to achieve a pH of 4 to 6 has been shown to give acceptable redox states and rheologies to the reference HWVP feed (Farnsworth et al. 1986). In the second stage, the compositions for which the redox state or rheology was not acceptable at a pH of 4 will be further evaluated after more formic acid is added. The third stage of testing is for any compositions still exhibiting an unacceptable redox state. Samples of those will first be formatted to an acceptable rheological level. Sugar will then be added to the melter feed until an acceptable redox state is achieved. Previous PNL experience has shown sugar to effectively control a feed's redox state.

Stage One Testing

Following preparation of the nine feed simulants, stage one testing will commence. In stage one testing, a 250-mL feed sample will be taken from each batch. The samples will then be heated to between 85 and 95°C, and formic acid will be added (under reflux) until the pH is at 4. After formatting, each sample will be boiled under reflux for at least 2 hr. Glass-forming

frit will then be added to each sample until a melter feed composition of 500 grams total oxides per liter is attained (~110 g of frit). Formic acid, equivalent to 1 wt% of the added frit, will also be added to the prepared feed. The samples will then be characterized physically and rheologically before being melted to determine redox state. Results of the rheological characterization and redox state analyses will be used to determine whether adding formic acid to a pH level of 4 is sufficient to control the feed's redox state and rheology. If sufficient, another 250-mL sample will be taken from the particular composition, then processed and characterized after undergoing formic acid addition to a pH of 6. This extra sample will show how sensitive the redox state is to pH.

Evaluation of the redox state of each batch after formic acid additions to pHs of 6 and 4 is based on previous work with a nominal composition of the HWVP reference feed (Farnsworth et al. 1986). Results from this work showed that acceptable feed rheologies and redox states could be attained at either pH. The amount of formic acid necessary to attain these pH levels was about one and two times the determined stoichiometric concentration of formic acid necessary to reduce all mono- and divalent hydroxides (0.092 g HCOOH/g waste oxides). Since a noticeable buffer effect exists upon approaching a pH level of 4, the stoichiometric quantities will be calculated before formic acid is added to the waste. These quantities can aid in adding the formic acid, but should not replace pH measurement.

Stage Two Testing

Stage two testing will be performed only on compositions that do not exhibit an acceptable redox and rheology at formic acid additions to a pH level of 4. In this stage, a 250-mL sample of the particular batch will have more formic acid than was added to the previous two samples. The amount for each particular batch will be determined by the redox state of the pH 4 sample from stage one testing. However, at no point should the amount of formic acid addition exceed nine times the determined stoichiometric amount.

This limit is based on laboratory-scale studies performed by Blair et al.^(a) that indicated excessive off-gassing during melting for formic acid additions equivalent to nine times the determined stoichiometric value. The addition of formic acid and glass-forming frit to the feed will be performed in the same manner conducted in stage one testing. After processing, characterization of the feed will also occur in the same manner as that of stage one. Other samples with different levels of formic acid addition will be evaluated, if necessary.

Stage Three Testing

Stage three testing will be performed only on compositions that did not have an acceptable redox state or rheology at any level of formic acid addition tested. In this stage, a 250-mL sample of each particular batch will be formatted to a pH level of 4. Formatting will be performed in a manner similar to that used during stage one testing. Following a 2-hr reflux, frit (and formic acid) will be added to the formatted feed. Sugar will then be added at a concentration of 3 g/L. This level is based on work performed by Nakaoka et al.,^(b) which showed that sugar levels of 2 to 3 g/L would acceptably reduce the redox state of HW-39 reference glass that had been formatted with a stoichiometric amount of formic acid. The samples will then be characterized. If necessary, batch samples with other levels of sugar addition can be performed.

NWTP BENCH-SCALE HEATING STUDY

Bench-scale heating tank tests using an internal steam coil bundle and an external steam jacket as heat sources were completed. These tests were designed to evaluate the performance of the testing equipment and the

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- (a) Blair, H. T., C. O. Harvey, and D. McCarthy. 1985. Feed Processing Section, February 1985 Monthly Report - HWVP Task V-02. Pacific Northwest Laboratory, Richland, Washington.
 - (b) Nakaoka, R. K., S. O. Bates, M. R. Elmore, R. W. Goles, J. M. Perez, Jr., P. A. Scott, and J. H. Westsik. 1985. Pilot-Scale Ceramic Melter Experiment HWVP-12/PSCM-22, Run Summary. Pacific Northwest Laboratory, Richland, Washington.

efficiency of the steam coil and jacket in heating Newtonian and non-Newtonian fluids in an agitated vessel.

CONCLUSIONS

The evaluation of the updated NCAW composition has led to the following conclusions:

- The change in the NCAW composition resulted in reduced apparent viscosity and yield stress values for all concentrations of both unformatted and formatted HWVP feed simulants.
- Rheological information contained in the HWVP feed processing data base cannot be applied directly to NCAW'86 slurry simulants. However, if the data base were utilized only for design purposes, it would prove to be conservative with reference to NCAW'86 simulant HWS9.
- The change in the NCAW composition had little effect on the physical properties of HWVP feed simulants.
- Physical property information contained in the HWVP feed processing data base is valid when applied to NCAW'86 simulants.
- Treatment with formic acid (forming) to a pH of 4 benefited the rheology of HWVP reference feed simulants more than that of NCAW'86 simulants.
- Heat treatment (after forming) of simulated NCAW'86 slurry for the reference two-hour period had no significant effect on rheological or physical properties.
- NCAW'86 simulants contained a higher ratio of dissolved solids to total solids than did simulations of HWVP reference feed.
- The ratio of total solids to total oxides increased more upon formic acid treatment of NCAW'86 simulants than with HWVP reference feed simulants.

Laboratory studies will be required to study the feed's process and compositional parameters. These will be performed by measuring the redox

state and the physical, chemical and rheological properties of the feed under varying feed compositions and process adjustments. Of primary emphasis is formic acid addition.

