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LFCM Vitrification Technology

Quarterly Progress Report
April-June 1985

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

January 1986

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

Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
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LFCM VITRIFICATION TECHNOLOGY

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QUARTERLY PROGRESS REPORT

April-June 1985

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

Contributing Authors

R. P. Allen	R. W. Goles
C. M. Anderson	W. L. Kuhn
G. A. Anderson	D. H. Mitchell
S. O. Bates	R. K. Nakaoka
H. T. Blair	K. H. Oma
L. A. Bray	J. M. Perez, Jr.
J. L. Buelt	M. E. Peterson
L. R. Bunnell	K. J. Schneider
J. G. Carter	K. L. Schuchardt
L. A. Chick	G. J. Sevigny
R. D. Dierks	D. H. Siemens
L. J. Ethridge	G. E. Spanner
D. W. Faletti	J. H. Westsik, Jr.
R. K. Farnsworth	B. M. Wise
D. S. Goldman	

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under Contract DE-AC06-76RL0 1830

Pacific Northwest Laboratory
Richland, Washington 99352

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ABSTRACT

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

SUMMARY

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

Pretreatment Systems - Due to curtailed activities in this area, no further contributions will be reported in this document.

Melting Process Chemistry and Glass Development - Melting rate data from laboratory testing agree with data measured in the experimental-scale ceramic melter (ECM). An initial HWVP reference glass was developed to incorporate Hanford Purex Plant neutralized current acid waste (NCAW) and cladding removal waste (CRW). Laboratory-scale scoping tests were performed to identify two candidate HWVP melter feeds for evaluation on an engineering scale.

Feed Preparation and Transfer Systems - The air displacement slurry (ADS) pump was used in a second radioactive test and in two other nonradioactive tests. A new system for measuring slurry level and specific gravity in feed tanks was successfully tested for 5 months. The addition of formic acid to HWVP waste was successfully demonstrated with pilot-scale equipment.

Melter Systems - Three radioactive liquid-fed ceramic melter (RLFCM) shakedown experiments were conducted. Analyses of test results from several nonradioactive experimental-scale, engineering-scale, and pilot-scale melter tests were completed.

Canister Filling and Handling Systems - A mass spectrometer leak detection system that will use helium as a tracer gas is being developed to test canisters of glass prepared for the Federal Republic of Germany (FRG).

Off-Gas Systems - Nonradioactive melter emission and off-gas system performance studies were conducted to evaluate operational conditions associated with RLFCM production of FRG glass canisters.

Process/Product Modeling and Control - Progress continued on process control instrumentation, process control algorithms, canister thermal modeling, and characterization of cracking in canisters.

Supporting Studies - Glasses containing reduced quantities of fluxing oxides are being considered as possible alternatives to borosilicate glass for use as high-level waste (HLW) forms. A study on a transportable vitrification process for low-level waste (LLW) was completed. Design criteria and the pre-conceptual design of the system were prepared, disposal costs were estimated, and utility interests in the transportable volume reduction service were assessed.

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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 (HLW), transuranic waste (TRUW), and other related wastes. This work includes developing waste treatment system technology and components, testing treatment systems, verifying the operability of the technologies through practical applications, producing waste packages for storage and disposal testing, assisting others to resolve specific problems in transferring the developed technologies, and maintaining a resource of radioactive waste treatment capabilities and facilities for DOE.

Major current activities include: developing waste glass formulations and vitrification equipment for HLW; operating a pilot-scale liquid-fed ceramic melter (LFCM) system under radioactive conditions; designing, fabricating, and installing canister closure, decontamination, destructive and nondestructive examination, and storage facilities for vitrified radioactive waste; providing heat and radiation sources to the Federal Republic of Germany (FRG) Asse Mine Test; developing and testing TRUW and second-generation HLW treatment technology; and providing processing technology and vitrification process equipment for treating West Valley wastes. These activities support the longer term goals of completing system design and operations documentation and production specifications for HLW treatment (vitrification) by 1992, for TRUW treatment by 1996, and for second-generation HLW treatment by 2000.

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

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

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

Progress in all program elements is reported through informal monthly status reports, formal annual reports (McElroy and Burkholder 1984; Burkholder and Rusin 1985), and formal topical reports. Recognizing both the magnitude of the first-generation HLW program element and the large number of applications currently under way, this quarterly report series was begun in FY 1985 to facilitate the transfer of LFCM vitrification technology between and among the central source (PNL) and the various user groups: the West Valley Demonstration Project (WVDP), the Hanford Waste Vitrification Program (HWVP), and the Defense Waste Processing Facility (DWPF) Project. Quarterly reports will be established for other program elements as the need arises.

The results of applicable technical work performed by PNL in direct support of the HWVP are included in this report. The HWVP is being conducted by Rockwell Hanford Operations (RHO) for DOE. DOE and RHO have assigned to PNL the responsibility for development of vitrification system technology for application to the HWVP. The HWVP facility, one of three major U.S. vitrification facilities for defense HLW and TRUW, will use PNL-developed vitrification technology. This technology will also be used for the DWPF and the WVDP. Progress in the development of waste- and site-specific technologies is reported in this quarterly report series to complement NWTP-supported activities. The PNL work is managed by J. E. Minor.

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

- Pretreatment Systems - L. A. Bray
- Melting Process Chemistry and Glass Development - D. S. Goldman and L. A. Chick
- Feed Preparation and Transfer Systems - H. T. Blair

- Melter Systems - R. D. Dierks and J. M. Perez, Jr.
- Canister Filling and Handling Systems - D. H. Siemens
- Off-Gas Systems - R. W. Gales
- Process/Product Modeling and Control - W. L. Kuhn
- Supporting Studies - K. J. Schneider.

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

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Burkholder, H. C., and J. M. Rusin, compilers. 1985. Nuclear Waste Treatment Program, Annual Report for FY 1984. PNL-5414, Pacific Northwest Laboratory, Richland, Washington.

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PRETREATMENT SYSTEMS

L. A. Bray

SUMMARY

Due to curtailed activities in this area, no further contributions will be reported in this quarterly report.

MELTING PROCESS CHEMISTRY AND GLASS DEVELOPMENT

D. S. Goldman, L. A. Chick, H. T. Blair, and S. O. Bates

SUMMARY

Melting rate data from laboratory testing agree with data measured in the experimental-scale ceramic melter (ECM). A shielded container was designed for the Mössbauer spectrometer to analyze radioactive glass, and tests are being conducted with radioactive glasses.

An initial Hanford Waste Vitrification Program (HWVP) reference glass was developed to incorporate Hanford Purex Plant neutralized current acid waste (NCAW) and cladding removal waste (CRW). Redox response and melting behavior have been evaluated for slurry feeds to be used in melter testing of this glass composition.

Laboratory-scale scoping tests were performed to identify two candidate HWVP melter feeds for evaluation on an engineering scale. One melter feed contained all the glass-forming chemicals as a premelted frit, and one contained two-thirds of the glass-forming materials as unreacted chemicals. A 1700-L batch of simulated HWVP reference feed was treated with formic acid and tested in the high-bay ceramic melter (HBCM); the results confirmed the laboratory-scale experience. Of the two melter feeds prepared with this waste simulation, the all-frit feed performed better and was selected for future testing in the pilot-scale ceramic melter (PSCM). In addition, methods were developed to measure the yield stress of HWVP melter feeds.

INTRODUCTION

The objectives of this work are to develop glass compositions that will produce glass products having acceptable chemical durability and to design feed formulations that can be processed in the liquid-fed ceramic melter (LFCM) at an acceptable rate. For the West Valley Demonstration Project (WVDP), the feed

includes simulated high-level waste (HLW), glass-forming chemicals, and (in some cases) ion-exchange material. Glass-forming chemicals and other chemicals used for redox control are selected to maximize melting performance and minimize problems due to foaming, metal precipitation, and other adverse phase separation. The resulting glass composition is designed to have a viscosity of 100 poise and an electrical conductivity between 0.18 and 0.5 (ohm-cm)⁻¹ in the temperature region between 1070°C and 1150°C. In addition, the glass is designed to minimize the tendency to form crystals above 900°C or other secondary phases on the melt surface.

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

The technical approach involves a close interaction among feed formulation, glass composition, and waste processing work being conducted at Pacific Northwest Laboratory (PNL). Hence, a glass composition is being developed to provide the appropriate high-temperature properties (viscosity, electrical conductivity) and low-temperature properties (elemental release rate, crystallization rate). Nitrate or hydroxide chemicals representing the waste fraction and glass former chemicals are made into a slurry in the laboratory. The redox state of the glass is then optimized using a reducing agent in the slurry until the ferrous/ferric ratio in the melted glass is between 0.1 and 0.3. Then, the melting rate of this feed is determined using the bottom-heated crucible test in the laboratory, which measures the rate at which the cold cap formed from this feed melts on molten glass.

Several variations are examined and the feed formulation with the best melting characteristics in this rapid, inexpensive test is recommended for small-scale testing in the ECM. The ECM test is used to corroborate the laboratory findings and to determine if melting problems occur over a longer time frame in a more continuous melting environment. If problems occur, additional

laboratory glass composition or feed formulation work is conducted. A successful ECM test leads to the development of an extended test in the PSCM.

Applicable technology developed in the HWVP is also presented in this section. The HWVP is dedicated to the vitrification of the liquid high-level and transuranic defense wastes produced and stored at the Hanford site, near Richland, Washington. The objectives of the HWVP are to:

- Develop a reference glass formulation incorporating NCAW/CRW. This glass composition should have the required physical properties for processing in LFCMs (viscosity, electrical conductivity, and phase behavior) and maximum chemical durability.
- Evaluate the effects of possible variations of selected waste components on the physical properties and chemical durability of the reference glass.
- Prepare a simulation of the HWVP reference feeds that represents the true chemical and physical properties of the waste, with the exception of radiation and heat generation, and creates no artificial difficulties.
- Determine whether the glass-forming materials that are added to the waste can all be added as a ground frit or whether some must be added as unreacted chemical compounds.
- Determine how the waste and glass-forming chemical blend can be processed before it is charged to the melter to achieve maximum melting rates, minimum foaming, and minimum phase separation in the melter.
- Determine ways to modify the rheology of the melter feed to improve homogeneity and minimize transport difficulties.
- Identify the critical rheological properties of the feeds and develop methods for evaluating these properties.
- Evaluate the maximum melter feed oxide concentration that exhibits acceptable rheological properties.

TECHNICAL PROGRESS

West Valley glass composition development, HWVP glass composition development, and HWVP feed development are discussed in the following sections.

WEST VALLEY GLASS COMPOSITION DEVELOPMENT

For West Valley, the melting properties of various glass compositions have been evaluated using the bottom-heated crucible method in both laboratory and ECM testing. As discussed in previous reports (Burkholder and Jarrett 1985; Burkholder, Jarrett, and Minor 1985), the laboratory tests measure the disappearance of the cold cap as a function of time. The melting rate is determined from the slope of a linear regression analysis of the data.

Most of the glasses shown in Figure 1 incorporate simulated West Valley waste; glass compositions are presented in Table 1. The designations N, n, and

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

TABLE 1. Target Compositions of West Valley and SRL Glasses

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

F represent feeds that are fully nitrated, partially nitrated, and formatted, respectively. The PSCM-16 feed has no added reductants and approximately 2 M nitric acid added. FRG+Z and FRG-Z represent the feeds recently evaluated for the Federal Republic of Germany (FRG) with and without zeolite, respectively. Although there is some data scatter, a reasonable correlation is indicated between the two tests, considering the difficulties in determining melting rates with both methods. These results support the viability of using the inexpensive laboratory test as a screening tool to refine feed formulations prior to more extensive testing in the continuous melters.

The correlation between the amount of oxides of alkali and boron (considered as melting aids or fluxes) and the ECM melting rate is illustrated in Figure 2. The viscosity of these formulations also decreases with an increasing flux content. Thus, the data in Figure 2 indicate that better melting is

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

achieved with additional flux components and with decreasing viscosity values. Results from earlier work indicated that additional flux components tend to decrease the chemical durability in aqueous solutions with WV203^(a) and WV202^(b) as the worst and best extremes, respectively.

HWVP GLASS COMPOSITION DEVELOPMENT

An initial candidate glass formulation was chosen using the 1985 HWVP reference waste and a borosilicate glass composition developed in FY 1984 for NCAW. Changes were made in this glass composition to adjust the viscosity and redox state to the desired levels. The resulting glass composition was designated HW35. However, the electrical conductivity of HW35 was unacceptably

(a) Similar to the earlier PSCM-16 working composition.

(b) Savannah River Laboratory (SRL) formulation with West Valley waste.

close to the upper limit at 1150°C. Three additional glass composition iterations were required to adjust the electrical conductivity and arrive at the initial reference glass composition (HW39).

The oxide composition of HW39 is shown in Table 2. HW39 glass has a waste loading of 25 wt% using the nominal reference HWVP waste. The oxide composition of the waste is shown in Table 3.

TABLE 2. HWVP Initial Reference Glass Composition (HW39)

Oxide	Waste, ^(a) wt%	Nominal Glass Former Oxide, wt%	Glass, wt%
SiO ₂	3.0	67.25	51.2
Na ₂ O	10.7	10.25	10.4
B ₂ O ₃	0.0	12.75	9.6
Li ₂ O	0.0	5	3.8
CaO	0.3	3.75	2.9
MgO	0.3	1	0.8
Fe ₂ O ₃	44.4		11.1
Al ₂ O ₃	17.2		4.3
FP _{0.125} ^(b)	5.7		1.4
Cr ₂ O ₃	5.3		1.3
NiO	2.4		0.6
ZrO ₂	2.4		0.6
La ₂ O ₃	2.2		0.6
Nd ₂ O ₃	2.1		0.5
SO ₄	1.8		0.4
F	1.2		0.3
CsO ₂	1.0		0.2
	100.0	100.0	100.0

(a) Waste composition used in glass development contains substitutions for radioactive components.

(b) Fission products and trace oxides.

TABLE 3. Nominal Oxide Composition of the HWVP Reference Waste^(a)

Oxide	As-Received Waste, kg/MTU	Normalized Waste, wt% oxide
Fe ₂ O ₃	7.50	43.95
Al ₂ O ₃	2.90	17.00
Na ₂ O	1.80	10.55
CrO ₃	0.90	5.27
SiO ₂	0.50	2.93
NiO	0.40	2.34
ZrO ₂	0.40	2.34
La ₂ O ₃	0.37	2.17
SO ₄	0.30	1.76
Nd ₂ O ₃	0.29	1.70
F	0.20	1.17
MoO ₃	0.20	1.17
CeO ₂	0.10	0.59
Cs ₂ O	0.10	0.59
CuO	0.10	0.59
MnO ₂	0.10	0.59
RuO ₂	0.10	0.59
TOC ^(b)	0.10	0.59
U ₃ O ₈	0.10	0.59
BaO	0.07	0.41
Pr ₆ O ₁₁	0.06	0.35
SrO	0.06	0.35
Tc ₂ O ₇	0.06	0.35
CaO	0.05	0.29
MgO	0.04	0.23
Rb ₂ O	0.04	0.23
PdO	0.03	0.18
Rh ₂ O ₃	0.03	0.18
Sm ₂ O ₃	0.03	0.18
Y ₂ O ₃	0.03	0.18
NpO ₂	0.02	0.12
Pm ₂ O ₃	0.02	0.12

TABLE 3. (contd)

Oxide	As-Received Waste, kg/MTU	Normalized Waste, wt% oxide
TeO ₂	0.02	0.12
BeO	0.01	0.06
SeO ₂	0.005	0.03
SnO ₂	0.004	0.02
Am ₂ O ₃	0.003	0.02
CdO	0.003	0.02
Eu ₂ O ₃	0.003	0.02
P ₂ O ₅	0.003	0.02
PuO ₂	0.003	0.02
Ag ₂ O	0.002	0.01
Gd ₂ O ₃	0.002	0.01
Nb ₂ O ₅	0.002	0.01
B ₂ O ₃	0.001	0.01
Ta ₂ O ₅	0.001	0.01
TiO ₂	<u>0.001</u>	<u>0.01</u>
Total	17.06	100.00

(a) Neutralized current acid waste/cladding removal waste (NCAW/CRW).

(b) TOC - total organic carbon.

The HW39 glass has the following physical properties:

- temperature at which the glass has a 100 poise viscosity (T100P) - 1124°C
- crystallinity - small cubic spinel crystals
- electrical conductivity - 0.30 (ohm-cm)⁻¹ at 1150°C
- chemical durability - similar to SRL TDS-165 and WV183.

This glass composition has acceptable viscosity values, phase behavior, and electrical conductivity for use in melter testing. Some leaching tests of HW39 have been completed and indicate that the chemical durability of HW39 is similar to that of SRL TDS-165 glass.

The temperature at which HW39 has a 100 poise viscosity (T100P) is 1124°C, and the viscosity is stable with time. This value is within the desired 1070 to 1150°C range required for PNL melter operation. The viscosity versus temperature curve for HW39 is shown in Figure 3.

Detectable crystallinity was found in the as-melted and heat-treated HW39 glass, as expected due to the relatively high Cr concentration in the waste. Optical and scanning electron microscopy/energy-dispersive x-ray (SEM/EDX) analysis indicated that the crystals are the cubic spinel (FeCr_2O_4) phase observed in previous HWVP glasses. It is estimated that these heat-treated samples are 1 to 5 wt% spinel crystals. It is not yet known if this level of crystallinity will cause problems during melting. If the crystals formed in

FIGURE 3. Viscosity Versus Temperature Curve for HW39 Waste Glass

the melter are small enough to be swept along with convection currents, settling would not be expected. It is also not yet known if the amount of crystalline material produced in the melter will be the same as that formed in laboratory glass samples. Laboratory samples of the WV182 glass also exhibited similar amounts of crystallinity, but glass samples taken from the PSCM-19 melter run using the WV182 glass had only small amounts of crystalline material. Future HWVP melter testing will evaluate the formation and effects of crystals within the melter.