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MELTER SYSTEMS: RADIOACTIVE TESTING

R. O. Dierks, L. K. Holton, and J. E. Surma

SUMMARY

The removal of the glass plug in the inner discharge tube between the radioactive liquid-fed ceramic melter (RLFCM) discharge section and the receiving canisters below the melter was completed. Final modifications were completed on the discharge section temporary silicon carbide heaters. The second and third ten-canister campaigns (RLFCM-8 and 9) were completed for the Federal Republic of Germany (FRG). Two FRG canisters for the FRG thermal fracturing tests were fitted with temperature and acoustic-emission sensing devices, transferred to B-Cell, and filled with glass. The operation of the RLFCM was terminated 950 days after radioactive operation began. Design verification testing of the remelt furnace that will be used in the FRG thermal fracturing tests was initiated and resulted in minor modifications to the furnace.

INTRODUCTION

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

An additional objective is to evaluate modifications of melter facility process equipment, first with simulated radioactive feeds in the PSCM and then with radioactive feeds in the RLFCM. The equipment modifications

include feed tank agitation, slurry sampling, glass sampling, feed delivery systems, off-gas treatment systems, process variable sensor development, and process control concepts.

TECHNICAL PROGRESS

RLFCM-8

As reported earlier, the second ten-canister FRG campaign, RLFCM-8, began in late December 1986, and after the first three canisters were filled, the inner discharge tube, the section connecting the melter and the canister turntable and through which the glass stream pours (Figure 1), filled with glass, temporarily suspending melter operation.

The campaign began erratically because feed tended to agglomerate into soft clumps that plugged the feed line and the feed nozzle. A routine water-flushing procedure was established to minimize plugging of the slurry feed system; however, the excess water from the flushing and the high slurry feed rates soon led to cold-cap bridging and pressurized discharges from the melter.

Erratic melter glass weight factor indications were frequently observed together with stable melter glass specific gravity and melter tank pressure indications during this period, generally after feed-line flushing or when feed rates were high. These observations were interpreted to indicate cold-cap bridging, in which the cold cap extends to the melter tank walls and leaves insufficient space for slurry evaporation steam and calcination gases to escape from under the cold cap. Pressurization under the cold cap increases the weight factor indication but does not affect the specific gravity or pressure indications. Sporadic release of these trapped gases through vent holes or cold-cap fissures results in unstable melter weight factor indications.

When the vent holes are sealed by continued high feed rates, or by excessive feed line water flushes, the trapped gas pressures are sufficient to cause unwanted glass discharges. Several stringy, minor pressurized

FIGURE 1. Plugged Melter Discharge Tube

discharges occurred during the start of RLFCM-8, generally causing glass "hair" to accumulate in the canisters and, probably to some extent, above the canisters. Three major pressurized discharges left unwanted glass on the discharge section floor and the walls of the inner discharge tube and probably an accumulation of glass hair in the lower portion of the inner discharge tube.

Glass transfers to the campaign's fourth canister went very slowly, generating some amounts of glass hair. Higher temperatures in the glass and the discharge section eventually permitted a satisfactory glass transfer rate. However, the glass-level detection system that monitored the receiving canister indicated that no glass was accumulating in the canister, and soon a liquid glass surface was seen in the inner discharge tube, confirming the lack of glass flow into the canister. With the discharge tube plugged by glass, the melting operations were terminated.

Several factors contributed to the plugging of the inner discharge tube:

- 1) Heat transfer to the feed slurry was poor, resulting in low glass melting rates, although both sugar and sulfate additions to the feed did improve the melting rate slightly.
- 2) Feed rates were generally higher than the melter could accommodate.
- 3) Sometimes too much water was used in flushing the feed line.
- 4) Occasional high glass discharge rates caused some glass to contact and stick to the inside of the inner discharge tube.
- 5) The frequent low discharge rates resulted in thin glass streams that generated enough glass hair catching onto the glass stuck on walls of the inner discharge tube to form a pocket or "nest." This nest eventually supported and cooled the bottom of the molten pool of glass that plugged the discharge tube.

GLASS PLUG REMOVAL

The RLFCM's original design included several concepts intended to prevent glass accumulation in the discharge tube, or to simplify its removal if it should occur. The inner discharge tube was designed to be cone-shaped, with the inside diameter at the bottom 1 in. greater than at the top. Also it was made of a special steel whose surface oxidized to form a loosely-held scale. These two features combined were intended to minimize the probability of a

plug forming in the discharge tube, and then to minimize the effort to dislodge any glass plug that did form. A glass plug did, however, form in the discharge tube, and several blows with a 60-lb slide hammer failed to dislodge it.

The inner discharge tube fits closely within the outer discharge tube, which is welded to the melter containment floor and is held in place with a set of three cam locks. A remote tool, positionable in any of the turntable thimbles, permits the inner discharge tube to be inserted or removed from the outer discharge tube. The possibility that the cam locks might have been damaged by the operation of the slide hammer precluded its use at this time. There was concern that the removal tool might not release the locks and might be irretrievably jammed into the removal attitude.

The RLFCM was, however, provided with one 4-in. nozzle in the discharge section lid that was on the centerline of the lid and slightly forward of the centerline of the inner discharge tube. This nozzle allowed overhead access to the discharge tube, through which mechanical tools could be brought to bear on any glass plug that formed in the tube. Through this opening the slide hammer was inserted to drive out the glass plug.

A rotary masonry bit was used to drill a small-diameter pilot hole through the glass plug, which was found to be about 18 in. deep. With successively larger diameter bits, the hole was enlarged to about 4 in. in diameter. Bayonet-type silicon carbide electrical heaters, 1-1/8 in. in diameter, with a power output of 6.5 kW, were suspended in the hole drilled in the glass plug, and these successfully melted the remaining glass from the discharge tube. Although most of the glass was removed from the discharge tube, the inside of the tube appeared to be wetted with tacky glass, which with a little glass hair could easily create another plug.

CONTINUATION OF RLFCM-8

RLFCM-8 was resumed late in January 1987 and progressed quickly, filling the remaining six canisters in 9 days. Water-flushing of the feed line was replaced with a feed-flushing technique to minimize sealing of the cold cap.

This technique periodically increased the feed rate by a factor of three by increasing the motive air pressure from the air displacement slurry pump for two or three cycles.

Adding sugar to the cold feed was determined to be ineffective and was discontinued, but the addition of sulfate to the cold feed was continued. This was done to raise the melting rate of the calcined feed and thus minimize the size of the cold cap and subsequent cold-cap bridging problems. However, near the end of the RLFCM-8, glass temperatures and melter tank electrical resistance indicated a molten sulfate layer was present on the glass surface when the cold cap was allowed to melt away. At this point sulfate additions to the cold feed were discontinued, and the only sulfate in the slurry feed was coming in with the radioactive components for the feed.