The electrical conductivity of the HW39 glass is $0.30 \text{ (ohm-cm)}^{-1}$ at 1150°C , which is well within the 0.18 to $0.5 \text{ (ohm-cm)}^{-1}$ range required for PNL melter operation. The electrical conductivity versus temperature curve for HW39 is shown in Figure 4.

FIGURE 4. Electrical Conductivity Versus Temperature Curve for HW39 Waste Glass

Results from 28-day MCC-1 and MCC-3 leach tests (MCC 1983, 1984) are summarized in Tables 4 and 5 for the HW39 glass. In Table 4, the results are for 28-day MCC-1 static leach tests in deionized water at 90°C with an SA/V (surface area-to-volume ratio) of 10 m^{-1} . The MCC-1 test is the most widely used test for comparing leaching performance.

In MCC-3 leaching tests, elemental concentrations in the leachate are representative of longer term extrapolation of MCC-1 test results and provide an indication of the concentrations under near-saturated conditions. Saturation is approached more rapidly in MCC-3 tests because the SA/V ratios are higher than those used in MCC-1 tests (approximately 1800 m^{-1} compared with 10 m^{-1}). The near-saturated conditions in the MCC-3 tests are thought to more closely approach the expected repository environment. Leachates from the MCC-3 tests are filtered through 45- μm and 18- $\text{\AA}$ filters, and each filtrate is analyzed. The analysis of the 45- μm filtrate indicates the amount of material that is in solution or is colloidal. Passing through an 18- $\text{\AA}$ filter, the colloidal material is removed from the filtrate and inductively coupled plasma (ICP) analysis of the filtrate provides the amount of material truly in solution. Results from 28-day MCC-3 leaching tests in deionized water confirmed previous MCC-1 tests (Table 5).

Slurry feed formulations were evaluated for redox response and melting behavior. The evaluation of redox response consists of determining the amount and type of reductant required for each feed formulation to produce a ferrous/ferric ratio between 0.1 and 0.3 in glasses melted from these feeds in the laboratory. This range is recommended to minimize the foaming tendency and the potential for metallic phase separation while maximizing melting efficiency. Reductants may be in the form of sugar, formic acid, and/or formated glass-forming chemicals. Evaluation of melting behavior consists primarily of determining the melting rate of a feed.

Currently, feeds are being evaluated in which one-third of the glass-forming chemicals are added as frit and the remaining two-thirds are added as frit or a nitrate-formate mixture. Both hydroxide and formated waste have been evaluated. The only observed difference between the two types of waste from a

TABLE 4. 28-Day MCC-1 Leaching Results for the HWVP Reference Glass HW39(a)

<u>Element</u>	<u>Normalized Elemental Release, g/m²</u>
Al	10
B	15
Ca	6.8
Cs	13
Fe	0.32
Li	15
Na	15
Si	14
Sr	5.7
Final pH	9.3

(a) Conditions: deionized water, 90°C, SA/V = 10 m⁻¹.

TABLE 5. 28-Day MCC-3 Leaching Results for the HWVP Reference Glass HW39(a)

<u>Element</u>	<u>Normalized Elemental Release, g/m²</u>	
	<u>18-A Filter</u>	<u>45-μm Filter</u>
Al	0.05	0.15
B	0.48	0.48
Ca	0.01	0.06
Cs	0.07	0.15
Fe	<0.01	0.15
Li	0.57	0.59
Mg	<0.01	0.28
Na	0.45	0.46
Si	0.26	0.28
Sr	<0.01	0.04
Final pH	9.8	9.8

(a) Conditions: deionized water, 90°C, SA/V = 1780 m⁻¹.

redox response and melting behavior standpoint is that the formatted waste required less added sugar to produce the desired ferrous/ferric ratio. Due to rheological considerations, the formatted waste has been chosen for melter testing. The redox response of these feeds is consistent with the expectation that less sugar will be required in feeds containing more carbon, such as those with formatted waste or formatted chemicals.

A feed containing 100% frit is one of two feeds that was tested in a short-term melter run in April 1985. For a feed containing the current formatted waste simulation with 100% of the glass-forming chemicals added as frit, the proper redox response can be obtained when 5 to 7 g/L of sugar are added. The amount of sugar that can be added to the feed and produce the desired ferrous/ferric ratio needs to be determined. For the feed with 100% frit, nearly 2 M formic acid was required to produce the desired redox conditions in the resulting glass. This feed melted violently in laboratory crucible tests. Hydrogen evolution is of concern with this amount of formic acid.

In feeds where two-thirds of the glass-forming chemicals were added as a nitrate-formate mixture, the redox response was complicated by the reaction of the nitrates with the reductant, requiring that more carbon be added for the desired redox response. When two-thirds of the glass-forming chemicals were added to the waste only as formates and few nitrates were present, the ferrous/ferric ratio was greater than 1. This redox level is in the region where the potential for metallic phase separation exists, thus eliminating this mixture from further consideration at this time. For feeds where the remaining two-thirds of the glass-forming chemicals were added only as nitrates, 40 to 50 g/L of sugar were required to adjust the ferrous/ferric ratio to the desired level.

In an attempt to eliminate the need to add sugar to the system, redox control was attempted by partial substitution of nitrated glass-forming chemicals for the formatted glass-forming chemicals. If the formate/nitrate ratio is used for redox control, a number of difficulties could occur. If the ferrous/ferric ratio of the feed is outside the desired limits, adjustment of the batch will be very difficult. In this situation, the number of degrees of freedom is severely reduced because the reductant is one of the glass components. The adjustment would require the addition of glass formers with a compensating formate/nitrate ratio. This adjustment would change the glass composition in the batch, requiring further additions of other glass-forming chemicals, waste, and water in the proper ratios. These adjustments would be difficult and could compound the problem if further errors or variations were encountered. Because of these problems, this method of redox control cannot be recommended.

What appears to be a viable alternative is the use of a formate/nitrate feed in which a reduced amount of sugar is used to produce the desired redox response. A feed could be developed with a formate/nitrate ratio such that the resulting glass would be slightly oxidizing. The redox response of the feed could then be adjusted using a reduced amount of sugar. Work is currently being conducted to optimize the formate/nitrate/sugar mixture.

Feed melting rates were analyzed using the bottom-heated crucible method in the laboratory. This test measures the rate at which the cold cap on the molten glass melts as a function of time. Feeds containing 33% frit and 67% chemicals exhibited similar melting behavior. Laboratory melting rates were similar to those measured for West Valley PSCM-16 feed. PSCM-16 feed processed at a rate of 45 L/h in the PSCM. Feeds containing 100% frit processed at about one-half to two-thirds of the rate of the 33% frit and 67% chemicals feeds. These results are consistent with earlier FY 1984 melting rate data on Hanford feeds containing frit or nitrate glass formers.

HWVP FEED DEVELOPMENT

Progress related to HWVP feed development is discussed in the following sections.

Waste Simulation

Two aliquots of the HWVP reference feed simulation described in the last quarterly report (Burkholder, Jarrett, and Minor 1985) and identified as HWS4 were treated with formic acid in excess of the stoichiometric amount of 0.092 g HCOOH/g of waste oxide. These tests were performed to assess the effects of increasing the amount of formic acid on viscosity and yield stress values. The results are presented in Table 6 and Figure 5. Boiling the simulated feed greatly reduced the yield stress of the slurry and also reduced the apparent viscosity measured at low shear rates. Assuming that the rheological properties of the boiled simulated waste are representative of the properties of real waste, it is recommended that waste simulations be boiled for several hours when prepared.

TABLE 6. Summary of Properties of HWVP Reference Feed Simulation HWS4.
When Treated with Formic Acid

Variables	Batch 0	Batch 1	Batch 2	Batch 5	Batch 4
Concentration, g oxides/L	140	140	140	140	140
Boiling time, h	0	2	2	2	2
Batch size, mL	15,000	200	200	200	200
g HCOOH/g waste oxide	0	0	0.092	0.23	0.46
Properties					
Density, g/mL	1.11	1.08	1.12	1.14	1.13
pH	--	11.5	7.1	--	--
Viscosity, cP					
at 183 s ⁻¹	53.8	37.7	29.3	16.8	11.9
at 608 s ⁻¹	19.0	15.5	12.9	9.1	7.0
at 824 s ⁻¹	14.6	12.4	10.4	8.0	6.2
Yield stress, dynes/cm ²	89	56	41	20	12

The addition of formic acid further reduced the apparent viscosity and yield stress values of the slurry. However, the effect began to diminish beyond the addition of about 0.23 g HCOOH/g of waste oxides or 0.5 mol HCOOH/L of melter feed prepared at a concentration of 400 g of total oxide/L. This result suggests that the waste may be concentrated in excess of 190 g oxides/L when HCOOH is added without exceeding the design value of 80 dynes/cm² set on the yield stress for the Defense Waste Processing Facility (DWPF). If this is possible, one instead of two concentration steps would be required in the waste process and melter feed preparation flowsheet.

Melter Feed Processing

Eight screening tests were performed with melter feeds prepared with HWS4 to assess the effects of the type and amount of frit and unreacted glass-forming chemicals on the rheological properties of each feed (Table 7). The unreacted glass-forming chemical formulations (A, B, C) listed in Table 7 are summarized in Table 8. These screening tests indicated that:

FIGURE 5. Effects of Formic Acid Addition on Rheological Properties of HWS4

TABLE 7. Summary of Properties of Melter Feed Batches Prepared with HWVP Reference Feed Simulation HWS4

Property	Batch							
	1F	2F	3F	4F	5F	6F	7F	8F
Concentration, g total oxides/L	400	400	400	400	400	400	400	400
g HCOOH added/g waste oxides	0.092	0.092	0.092	0.092	0.092	0.092	0.46	0.23
Coarse frit, ^(a) fraction of TGF ^(b)	1/1	1/3	1/3	1/3	1/1	1/3	1/3	1/3
Fine frit, ^(c) fraction of TGF	0	0	0	0	0	2/3	2/3	2/3
Unreacted GF, ^(d) fraction of TGF	0	2/3	2/3	2/3	0	0	0	0
Type of unreacted GF ^(d)	--	A	B	C	--	--	--	--
Sugar added, g/L	0	0	0	0	5	0	0	0
Density, g/mL	1.31	1.32	1.32	1.33	1.28	1.27	--	--
pH	5.08	8.01	8.04	8.4	6.8	6.3	--	--
Dissolved solids, wt%	2.78	10.77	12.37	11.6	3.6	2.9	--	--
Suspended solids, wt%	29.91	27.58	25.98	27.8	30.6	32.3	--	--
Total solids, wt%	32.69	38.35	38.36	39.5	33.6	35.2	--	--
Viscosity, $\text{cp}^{(e)}$ at 183 s ⁻¹	11	22	22	27	13	17	14	12
at 608 s ⁻¹	5	10	10	13	5	7	6	6
at 824 s ⁻¹	4	9	9	11	4	6	5	5
Yield stress, dynes/cm ²	15	28	28	36	19	27	20	15

(a) -80/+200 mesh.

(b) TGF - total glass-forming oxides.

(c) -200 mesh.

(d) GF - glass-forming chemicals (see Table 8).

(e) Pseudoplastic model.

TABLE 8. Unreacted Glass-Forming Chemicals Used to Prepare Melter Feeds with HWS4

Chemicals, g/L	Glass-Forming Chemical Batch Type		
	A	B	C
SiO ₂	134.4	134.4	134.4
Na ₂ B ₄ O ₇ • 10H ₂ O	69.9	69.9	69.9
LiCO ₂ H • H ₂ O	46.9	46.9	46.9
NaCO ₂ H	20.0	20.0	20.0
Mg(CO ₂ H) ₂ • 2H ₂ O	7.4	--	--
Mg(NO ₃) ₂ • 6H ₂ O	--	12.9	12.9
Ca(CO ₂ H) ₂	17.4	--	8.7
Ca(NO ₃) ₂ • 4H ₂ O	--	31.6	15.8

- The addition of sugar (Batch 5F) to feed previously treated with formic acid (Batch 1F) had a negligible impact on measured apparent viscosity and yield stress values.
- The addition of unreacted glass-forming chemicals (A, B, or C) increased the measured apparent viscosity and yield stress values.
- The addition of fine frit (Batch 6F) appeared to increase measured apparent viscosity and yield stress values above levels achieved when all coarse frit (Batch 1F) was used.

These laboratory batches were also evaluated for ferrous/ferric response and melting rate. Based on the results of these screening tests, Batch 3F and Batch 6F were selected for evaluation in a melter test conducted during April 1985 in the HBCM. The run was designated HBCM-11.

The reaction of HWS4 with formic acid was studied to establish an allowable acid feed rate for formating the feed for the HBCM run. The reaction appears to be concentration dependent. There is no visible sign of reaction with the initial acid addition. In feeds formated to the estimated stoichiometric level of 0.92 g HCOOH/g waste oxide, there are no signs of reaction until 50% or more of the acid has been added; then gas release starts and

proceeds in relation to the rate of the formic acid addition. Methods are now being developed to remotely monitor this reaction in the makeup tank.

The HBCM-11 experiment was the first engineering-scale test that used the rigorous HWVP reference feed simulation and the DWPF forming process for waste property adjustment. The melter feed was prepared in three steps: preparation of the simulated waste, treatment of the simulated waste with 90 wt% formic acid, and addition of glass formers. A total of 1700 L was prepared. The simulation was then heated to 90°C using 20- to 30-psig steam in the coils in the makeup tank. Heatup time was about 3 h.

Once the final temperature was reached, 90 wt% formic acid was added using a diaphragm metering pump. The addition rate of 20 L/h was based on laboratory experiments conducted using samples of the simulate from the 1700-L batch. During this experiment, no signs of reaction were visible until approximately 70% of the total acid had been added. Additional formic acid caused surface foaming. The addition of formic acid to the tank followed the laboratory experiment very closely. The acid addition had to be stopped after 68% of the formic acid had been added. The foam had covered the entire liquid surface and had risen approximately 2 to 3 in. The foam dissipated in 8 to 10 min, and the addition of acid continued at 20 L/h. After 3 min, the surface foam had returned and the pump was stopped to allow the foam to recede. The addition rate was reduced to 10 L/h. The foaming continued at this rate, but the height of the foam was only 1 in. and did not increase. The remaining formic acid was added without interruption. A total of 56.3 lb of 90 wt% formic acid was added over a 2-h period and the temperature of the waste was maintained at 90°C $\pm$ 2°C. Following the forming step, 550 lb of -80/+200 mesh HW39 frit was added to the simulated waste.

After the batch had cooled, it was split; 645 L was sent to Tank HB-11 and 1065 L remained in Tank 311. The waste in Tank 311 was designated as the all-frit feed and 685.5 lb of -200 mesh frit was added to this batch. The final volume of the all-frit feed was 1550 L. The second batch was combined with unreacted glass-forming chemicals. Just prior to running the feed to the melter, sugar was added to each feed to insure an appropriate redox level. The all-frit feed required 3 g of sugar/L of feed; the frit/unreacted chemicals

feed, 4.5 g/L. The total oxide loadings in the melter feeds were 396 g/L for the all-frit feed and 365 g/L for the frit/unreacted chemicals feed. The reduced oxide loading in the latter feed was due to overdilution that occurred during a transfer.

Three samples (17, 18, 19) of the one-third coarse frit and two-thirds fine frit melter feed were obtained from the melter feed line during HWVP-11. The samples were collected at the same time and exhibited similar rheological behavior (Table 9). This behavior was very similar to that exhibited by a related laboratory prepared sample (see Batch 6F in Table 7).

After the melter feed was changed to one similar to Batch 3F, Samples 93, 94, and 95 were obtained from the melter feed line. The feed tank was agitated by an axial marine propeller agitator. Sample 141 is the same feed as Samples 93, 94, and 95 but was obtained by dipping a wide-mouth jar through a port in the feed tank top to collect a gel that had formed beyond the influence of the agitator. Sample 141 exhibited essentially the same rheological properties as Samples 93, 94, and 95 (Table 9). The rheological properties exhibited by Samples 93, 94, 95, and 141 are markedly different from the properties of

TABLE 9. Properties of Melter Feed Samples Obtained During HWVP-11

Properties	Sample						
	17	18	19	93	94	95	141
Density, g/mL	1.30	1.31	1.31	1.31	1.23	1.26	1.33
pH	8.8	8.8	8.8	7.6	7.6	7.6	7.6
Dissolved solids, wt%	3.2	3.2	3.3	11.4	11.0	11.3	11.4
Suspended solids, wt%	31.2	30.4	31.2	24.1	24.7	24.0	24.0
Total solids, wt%	34.4	33.6	34.5	35.5	35.7	35.3	35.4
Viscosity, cP							
at 183 s ⁻¹	15	15	14	165	163	171	157
at 608 s ⁻¹	9	7	7	61	60	63	57
at 824 s ⁻¹	8	6	6	47	47	49	44
Yield stress, dynes/cm ²	19	18	19	280	280	287	256

laboratory-prepared melter feed. These substantial differences may have been induced by 1) differences in bulk and laboratory chemicals; 2) changes in bulk chemical preparation techniques (i.e., digestion at 90°C instead of boiling), storage time, and type and degree of agitation; or 3) other factors that occur when laboratory preparation techniques are scaled to pilot-scale equipment. Scaleup factors for HWVP melter feed preparation have not been determined.