RLFCM DISCHARGE SECTION HEATERS

The temporary heaters in the discharge section continued to fail as RLFCM-8 was resumed. These failures were attributed to electrical arcing through conductive volatile salts that condensed in the relatively cool nonheating sections of the heaters and to mechanical breakage caused by movement of the in-cell power cables.

The movement of the volatile salts from the discharge section to the cooler upper ends of the heaters was minimized by stuffing the inside of the heaters with a low-density ceramic fiber insulation. The probability of electrical arcing was reduced significantly by increasing the nominal spacing between the two halves of the heaters from 3/32 in. to 8/32 in., with a minimum clearance of 6/32 in.

The probability of mechanical breakage of the heaters caused by movement of the heavy in-cell power cables was eliminated by connecting these cables to the heater power straps through electrically insulated, plug-and-socket power transfer boxes solidly mounted onto the discharge section lid. With this system the in-cell cables remained permanently connected to the transfer boxes while the heater assemblies were connected and disconnected from the boxes as required.

Before the start of RLFCM-9, the three existing temporary discharge section heaters were replaced with three new heaters. The new heaters met the specification for a minimum 6/32-in. gap, they had been stuffed with a low-density ceramic fiber blanket, and they were connected to the power cables through the new power transfer boxes. No further heater failures were experienced.

RLFCM-9

The third FRG canister production campaign (RLFCM-9) was initiated during the first week of March and was completed 3 weeks later. The major problem encountered during this campaign was an increased frequency of off-gas line plugging due to the increased cesium concentration in the feed slurry. Although a rotary chain flail mounted in the melter off-gas nozzle kept this section of the off-gas line clear, the line section leading into the ejector venturi scrubber became a problem. A water-spray technique, later augmented with a rotating cable flail, periodically cleared this line section effectively. In general, operation of the melter system proceeded smoothly during this last campaign.

FRG THERMAL FRACTURING TESTS

Two standard FRG canisters, fitted with identical temperature and acoustic-emission sensor arrays and filled with glass containing heat-emitting nuclides, will be subjected to heating and cooling cycles. Data from these self-heating glasses will be compared with existing data on thermal conductivity of nonradioactive glasses.

During the report period, two standard FRG canisters, Nos. 13 and 19, were fitted with identical arrays of temperature and acoustic-emission sensors. Figure 2 shows the sensor arrays within canister 13 before it was filled with radioactive glass. Canister 19 is identical except that it does not contain the 1/8-in.-thick ceramic liner shown in canister 13. Figure 3 shows an instrumented canister and the cable that carried temperature signals from the glass to the remotely operable, ten-thermocouple connector blocks.

8701813-13CN

FIGURE 2. Instrumented Canister Showing Internal Thermocouples and Acoustic Waveguides

8701813-10CN

FIGURE 3. Instrumented Canister Showing Canister and Instrument Cable

At completion of the third campaign, RLFCM-9, the glass remaining in the melter was diluted with nonradioactive glass-formers. Then the two instrumented canisters were filled with glass having a decay heat specification of about 19 W/L.

Figure 4 shows the remelt furnace that will be used to fuse any cracks present in the glass in preparation for each cooling cycle that results in glass cracking. During the report period the design verification tests on the two-zone remelt furnace were completed. These tests showed that nonisothermal conditions existed in the furnace, due primarily to large heat losses

88A929-1

FIGURE 4. Instrumented Canister Reheat Furnace

from the top and bottom. Modifications to the furnace were completed, including added insulation at the top and bottom and the installation of a thermal baffle device in the annulus between the canister and the furnace wall.

RLFCM SHUTDOWN

Power to the RLFCM electrodes was terminated on March 30, 1987, at 0810 hours, approximately 950 days after conduction was realized on August 16, 1984, at 0400 hours during the melter startup procedure.

CONCLUSIONS

Cold-cap bridging can be detected from indications of glass-tank weight factor. Cold-cap bridging can cause inappropriate pressurized glass discharges from a melter.

Bayonet-type silicon carbide heaters fail due to the condensation of volatile, electrically conductive salts on their nonheating sections. They can be made less susceptible to failure by filling the inside of the nonheating sections with a low-density ceramic fiber insulating material and increasing the gap between the two halves of the heater elements.

In the design of glass-melting facilities, consideration should be given to the possibility of glass hair accumulations obstructing the free flow of glass into the receiving canister, to detecting the loss of flow into the canister, and to remote means for removing these obstructions.

from the top and bottom. Modifications to the furnace were completed, including adding insulation at the top and bottom and the installation of a thermocouple device in the annulus between the catalyst and the furnace wall.

ALFON SHUPOMAN

Power to the ALFON electric motor was terminated on March 30, 1985, at 0800 hours; approximately 900 days after construction was initiated on August 15, 1983, at 0400 hours during the reactor starting procedure.

CONCLUSIONS

Gold-cap bridging can be detected from indications of glass-tank height factor. Gold-cap bridging can cause inappropriate pressurized glass changes from a reactor.

Reactor-type silicon catalyst behavior will due to the condensation of volatile, electrically conductive salts of their nonreacting reactants. They can be made less susceptible to bridging by filling the inside of the nonreacting sections with a low-density, electrically insulating material and increasing the gap between the two layers of the heater elements.

In the design of glass vessels for liquid, consideration should be given to the possibility of glass tank wall cracking obstructing the flow of glass into the receiving container and detecting the loss of flow into the reactor, and to rotate means for removing these obstructions.

CANISTER FILLING AND HANDLING SYSTEMS

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SUMMARY

Reference conceptual design of the Hanford Waste Vitrification Plant (HWVP) is nearing completion. Pacific Northwest Laboratory (PNL) recently conducted a preliminary failure mode evaluation of the HWVP melter/turntable based on the current conceptual design of that system. Potential failures were postulated, and impacts on operations were assessed. As part of this evaluation, a limited operational analysis of the turntable was performed to evaluate the potential for pouring glass from the melter at the wrong time (such as pouring glass into a thimble position not containing a canister, overflowing an overfilled canister, etc.). Design features were identified that would limit the potential for this type of problem, and a logic chart was developed to illustrate possible interactions of those features with operational control of the turntable. This study will provide input into a formal Failure Modes and Effects Analysis recommended to be performed near the beginning of definitive design for the plant.