Even though the apparent viscosity and the yield stress of the melter feed made with unreacted glass-forming chemicals exceeded the maximum limits of 40 cP and 150 dynes/cm² set for the DWPF feed, no melter feeding difficulties that could be attributed to feed properties were experienced during the run. However, it should be noted that a centrifugal pump, which is the DWPF reference feed pump, was not used.

During the 65 h of operation, a total of 687 L of all-frit feed was processed at feed rates from 9.5 to 13.7 L/h. The performance of the all-frit feed was evaluated as acceptable based on cold cap behavior and glass quality. The cold cap was usually 1 to 1.5 in. thick with a 50% to 80% melt surface coverage. Satisfactory cold cap flexibility and venting were observed.

The one-third frit and two-thirds glass-forming chemicals feed was processed for 48 h with no downtime. A total of 407 L was fed to the melter and approximately 150 kg of glass was produced. The one-third frit and two-thirds chemical slurry was much thicker than the 100% frit case. The slurry seemed to suspend solids better, but the pseudoplastic nature also made agitation difficult. The cold cap coverage was higher (70% to 100%) at lower feed rates. The feed rate varied from 8.0 to 8.9 L/h with the nominal rate being 8.4 L/h. The cold cap was very rigid and had little venting. It was usually 1 to 3 in. thick and took longer to burn off at the end of the run. No equipment problems were encountered using the thicker feed.

The all-frit slurry processed at a rate about 30% higher than the slurry containing a mixture of frit and unreacted glass-forming chemicals. Therefore, the all-frit melter feed was selected for further testing in a PSCM run scheduled for July 1985.

Because the design operating temperatures for HWVP melter feed processing are 35°C and above, the effects of temperatures above 25°C on the yield stress and apparent viscosity of the two melter feeds used during HWVP-11 were evaluated. The effects of temperature on rheological properties are shown in Tables 10 and 11. Even though these data are from a single test, the data indicate that the temperature at which the properties are measured has a very minimal effect on melter feed rheological properties.

Rheological Properties

SRL has identified the yield stress of melter feed slurries as a significant design criteria for the slurry transportation and handling systems at the DWPF. A nominal design yield stress of 80 dynes/cm² has been established by SRL. The extrapolation procedure adopted at SRL to measure yield stress was described in Burkholder, Jarrett, and Minor (1985). The procedure is based on the fact that the SRL melter feeds are treated as if they were Bingham plastic fluids.

TABLE 10. Effect of Temperature on Rheological Properties of HWVP-11 Feed Made with All Frit

Temperature, °C	Yield Stress, dynes/cm ²	Viscosity, cP		
		824 s ⁻¹	608 s ⁻¹	183 s ⁻¹
25	8.1	4.4	4.8	8.2
30	7.4	3.8	4.3	7.9
35	7.7	3.4	4.0	8.2
40	8.4	3.6	4.2	8.1
45	9.0	3.4	4.0	8.1

TABLE 11. Effect of Temperature on Rheological Properties of HWVP-11 Feed Made with Unreacted Glass-Forming Chemicals

Temperature, °C	Yield Stress, dynes/cm ²	Viscosity, cP		
		824 s ⁻¹	608 s ⁻¹	183 s ⁻¹
25	106	26.6	32.4	78.4
30	98	23.9	30.0	77.2
35	104	26.4	32.3	78.5
40	101	24.9	30.6	75.8
45	99	25.4	30.7	72.9

HWVP feed slurries exhibit yield-pseudoplastic non-Newtonian rheological properties (Burkholder, Jarrett, and Minor 1985). The extrapolation procedure used by SRL to measure yield stress produces conservative estimates for yield-pseudoplastic materials like simulated HWVP waste and melter feeds. Several methods that appear to be more appropriate for yield-pseudoplastic slurries were evaluated this quarter.

Yield-pseudoplastic fluids are characterized by a yield point; a force is required to start the fluid in motion; and once in motion, the viscosity decreases with increasing shear rate. Determination of the exact yield point is very difficult in some materials because of the nonideal behavior of the slurry and/or the viscometer. In the Haake^(a) rotational viscometer, torque (or shear stress) is measured by rotational displacement of a spring. As the motor starts to rotate, a slurry with a yield point will inhibit the rotor from moving, causing a displacement of the spring and a resultant stress to be recorded. In an ideal fluid, as soon as the yield stress had been surpassed, the rotor will begin to turn. This event will be indicated by a change in the shape of the flow curve from a nearly perpendicular line to one of constantly decreasing slope. In several of the melter feeds, the shear stresses immediately following the linear region are lower than the yield stress. This may be due to a combination of the acceleration of the rotor as the yield stress is surpassed and the viscous nature of the slurry, which tends to dampen the response. In an effort to minimize these effects and to better define the yield point, a series of runs were conducted in which the acceleration of the rotor was slowed during the initial phase of testing. In preliminary tests, very slow acceleration rates resulted in increased noise at the lower shear rate ranges, making the distinction of yield points less clear. The best transition through the yield stress to the fluid flow portion of the curve occurs at an initial rotor acceleration of approximately 3 rpm/min for the first 10 s. The yield stress is then determined by the intersection of the tangents of the straight line and curved portions of the initial flow curve.

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

The yield stress values reported in this and previous reports were obtained by the conservative SRL extrapolation procedure. These conservative values will probably decline once a procedure application to yield-pseudoplastic materials is developed and verified.

CONCLUSIONS

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

- Simulated HWVP reference feeds should be boiled for several hours as part of the preparation to obtain representative rheological properties.
- Treating simulated HWVP reference feed with formic acid reduces the apparent viscosity and yield stress of the slurry up to 0.23 g HCOOH/g of waste oxides. Beyond this level of acid addition, the effect is small.
- The addition of selected unreacted glass-forming chemicals to the simulated waste increases measured values of apparent viscosity and yield stress above levels achieved by melter feed prepared with all -80/+200 mesh frit.
- The substitution of two-thirds by weight -200 mesh frit for the coarser frit appears to increase measured values of apparent viscosity and yield stress above those achieved using all coarse frit.
- The results of treating simulated HWVP reference feed with formic acid on a laboratory-scale were verified on an engineering scale.
- HWVP melter feed prepared on an engineering scale with selected unreacted glass-forming chemicals exhibited rheological properties that were much different than laboratory-prepared batches and that exceeded DWPF limits. However, no feed processing or transport difficulties were experienced with these feeds.

- HWVP melter feed prepared with the all-frit glass-forming material processed in the HBCM at an approximately 30% higher rate than the feed made with unreacted chemicals.
- The measured values of melter feed apparent viscosity and yield stress were not affected by changes in temperature between 25°C and 45°C.
- Yield stress values for HWVP melter feeds are best measured at initial viscometer rotor accelerations of 3 rpm/min.

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FEED PREPARATION AND TRANSFER SYSTEMS

H. T. Blair, D. H. Mitchell, R. K. Nakaoka,
M. E. Peterson, and G. J. Sevigny

SUMMARY

The air displacement slurry (ADS) pump was used in a second radioactive test and in two other nonradioactive tests. A new system for measuring slurry level and specific gravity in feed tanks was successfully tested for 5 months. The addition of formic acid to Hanford Waste Vitrification Program (HWVP) waste was successfully demonstrated with pilot-scale equipment.

INTRODUCTION

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

Activities and results of the work being performed at Pacific Northwest Laboratory (PNL) to support the development, design, selection, and operation of the feed preparation and transfer systems are discussed. During FY 1985, specific activities concerning feed preparation and transfer systems include:

- Long-term demonstration of the ADS pump designed by PNL for charging slurry to melters.
- Radioactive demonstration of melter feed transfer equipment in support of radioactive demonstration of the liquid-fed ceramic melter (LFCM).

- Design of a fully remote ADS pump and a slurry sampler for the West Valley Demonstration Project (WVDP).
- Development of a melter feed tank design including the agitator and heat transfer system.
- Demonstration of a slurry level and specific gravity measuring system that will work in concentrated slurries and high radiation fields.
- Evaluation of remote liquid sampling devices for concentrated slurries.

TECHNICAL PROGRESS

Progress on feed preparation and transfer system work is reported in the following sections.

PILOT-SCALE TANK FOR TREATING WASTE WITH FORMIC ACID

The addition of formic acid to simulated radioactive liquid waste enhances the rheological properties and more realistically simulates actual Hanford waste. Formic acid addition was a part of the feed preparation procedures adopted prior to the pilot-scale ceramic melter (PSCM) experiments conducted this quarter. The tank in which the waste is treated with formic acid has an internal six-wrap hexagonal steam coil around its perimeter. The tank uses an axial agitator with turbine blades and a paddle wheel. The acid introduction system consists of an acid weigh tank on a scale, a positive displacement diaphragm pump for metering formic acid, a water flush line, and a submerged acid addition line.

A total of 1575 L of simulated HWVP waste treated with formic acid were prepared for high-bay ceramic melter (HBCM) experiment 85-1 (HWVP-11), while 11,500 L of simulated Hanford waste were prepared for a PSCM experiment (PSCM-22; HWVP-12). During the forming procedure, the tank contents were heated to 90°C, then 90 wt% formic was added at 20 L/h over a 2-h period. The acid was added below the liquid level to prevent vaporization on the surface. When 70% of the formic acid was added to the waste concentrate, surface foaming

was observed. Subsequent reduction of the acid addition rate after 60 wt% of the acid was added mitigated foaming. The addition of formic acid to simulated Hanford waste was successfully demonstrated.

AIR DISPLACEMENT SLURRY PUMP

The ADS pump was used for an experiment with the radioactive LFCM. The experiment lasted 90.4 h with the ADS pump feeding to the melter for ~62.5 h. Equipment failure caused 14 h of downtime; the flexible coupling connecting the master and slave shafts of the ADS pump air cylinder assembly came loose. The coupling had not been back-welded during fabrication. During this experiment, the feed line became plugged. Attempts at water flushing were unsuccessful and the experiment was, therefore, terminated. The air cylinder assembly design is being modified to avoid this source of downtime in the future.

The ADS pump was also used for two PSCM experiments. During PSCM-20, the ADS pump was used for 220 h. Feed rates ranged from 21 to 32 L/h. To achieve lower flow rates without long periods of dead time, a 0.25-in. orifice was placed in the air supply line to reduce airflow. Water flushing of the feed nozzle was required because of decreasing flow rates and solids collecting on the tip. The ADS pump performed well during this experiment. Similar successful performance was demonstrated during PSCM-21.

MEASURING SYSTEM FOR SLURRY LEVEL AND SPECIFIC GRAVITY

An accurate and reliable system is needed for tank level measurement and specific gravity determination for slurries. Conventional systems have disadvantages because of problems with radiation damage to components, plugging and fouling, and the need to be remotely operable. A system was tested that uses metal diaphragms that pneumatically balance the pressure on the diaphragm. The system consists of Holledge^(a) pneumatic diaphragm sensors and Gould^(b) pressure transducers (see Figure 1). The metal diaphragm sensors were not damaged by simulated melter feeds during 5 months of use. During system use,

(a) Holledge Ltd., Crawley, England.

(b) Gould, Inc., Oxnard, California.

FIGURE 1. Holledge Sensors Integrated with Differential Pressure Cells and Air Supply

electronics were moved and not recalibrated, which led to inaccuracies in measurements. Although a significant bias was detected in all readings, the overall precision was greater than 98%.

Based on the experience gained in 5 months of testing, the following recommendations are made:

- All-welded construction is recommended to reduce the potential for the seepage into the sensor that occurred during this experiment.
- All tubing connecting to the sensors (supply and vent lines) should be cleaned and inspected prior to assembly with the sensors to reduce the possibility of foreign particles affecting sensor performance.
- The sensors can be easily damaged mechanically or by obstructions of the orifice or vent lines. Care should be taken to assure that vent lines are never plugged and that supply lines never exceed allowable pressures. The sensors should be protected from mechanical damage.
- Level and specific gravity readings should be taken with the agitator off; however, readings with the agitator on should be adequate to sense alarm conditions.
- Redundant filters on instrument air should be used.
- The sensors are subject to a dead band effect at less than 25 in. of head. The dead band of the sensor could be connected with a microprocessor to account for the effect, thereby giving more accurate readings at less than 25 in. of water. The microprocessor could also account for the offset of the bottom sensor from the tank floor.
- Calibration data for each sensor should be included in the procurement documents.
- Electronics should be recalibrated if the sensors are moved.

CONCLUSIONS

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

- Over 15,000 L of simulated radioactive melter feed was treated with formic acid to enhance rheological properties. Reducing the formic acid addition rate after 60 wt% of the formic acid has been added mitigates excessive foaming of the feed.
- During a radioactive experiment, ADS equipment failure resulted in significant downtime. The experiment was eventually terminated due to plugging in the feed line. The air controller elements that caused this failure are being redesigned. The ADS pump operated successfully during extended nonradioactive tests.
- To eliminate feed tank pressurization, mechanical agitators are being evaluated as substitutes for the existing pulse agitators in the radioactive LFCM system.
- The Hollledge pneumatic system for level and specific gravity measurement was successfully operated for 5 months.

MELTER SYSTEMS

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

SUMMARY

Three radioactive liquid-fed ceramic melter (RLFCM) shakedown experiments were conducted this quarter (RLFCM-3a, -3b, and -3c). These experiments were compromised by feed system problems that limited the transfer of feed to the melter. During RLFCM-3c, the melter operated for approximately 90 h with an on-line efficiency of 63%. The final continuous operating period lasted 27.4 h.

Analyses of test results from several nonradioactive experimental-scale, engineering-scale, and pilot-scale melter tests were completed this quarter. The results of these analyses are discussed.

INTRODUCTION

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

An additional objective of this work is to evaluate melter facility process equipment modifications, first with simulated nonradioactive feeds in the PSCM and then with radioactive feeds in the RLFCM. The process equipment modifications include feed tank agitation, slurry sampling, glass sampling,

feed delivery systems, off-gas treatment systems, process variable sensor development, and process control concepts.

TECHNICAL PROGRESS

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

RADIOACTIVE TESTING

During the RLFCM-3 shakedown experiment, a leak at the flange connection between the air displacement slurry (ADS) pump discharge and the feed line jumper to the melter limited feed transfer to the melter. During both RLFCM-3a and -3b, the feed system operated for only a few minutes before the flange leak forced the termination of the experiment. After the flange problems were corrected, the melter operated for 90.4 h (RLFCM-3c); however, ADS pump feed delivery problems limited the on-line efficiency to only 63%.

For the RLFCM-3 experiment, the ADS pump configuration used an air-cylinder-driven 1-L capacity syringe to supply the air pressure to force the slurry out of the submerged pump cavity to the melter feed nozzle. With the fixed 1-L pulsed air volume, long jumpers and leaky jumper block connectors reduced the volume of slurry transferred to the melter to only a few milliliters per pump cycle. Feed rates during this period were erratic; and on several occasions feeding stopped altogether, necessitating a time-consuming feed nozzle flushing operation.

The final feed system failure occurred when the coupling between the drive cylinder and the syringe vibrated loose and finally separated completely. When this problem was repaired and the syringe system was reinstalled, the feed delivery system ran continuously for 27.4 h. RLFCM-3 was terminated when the allotted time for the experiment was reached.

NONRADIOACTIVE TESTING

Test results from a number of melter experiments were analyzed this quarter. These analyses are discussed in the following sections.

Experimental-Scale Melter Testing

The ECM is a small test melter with a melter cavity measuring 15 cm wide by 36 cm from electrode face-to-electrode face. At the nominal overflow level, the melt depth is 15 cm. A complete description of the ECM is given in Burkholder and Jarrett (1985).

During FY 1984 and FY 1985, 18 experiments have been performed in the ECM with West Valley or related feeds. The objective of the tests was to identify a feed composition that would incorporate the West Valley Purex sludge, Thorex waste, and the zeolite ion exchanger used to decontaminate the Purex supernatant. A major objective of FY 1985 testing was to investigate the formation of a Ca/rare-earth/ PO_4 phase on the glass surface during processing. The following variables have been investigated: reductant level; incorporation of zeolite; acid type and level; alkali type and level; boron level; and rare-earth, Ca, Cr, and P concentrations. The results of FY 1984 research are documented in Burkholder and Rusin (1985). The results of FY 1985 ECM testing are summarized in the following sections. Operating data are presented in the Appendix (see p. 56).

In FY 1985, 13 separate ECM tests have been performed with West Valley or related feeds. These tests are summarized in Table 1, and the glass compositions are listed in Table 2. Operating data for these tests are given in the Appendix to this section. The first three tests (ECM-85-1, -2, and -3) and ECM-85-6 were performed to optimize the WV183 glass formulation. In ECM-85-4 and -5, a high Cs glass that was designed after the WV183 composition was tested (Burkholder, Jarrett, and Minor 1985). Zeolite was added to one of these glasses to determine its effect on melt performance. A Savannah River Laboratory (SRL) analog glass with formatted waste was tested in ECM-85-7. Several glass formulations with partially and fully nitrated feeds were tested in ECM-85-8 through -13.