As molten glass is poured from a melter into a waste canister, radioactive aerosols evolve from the glass stream. These aerosols cool and condense and can contaminate the outer surface of a waste canister. Contamination on the exterior of a canister then creates a problem for subsequent canister decontamination, welding, storage, and shipping operations. During the recent canister-filling campaign PNL conducted for the Federal Republic of Germany (FRG), stainless steel coupons were installed on certain canisters and later analyzed to provide information on the extent and characteristics of canister contamination acquired during filling. Little contamination (primarily cesium) was deposited on the coupons when the turntable was vented during glass pouring. Canister contamination was found to depend mostly on glass temperature; the higher the glass temperature, the more contamination accumulated on the coupons.

Some contaminated coupons taken from the FRG canisters were later used to demonstrate the Ce(IV) decontamination method being developed for use at West Valley Nuclear Services. The coupons were first counted for initial gamma activity. Various decontamination schemes were applied, and the coupons were then recounted to determine decontamination factors. The calculated overall cesium decontamination factor ranged up to 2040 using the Ce(IV) technique. Preliminary results indicate that the Ce(IV) technique will decontaminate canisters sufficiently to meet the waste acceptance standards. Similar testing is continuing on additional contaminated coupons.

INTRODUCTION

The objectives of this work are to develop and demonstrate systems to position waste canisters under the melter glass discharge, monitor glass level in the canisters during filling, seal and leak-test the canisters, and decontaminate the canister exteriors. Activities during this quarter included: a failure modes evaluation of the conceptual design for the HWVP melter/turntable system; a study of canister contamination occurring during canister-filling operations in the B-Cell turntable; and a demonstration of the Ce(IV)/HNO₃ canister decontamination process planned for use at West Valley.

TECHNICAL PROGRESS

CANISTER TURNTABLE DESIGN EVALUATION

For the HWVP and the West Valley Demonstration Project, a turntable is used to position the canisters under the melter. The carousel is enclosed in a tank sealed to the melter, thereby providing the required canister-to-melter seal without connecting each individual canister to the discharge chamber during filling and subsequent cooldown.

Throughout the design of a system such as the melter/turntable, potential deficiencies and hazards associated with the design need to be reviewed. In particular, effective, reliable, and safe equipment must be designed to eliminate these deficiencies or hazards. One technique used to accomplish such a

review is a Failure Modes and Effects Analysis. As a precursor to such an analysis, a need was determined for a preliminary review of possible failures in the HWVP melter/turntable system, based on review of the current conceptual design. The purpose of this evaluation was fivefold:

1. Identify potential component failures associated with the melter/turntable system.
2. Describe the means for detecting indications of component failures.
3. Outline preventive features that have been designed into the current system to eliminate or minimize the probability of a component failure.
4. Identify proposed recovery schemes should a specific component failure occur.
5. Assess the potential adverse impact of a failure on waste processing operations.

A milestone report Preliminary Melter/Turntable Failure Mode Evaluation for the Hanford Waste Vitrification Plant (HWVP-87-V110402E) was issued summarizing the results of this review. Various potential failures were postulated and evaluated, and their degree of impacts to continued operations ranged from insignificant to "requiring replacement of the melter or turntable." Presently undecided issues in technology development that might modify the design of the melter/turntable, and therefore the results of this evaluation, were also summarized.

As a supplement to this study, PNL was requested to perform a partial operational evaluation of the melter turntable. The scope of this evaluation was to determine the following:

- Can glass be poured into a canister position in the turntable that does not contain an empty canister?
- If so, what mitigating features are incorporated into the design to preclude this from happening?
- What would be required to recover from this type of problem should it occur?

The evaluation concluded that without certain features in the design, glass could be poured inadvertently into a canister position not containing an empty canister. Because of this potential, four features that would minimize the potential for, and impact of, this type of problem have been incorporated into the HWVP design:

- A gamma-level detection system to monitor the level of glass in a canister as it is filled.
- A load cell to transmit the weight of the thimble, liner, and canister to determine whether a canister is in the thimble, and whether it is empty, partially filled, or full.
- A linear variable differential transmitter to indicate which carousel position is under the glass discharge, and whether it is accurately centered under the discharge port.
- Visual verification of the carousel position through the access port cover to indirectly indicate that the thimble position under the glass discharge is accurately centered.

As a result of this review, another feature is being considered for the turntable design to increase the reliability of canister positioning: a thimble source position detector to signal the proper alignment of each canister thimble with the melter discharge.

If glass were poured outside the waste canister, the primary protective features are liners between the canisters and thimbles and the turntable enclosure. The liners are removable to permit replacement with clean ones and continue operation. If glass were somehow poured into the turntable between the canister positions, glass would then be contained by the turntable vessel itself, thereby minimizing the spread of contamination into the cell.

CANISTER DECONTAMINATION

As molten glass is poured from a melter into a waste canister, radioactive aerosols evolve from the glass stream. These aerosols cool and condense, and can contaminate the outer surface of a waste canister, creating a problem

for subsequent canister decontamination, welding, storage, and shipping operations. The effectiveness of canister decontamination can be optimized only when the characteristics of the contaminants are known.

Numerous studies have focused on the volatility characteristics of borosilicate glass components. Several of these studies have observed cesium to have the highest volatility of the glass components, which is of concern in subsequent contamination control. No study was found, however, that seeks to quantify and characterize volatile materials condensing on waste canisters or how process parameters affect their deposition.

A study has been initiated at PNL to characterize the amounts and composition of contamination occurring on the exteriors of canisters filled with radioactive waste glass. During the recent FRG canister-filling campaign conducted at PNL, stainless steel coupons were installed on both vertical and horizontal exterior surfaces of certain canisters. These canisters were then placed in the sealed turntable enclosure, which was vented to the off-gas system during pouring. The coupons were to provide samples from which information could be obtained on the extent and characteristics of canister contamination acquired during filling.

Initial coupons were removed from the canisters before being placed in the turntable to determine the contribution of airborne cell contamination to the total accumulation on the canisters. The remaining coupons were inserted with the canisters into the turntable. After the canisters were filled and removed from the turntable, the coupons were removed remotely and placed into bottles for later counting of gamma activity. Examination of the contaminated coupons yielded the following preliminary conclusions:

- Only a relatively small amount of contamination was deposited on the coupons when the turntable was vented during glass-pouring.
- Most of the contamination occurred as water-soluble compounds. The primary elemental component of the contamination was cesium.
- No significant pattern of contaminant condensation was noticed on coupons placed in various locations on the canisters. There were

some indications of declining contamination levels with increasing distance from the canister mouth, as might be expected.

- Canister contamination was found to be mostly dependent on the molten glass temperature; the higher the glass temperature, the more contamination that accumulated on the coupons. Other factors, including relative pour-surface area, process upsets, and residual turntable and cell contamination, were found to have little or no effect on contamination levels on the coupons.

Following analyses of the coupons for quantities and characteristics of the contamination, a program was initiated to evaluate the effectiveness of a Ce(IV)/nitric acid solution as a canister decontamination agent. The Ce(IV) solution had been shown earlier to be effective at chemically milling the surface of stainless steel, similarly to the electropolishing process, but without the aid of an applied electrical current. The contaminated coupons from the B-Cell operations provided the opportunity to evaluate the effectiveness of the process under radioactive conditions.

After receipt and initial counting of the coupons, each specimen was soaked in distilled water at 25°C for 1 min, air-dried, weighed, and recounted. Two of the coupons were then further decontaminated by soaking in nitric acid solution or nitric acid/Ce(IV) solution.

The initial coupon activity varied from 10^7 to 10^{10} disintegrations per minute per 100 cm^2 of surface. Decontamination factors for the initial water soak ranged from 3 to 44. Later smear tests of the water-soaked coupons showed that all were greater than waste acceptance standards of <2200 dpm beta-gamma/ 100 cm^2 . Decontamination factors for the nitric acid solution and Ce(IV)/nitric acid solution washes were around 2000. Only the coupon treated with the Ce(IV) solution had smearable beta-gamma contamination levels low enough to meet waste acceptance standards as determined by smear-testing. Further investigation of the Ce(IV)/HNO₃ decontamination process is now being conducted.

PROCESS/PRODUCT MODELING AND CONTROL

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SUMMARY

A process simulation model (PSM) is being developed under the Nuclear Waste Treatment Program (NWTP) to demonstrate the role of mass balance computations in the Pacific Northwest Laboratory (PNL) approach to waste-form qualification. The simulation is being based on the vitrification system and control strategy of the West Valley Demonstration Project because significant exchanges of technical information regarding this system already occur as part of PNL's West Valley Support Task under the NWTP. Emphasis during the past report period was placed on obtaining an understanding of how West Valley plans to operate their system and on translating this into a control logic in the simulation.

In developing the process simulation model, previous work on simulating a liquid-fed ceramic melter (LFCM) vitrification system has been reformulated to simplify programming changes to the simulation. This approach allows all subroutines to be written in a form that makes the "physics" of the simulation evident. This facilitates interpreting and maintaining the FORTRAN subroutines and makes them independent of the number and arrangement of tanks and connecting streams that constitute the process.

An analysis of the failed electrodes of the pilot-scale ceramic melter (PSCM) and their corrosion products indicates that the electrode bus connection welds may have failed due to a combination of chemical and mechanical effects. The evaluation of PSCM electrode corrosion suggests that although Inconel 690 has excellent corrosion resistance to defense waste glass, corrosion at the melt line in stagnant regions is a significant concern. Future melter designs should address this problem by placing the electrodes in the walls or by other design modifications that minimize contact between the glass and the Inconel components at the melt line, especially in the area between the electrodes and the wall.

A study was conducted to evaluate the techniques currently available for melter scale-up with respect to melter processing rates. The goal of the study was to provide insight for future designers of glass melters by evaluating processing data from several sizes of melters using different scale-up techniques and models. By comparing rate data from five different melters from laboratory-scale to pilot-scale, with three glass formulations, it was determined that the nominal melt rate can be reasonably correlated to the melter glass surface area.

A topical report entitled Development of a Continuous Liquid-Fed Laboratory-Scale Mini-Melter for Nuclear Glass Development was published describing the development and initial testing of the liquid-fed mini-melter.

INTRODUCTION

The principal objective of this work is to demonstrate and document a technical approach to waste-form qualification. However, special attention is being given to the applicability of the technical approach to the West Valley Demonstration Project. A technical approach has been developed that calls for development of product and process models as means for relating product quality to process measurements. Because the NWTP is not responsible for qualifying a specific vitrification process, its contribution is principally to provide and demonstrate waste-form qualification methodology in a manner that will assist waste-form producers to develop their waste-form qualification reports.

The process models consist of a mass balance model predicting the glass composition and a thermal model predicting the temperature history in glass poured into a canister. Work on product models is limited to integrating general relationships between the composition and the durability of a glass and between the extent of devitrification and the temperature history of a glass into the process model. Work on process and product models is described below.

TECHNICAL PROGRESS

PROCESS MODELING

A process simulation model (PSM) is being developed under the NWTP to demonstrate the role of mass balance computations in the PNL approach to waste-form qualification. Previous work on simulating an LFCM vitrification system was described during FY 1986 in the report Demonstration of an Approach to Waste Form Qualification Through Simulation of Liquid-Fed Ceramic Melter Process Operations. At that time the simulation activities were implemented using the commercial simulation software package "SIMAN." We are continuing to use SIMAN but have changed the approach slightly, circumventing some of the SIMAN options by writing our own replacement FORTRAN subroutines. This has been done to simplify programming changes to the simulation; the tanks and streams of the process are now described using names in an input file rather than being coded directly into FORTRAN subroutines and identified by positions in variable arrays in SIMAN, as was done previously.

A key part of a simulation using SIMAN is the "STATE" subroutine, which is written by the user and is called by SIMAN in order to compute values of the time derivatives of state variables. SIMAN requires the derivatives to be supplied in the form of a one-dimensional array corresponding element by element to its one-dimensional array of numbered state variables. In our simulation, the state variables are the masses of individual components in individual phases in each tank. However, we treat the masses, volumes, etc., separately from the numbered SIMAN state variables, and then translate our "physical" state variables into SIMAN's one-dimensional numbered state variable array as needed. The derivatives of the masses are computed by a set of subroutines called by STATE in which a three-dimensional array is used to describe the masses, where the array dimensions correspond to tank, component (e.g., silica, water, boron, iron, etc.), and phase (e.g., water, dissolved solids, suspended solids, settled solids, etc.).