TABLE 1. Summary of FY 1985 West Valley-Related Experimental-Scale Ceramic Melter Tests

ECM Test	Glass Formulation	Feed Formulation	Test Duration, h	On-line, %	Average Feed Rate, L/h	Average Glass Temperature, °C	Cold Cap Behavior	Comments
ECM-85-1	WV183	Nitrated plus sugar	23.8	57	2.3 ^(a) 1.5 ^(b)	1160	Rigid; tendency to bridge; average ~70%	Viscous surface layer
ECM-85-2	WV183	Nitrated plus sugar, sulfate	24.0	98	2.1 ^(a) 2.8 ^(b)	1160	Thin; less rigid; some venting; average ~80%	Viscous surface layer
ECM-85-3	WV183	Nitrated plus sugar, sulfate	76.8	88	1.7 ^(a) 1.8 ^(b)	1160	Similar to ECM-85-2 but with bridging; average ~55%	Viscous surface layer
ECM-85-4	FRG-8	Glass formers for zeolite	40.3	100	3.4	1150	Rigid but thin with many vents; average ~60%	Very good melt behavior
ECM-85-5	FRG-8	Zeolite	27.8	100	3.5	1160	Rigid but thin with many vents; average ~70%	Melt behavior identical to ECM-85-4
ECM-85-6	WV192 WV183 Update	Nitrated	46.3	92	3.0	1175	Rigid but thin with many vents; average ~50%	WV192 is WV183 with less rare-earth elements used for U and Th substitution
ECM-85-7	WV202 SRL TDS-165 analog	Formated	24	100	2.8	1180	Rigid but thin with many vents; average ~75%	Some scum and molten salts
ECM-85-8	WV199	Partially nitrated	34	94	2.1	1150	Rigid but thin with many vents; average ~70%	Formed glassy insoluble phase; rubbery
ECM-85-9	WV199	Fully nitrated	18.6	100	2.4	1160	Very rigid; little venting; average ~60%	Formed glassy insoluble phase; rubbery
ECM-85-10	WV203 PSCM-16 analog	Partially nitrated	41.4	100	3.0 ^(a) 3.4 ^(c)	1130	Very active; flexible; average ~40%	Small amount of scum
ECM-85-11	WV202 SRL TDS-165 analog	Partially nitrated	36.5	100	2.3	1170	Rigid; some venting; average ~70%	Surface scum very rigid
ECM-85-12	WV204	Partially nitrated	37.8	97	2.5	1160	Rigid; thick; moderate venting; average ~60%	Surface scum very rigid
ECM-85-13	WV205 SRL interim glass	Partially nitrated	42.5	98	2.8 ^(a) 3.2 ^(b)	1150	Thin; flexible; active venting; average ~60%	Small amount of scum

(a) Average for entire test.

(b) Stable feed rate for last 8 h.

(c) Average for last 20 h of test.

TABLE 2. Glass Compositions for FY 1985 Experimental-Scale Ceramic Melter Tests

Glass Oxides	FY 1985 Experimental-Scale Ceramic Melter Tests								
	1, 2, and 3 ^(a)	4 and 5 ^(b)	6 ^(c)	7 and 7E ^(d)	8 and 9 ^(e)	10 ^(f)	11 ^(g)	12 ^(h)	13 ⁽ⁱ⁾
Al ₂ O ₃	2.36	2.39	3.29	2.80	3.31	3.31	3.31	3.31	3.31
B ₂ O ₃	15.53	14.93	15.58	7.50	15.56	8.80	7.56	7.50	9.96
BaO	0.06	1.29	0.06	0.07	0.06	0.06	0.06	0.06	0.06
CaO	0.63	0.81	0.61	0.62	0.61	0.61	0.61	0.61	0.61
CaO ₂	0.17	0.29	0.16	0.07	0.16	0.16	0.16	0.16	0.16
Cr ₂ O ₃	0.68	0.70	0.22	0.71	0.22	0.22	0.22	0.22	0.22
Cs ₂ O	0.10	5.75	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Fe ₂ O ₃	12.23	10.04	11.75	11.90	11.84	11.84	11.84	11.84	11.84
K ₂ O	0.08	--	0.07	0.08	0.07	0.50	0.07	0.50	3.51
Li ₂ O	--	--	--	4.50	--	3.75	4.55	4.00	3.05
MgO	0.08	0.53	0.16	0.08	0.16	1.30	0.16	1.16	1.31
MnO ₂	0.48	0.77	1.71	0.91	1.73	1.73	1.73	1.73	1.73
Na ₂ O	14.74	11.95	14.76	10.50	14.23	14.65	10.22	12.50	11.03
NiO	0.45	0.30	0.69	0.85	0.70	0.70	0.70	0.70	0.70
P ₂ O ₅	2.60	--	2.50	2.72	2.52	2.52	2.52	2.52	2.52
RE ₂ O ₃	2.92	2.29	0.12	0.25	0.12	0.12	0.12	0.12	0.12
RuO ₂	--	--	0.08	0.10	0.08	0.08	0.08	0.08	0.08
SiO ₂	44.67	44.80	44.73	52.30	45.22	45.64	52.68	49.50	45.20
SO ₃	0.14	0.50	0.13	0.64	0.50	0.50	0.50	0.50	0.50
SrO	0.03	1.91	0.03	0.04	0.03	0.03	0.03	0.03	0.12
TiO ₂	--	--	--	--	--	0.60	--	--	0.97
Y ₂ O ₃	0.02	--	0.02	--	0.02	0.02	0.02	0.02	0.02
ZrO ₂	1.68	0.07	3.10	3.16	3.12	3.12	3.12	3.12	3.12
Other	0.35	0.68	0.13	--	--	--	--	--	--
Total	100.00	100.00	100.00	100.00	100.36	100.00	100.00	100.00	100.00

- (a) ECM-85-1, -2, and -3; WV183 glass; fully nitrated feed with no HNO₃ added; ~10 wt% IE-96 zeolite.
 (b) ECM-85-4 and -5; FRG-8 glass (WV192 with high Cs and no P); nitrated feed with no zeolite (ECM-85-4) or ~10 wt% IE-95 zeolite (ECM-85-5).
 (c) ECM-85-6; WV192 glass (updated WV183); nitrated feed.
 (d) ECM-85-7 and -7E; WV202 glass, SRL TDS-165 analog glass with old waste; formatted hydroxide feed.
 (e) ECM-85-8 and -9; WV199 glass; partially (ECM-85-8) and fully (ECM-85-9) nitrated hydroxide feed; 25 and 50 g/L sugar; ~10 wt% IE-96; Na oxalate glass former.
 (f) ECM-85-10; WV203 glass, PSCM-16 analog; partially nitrated hydroxides; 50 g/L sugar; ~10 wt% IE-96; Na oxalate glass former.
 (g) ECM-85-11; WV202; SRL TDS-165 analog; partially nitrated hydroxides; 22 g/L sugar; ~10 wt% IE-96; Na oxalate glass former.
 (h) ECM-85-12; WV204, PSCM-16, SRL TDS-165 hybrid; partially nitrated hydroxides; 22 g/L sugar; ~10 wt% IE-96; Na oxalate glass former.
 (i) ECM-85-13; WV205, SRL Interim glass analog; partially nitrated hydroxides; 36 g/L; ~10 wt% IE-96; Na oxalate glass former.

High B, No Li Glasses

The ECM-85-1, -2, -3, -6, -8, and -9 tests all used glass formulations with high B and no Li contents. The WV183 glass formulation was derived from the WV182 glass used in the August 1984 PSCM melter test (Burkholder, Jarrett, and Minor 1985). The major difference was that the Ca glass former used in WV182 was eliminated and IE-96 zeolite ion exchanger^(a) was used instead of IE-95 to further reduce the total Ca content. The WV192 glass is closely related to WV183 except that the substitution formula for U and Th simulants was changed. Formerly, the U and Th oxides were replaced by a mixture of 65% rare-earth oxides and 35% ZrO_2 . The WV192 substitution formulation was a mixture of 70% ZrO_2 , 10% Al_2O_3 , and 10% MnO_2 . The WV199 formulation is essentially the same as WV192 except that the waste fraction composition was updated based on input from West Valley.

The ECM tests with the high B, no Li glasses showed similar rigid, easily bridging cold cap behavior, except for ECM-85-2 and -6. The ECM-85-2 and ECM-85-6 tests were run after the melter was flushed using an earlier West Valley glass (WV131S flush glass). In these tests, melting rates and the cold cap behavior were improved probably because of the high alkali content and low viscosity of the WV131S flush glass. Replacement of the rare-earth substitute for Th and U and elimination of the major part of the Ca in the feed formulation appeared to help eliminate the Ca/rare-earth/ PO_4 phases from the surface scum.

High B, No Li, High Cs Glasses

ECM-85-4 and -5 processed a feed that produced a glass (FRG-8) that was essentially a high-cesium version of WV192 with no phosphorus. The final glass formulations for the ECM-85-4 and -5 tests were identical; however, in ECM-85-5 about 10 wt% zeolite was added to the feed replacing some of the unreacted mineral glass formers. Both feeds melted very well, forming a thin, very active cold cap. There was no discernible difference between the melting behavior of the feeds. The glass surface after each test was clean and no secondary phases were noted.

(a) Linde IE-96 and IE-95 are registered tradenames of the Union Carbide Corporation.

Low B, High Li Glasses

Three tests (ECM-85-7, -7E, and -11) were run to determine the processability of an SRL TDS-165-type glass with West Valley waste. These tests compared the WV202 glass formulation as a formatted slurry (85-7 and -7E) and as a partially nitrated slurry (85-11). The first two experiments were compromised because IE-95 (labeled as IE-96) was added to the feed, doubling its CaO content. These runs also used the previous West Valley feed formulation and, thus, had a higher Cr level. The feed rates for ECM-85-7 and -7E were moderately higher. It appeared that the cold cap behavior was improved with the nitrated waste in ECM-85-11. During the ECM-85-7 and -7E tests, the cold cap was quite rigid with a tendency to cone; little gas venting was observed. The ECM-85-11 feed produced a moderately flexible cap with some venting. Heavy scum was found on the melt surface after each run. In ECM-85-7 and -7E, this scum consisted primarily of apatite, spinel, and hematite phases; in ECM-85-11, the scum contained no PO_4 phases but did contain spinel and ZrO_2 . The differences in apatite phases were attributed to the extra Ca in the ECM-85-7 feed. The ZrO_2 found in the ECM-85-11 scum was attributed to the ZrO_2 used to make a final feed composition adjustment. Normally, zirconyl nitrate is added as a Zr source. No Zr has been found in surface phases except when the ZrO_2 was used.

The conclusions from these tests were that formatted and nitrated feeds behave similarly and that there is no real incentive for West Valley to switch to a formate flowsheet based on melter considerations.

High Alkali Plus Boron Glasses

In ECM-85-10, -12, and -13, partially nitrated feeds were processed that produced glasses with a high alkali plus boron content. The WV203 composition used in ECM-85-10 was based on the WV131S glass. The WV204 glass used in ECM-85-12 was a hybrid between the WV203 and WV202 compositions (SRL TDS-165 analog). The WV205 glass used in ECM-85-13 is the new SRL interim glass and contains about 3.5% K_2O , adapted for West Valley waste.

The WV203 glass processed very well; this glass had the highest feed rates observed in the ECM with West Valley wastes. The cold cap was very active and flexible, and many vents were produced. A very minimal second phase was found

after ECM-85-10 that contained mostly spinel and ZrO_2 with no PO_4 phases. The ZrO_2 was attributed to the adjustment of the feed with ZrO_2 .

The WV204 feed (ECM-85-12) processed very much as expected based on its hybrid origins. The feed rate was between that of WV202 and WV203 partially nitrated feeds. The cold cap tended to be somewhat rigid, and the surface phase that remained after the tests was rigid and similar to that left after ECM-85-11 with WV202 feed. The ECM-85-12 surface phases were not analyzed; however, they probably contain mostly spinel and ZrO_2 with very little PO_4 .

Partially nitrated WV205 was processed in the ECM-85-13 test. This feed produced a moderate to very active flexible cold cap with vigorous vents that tended to splatter molten glass. This behavior would be expected with the low viscosity of the WV205 glass. Surface phases after the test were minimal and very similar to those found with WV203 (mostly ZrO_2 and spinel with small amounts of apatite).

Engineering-Scale Melter Testing

An engineering-scale melter run was completed on April 22, 1985, in support of the Hanford Waste Vitrification Program (HWVP). The 5-day experiment was conducted in the high-bay ceramic melter (HBCM). This experiment was the first one to be completed in the HBCM in FY 1985 and the eleventh melter experiment conducted in support of HWVP. Thus, the experiment was designated HWVP-11/HBCM-85-1.

The test was designed to evaluate the processability and product quality of the newly designated initial reference glass (HW39) and reference waste feed (HWVP-RF). The current reference waste for HWVP is envisioned to be a blend of washed neutralized current acid waste (NCAW) and the transuranic (TRU) fraction of cladding removal waste (CRW). The majority of the components of the simulated waste are added as hydroxides or fluorides. The target oxide waste loading of the simulated glass is 25 wt%.

In November 1984, it was determined that the reference method for canister decontamination would be the Savannah River Defense Waste Processing Facility (DWPF) process of slurry frit blasting. In this scheme, the spent contaminated frit will be combined with simulated waste as a glass-forming component. The

contaminated frit will make up one-third of the total glass formers needed, which provides the flexibility of adding the remaining glass formers as frit or as unreacted bulk chemicals. Both of these options offer certain advantages. The addition of 100% frit insures that the glass formers will be present in the proper chemical ratios and reduces the number of bulk chemicals to be handled during feed preparation. During processing in the melter, glass-former component volatility is less than that of unreacted chemicals. The conversion of nitrate and carbonate bulk chemicals to glass-forming oxides causes the release of NO_x and CO_2 . However, adding the glass formers as unreacted chemicals introduces more flexibility in adjusting to variations in the HWVP reference waste stream composition. In addition, the redox level of the glass can be adjusted using a carbon reductant added as a constituent of the glass-forming chemicals.

The two options for adding glass formers were tested during HBCM-85-1. For the first three days of the run, the feed consisted of simulated waste and 100% of the glass formers added as solid frit. For the remaining two days, the feed consisted of simulated waste and glass formers added as one-third frit and two-thirds unreacted chemicals. The two compositions were evaluated based on their processability, cold cap characteristics, slurry rheology, and melt performance.

An additional objective of HBCM-85-1 was to evaluate the procedure and equipment used to react the simulated waste with 90 wt% formic acid prior to the addition of glass formers. The composition of the simulated HWVP reference feed prior to forming is presented in Table 3. The forming of the simulated waste, which is part of the DWPF processing scheme, improves the rheology of the feed and decreases the amount of additional reductant (sugar) needed to maintain the appropriate redox level in the glass melt to prevent foaming. The forming process includes the preparation of the waste, followed by heating the slurry to over 90°C prior to acid addition. The glass formers (Tables 4 and 5) are then blended into the slurry.

The HBCM is an engineering-scale, joule-heated, ceramic-brick-lined glass furnace (Figure 1). The internal cavity, with respect to the nominal glass level, is 66 cm long by 41 cm wide by 23 cm deep. After accounting for the

TABLE 3. Composition of Simulated HWVP Reference Feed in Melter Feed Slurry^(a)

Compound	Concentration, g/L	Assumed Oxide	Concentration, g/L	Glass, wt%
Fe(OH) ₃	59.5	Fe ₂ O ₃	44.4	11.10
Al(OH) ₃	26.3	Al ₂ O ₃	17.2	4.30
NaNO ₃	13.4	Na ₂ O	10.7	2.68
Cr(OH) ₃	7.21	Cr ₂ O ₃	5.3	1.33
NaOH	3.58	ZrO ₂	2.4	0.60
Na ₂ C ₂ O ₄ ^(b)	3.37	SiO ₂	3.0	0.75
Zr(OH) ₄	3.11	NiO	2.4	0.60
SiO ₂	3.00	SO ₃	1.5	0.38
Ni(OH) ₂	3.00	La ₂ O ₃	2.2	0.55
Na ₂ SO ₄	2.32	MoO ₃	1.2	0.30
LaF ₃	2.16	Nd ₂ O ₃	2.1	0.53
Na ₂ MoO ₄ • 2H ₂ O	2.00	Cs ₂ O	1.0	0.25
Nd(OH) ₃	1.84	CeO ₂	0.7	0.18
CsOH	1.05	CuO	0.6	0.15
Ce(OH) ₃	0.79	MnO ₂	0.7	0.18
Cu(OH) ₂	0.74	BaO	0.4	0.10
Mn(OH) ₂	0.74	F ⁻	1.2	0.30
BaSO ₄	0.63	SrO	0.4	0.10
NdF ₃	0.58	Pr ₆ O ₁₁	0.4	0.10
Sr(OH) ₂	0.47	MgO	0.3	0.08
Pr(OH) ₃	0.47	CaO	0.3	0.08
La(OH) ₃	0.47	Y ₂ O ₃	0.2	0.05
NaF	0.47	Sm ₂ O ₃	0.2	0.05
Mg(OH) ₂	0.42	TOC	0.6	0.15
CaF ₂	0.42			
Y(OH) ₃	0.26			
Sm(OH) ₃	0.21			
	138.51		99.6	24.89

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

(b) TOC substitute.

TABLE 4. Glass-Forming Fraction in Melter Feed Slurry with 100% Frit

Compound	Concentration, g/L	Oxide Form	Concentration, g/L	Glass, wt%
HW39 frit ^(a)	300.0	SiO ₂	201.8	50.44
		B ₂ O ₃	38.2	9.56
		Na ₂ O	30.8	7.69
		Li ₂ O	15.0	3.75
		CaO	11.2	2.81
			3.0	0.75
			300.0	75.0

(a) HW39 frit size distribution: one-third -80/+200 mesh; two-thirds -200 mesh.