The subroutines consider changes in masses caused by flow into and out of streams, precipitation, resuspension, and settling. Any separation of components can be specified in terms of the partial acceptance of different phases

upon entrance into a stream (e.g., only the "water" phase enters the condensate stream during an evaporation step), or in terms of the distribution of components among the various phases upon exiting from a stream into a tank (e.g., classifying molten glass in the melter as the "solid" phase and distributing none of the water to this phase). The causes of any settling, resuspension, or caking of solids are currently not modeled, but rather are treated as processes whose rate and criterion for occurrence (e.g., randomly) must be specified by the programmer. The volumes of slurry (or glass, or cold cap, etc.) in tanks can be computed from phase densities. This approach allows all subroutines to be written in a form where the "physics" of the simulation is evident. This facilitates interpreting and maintaining the FORTRAN subroutines and makes the FORTRAN subroutines independent of the number and arrangement of tanks and connecting streams that constitute the process.

The vitrification system chosen for simulation is the one being tested as part of the West Valley Demonstration Project because significant exchanges of technical information regarding it already occur as part of PNL's West Valley Support Task under the NWTP. During this reporting period we emphasized obtaining an understanding of how West Valley plans to operate their system and translating this into a control logic in the simulation.

The information gained from West Valley indicated that the following approach is best. The mass balance for the West Valley Nuclear Services system will be simulated from the waste tank to the canisters. (Current plans call for placing all waste in one tank before conducting the vitrification campaign.) The components being modeled will include the waste tank, the cold chemical make-up tank, the concentrator feed make-up tank, the main feed tank, the melter, the off-gas system, and the canister-filling operation. The addition of chemicals to the waste to make the feed will be computed by using the RECIPE code as a subroutine.^(a)

(a) The RECIPE code was developed during FY87 and FY88 under the West Valley Subtask of NWTP. This code computes the amount of oxide-bearing additives that needs to be added to a batch of waste to obtain the specified glass composition.

The RECIPE code has been converted to a subroutine for the PSM. The subroutine is about 80% checked out; what remains is 1) to verify the portion of the computation for checking out a slurry and 2) to check whether the subroutine's outputs are adequate.

Based on the information gained from West Valley, the following operational activities will be simulated in the PSM:

- Off-specification feed will be returned to the waste tank; i.e., no attempt to correct its composition will be made.
- Off-specification mixtures of chemicals to be added to the waste will be dumped to a cold chemical tank.

The PSM code will be able to simulate entire waste vitrification campaigns. The length of the campaigns, the total amount of feed make-up chemicals required, and the amount of glass produced will vary, depending upon how well the feed composition is controlled. This is because rejected feed batches will be returned to the waste tank and rejected cold slurry will be dumped. These actions will:

- increase the total run time because additional batches of cold slurry and/or feed will have to be prepared
- increase the amount of glass that needs to be produced because non-radioactive waste species will be added to the concentrator feed makeup tank during feed makeup.

Conducting multiple campaign simulations using a given set of statistical inputs (standard deviations, etc.) will provide a statistical body of data on factors such as variations in the length of the campaign and in the amount and quality of glass produced.

An improved logic has been developed to simulate operations of the vitrification system. The improved logic uses a unique set of flags for each foreseeable situation to be modeled. This approach will result in simpler subroutines, many of which will not require modifications even if subsequent substantial changes in system logic are made.

Work during the next report period will emphasize a) finishing conversion of the RECIPE code to a subroutine, b) completing the coding of the logic subroutines, c) combining items a and b with the modules for solving the composition of the material in the tanks to obtain a deterministic (i.e., nonstochastic) version of the code. This will be followed by addition of statistical modules that will permit the PSM to perform stochastic computations that allow uncertainty computations to be propagated.

CORROSION PRODUCT ANALYSIS - PILOT-SCALE CERAMIC MELTER (PSCM)

The PSCM was drained and inspected in September 1985 and was rebuilt the following year. Corroded and failed components were replaced and the structural design of the lid was improved. The melter tank walls, electrodes, and lid refractories showed corrosion damage consistent with 5 years' operation at high temperature with exposure to molten glass. Severe corrosion occurred on the back sides of the Inconel 690 electrodes, especially at the glass operating level.

Later sand blasting of the electrodes revealed vertical cracks penetrating the electrodes where cooling channels were machined into the rear of the electrodes and vertical holes for instrumentation had been drilled. Subsequently the corrosion products in and around the electrode bus connection were analyzed to determine a mechanism for the severe electrode corrosion. This evaluation was completed in the second quarter of FY 1987 and is discussed here.

Corrosion products removed from below the south electrode bus bar show much higher ratios of iron and manganese to chromium than are found in Inconel 690. Also, corrosion-product samples from both electrodes showed nickel and chromium levels significantly below those of Inconel 690. Although these analyses indicate corrosion, they give no strong evidence of a particular corrosion mechanism. The fluorine, chlorine and sulfur levels in the corrosion products were below 0.2% in all but the north electrode corrosion sample, which was 0.5%. The fluorine, chlorine and sulfur levels are close

to the concentrations of these elements in the sludge that was removed from the melter floor and do not offer additional information on a corrosion mechanism.

A possible mechanism, however, for the corrosion seen at the rear of the electrodes is suggested by their appearance after sand-blasting. As the electrodes were pushed away from the walls, mechanical stress (and possibly heating and cooling cycles) may have opened small cracks at the cooling channel welds on the back of the electrodes and breached the vertical holes that had been drilled for measuring weight factor and specific gravity. The cooler, stagnant area behind the electrodes allowed oxidizing salts to accumulate, especially at the melt line, accelerating the attack on the Inconel 690.

A portion of the melter lid fell into the melter cavity during later operation. The melter lid refractory had failed because of inadequate support from the Inconel 690 anchors welded to it. These were replaced with ceramic anchors, which are more resistant to corrosion.

The evaluation of the corrosion of the PSCM electrodes suggests that although Inconel 690 has excellent corrosion resistance to defense waste glass, corrosion at the melt line in stagnant regions is a significant concern. Future melter designs should address this corrosion problem by placing the electrodes in the walls or by other design modifications to minimize contact of the glass with Inconel components at the glass surface, especially in the area between the electrodes and the wall.