TABLE 5. Glass-Forming Fraction in Melter Feed Slurry with One-Third Frit and Two-Thirds Unreacted Chemicals

Compound	Concentration, g/L	Oxide Form	Concentration, g/L	Glass, wt%
HW39 frit ^(a)	100.0	SiO ₂	201.8	50.44
SiO ₂	134.4	B ₂ O ₃	38.2	9.56
NaCHO ₂	20.0	Na ₂ O	30.8	7.69
Na ₂ B ₄ O ₇ · 10H ₂ O	69.9	Li ₂ O	15.0	3.75
LiCHO ₂ · H ₂ O	46.9	CaO	11.2	2.81
Mg(NO ₃) ₂ · 6H ₂ O	12.8	MgO	3.0	0.75
Ca(NO ₃) ₂ · 4H ₂ O	31.6			
	425.6		300.0	75.0

(a) HW39 frit size distribution: -80/+200 mesh.

sloping side walls, this corresponds to a glass capacity of approximately 55 L. During the test, 1095 L of feed was processed and 390 kg of glass was produced. The oxide loading of the feed, determined by analyses of feed samples collected during the experiment, was 365 g/L (the target oxide loading was 400 g/L). Assuming a glass density of 2.5 kg/L, 156 L of glass was produced. If the melter is assumed to follow perfectly mixed tank kinetics, the calculated

FIGURE 1. Engineering-Scale High-Bay Ceramic Melter

turnover is 94%. The actual turnover, based on calcium and boron concentration analyses found in final glass samples, was 90% to 96%.

The results of this test indicate that the 100% frit reference feed is more desirable than reference feed with glass formers added as one-third pre-made frit and two-thirds unreacted bulk chemicals. This conclusion was based on a higher processing rate and superior cold cap characteristics experienced using the 100% frit feed. The nominal feed rate was 11 L/h (44 L/h-m^2), and the maximum rate was 14 L/h (56 L/h-m^2) during the 100% frit processing phase of the test. Nominal and maximum feed rates using the one-third frit and two-thirds chemical feed were 8 L/h (32 L/h-m^2) and 9 L/h (36 L/h-m^2), respectively.

The major differences between the cold caps generated by the feeds were coverage of the melt surface, thickness, flexibility, and venting behavior. The 100% frit feed produced a cold cap that ranged from 50% to 80% coverage and was 1 to 2 in. thick. The flexibility of the cap was maintained, and numerous

vents were present during this portion of the test. These characteristics are very conducive to stable melter operations. With the unreacted chemical feed, a very rigid cold cap formed and little or no venting was visible. The thickness of the cold cap varied from 1 to 3 in., and it covered 70% to 100% of the glass surface. The cold cap of the 100% frit feed melted faster than the unreacted chemical feed once the feed was terminated, indicating a thinner and more easily dissolvable material.

The use of sugar as a reductant was successfully demonstrated with both slurry compositions to achieve slightly reduced glass melt conditions. For the slurry containing 100% frit, 3 g/L of sugar was required. For the slurry containing a mix of frit and unreacted glass-forming chemicals, 4.5 g/L of sugar was required. This higher concentration was required to counter oxidizing nitrates that comprised a portion of the unreacted glass-forming chemicals.

Based on post-test analysis of the product glass using scanning electron microscopy/energy dispersive x-ray microanalysis (SEM/EDX), the only crystalline material present in the glass is the cubic spinel phase: $(\text{Fe:Ni})(\text{Fe:Cr})_2\text{O}_4$. The spinel phase has been observed in previous HWVP glasses and is the result of the high Cr content in HWVP waste. The spinel crystals tended to agglomerate, forming crystal diameters in the range of 20 to 50 μm . Because of the larger size, there is more concern that the spinel crystals may be more prone to settling in the melt tank. Product glass analyses indicate that some spinel settling (up to 15%) may have occurred in the melter. Therefore, a major objective of the planned July PSCM-20 experiment is to quantify the amount of Cr holdup using in-tank crystal collection boats and mass balance calculations.

Based on the results of this experiment, premade frit has been chosen for glass-former addition for the long-term PSCM experiment. The primary objective of the PSCM experiment will be characterization of the HW39 processability on a pilot scale. Testing will determine nominal and maximum processing rates, off-gas system component performance evaluations, processability with and without sugar as a reductant, and extensive glass sampling to quantify the extent of spinel settling in the melt tank.

Pilot-Scale Melter Testing

A 10-day PSCM experiment (PSCM-20) was completed in April 1985 for the Federal Republic of Germany (FRG) under the NWTP. This experiment was designed to provide support for the radioactive canister production run scheduled for late FY 1985 in the RLFCM. The primary objectives of the experiment were to:

- verify acceptable melting behavior of a waste glass composition containing high levels of cesium and strontium
- define the melter operating parameters and procedures
- verify cesium volatility and off-gas system equipment performance
- determine a filling and cooling scheme that will produce a glass product with acceptable voids and glass fracture.

Results from off-gas studies and analysis of the eight test canisters filled during the experiment are discussed elsewhere in this report. Where appropriate, the test results are compared with results obtained from the two small-scale ECM tests (ECM-85-4 and -5). The ECM tests were conducted prior to PSCM-20 to confirm the glass selection. Many of the operating parameters and objectives were defined by the information required for RLFCM operation.

In an attempt to avoid melting problems, the FRG canister glass was modeled after typical U.S. waste glasses with known processing behavior. The reference glass selected was an interim West Valley waste glass composition that included 10 wt% zeolite ion-exchange resin. The major difference between the designed glass composition (FRG-8) and the interim West Valley composition was the high cesium and strontium levels and the lack of phosphate in the FRG-8 composition. Phosphate was eliminated to assure that insoluble alkaline earth phosphate phases would not separate from the melt. Sugar was added to the slurries as a reductant to reduce the glass melt and minimize the potential for melt foaming problems.

For efficient use of the radioactive cesium and strontium during production of the actual radioactive canisters, the experiment was also designed to demonstrate a means to achieve target levels of cesium and strontium in the

first canister filled. To accomplish this, a procedure was developed that reduced the melter glass inventory to the extent that was easily achievable (approximately two-thirds full); and a slurry containing approximately three times the nominal cesium and strontium waste concentrations was fed to the melter until the normal operating level was reached. This slurry is designated the spike feed. Glass sampling to define the mixing time and off-gas sampling to determine the cesium and strontium losses were conducted during this portion of the experiment.

During the FRG canister filling, the average feed rate was 21 L/h. This rate was selected to duplicate the expected RLFCM processing rate. At other periods, the feed rate was increased to determine the maximum stable feed rate (per unit area) and further characterize off-gas emissions. The off-gas flow was treated with an ejector venturi scrubber and a high-efficiency mist eliminator to duplicate the system that will be used during the radioactive production run.

Spiked Feed Processing Results

With one-third of the glass in the melter removed, the spiked feed was added until the normal melter operating level (at a melter vacuum of 5 in. water) was achieved and the tank inventory contained Cs and Sr levels that were representative of steady-state feeding. About 830 L of slurry was fed to the melter over a 22-h period at an average rate of 34 L/h (45 L/h-m^2). Processing was stable with 70% to 80% cold cap coverage. Based on these results, the average stable feed rate expected in the RLFCM is 23 L/h. Although this feed rate is 25% lower than predicted based on ECM results, it is still considered acceptable. The glass melt was stable with no foaming. A thin cold cap over the glass surface prevailed throughout the experiment. Little or no active venting was observed. The cold cap dissolved completely in approximately 50 min after feeding was stopped.

Analytical results of glass core samples taken of the melt tank after the spiked feed addition showed that the glass tank was mixed and homogeneous after only 8 h of idling. Therefore, convection bubblers to enhance mixing are not considered necessary.

FRG-8 Feed Processing Results

Approximately 4750 L of slurry was fed to the melter, producing 1700 kg of glass over a 218-h period. The maximum stable feed rate achieved during the first 24 h was 32 L/h (43 L/h-m^2). Cold cap coverage was maintained at 70% to 80%. Therefore, the RLFCM can expect to achieve a stable feed rate of 21 L/h. Although this feed rate is 25% lower than predicted based on ECM results, it is still considered acceptable. Higher feed rates are considered possible, however, because of the thin cold cap coverage.

No significant crystallization was seen in the glass samples. The eight FRG canisters were filled at an average slurry feed rate of 21 L/h with a cold cap coverage of approximately 50%. At both the 50% cold cap coverage and 70% to 80% coverage, the glass melt was stable and there was little venting action observed through the 0.25- to 0.50-in. cold cap.

Two sugar levels (90 g/L and 70 g/L) were used in the experiment to obtain reducing melt conditions as indicated by product glass ferrous/ferric ratios greater than zero. At 90 g/L, the ferrous/ferric ratio was 0.25; at 70 g/L, the ferrous/ferric ratio was 0.01. The ferrous/ferric ratio at the 90 g/L sugar loading is within the range recommended in previous laboratory work to assure a stable glass melt (0.1 to 0.3). Recent melter tests have shown that higher processing rates and stable glass melts can be achieved under less reducing conditions. Because no glass foaming occurred in either case, it is recommended that the RLFCM use the lower sugar level. The variation in sugar level did not alter the processing rates or observed cold cap behavior. The maximum average feed rate during the low sugar period was 31 L/h (41 L/h-m^2) with 70% to 80% coverage.

The melter was operated under both constant power control and automatic resistance feedback control. The glass temperatures tended to be more stable under automatic resistance feedback control.

CONCLUSIONS

The RLFCM feed delivery system problems need to be investigated, and operation of the ADS pump with a fixed-volume syringe drive is marginal for remote operations. A constant-pressure-driven ADS pump will be evaluated next quarter.

The significant conclusions from ECM testing are as follows:

- The formation of Ca/rare-earth/ PO_4 phases on the glass surface is the major cause of poor melting performance.
- Cr phases appear to have little or no impact on melting performance.
- PO_4 phases continue to exist while idling.
- Zeolite does not degrade melting performance.
- Formate-based feeds melt comparably to nitrate-based feeds.
- Higher alkali, lower viscosity glasses improve melter performance through increased flux rate and suppressing phase separations.

A 120-h engineering-scale melter run was conducted in support of the HWVP. The experiment evaluated the processability and product quality of the current waste and glass-former composition. Testing demonstrated the acceptable processing of the slurry containing simulated waste and glass-forming frit addition. A nominal process rate of 44 L/h-m^2 and maximum rate of 56 L/h-m^2 were determined. As a result of testing, a long-term pilot-scale experiment was recommended. Pilot-scale testing will determine nominal and maximum processing rates, off-gas system component performance evaluations, processability with and without added reductant, and extensive glass sampling to quantify the extent of spinel settling in the melt tank.

A 10-day PSCM test was completed in April 1985 for the FRG under the NWTP. The work supports planned production of radioactive canisters in the RLFCM. Testing demonstrated a processable feed composition and suitable glass product. A method of quickly bringing the melt tank contents to correct specifications was demonstrated whereby the tank inventory was initially reduced followed by feeding of a slurry concentrated in waste components.

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APPENDIX - ECM OPERATION DATA

The following figures present electrode powers, feed rates, and temperatures for ECM-85-1 through ECM-85-13.

ECM 85-3

Runtime 18:15

ECM 85-6

ECM 85-7

Runtime 18:40

ECM 85-11

Runtime 22:00 0

ECM 85-12

ECM 85-13

CANISTER FILLING AND HANDLING SYSTEMS

D. H. Siemens and R. P. Allen

SUMMARY

One of the major activities of the radioactive liquid-fed ceramic melter (RLFCM) program is to prepare canisters of glass for the Federal Republic of Germany (FRG). Prior to shipment, the canisters must be leak tested to ensure that there are no weld defects that could result in contamination release during transport or subsequent repository experiments. A mass spectrometer leak detection system that will use helium as tracer gas is being developed to satisfy this requirement.

INTRODUCTION

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

TECHNICAL PROGRESS

The following sections discuss progress during this quarter on helium leak testing of FRG canisters.

HELIUM LEAK TESTING OF FRG CANISTERS

After filling and welding, the FRG canisters must be leak tested to ensure that there are no weld defects that could result in contamination release during transport or repository experiments. The FRG has requested that this leak testing operation include:

- use of a mass spectrometer leak detection system with helium as the tracer gas
- placement of the canister in a special vacuum chamber to provide maximum leak detection sensitivity
- preparation of a leak testing approach and procedures that provide the type of data and associated quality assurance validation required for FRG repository experiments
- provision for independent third-party review of the approach, procedures, and leak testing operations.

HELIUM LEAK TESTING STANDARDS

The following leak testing standards are relevant to the testing of FRG canisters:

- American National Standard for Leakage Tests on Packages for Shipment of Radioactive Materials (ANSI N14.5-1977) - This standard specifies methods for demonstrating that Type B(U) or Type B(M) packages comply with the package containment requirements of the International Atomic Energy Agency (IAEA) Regulations of the Safe Transport of Radioactive Materials, Safety Series No. 6, Revised. This standard specifies:
1) minimum leakage test requirements for package containment systems;
2) methods for relating leakage test procedures to package containment requirements; and 3) minimum requirements for leakage test procedures.
- Standard Methods of Testing for Leaks Using the Mass Spectrometer Leak Detector in the Inside-Out Testing Mode (ASTM E-493) - This standard covers procedures for testing sealed components for leakage

by placing the components inside a vacuum chamber connected to a helium leak detector. Two methods of introducing the helium are described: 1) prefilling--establishing a known pressure of helium inside the component during the sealing operation or 2) bombing--introducing helium into the sealed component through any existing leaks using a helium pressure chamber.

- Standard Methods of Testing for Leaks Using the Mass Spectrometer Leak Detector in the Detector Probe Mode (ASTM E-499) - This standard covers procedures for leak testing helium-containing components using a "sniffer" probe to sample the effluent side of the leak.

Valuable information relating to helium leak testing methods and procedures was also obtained from the following publication:

- Introduction to Helium Mass Spectrometer Leak Detection. 1980.
Varian Associates, Inc., Palo Alto, California.

Based on the information given in these sources, the following definitions, limits, and capabilities should be considered in establishing and implementing a helium leak testing procedure and system for the FRG canisters:

- Leaktightness - A leak rate of 10^{-7} atm cc/s or less, based on dry air at 25°C and a pressure differential of 1 atm against a vacuum of 10^{-2} atm or less, is considered to represent leaktightness.
- Sensitivity Considerations - To demonstrate leaktightness, the sensitivity of the leakage test procedure must be 5×10^{-8} atm cc/s. It should be noted that there is a difference between leak detector sensitivity and the sensitivity of a leak test procedure. The sensitivity of a helium leak detector is the measured response to the flow from a calibrated helium leak, whereas the sensitivity of a test procedure is the minimum detectable leakage rate.
- Leak Size Distribution - Although industrial leak rate specifications range from 10^{-9} to 1 atm cc/s, the majority of products have leak rate specifications from 10^{-6} to 10^{-1} atm cc/s. Leaks larger than 10^{-1} atm cc/s can usually be detected visually. The large class of leaks caused by incomplete welds, brazes, and seals does not usually

extend below 10^{-7} atm cc/s. Leak paths with leakage rates of 10^{-7} atm cc/s are small and close easily with liquids or minute particles. Although such small leaks can be detected, they are rarely found in practice.

- Helium Leak Detection Capabilities - Helium methods can be used to detect leaks as large as 1 atm cc/s. The theoretical minimum detectable leak rate is 10^{-11} atm cc/s; however, practical limits are about 10^{-5} to 10^{-7} atm cc/s for the probe method, 5×10^{-8} atm cc/s for the bombing method, and 10^{-8} atm cc/s for the prefill method. Sensitivity is limited for these latter techniques by the desorption of helium from the component and test system surfaces.

SELECTING A HELIUM LEAK TESTING APPROACH

Sensitivity Requirement

The first step in defining a helium leak testing approach is to establish the required sensitivity for the leak test procedures. The official definition of leaktightness is a leak rate of 10^{-7} atm cc/s or less, although leaks this small clog easily, particularly with liquids. Since the FRG canisters will be electropolished in viscous phosphoric acid before leak testing, a leak rate of 1×10^{-6} atm cc/s will probably represent a practical detection minimum. The corresponding required sensitivity of the leak test procedure for this size leak is 5×10^{-7} atm cc/s.

Basic Considerations

The following canister- and process-related factors must be considered in selecting a helium leak testing approach:

- The canisters will be welded in a hot cell, transported to an adjacent hot cell, and decontaminated before final leak testing.
- A preliminary helium leak check using a sniffer probe will be performed in the cell where the canister is welded to detect gross leaks.

- It is not practical to weld the canisters in a helium atmosphere; some other helium introduction method must be used.
- The time to complete the welding operations after introduction of a helium source could be as long as 6 h.
- The elapsed time after closure until the final helium leak check could be as long as 170 h.
- The canisters will be filled with glass to a target level of 85%. The actual level, however, will vary from canister to canister and, combined with the formation of a shrinkage cavity, will result in an undefined volume between the glass and the lid that could range from a few hundred to several thousand cubic centimeters.
- The temperature within the canister head region will be relatively undefined, ranging from the centerline temperature of the glass to that of the outer canister surface. These values will change as a function of the decontamination treatment, the decay heat, and storage and test environments.

Bombing Techniques

The bombing technique is useful for leak testing components that cannot be prefilled with helium before sealing or that may have leaks large enough to lose the helium inventory before testing. The sealed component is exposed to helium inside a pressure chamber and held to allow helium to flow into the internal volume through any existing leaks. The component is then removed from the pressure chamber and placed in a vacuum chamber connected to a helium leak detector. The helium that has accumulated inside the component will leak out at a measured leak rate that is related to the actual leak rate under standard conditions by:

$$S = P(1 - e^{-3600aT})(e^{-at})L$$

where S = measured leak rate, atm cc/s

P = helium bombing pressure, atm

T = bombing time, h

t = time interval between bombing and testing, s

L = actual leak rate for a cavity containing helium at 1 atm, cc/s

V = internal volume, cc

$a = L/V$.