LIQUID-FED CERAMIC MELTER SCALE-UP STUDY

A study to evaluate melter capacity prediction techniques was completed in the second quarter of FY 1987. The study consisted of three parts:

- 1) identification of possible techniques and models for melter scale-up,
- 2) compilation and evaluation of melter processing data for five different melters with three different glass formulations, and 3) evaluation of the melter data using the scale-up techniques.

Available Techniques and Models for Melter Scale-Up

Considerable attention has been given to various techniques to scale up a slurry-fed, Joule-heated ceramic melter. Rules of thumb and criteria based on melt surface area and volume have been used by the radioactive waste vitrification research and development programs and by the commercial glass industry. The expected output for a small (less than 20 ton/day) commercial electric furnace, melting colored glass, is about 1000 kg/m^2 of surface area per day or 1250 kg/m^3 of melter volume per day (Stanek 1977). For clear glasses the expected output increases by about 50% because of the increased infrared transmission through the glass. This situation is somewhat different for the slurry-fed melter that has a feed pile or cold cap of liquid and solid material covering most of the glass surface. Little radiant heat penetrates the volume of the glass, and heat travels through the glass to the cold cap by convection or by transfer of radiant heat from the exposed walls to the cold cap. The performance of a slurry-fed ceramic melter is therefore quite different from the glass industry rule of thumb given above.

Several researchers (Quigley and Kreid 1979; Routt 1982; Robinson 1984) have studied melter tank fluid dynamics using scale models in which dimensionless similarity parameters were developed from simplification of the differential equations describing heat and mass transfer. Flow patterns were determined by photographing illuminated particles. Other investigators (Hjelm and Donovan 1979; Trent et al. 1983; Eyler 1985) have developed two- and three-dimensional computer models to predict mixing patterns in the melter tank under different conditions and with various electrode configurations. Although both the physical and numerical simulations give insight into melter performance, neither addresses the design considerations of processing rate and cold-cap performance because both are based on a static system which does not include inflow and outflow of material or changes to the thickness and area of the cold cap.

Routt and Porter (1980) modeled the cold cap using a mass balance, heat transfer equations, and the calculated buoyancy of the cold cap. The heat transfer between the bottom of the cold cap and the bulk glass was calculated using boundary-layer theory. Routt's model predicts that heat transfer from

the lid to the cold cap is important and that melt rate should therefore be a function of wall temperature. Melter rate data were correlated using the Roult model and the melt surface area for three glass formulations and five different melters.

Experimental Work

Data from previous melter experiments were examined to select experiments that were run in melters of different scale but under the same operating conditions. Three melter feed compositions were selected for study: a Savannah River Laboratory (SRL) composition (SRL-TDSF-131) and a Hanford composition (HWVP) with and without sugar added for control of foaming. Because none of the feeds had been run in all four of the PNL melters, experiments were conducted to fill in gaps in the experimental data base. Experimental data from a large-scale SRL melter experiment were also included in the study. The melters included in the study were the PSCM, high-bay ceramic melter (HBCM), experimental ceramic melter (ECM), and liquid-fed mini-melter (LFMM) at PNL and the large slurry-fed melter (LSFM) at SRL. Table 1 summarizes their major design characteristics.

Ten experiments were used for the scale-up study as shown in Table 2. Included in the data matrix were experiments that were performed from 1981 to 1986 and those that were designed specifically to fill in gaps in the data. In the latter category were ECM experiment ECM-86-1 and the LFMM experiments conducted in May and June of 1986. The PNL experimental run data were

TABLE 1. Melter Characteristics

<u>Characteristic</u>	<u>PSCM</u>	<u>HBCM</u>	<u>ECM</u>	<u>LFMM</u>	<u>LSFM</u>
Surface Area, m ²	0.73	0.25	0.054	0.0029	1.10
Glass Depth, cm	42	22	15	10.6	61
Glass Volume, L	290	50	8.2	0.3	670
Nominal Feed Rate, L/hr	44	15	3	0.1	66
Maximum Feed Rate, L/hr	58	20	4	0.2	99

TABLE 2. Experiments Included in Scale-up Study

<u>Melter</u>	<u>SRL Feed</u>	<u>HWVP Feeds</u>
PSCM	PSCM-4	PSCM-22
HBCM	HBCM-86-1	HBCM-85-1 & 86-2
ECM		ECM-86-1
LFMM	LFMM-86-1	LFMM-86-2 & 3
LSFM	LSFM-9	

analyzed to obtain a nominal or average processing rate and a maximum processing rate. The nominal feed rate is the rate that can be maintained indefinitely because all operating parameters fall within accepted ranges. A maximum feed rate pushes the system to the limit; one or more of the standard operating parameters is on the verge of being exceeded. Feed surges may then lead to instability because minimal excess capacity remains. At the nominal rate, the cold-cap coverage was about 80%, with good venting and flexibility. At the maximum rate, the cold-cap coverage was approaching 100%. The nominal feed rate for the LSFM experiment was 50% cold-cap coverage.

Correlation of Results

The traditional method for LFCM scale-up is by melter surface area. Since the heat transfer from the bulk glass to the cold cap is through the glass surface, this approach makes intuitive sense. Figure 1 shows the nominal glass production rate divided by the melter surface area for the experiments studied. The melter data are plotted in order of increasing size from the LFMM (surface area = 0.0029 m^2) to the LSFM (surface area = 1.12 m^2). The correlation between surface area and melt rate is very good for the larger melters. Figure 2, a plot of melt rate as a function of surface area, shows the melt rate as a nearly linear function of surface area for each type of feed.

The data generated from the mini-melter, which is now under development, show a much higher throughput than would be expected from the data on the larger melters. This may be due to edge effects; heat transfer to the cold cap from the walls is probably much more important in the 2.5-in.-dia vessel than in larger melters. The mini-melter height to width (aspect ratio) is

FIGURE 1. Nominal Glass Melt Rate (Melt Rate/Surface Area)

FIGURE 2. Melt Rate Versus Surface Area

much larger than in the other melters, and its plenum space is in the heated zone. These factors should increase processing rate by radiant heat transfer to the cold cap.