This equation was used to evaluate the sensitivity of the bombing technique for canister testing assuming an internal volume of 1000 cc, a bombing pressure of 1 atm, a bombing time of 20 h, and a 10-min delay. The results for the expected range of leak rates were:

<u>Actual Leak Rate, atm cc/s</u>	<u>Measured Leak Rate, atm cc/s</u>
1.0×10^{-1}	9.4×10^{-2}
1.0×10^{-2}	5.1×10^{-3}
1.0×10^{-3}	6.9×10^{-5}
1.0×10^{-4}	7.2×10^{-7}
1.0×10^{-5}	7.2×10^{-9}
1.0×10^{-6}	7.2×10^{-11}

These calculations show that the bombing technique does not have the required sensitivity under reasonable times and pressures because of the comparatively large internal volume. The sensitivity could be increased by filling the volume with stainless steel shot or another inert material. However, even reducing the void volume to 1 cc would not provide the required sensitivity for smaller leaks.

Based on this evaluation, it is concluded that bombing is not a suitable technique for leak testing the canisters. In addition, the bombing technique would not provide a source of helium for the initial gross leak testing in B-Cell.

Prefilling Technique

In the standard prefilling technique, the component is sealed in a helium environment to provide a known internal volume and pressure of helium. Because this would not be possible for canister operation, the helium must be introduced before welding in a form that will release helium after completion of the sealing operation.

One possible method would be to contain the helium in a small capsule that could be placed in the canister before welding and then vented after sealing by controlled melting of a seal. This method would be difficult, if not impossible, to implement and control. There would be no way to verify venting of the capsule, and the inventory could be lost through a gross leak if the initial leak testing were delayed.

The only suitable alternative, although it is not standard procedure, is to introduce the helium just prior to welding in the form of a source with a controlled leak rate. The source helium inventory and leak rate must be balanced to avoid excessive loss during the welding period and yet provide adequate sensitivity for the gross leak testing in the cell where the canister is welded and for delayed leak testing in the cell where it is stored.

Source Optimization Calculations

A computer program was prepared to calculate the measured canister leak rate as a function of source leak rate for the following sequence of events and assumed conditions:

- A source containing 500 cc of helium at 10-atm pressure is placed on top of the glass before installation and welding of the lid.
- All of the helium released during the 6-h welding period is lost.
- After completion of the weld, the helium released from the source pressurizes the canister void volume at a rate that is a function of the decrease in source inventory and the loss of helium through leaks in the weld.
- The leak rate for the source and the weld region is given by the following combination equation derived from Poiseuille's law for viscous laminar flow and Knudsen's law for molecular flow:

$$L = 3810(D^3/a)[323(D)(P_u^2 - P_d^2)/\mu + (T/M)^{0.5}(P_u - P_s)]$$

where L = gas leak rate, atm-cc/s

D = leakage hole diameter, cm

a = leakage hole length, cm

P_u = upstream gas pressure, atm
 P_d = downstream gas pressure, atm
 μ = gas viscosity, cP
 T = absolute temperature, K
 M = gas molecular weight, amu.

- The upstream gas pressure for the source is the source pressure and is calculated by dividing the remaining inventory by the source volume.
- The downstream gas pressure for the source is the same as the upstream gas pressure for the canister and is calculated by dividing the net change in gas inventory (gas input from the source minus loss through the weld) by the canister void volume.
- The downstream gas pressure for the canister is zero.
- Because of the good thermal conductivity of helium, the glass center-line temperature (280°C) is used as the basis for gas pressure and viscosity calculations.
- Helium viscosity data (0.020 cP at 20°C and 0.034 cP at 280°C) are from the Handbook of Engineering Fundamentals, O. W. Eshbach, Ed., John Wiley & Sons, New York.

The pressure and leak rates as a function of time from weld closure were calculated for source leak rates ranging from 10^{-1} to 10^{-5} atm cc/s. Almost all of the helium inventory would be lost during the welding period for the highest source leak rates, resulting in reduced sensitivity for the preliminary examination and marginal sensitivity for the final testing. For source leak rates in the 10^{-4} to 10^{-3} -atm cc/s range, inventory loss would be modest and the sensitivity for the preliminary sniffer tests would be nearly adequate to detect the smallest leaks. Moreover, the measured leak rates for the final testing at the longer time intervals would be greater than the standard 1-atm rate for the smallest leaks due to accumulative pressurization to greater than 1 atm. For lower source leak rates, inventory loss would be negligible; but the sensitivity for the specified measurement times would decrease aging due to the slow buildup of pressure in the canister void volume.

Additional calculations were made for a sensitivity analysis of the possible effects of the uncertainties in canister void volume, actual gas temperature, and the length of the leak. This sensitivity analysis shows that increasing the canister void volume by a factor of five results in a factor of seven decrease in the measured leak rate for the smallest canister weld leak. However, even the reduced rate is still more than an order of magnitude greater than the expected sensitivity limit for the measurement system. The effects of the temperature and path length uncertainties are comparatively negligible.

Approach Recommendation

Based on the results of the source optimization calculations, the use of a helium source with the following characteristics should provide adequate detection sensitivity for hot cell leak tests:

- 500-cc minimum volume
- 10-atm minimum pressure
- an approximately 5×10^{-4} -atm cc/s leak rate for standard temperature and pressure conditions (a 1-cm long by 0.0015-cm diameter leak).

With this approach, the time required for welding, initial testing, and final testing could be varied significantly without serious effects on the ability to detect the smallest defect. Similarly, this approach would be relatively insensitive to the uncertainties in canister void volume, temperature distribution, and leak path length. The major requirement would be ensuring sufficient space for placement of the source.

CONCLUSIONS

Possible helium leak testing approaches for the FRG canisters have been evaluated including various pre- and post-weld helium introduction methods. Extensive calculations were performed to identify the effect of process and canister variables on achievable test sensitivities and to define the optimum set of test parameters. The results of this work indicate that adequate detection sensitivity for both the preliminary leak tests and the more stringent final measurements can be obtained by the preweld introduction of a helium

source with an approximate leak rate of 5×10^{-4} atm cc/s. Substantial variations in welding and subsequent handling/decontamination times, canister void volumes, and other process parameters can be tolerated without seriously impacting the required leak detection sensitivity.

OFF-GAS SYSTEMS

R. W. Goles and C. M. Anderson

SUMMARY

Nonradioactive melter emission and off-gas system performance studies have been conducted to evaluate operational conditions associated with radioactive liquid-fed ceramic melter (RLFCM) production of Federal Republic of Germany (FRG) glass canisters. The following data were collected during nonradioactive emission and off-gas system performance studies:

- Cesium activity losses to the off-gas system of 5% should be expected during spike feeding due to an aerosol emission loss mechanism. Since other loss mechanisms are possible, if not probable, total losses may be greater than 5%.
- Projected RLFCM cesium-137 idling losses to the off-gas system after spike feeding could be 10 kCi/day for several days. This rate will decay to a more or less stable rate of 4 kCi/day, which is characteristic of 5% cesium-loaded glass.
- Melter decontamination factors (DFs) for cesium and strontium averaged 140 and 1200, respectively, based on off-gas sampling.
- Ejector venturi scrubber (EVS) processing DFs for cesium and strontium averaged 1.7 and 44, respectively. Similar EVS cesium DFs were obtained during melter idling; no strontium emissions were observed during idling.
- Projected cesium-137 penetration of the EVS represents an activity loss rate of 1000 Ci/day irrespective of melter operating conditions. High-efficiency in-cell aerosol removal devices are required to deal with cesium emissions.
- High-efficiency mist eliminator (HEME) cesium DFs were approximately 50 under dry operating conditions and about 5 under continuous water

flushing conditions. Dry HEME operation is required in LFCM applications involving submicron cesium aerosols.

INTRODUCTION

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

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

TECHNICAL PROGRESS

One of the major tasks associated with the RLFCM is to produce canisters of radioactive glass containing high cesium-137 and strontium-90 loadings for the FRG. Because FRG melter feed and resultant glass composition are sufficiently different from conventional LFCM feed compositions, a cold melter test (PSCM-20) was conducted during the second quarter of FY 1985. One objective of the test was to characterize melter emission characteristics and off-gas system performance to provide a data base from which radiological implications of processing the FRG feed could be assessed.

Three melter operational modes were evaluated during PSCM-20: spike feeding, reference feeding, and melter idling. Spike feeding quickly increased the cesium and strontium contents in the melter glass and was followed by an idling period. Then, reference feed was processed for 240 h followed by another period of melter idling. The off-gas system components studied during PSCM-20 included an EVS and a HEME used as a deep bed washable filter. The HEME was

operated with a continuous spray mist as well as completely dry. The results from these off-gas studies were evaluated this quarter and are summarized below.

MELTER/OFF-GAS SYSTEM PERFORMANCE

To characterize the pathways and magnitudes of melter feed component losses, a differential sampling system composed of an aerosol filter, a condenser, and a series arrangement of three gas-scrubbing units was used. The manner in which any given element is distributed across the five discrete sampling fractions of this device indicates the physical state or states assumed by the effluent. Data generated with this sampling system are summarized in terms of DFs (ratios of the rate at which feed components enter a device to the rate at which they are evolved from it). Particulate DFs are partial DFs relating to only a single loss mechanism: aerosol emission. The PSCM-20 data collected by the differential sampler clearly indicated that melter gas phase losses to the off-gas system were only significant for boron, carbon, nitrogen, and the halogens that readily form volatile acid gases. Ruthenium volatility was effectively suppressed by the sugar loading in the feed. Furthermore, no gas phase losses of ruthenium were observed during melter idling. Consequently, with the exception of the above acidic gases, the major feed component loss mechanism associated with PSCM-20 is particulate transport through the off-gas system.

Since most melter off-gas system losses have been shown to be associated with aerosol emission, the off-gas performance (DF) of the LFCM can be conveniently measured in terms of gross off-gas aerosol loading. Melter emission and off-gas performance data are summarized in Table 1 for gross particulate effluent and cesium and strontium feed components.

The gross emission performance of the melter appears to be affected by all feed compositional changes that occurred during PSCM-20. The average overall melter DF during FRG reference feed processing was a factor of six higher than during spike feeding. This difference is totally ascribable to cesium, whose average DF also varied by the same factor (Table 1). Similar but less dramatic

TABLE 1. Melter Emission and Off-Gas Performance Data During the PSCM-20 Experiment

Date	Condition	Aerosol Decontamination Factors								
		Melter			EVS			HEME		
		Total	Cs	Sr	Total	Cs	Sr	Total	Cs	Sr
3/27	Spike feed	100	23	370	4.0	3.4	15	--	--	--
3/28	Spike feed	110	21	630	1.1	5.1	29	--	--	--
3/28	Idling	--	--	--	3.1	2.9	--	--	--	--
3/29	Idling	--	--	--	2.4	2.2	--	--	--	--
3/30	Idling	--	--	--	2.0	1.9	8.2	--	--	--
3/31	Idling	--	--	--	2.0	3.4	--	--	--	--
4/2	Reference feed	530	120	450	3.2	1.8	58	--	--	--
4/3	Reference feed	280	72	300	2.7	1.4	17	1.6	--	--
4/4	Reference feed	440	110	880	2.1	2.0	12	0.8(a)	--	--
4/5	Reference feed	550	170	500	2.3	1.3	33	2.7	--	--
4/6	Reference feed	730	160	920	2.2	2.0	30	0.8(a)	--	--
4/7	Reference feed	920	220	900	2.1	1.0	110	1.8	--	--
4/8	Reference feed	820	200	810	2.3	1.2	95	1.4	--	--
4/9	Reference feed	620	79	2200	2.7	2.4	29	6.9	2.6	3.2
4/10	Reference feed	890	100	3800	1.9	1.8	13	5.4	2.7	4.0
4/11	Idling	--	--	--	2.0	1.7	--	16 ^(b)	17	--
4/13	Idling	--	--	--	1.6	1.2	--	31	34	--
4/14	Idling	--	--	--	3.0	2.2	--	42	38	--
4/15	Idling	--	--	--	2.8	2.2	--	39	39	--
4/16	Idling	--	--	--	3.2	2.4	--	90	110	--
4/17	Idling	--	--	--	3.4	3.0	--	57	11	27

(a) Influenced by water spray and/or re-entrainment.

(b) Dry operation of HEME from April 11 through April 17.

differences were also observed during previous experimental-scale ceramic melter (ECM) testing of spike and reference feeds.

On April 7, 1985, the sugar content of the feed was reduced from 90 to 70 g/L. The average melter DF increased after this change. Because overall melter DFs were steadily increasing prior to this change, it is difficult to claim that a correlation exists between gross melter DF and reductant feed loading. However, melter performance increased for essentially all nonvolatile feed components after the sugar feed loading was reduced.

The performance of the EVS was low and stable throughout all phases of PSCM-20 testing. Except for the 2-day period of spike feeding when melter emissions were quite high, the melter behaved as a stable aerosol generator

independent of processing conditions. The average overall EVS DF throughout PSCM-20 testing was $2.5 \pm 25\%$. The reason for such low performance is the nature of the aerosols generated during PSCM-20, which were predominantly alkali salts. Past melter tests have shown that alkali elements are predominantly associated with submicron aerosols. This melter test was no exception as shown by the cyclonic sampling data in Table 2. About 10% of the aerosol mass leaving the melter was effectively treated by the low-efficiency EVS; thus, its low DF. Since most of the mass associated with submicron aerosols is associated with the alkali element cesium, this element has an influence on the performance of the EVS as is shown in Table 1.

The operational characteristics of a HEME used as a deep bed washable filter for high-efficiency removal of submicron aerosols were also investigated during this test. The size distribution of aerosols that the HEME had to deal with was established with a cascade impactor. Approximately 100% of the aerosol mass impinging on the HEME was associated with submicron particulate matter (Table 3).

Two HEME operational modes were evaluated during this test: a low flow continuous flush and dry conditions. The continuous flushing operation was prompted by apparent cesium solution breaching of the HEME filter during the PSCM-19 test. It was hoped that continuous water flushing of the HEME filter element would suppress re-entrainment; therefore, water flushing was used

TABLE 2. Size Distribution of Melter Aerosols

<u>Sample Date</u>	<u>Sample wt% Versus Cut Point</u>			
	<u>16 μm</u>	<u>6 μm</u>	<u>1 μm</u>	<u><1 μm</u>
4/9/85	6.4	0	15.1	78.5
4/10/85	1.7	0	12.5	85.8

TABLE 3. Size Distribution of Aerosols Penetrating the Ejector Venturi Scrubber

<u>Sample Data</u>	<u>Sample wt% Versus Cut Point</u>				
	<u>1.5 μm</u>	<u>0.86 μm</u>	<u>0.57 μm</u>	<u>0.35 μm</u>	<u><0.35 μm</u>
4/9/85	1.2	5.7	14.9	29.9	48.3

throughout processing of the FRG reference feed formulation (April 2 through April 10). The unrealistically low HEME performance from April 1 to April 8 was due to a seal pot operational problem. However, the performance of the HEME did not improve significantly after this problem was resolved. Consequently, the flushing operation was terminated on April 11. HEME DF performance improved significantly when dry operation was initiated (Table 1); overall and cesium DFs improved by a factor of approximately 10. All pertinent PNL melter off-gas data to date suggest that adequate HEME performance for LFCM-generated aerosols can only be achieved by maintaining a dry filter element.

MELTER IDLING EMISSIONS

Elemental melter-generated effluent emission rates were studied during the processing of spike and reference feeds and during the idling periods between the processing campaigns and following melter testing. Compositionally, melter feeding and idling emissions were essentially nonoxide salts of the alkali elements sodium and cesium. Consequently, the time-dependent loss rates associated with the alkali elements will determine the functional behavior of the total melter aerosol emission rate. This fact distinguishes PSCM-20 from all other melter idling studies.

For the FRG high cesium-loaded glass, the melter glass pool is apparently a dominating influence on the overall cesium melter source term under both feeding and idling conditions. Consequently, when melter processing was terminated after 10 days of feeding, melter emission rates for cesium continued without significant change for approximately 12 days. A small and presumably temperature-dependent increase in cesium emission rates was observed; the rate peaked after 3-1/2 days of idling followed by a very slow decrease in subsequent emission rates. The emission behavior of sodium was essentially identical to that of cesium.

Only semivolatile elements contributed significantly to overall melter emissions. For PSCM-20, these elements were boron, chromium, cesium, sodium, lead, and ruthenium. During idling, ruthenium melter losses were associated with aerosol emissions, where sampled. In addition, no significant strontium emissions were observed during either PSCM-20 idling period.

CONCLUSIONS

The PSCM-20 off-gas characterization studies were conducted primarily to provide a data base from which FRG RLFCM operational parameters could be derived. The first pertinent result from the cold testing is that during spike feeding 5% of the activity fed to the melter was lost to the off-gas system due to an aerosol emission. This loss mechanism is important but is, by no means, the only one. Surface deposition on the melter lid and walls as well as on off-gas lines cannot be accounted for by off-gas sampling data. Consequently, a minimum of 5% excess cesium activity will be required during spike feeding to account for airborne off-gas system losses.