Glass melt rates for each melter experiment studied were calculated using the heat-transfer model developed by Routt (Routt 1980). Glass and plenum

temperatures were available from run summaries, while some of the other parameters were estimated from available data. An important element of the heat-transfer calculation is the heat-transfer rate between the molten glass and the bottom of the cold cap or feed pile. Routt used boundary-layer theory to predict this heat transfer rate. The boundary-layer thickness, however, depends on the velocity of the molten glass below the cold cap, and this velocity is not measured. Depending on the glass melt velocity used, the calculated heat-transfer rate will vary and will strongly affect the predicted melt rate capacity.

A plot of actual versus calculated glass melt rates (glass melt rate/surface area) appears in Figure 3 for the SRL feed composition. The model under-predicts the glass melt rate by a large margin. The model can be adjusted to better predict melter performance by changing the thermal boundary-layer thickness, and hence the rate of heat transfer from the glass to the cold cap. Figure 4 shows actual versus calculated glass melt rates assuming a bulk glass velocity of 10 cm/sec (a factor of 40 times the calculated velocity). Except for the mini-melter, the calculated numbers are fairly close to the actual measurements. The correlation for the other feed types was similar. The correlation based on surface area, however, is a better predictor of melter processing rate than is the heat-transfer model in its present form.

A topical report entitled Development of a Continuous Liquid-Fed Laboratory-Scale Mini-Melter for Nuclear Glass Development, authored by M. A. H. Reimus, S. C. Marschman, and G. L. Graff, was published in February 1987. This report describes the development and initial testing of the liquid-fed mini-melter (LFMM). The LFMM was developed to aid in waste glass feed slurry development and offers several advantages over testing in large-scale melters. The LFMM requires little lead time in preparing for a test run, and requirements for labor and material are low. Real-time melting behavior of liquid feed slurries can be investigated, and feed rates can be estimated for larger-scale melters. The glass produced is representative of that produced by a larger-scale melter, as well as representative of the processing operation itself. Glass produced by the LFMM may subsequently be analyzed for metallic

FIGURE 3. Actual and Calculated Glass Melt Rate for SRL-TDSF-131 Feed ($V = 0.25$ cm/sec)

FIGURE 4. Actual and Calculated Glass Melt Rate for SRL-TDSF-131 Feed ($V = 10$ cm/sec)

and other secondary phase formation. In contrast to larger-scale melters, the LFMM may be easily and inexpensively installed in a hot cell because of its relatively small size and simple configuration, enabling testing of radioactive feeds.

CONCLUSIONS AND RECOMMENDATIONS

PROCESS MODELING

Simulation of a vitrification process can be implemented using a computer code that is not specific to the process and which utilizes an input file describing the tanks, streams, and parameters constituting the process. A computer code has been written that will be tested for a simulation of the West Valley vitrification process. A description of the process has been obtained informally from West Valley personnel and is being successfully translated into a control logic to be used as part of the simulation.

PSCM REBUILD

The PSCM is an important part of the melter testing program, providing the nonradioactive test facilities for correlation with the radioactive liquid-fed ceramic melter (RLFCM) and other experimental melters. Completion of the rebuild ensures the availability of the PSCM for testing into the 1990s. Several conclusions important to the Technology Testing Program can be drawn from the PSCM disassembly and rebuild project:

- The type and configuration of the melter tank ceramics are suitable for use with the glass types tested. Corrosion of the K-3 refractory used in the walls was consistent with corrosion rates expected for the 5-year operation.
- The melter lid refractory failed because of inadequate support from the Inconel 690 anchors welded to the lid. The ceramic anchors used to replace them will be more corrosion-resistant.
- The electrodes failed at the upper bus connection and showed severe corrosion at the glass melt interface. Corrosion was worst where cooling channels had been machined into the rear of the electrodes. Corrosion penetrated into the vertical holes drilled for weight factor and specific gravity measurements. The severe electrode corrosion may have been due to a combination of oxidizing material buildup and mechanical stress at the channel welds on the rear of the electrodes.

Implications of the PSCM electrode corrosion are that although Inconel 690 normally has excellent corrosion resistance to defense waste glass, corrosion at the melt line in stagnant regions is a significant concern. Future melter designs should place the electrodes in the walls or use other design modifications to minimize dead-area glass contact with Inconel components at the glass surface.

MELTER SCALE-UP STUDY

The run summaries from ten LFCM experiments in five different melters give a broad range of melter performance data. The historical feed and temperature data were particularly useful in comparing melter processing capacities. Nominal melter feed rate divided by melter surface area gives a fair estimate of melter capacity and is reasonably independent of melter size. The slope of the rate-surface area curve differs for different feed compositions.

Calculations using heat transfer through the cold cap is a potentially useful method for predicting melter capacity, although the correlation based on existing measured data was not as good as the simple surface area correlation. The heat transfer model takes into account glass and cold cap properties and melter physical parameters. Heat transfer at the glass/cold cap boundary, however, is not adequately handled by boundary-layer theory.

The mini-melter rate data do not follow the trends of the larger melters. The mini-melter has a much larger throughput than would be expected for its surface area. The discrepancy may be due to geometric differences and to heat transfer directly from the walls to the cold cap.

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APPENDIX

ACRONYMS AND ABBREVIATIONS

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°C - degree Celsius
cm - centimeter
CRW - cladding removal waste
DOE - U.S. Department of Energy
E1150 - electrical conductivity at 1150°C
ECM - experimental ceramic melter
EDX - energy-dispersive x-ray
FRG - Federal Republic of Germany
g - gram
HBCM - high-bay ceramic melter
HW - Hanford waste
HWVP - Hanford Waste Vitrification Plant
kg - kilograms
kW - kilowatts
L - liter
LFCM - liquid-fed ceramic melter
LFMM - liquid-fed mini-melter
LSFM - large slurry-fed melter
m - meter
MCC - Materials Characterization Center (at PNL)
min - minute
mL - milliliter
NCAW - neutralized current acid waste
NWTP - Nuclear Waste Treatment Program
PNL - Pacific Northwest Laboratory
PSCM - pilot-scale ceramic melter
PSM - process simulation model
redox - chemical reduction oxidation
RLFCM - radioactive liquid-fed ceramic melter
s (or sec) - second
SEM - scanning electron microscopy
SRL - Savannah River Laboratory
T100P - the temperature at which viscosity is 100 poise
TDSF - Technical Data Summary Formated (SRL melter feed)
T_g - glass transition temperature
wt% - weight percent
WO/L - waste oxides per liter
XRD - x-ray diffraction (analysis)

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