Further losses during idling after spike feeding could be as high as 10 kCi/day due to off-gas aerosol emissions. This rate would quickly decay to a more or less stable rate of 4 kCi/day, which amounts to 0.4% of the total cesium-137 melter inventory per day. The loss rate would be a function of cesium glass concentration and would, consequently, decrease with time. Escape mechanisms other than airborne aerosol emission were not considered; thus, the loss rate represents a minimum value.

During melter processing of reference FRG feed, cesium aerosol losses would account for 0.7% of the cesium activity fed to the melter, and strontium losses would represent only 0.08% of the activity processes. Much of this airborne activity would be collected by the EVS. Under steady-state conditions, if no dilution water is added other than melter steam, scrub solution activities would be 2 Ci/L and 0.22 Ci/L for cesium-137 and strontium-90, respectively. The cumulative effects of idling would increase scrub solution specific activity above these values.

The impact of cesium aerosol penetration of the EVS can also be estimated from PSCM-20 operating data. For a melter feeding rate of 20 L/h, cesium penetration of the EVS could result in activity loss rates as high as 2000 Ci/day, which would necessitate further in-cell processing or filtration. Melter idling would be expected to produce the same general off-gas effects. Strontium penetration of the EVS would amount to only about 2.7 Ci/day during melter feed processing and would be insignificant during idling.

PROCESS/PRODUCT MODELING AND CONTROL

W. L. Kuhn, G. A. Anderson, L. J. Ethridge,
D. W. Faletti, R. K. Farnsworth, K. L. Schuchardt,
G. E. Spanner, B. M. Wise, and J. H. Westsik, Jr.

SUMMARY

Progress continued on process control instrumentation, process control algorithms, canister thermal modeling, and characterization of cracking in canisters. Process control instrumentation work included installation and testing of an infrared television camera for viewing inside a melter, interpretation of thermocouple measurements in molten glass, and testing of a time domain reflectometer (TDR) and an acoustic probe.

A process control algorithm for controlling the glass temperature was devised and tested during PSCM operation. The algorithm was made a subroutine of the data acquisition and control software used to monitor the melter.

Thermal experiments were designed and conducted for the PSCM-20 and PSCM-21 tests that investigated thermal behavior in instrumented canisters as they were filled with molten glass. These experiments supported both the validation of a heat transfer code and the validation of procedures to be used in the radioactive liquid-fed ceramic melter (RLFCM). Eight canisters that were filled during PSCM-20 were visually examined to determine the extent of cracking.

INTRODUCTION

The purpose of this work is to develop correlations and models that can be used to 1) adapt LFCM technology to new high-level waste (HLW) compositions and processing rates and 2) operate the adapted LFCM processes. During FY 1985, the focus will be on process control. Procurement of developmental control

instrumentation is included in this work; data from nonradioactive and radioactive testing conducted by PNL, Savannah River Laboratory (SRL), or West Valley will be used.

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

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

TECHNICAL PROGRESS

Technical progress for this quarter is presented in the following sections on process control instrumentation, in which interpretation of instrumentation is discussed; process control algorithms, in which work to improve temperature control is discussed; canister thermal data and modeling, in which measurements and analyses of temperatures in canisters are discussed; and characterization of cracking in canisters, in which examination of glass is discussed.

PROCESS CONTROL INSTRUMENTATION

The objective of this work is to develop instrumentation that will improve control of an LFCM process. All instrumentation packages currently under evaluation including infrared camera, glass thermowell, TDR, bubbler, and acoustic probe were installed and tested during the PSCM-21 run. Analysis of the information obtained with each instrument is continuing.

Installation of the infrared camera was delayed because of difficulties in cooling the lens and mirror portion of the camera that extends into the melter

plenum. Video tapes were made of the growth and dissolution of the cold cap, overfeeding, and the early stages of foaming. For the run, the camera was rotated to observe drifting of the cold cap along the melt surface. Neither the view from the camera nor from the viewport gives an accurate indication of the cold cap coverage in areas that are not visible. It will, therefore, be difficult to use the camera to obtain quantitative data on the growth and consumption of the cold cap. The camera should be redesigned to look at more of the melt surface than is currently possible.

For PSCM-21, thermocouples in the glass thermowell were located at the 5.5-, 8-, 11-, 14-, 15-, 16-, and 17-in. levels above the melter floor. The first three levels were used to indicate the glass temperature. The other four thermocouples were placed near the melt surface to be tested as indicators of glass level, cold cap coverage, and foaming. Foaming caused a characteristic temperature increase at all thermocouple levels; temperatures at all levels were nearly the same at the height of foaming. This temperature increase may provide a method for the early detection and correction of foaming. During idling, temperatures at the 17-, 16-, 15-, and 14-in. glass levels were about 1050, 1095, 1130, and 1175°C, respectively. The average glass temperature was 1175°C. These temperatures represent the maximum levels that should be registered by these thermocouples unless they are in contact with the glass. Therefore, foaming would be indicated if these maximum temperatures were exceeded. A temperature control algorithm will be designed that will issue an alarm if these limits are exceeded.

Data from the TDR decreased throughout PSCM-21. Indicated glass levels were frequently higher or unchanged after an air lift of glass from the melter. Glass hairs formed a large bridge across the exposed portions of the two Inconel rods comprising the TDR probe. This situation should have resulted in indicated glass levels that were unreasonably high rather than levels of typically 11 in. or less. Actual glass levels were about 15 in. The TDR was located further from the feed nozzle than in previous runs, and no blocking of the cold cap by the probe was observed.

The acoustic probe was used to monitor the run from the main melter cavity through the cold cap and from the air-lift riser. Work is ongoing to develop a computer program to access and analyze the data.

PROCESS CONTROL ALGORITHMS

The objective of this work is to develop algorithms for LFCM process control that are based on available and developing process instrumentation and to propose tests to validate the algorithms. A computer algorithm using glass temperature feedback for controlling electrical power to the melter has been developed and was tested during the PSCM-21 melter run.

The PSCM has been operated using constant power, resistance or current as the method to maintain glass temperatures within the desired range. Each of the control methods has its drawbacks, however. Since a constant temperature or at least a temperature within a specific range is required, a controller using the glass temperatures as the feedback should provide the necessary control. Temperature fluctuations associated with the convective currents in the melter have precluded using this scheme in the past. The addition of a computer to the PSCM instrumentation/data acquisition system now permits more sophisticated control systems.

Figure 1 shows the flow diagram for the temperature control algorithm. The algorithm is a subroutine of the data acquisition and display program currently used with the PSCM. The subroutine is called each time a data scan is performed by the computer, although the algorithm can be implemented at any integral multiple of the scan rate. Even if the algorithm is not implemented on a particular scan, the controller parameters are stored with the other run data.

The algorithm starts by reading the glass temperatures and determining if a thermocouple has burned out. A thermocouple is assumed to have burned out if the indicated temperature is outside the 800 to 1250°C range. The average glass temperature is then calculated from those temperatures within the acceptable range. A digital filter (Equation 1) is then used to smooth the average glass temperature:

FIGURE 1. Temperature Control Algorithm Flow Diagram

$$T_{\text{filter}}(n) = (1 - a)T_{\text{filter}}(n - 1) + aT_{\text{avg}} \quad (1)$$

The smaller the value of the filtering parameter (a), the more smoothing. A value of 0.3 for the filtering parameter produces about the same smoothing as a 1-h time average of data taken every 5 min. The digital filter does introduce a time delay between the measured and filtered glass temperatures.

The error between the set point temperature and the filtered average glass temperature is then calculated. If the error is less than an acceptable deviation from the set point (i.e., the melter has frequently been operated at $1150^{\circ}\text{C} \pm 25^{\circ}\text{C}$), then no further changes are made and the controller parameters are stored. The algorithm does not adjust the power set point if the glass temperature error is too large unless either the last power set point change is a minimum time in the past or the temperature error for the present scan is significantly larger than the error for the previous scan. These checks are necessary to allow for time delays in the response of glass temperatures to changes in power and to permit power changes if the glass temperatures are changing rapidly as might occur during foaming.

The control algorithm can function as a proportional (P), proportional-integral (PI), proportional-derivative (PD), or proportional-integral-derivative (PID) controller. The controller calculates the necessary set point change, which the computer sends as a 0 to 10-volt signal to the power controller. The controller then provides PID control of the power at the specified set point. This dual controller scheme is called cascade control with the power in the secondary control loop and temperature in the primary control loop. SRL also plans to use cascade control with their melter system. Finally, the algorithm prints a record of the power set point change and stores the control parameters with the other run data.

A PSCM experiment was conducted prior to PSCM-21 to determine estimated values for the proportional gain and integral and derivative time constants for the temperature control algorithm. With the melter idling and no feeding, set point changes of 20 and 30 points on the main power controller were made. Glass temperatures were then measured as a function of time. Using the method

of Cohen and Coon (D. R. Coughanowr and L. B. Koppel, 1965, Process Systems Analysis and Control, McGraw-Hill) the following values were estimated:

Proportional gain	2.5 kW/°C
Integral time constant	1800 s
Derivative time constant	200 s

It must be noted that the 20-point power set point increase did not show the "well-defined" temperature increases observed with the 30-point change. The temperatures did not decrease after a 30-point set point decrease but were actually higher 24 h after the set point decrease. This indicates that, at least during idling, steady state may not be reached for several days rather than several hours. An experiment is planned for a melter run to verify this observation for the case of feeding the melter.

The temperature control algorithm was used throughout PSCM-21. Proportional control was used for most of the run with PID control used during the last days of the run. The proportional control worked well during steady-state operation, although the PID control appeared to provide better temperature control during transients associated with starting and stopping feeding. Some operator adjustments may still be required during these transients. The algorithm did not reduce the power fast enough during foaming, and operator intervention was required to make the necessary power reductions to reverse foaming. The temperature control algorithm on the computer will be programmed to recognize temperature changes characteristic of foaming (see Process Control Instrumentation Section) and then make the appropriate power changes.

PRODUCT QUALITY CONTROL ANALYSIS

Canister Thermal Data and Modeling

The major activities this quarter were designing and conducting thermal experiments for the PSCM-20 and PSCM-21 runs and formulating recommendations for filling the FRG canisters in the RLFCM. The major purpose of the PSCM-20 experiment was to gather information required for determining the filling procedures to be used in the RLFCM; however, this experiment also provided an

opportunity to obtain thermal data required to validate an application of the TEMPEST computer code (Trent et al. 1983) to predicting temperatures in LFCM canisters. Furthermore, the experiment provided an opportunity to apply thermal models and glass cracking estimation methods and to evaluate them prior to use in the RLFCM.

Six canisters were filled during PSCM-20 that provided information for TEMPEST code validation; three additional canisters were filled in PSCM-21. All but two of these nine canisters had internally mounted thermocouples for determining the temperature history within the canister. The other two canisters were filled while located in a simulated turntable. This turntable had heat transfer characteristics similar to the RLFCM turntable and therefore provided data on the heat transfer between the canister and the turntable as it was affected by the overpack, liner, and thimble.

Data from PSCM-21 are currently being reduced. Work is continuing on the PSCM-20 data; comparisons between computer predictions and experimental data have been made for one turntable simulant fill and two internally instrumented canisters. The turntable simulant fills were made for three reasons:

- to determine if the TEMPEST limitation of symmetry results in computational error when applied to a turntable
- to determine if the emissivity values were correct
- to determine the correctness of the contact coefficients used to model convective heat transfer.

The simulated turntable was instrumented with arrays of thermocouples to determine axial and radial temperature gradients. The TEMPEST requirement for symmetry was found to be acceptable since circumferential variations in temperature gradients seldom exceeded 40°C and were generally less than 10°C. Furthermore, this variation existed over less than 25% of the turntable shell. Thus, lack of symmetry in the thermal gradients should affect the overall heat transfer by less than 1% to 5%.

A steady-state analysis of the transient cooling profiles (judged to be acceptable because of the relatively slow cooldown rates compared with system thermal lag time) was made to permit comparison between the experimental data

and TEMPEST predictions. As shown in Table 1, there is good agreement between the temperature differences predicted by the code and those observed within the turntable simulant. These predictions were sufficiently accurate for the purposes of developing RLFCM filling recommendations for FRG canisters. However, the canister wall-to-overpack and thimble wall-to-ambient temperature differences were not in good agreement, even when lowered emissivity values were used to try to reduce the difference (see Column 3 of Table 1). In addition, axial temperature gradients were overpredicted because of the modeling simplifications required by TEMPEST. However, code development would be required for improved performance.

Two of the PSCM-20 canisters with internal thermocouples were analyzed. The TEMPEST code appears to reasonably predict temperature trends. The major discrepancy that has been observed is that TEMPEST predicts a significantly slower cooldown rate than is observed experimentally. Thus, the code-predicted temperatures are about 100°C high during most of the cooldown phase. Examination of the results indicates that, in many but not all cases, this discrepancy occurs because TEMPEST predicts a slower cooldown in the newly poured glass in the first hour or two after a pour is made. An example is shown in Figure 2 where TEMPEST and experimental temperature profiles are essentially parallel but are offset by about 150°C for all times greater than 1 h after the third pour, i.e., times greater than 7.5 h.

The validation efforts showed that TEMPEST gave results accurate enough for formulating RLFCM filling and cooling recommendations. However, there was a clear need to develop a better input model for TEMPEST since the radiation model was underpredicting the heat loss from the glass surface and the existing input model required large numbers of restarts. These restarts required up to a person-week of effort for a single simulation. Therefore, a new input model is currently under development. In addition, potential sources of error are being examined including thermocouple conduction error (preliminary studies indicate that it is relatively small) and obtaining improved physical property data. Finally, the data obtained from PSCM-21 are being put into a form for use in code validation. These efforts will culminate in a major code validation effort in August-early September.

FIGURE 2. Comparison Between TEMPEST Predictions and Experimental Conditions in Canister 7 at 15.38 in. from the Bottom of the Glass. The radial location is 4.25 in. from the wall.

Characterization of Cracking in Canisters

The activities on the cracking model have been limited to examining the FRG canisters and several canisters that were the bases of prior PNL reports. Cracking is clearly stochastic in nature with few predictable trends as far as the geometric shape of the cracks (i.e., radial or circumferential). Consideration is being given to recording the disassembly of a canister with a TV camera to illustrate typical cracking.

The eight canisters filled during PSCM-20 were cut for inspection over the radial-axial cross section. The longitudinally cut surface of each canister was visually inspected and a qualitative estimate of the cracking was made. Most of the following discussion centers on Canisters 4, 6, and 7, which had 3 in. of insulation, and Canister 2, which had 1/4-in. of insulation. Canisters 3 and 8 were similar to Canister 2 and are not specifically discussed here. Canisters 1 and 5, which were filled within the turntable simulant, were not inspected because of the absence of internal thermocouples to correlate temperature differences with cracking behavior.

The cut surface of Canister 6 can be seen in Figure 3. Canister 6 is a typical example of cracking in canisters insulated with 3 in. of external insulation during the filling and cooling process. The cracking appears random and not centralized in any specific area such as pour interfaces or canister walls. The cracks appear to be an average of 7 in. long, creating very large pieces of glass that weigh as much as 5 to 10 kg. Canisters 4 and 7 display cracking behavior similar to that observed in Canister 6.

Canister 2 was insulated with 1/4-in. insulation during filling and cooling. The cracking in Canister 2 is typical of all the canisters with 1/4-in. insulation. The amount of cracking was judged to be somewhere between 3 and 15 times greater in these canisters than in the canisters with 3 in. of insulation. The cracking also produced a much greater quantity of shards and other small pieces of glass. The glass was much more likely to fall from the bulk

FIGURE 3. Cut Surface of Canister 6

glass when the canisters were opened. However, as with the 3-in. insulated canisters, there was no increased cracking found at the batch pour interfaces.

Crack surface area and size distribution measurements on the glass in the canisters were beyond the scope of this initial inspection. However, the following observations were made. The cut surface of the glass was observed and the pieces of glass formed by the cracking were placed into two general categories: those with minimum dimensions larger than 3 x 3 in. and those with at least one dimension smaller than 3 in. An average of one or two pieces of the larger size were observed in each quarter of the canisters with 1/4-in. insulation. The remaining glass appeared to be in smaller pieces. In the canisters with 3 in. of insulation, at least 75% of the glass pieces were of the larger size.

Canister 4 was filled using an interrupted pour procedure. Approximately one third of the canister was filled and allowed to cool for 29 h before the next batch of glass was poured. There was a noticeable increase in the cracking for approximately 1 in. at the interface between the pours. However, there was not enough of an increase in cracking to cause concern if the RLFCM was required to stop feeding for a short time.

Work is continuing on the PSCM-20 canisters. Additional inspection is necessary to draw conclusions concerning the cracking behavior due to internal thermocouples, internal insulation, and other variables experienced during the filling of the canisters. Other canisters filled by the PSCM may be used for additional cracking data.

CONCLUSIONS

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

- The infrared camera system needs to be redesigned to provide a better view of the glass melt surface; with modification, it should be useful for monitoring the cold cap and foaming incidents.

- While testing a new temperature control algorithm, it appeared that melter idling steady-state temperatures may be reached after days, rather than after a few hours as expected.
- Temperature predictions made using the TEMPEST code were about 150°C higher than measured but followed the pattern of the measured temperatures very closely.
- Cracking in insulated 12-in. canisters was not significantly enhanced at walls or the bottom of the canister. The extent of cracking decreased significantly with increasing insulation applied to canisters during filling and cooling.

REFERENCES

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SUPPORTING STUDIES

K. J. Schneider, J. L. Buelt, L. R. Bunnell,
J. G. Carter, and K. H. Oma

SUMMARY

Glasses containing reduced quantities of fluxing oxides are being considered as possible alternatives to borosilicate glass for use as high-level waste (HLW) forms. These glasses require higher processing temperatures but probably offer leaching performance that is superior to borosilicate glass. An analysis of the impact of higher processing temperatures (up to 1400°C) in a joule-heated ceramic melter indicates that the high-temperature glass could be processed with fairly straightforward melter modifications. The main penalties involve somewhat more expensive materials for some components and probably shorter overall lifetimes for the melter and associated hardware.

A study on a transportable vitrification process for low-level waste (LLW) was completed. Design criteria and the preconceptual design of the system were prepared, disposal costs were estimated, and utility interests in the transportable volume reduction service were assessed. In the preconceptual design, a joule-heated glass melter is used to convert the wet LLW into glass. The Mobile Encapsulation and Volume Reduction System (MEVS) can process 12,700 ft³/year of resins or 38,100 ft³/year of concentrated liquids from a minimum of three reactors. The capital cost for the MEVS is estimated to be \$4,700,000; the annual operating costs of the system based on servicing three reactors is \$1,500,000 for resins or \$2,300,000 for concentrated liquids. Total costs for transportation and burial are \$190 to \$220/ft³ of waste.

INTRODUCTION

The objective of these supporting studies is to carry out technical analyses that provide input and guidance for development of vitrification technology. Studies are being performed that support various aspects of

development of nuclear waste vitrification technology. These paper studies include generic assessments of vitrified waste performance during subsequent waste management operations, development of requirements/criteria for vitrified wastes, assessment of alternative waste forms, and documentation of vitrification technology and plans for specific applications.

TECHNICAL PROGRESS

Progress on second-generation nuclear waste forms and vitrification systems for non-HLW are presented below.

SECOND-GENERATION NUCLEAR WASTE FORMS

In FY 1985, Pacific Northwest Laboratory (PNL) began a study to conceive and evaluate several second-generation high-level nuclear waste forms that were not based on current borosilicate glass. For such a form to eventually replace borosilicate glass, it would have to offer performance and/or processing advantages. Initial efforts have been directed at other glass-based forms: one processed at lower temperatures (lead-iron-phosphate glass) and the other processed at higher temperatures. The lead-iron-phosphate glass has been evaluated, and the results have been reported (Burkholder, Jarrett, and Minor 1985). Work has just begun on the second alternative, and test compositions are presently being formulated. Even at this early point, it was judged prudent to analyze whether a high-temperature glass could be processed in a joule-heated ceramic melter by determining what changes would have to be made and evaluating the effect on the glass melting system.

There are clear indications from both general knowledge concerning glass durability and recent studies (Chick et al. 1984) that glasses processed at higher temperatures would generally be more resistant to aqueous corrosion than glasses processed at lower temperatures. This generalization ignores mechanism changes such as protective layers that may be operative in the high durability noted for lead-iron-phosphate glasses. Decreasing the amount of fluxing oxides so that processing temperatures must be increased by 200 to 300°C would probably result in an order-of-magnitude increase in leaching performance (Chick et al. 1984). The processing temperature is defined as that temperature at

which the glass has a viscosity of about 100 poise. Temperatures of 1350 to 1400°C are therefore indicated. It was desired to determine whether a joule-heated ceramic melter could cope with such temperatures and what would be the foreseeable penalties of such operation.

To assess the effects of higher processing temperatures on all major components, the following subsystems were evaluated: feed system; melter cavity; electrodes; routine glass discharge system; terminal glass draining system; off-gas treatment system; and instrumentation. The designs and materials used in each subsystem were evaluated, the effects of higher temperatures were determined, and standard "fixes" were identified. Some of these fixes are presently used in the commercial glass industry, where higher processing temperatures are used in the interests of higher throughput. Other fixes consist of merely increasing cooling, which can be accomplished with some redesign. The results of this work are summarized below:

- Current high-alumina lid refractories and K-3 glass contact refractories have a maximum temperature rating of over 1500°C and are routinely used in the commercial glass industry at 1400 to 1500°C. Therefore, no change to the primary refractory lining would be necessary.
- Cooled nickel-chromium electrodes are limited to temperatures of about 1200°C and have typically been run below 1100°C. With air cooling, the bulk glass temperature can be about 1300°C. Above this temperature, alternate electrode materials such as molybdenum, tin oxide, or Union Carbide UCAR^(a) Grade LT-1 metal-ceramic should be considered. Molybdenum is the industry standard for these melters. Replaceable electrode designs will probably be needed to obtain a reasonable melter life.
- Inconel^(b) parts used in current LFCM designs have a temperature limit of about 1100 to 1200°C. Substituting platinum-rhodium or

(a) Registered trademark of the Union Carbide Corporation, Carbon Products Division, Cleveland, Ohio.

(b) Inconel is a registered tradename of the Huntington Alloy Products Division, International Nickel Co., Huntington, West Virginia.

molybdenum parts can increase the temperature limit to above 1500°C. However, platinum-rhodium should not be used in a reducing environment, and molybdenum is not suited for oxidizing environments. Molybdenum melter electrodes are inserted through the melter floor; if there is contact with air, the electrodes are water cooled. The parts in question are those that would be exposed to the molten glass or high-temperature vapor spaces (the air-lift tube, pour trough, pour tip, drain valve, suction tube, thermowells, and pressure ports). The K-3 refractory, which has been demonstrated for this application, is a suitable substitute for the pour trough and pour tip.

- Silicon carbide heating elements used in the overflow section of the melter can be used for continuous service in air up to 1500 to 1650°C. More frequent replacement of the heating elements will be required for operation, but acceptable service life is anticipated.
- Standard stainless steel canisters should accommodate high-temperature glass at present fill rates with no adverse effects. The canister design may need to be revised to compensate for additional thermal stresses and increased surface oxidation.
- Cooling systems required for the melter will need to be redesigned for the increased heat load due to the higher temperature application (cooling systems for the feed nozzle, electrodes, melter shell, canister turntable, and off-gas line film cooler, etc.). No technical difficulties or limitations are expected.
- Additional fission product sorbers and particulate scrubbers may be required because the feed-to-off-gas decontamination factors are expected to be slightly lower for the higher temperature melting process.

TRANSPORTABLE VITRIFICATION PROCESS

The Mobile Encapsulation and Volume Reduction System (MEVS) is a conceptual liquid-fed glass melting system with enough peripheral equipment to be

self-sufficient in various environments (for example, during transportation, operation, or maintenance). The MEVS is based on an adaptation of previous high-level nuclear waste vitrification technology (Bjorklund and Brouns 1982).

Preconceptual Design

The MEVS is specifically adapted for slurries of filter sludges, evaporator bottoms, and ion-exchange resins. Both noncombustible and combustible slurries can be handled without pre-evaporation or other pretreatment. The conceptual MEVS consists of a joule-heated glass melter, its associated feed system, an off-gas treatment system, and a product handling and transfer station. The system is located in mobile trailers that can be transported to a number of nuclear reactor sites to process wet LLW generated and stored at the sites. The end product incorporates the noncombustible portions and the inherent radionuclides into glass, a stable monolithic and inert solid. The glass is poured into drums to minimize onsite storage requirements and reduce transportation and burial costs.

The joule-heated glass melter has been adapted to process both noncombustible and combustible slurries. Special feeding techniques help incorporate the radionuclides directly into the glass, minimizing particulate carryover and volatilization into the gaseous effluent stream. Radionuclides that are volatilized are scrubbed from the gaseous effluent via an off-gas treatment system. The scrub solution is decontaminated and recycled to the plant through anion-exchange column in the MEVS. After being fully loaded, the ion-exchange resins in the column are recycled to the melter, thereby eliminating any secondary waste stream generation.

The process can be categorized into six groups: the feed system, the melter system, the product handling area, the off-gas treatment system, the control area, and the electrical and cooling support equipment. All components of the process are located in three transportable semitrailers (the process trailer, the support trailer, and the control trailer). The trailers have undercarriage assemblies so they can be transported by rail, if desired. The MEVS is entirely self-contained and requires no facility-type services from the reactor for operation.

Process Trailer

Radioactive processing equipment is contained within the process trailer (Figure 1). This standard highway semitrailer measures 14.6 m long by 2.6 m wide by 4.1 m high (48 by 8.5 by 13.5 ft). The maximum weight of the trailer (including all process equipment, the trailer, and the towing vehicle) does not exceed 39,000 kg (86,000 lb).

A double containment philosophy is applied to all radioactive processing equipment. The first level of containment is the radioactive processing equipment and piping; the second level is a module that completely envelops the radioactive processing equipment. The containment module and trailer are designed with removable panels at selected locations to allow contact maintenance of the radioactive processing equipment. The processing equipment includes:

- recirculating slurry pump that pumps wet waste from the plant to the melter feed tank
- 110-L (40-gal) feed tank with air sparger, in which glass formers are added to the wet waste
- air displacement feed pump that meters slurry to the melter
- melter

FIGURE 1. Process Trailer for the Mobile Encapsulation and Volume Reduction System

- single-pass heat exchanger and pump for the melter cooling water
- turntable that provides a sealed drum filling and changeout station for glass-pouring operations
- receiving canister station that places filled drums into an overpack for storage and/or transport
- venturi scrubber to provide the first stage of cooling and cleanup of gaseous effluents
- two tandem nozzle scrubber units: one with a 12-in. inlet and the other with a 6-in. inlet
- two mist eliminators, one for each scrubber system, to remove water droplets from the gaseous effluents
- two single-pass heat exchangers to remove heat from the scrub solution
- scrub recirculation tank
- two scrub recirculation pumps
- resin column for discharge of the scrub solution back to the reactor plant
- condenser to remove additional heat from the gaseous effluents
- mist eliminator after the condenser to remove droplets generated in the condenser
- heater to preheat the air prior to entry to the filtration system
- two redundant high-efficiency particulate air (HEPA) filter and iodine absorber systems to provide primary and secondary filtration and iodine removal before the gases are exhausted to the reactor.

The containment module is vented through a blower and HEPA filter system with the same capacity as that of the process effluent system. Therefore, the containment module ventilation system acts as a full-capacity backup to the main process effluent system.

A glass former feed system is mounted on the top of the process trailer and removed before transport. Although the process trailer does not include the induced draft blowers for the containment module and process effluent stream, the gases leaving the process trailer are fully decontaminated, thereby meeting the criteria of keeping all radioactive processing equipment in one trailer.

Lead shielding is installed around the melter, product handling areas, and feed tank prior to operation. The 5-cm-thick shielding is removed before transport to maintain the weight limitations of 39,000 kg. At the reactor site, the shielding is mounted outside the process trailer around the melter and mounted internally between the melter and effluent treatment system. The internal shielding can be dropped into place through a baffle in the roof of the containment module. The off-gas treatment system requires no shielding. The radioactive source in the melter and feed tank is conservatively assumed to be 100 R/h using 100% cobalt-60 as the source. The shielding thickness is based on a maximum dose rate of 100 mR/h 1 m from the outside of the trailer. After operation, the melter is drained, the glass product removed, and the system decontaminated to meet the 10 mR/h transportation criterion at 2 m away from the trailer with the shielding removed.

Control Trailer

The control trailer (Figure 2) measures 13.7 m long x 2.4 wide x a maximum height of 4.1 m (45 by 8 by 13.5 ft); its weight is within the legal weight in most states of 36,000 kg (80,000 lb). A 5.5-m x 2.4-m control room houses the distributed process control system that controls all critical operating functions and monitors and records all operating functions of the process. The distributed control system contains inherent redundancy features such as multiple operator interface units, dual plant communication loops, and backup multifunction controllers to ensure safe operation. The control trailer also contains the induced draft blowers for the containment module ventilation and process effluent stream. The two blowers are interconnected such that the two ventilation streams can be directed through either blower should the other one fail. Therefore, the blowers for the process effluent system and the containment module ventilation system are completely redundant. A chemical makeup

FIGURE 2. Control Trailer for the Mobile Encapsulation and Volume Reduction System

tank that is used for storage and makeup for new scrub solutions is located between the blower system and the control room. The plasma torch power supplies used for restarting the melter are also located in this area.

Support Trailer

The support trailer (Figure 3) is a standard flat bed trailer that measures 14.6 m long x 2.6 m wide (48 by 8.5 ft) with a total system capacity including tractor/trailer and load of 39,000 kg (86,000 lb). It houses all peripheral support equipment, including the electrical and off-gas cooling units. The heat exchangers in the process trailer use glycol as a cooling fluid, which is recirculated from the glycol cooler unit located on the support trailer. Blowers located in the glycol cooler unit discharge the heat from the glycol loop to the atmosphere. Three diesel generators provide primary and emergency electrical power. The first is a 400-KVA single-phase diesel generator for melter power. The other two are 230-KVA generators for primary and emergency backup power to the off-gas system. The support trailer also contains the 400-KVA transformer and silicon-controlled rectifier (SCR), which provide the varying voltage and current required for operation. The off-gas system generators are connected directly to an automatic transfer switch and a motor control center that provides 480-V power to the blowers and motors of the off-gas treatment system. They also provide 480-V power to a step-down 50-KVA

FIGURE 3. Support Trailer for the Mobile Encapsulation and Volume Reduction System

transformer that supplies lower voltage servicing through the distribution panel. The support trailer also contains a 10-hp air compressor to actuate the pneumatic valves located throughout the process.

Melter

The joule-heated glass melter (Figure 4) is designed to reduce the volume of both noncombustible and combustible slurries and incorporate their residual radionuclides into a stable glass matrix. The wet wastes are fed to a molten glass pool that is kept at 1000 to 1100°C by introducing an electrical current between Inconel 690 electrodes at opposite ends of the melting cavity. The glass is contained within the melting cavity lined by a fused-case refractory known as Monofrax K3.^(a) As electrical potential is applied to the electrodes, an electrical current is established through the conductive molten glass, thereby acting as a resistive heating element and introducing power to the melt.

When feeding combustible slurries, a drop tube in the lid of the melter is lowered 10 cm into the melt. As the slurry dries and combusts in the drop tube, the combustion gases are forced into contact with the molten glass, thereby allowing mass transfer of radionuclides and particulates into the glass

(a) Monofrax K3 is a registered trademark of the Carborundum Co.

FIGURE 4. Joule-Heated Glass Melter for the Mobile Encapsulation and Volume Reduction System

and attaining a high retention of radionuclides in the glass. This feeding technique has been tested in an experimental-scale glass melter with a drop tube diameter of 3.8 cm at feed rates as high as 3 kg/h. The 86-cm drop tube diameter in the MEVS conceptual design was scaled linearly with the diameter of the experimental melter drop tube to maintain identical residence times in the glass to achieve high retention values. The MEVS melter can process 70 kg/h of resin slurries (which corresponds to the criteria given in the summary). Air cooling is provided at the bottom of the MEVS drop tube to maintain a viscous, relatively nonconductive layer between the drop tube and the molten glass to minimize the electrical shorting potential through the drop tube.

When feeding noncombustible slurries, the drop tube must be raised above the glass melt to allow cold cap formation. The drop tube is extracted 10 cm above the glass level via the air cylinder located on the lid of the melter. The overflow's air lift can reduce the glass level to attain additional separation between the bottom of the drop tube and the glass, if necessary. The

noncombustible slurry is premixed with glass frit in the mixing tank before being introduced to the surface of the glass melt. The heat from the glass pool evaporates the moisture and establishes a cold cap in which the glass formulation reactions take place. The nonvolatile waste constituents flux with the glass formers, making a borosilicate glass composition.

The process is not amenable to waste solutions with significant concentrations of sulfates. Sulfate solubility in glass is limited to 0.5 to 1.0 wt%. Na_2SO_4 regeneration solutions could not be processed using the MEVS process. The resins could, however, be disposed of directly in the melter instead of being regenerated.

The melter cavity measures 1.37 m x 1.67 m x 0.41 m deep, resulting in an exposed surface area of 2.3 m^2 . The maximum concentrated liquid rate for a deep bed condensate polishing system for a BWR results in a required rate of 210 L/h. At maximum production rates, a minimum glass production rate of 200 kg/h would fill a canister of glass every 2 h. These rates assume a 70% production factor with a 3-week shutdown period for transport and setup at each of three reactor sites. The melter was designed for a 90 L/h-m^2 flux rate. The rates demonstrated for HLW vitrification range from 30 to 100 L/h-m^2 ; however, HLW generally contains many more refractory components than LLW (LLW contains little if any iron, zeolite, and other refractory components). Therefore, the 90 L/h-m^2 rate will be easily achievable for LLW.

Cost Estimate and Systems Analysis

The preconceptual design of the MEVS provided the basis for a capital and operating cost estimate of the process. The estimates were used to determine the total disposal costs on a waste volume basis for comparative purposes.

The capital cost estimate was prepared by Kaiser Engineers Hanford Company (KEH). Capital costs include all labor and materials required to design, procure, fabricate, inspect, and license the MEVS process. All procurement and fabrication items are assumed to be fixed-price competitive procurements. A 26% contingency and an 8.6% escalation factor are included so that the costs represent a January 1987 completion date. Engineering and inspection services comprise 30% of the construction costs, based on past experience by PNL and

KEH. These costs also include escalation and contingency factors. When comparing the estimated capital cost with those for other processes, one must carefully observe which factors are included. The combined procurement and fabrication costs for the MEVS were estimated to be \$2,700,000; accounting for escalation, contingency, engineering and inspection services, and licensing activities results in a total cost of \$4,700,000.

The annual operating cost for combustible slurries (resins and combustible filter sludges) is \$1,500,000. The annual operating cost for noncombustible slurries (concentrated liquids and noncombustible filter sludges) is \$2,300,000.

A conservative estimating approach was used for the operating cost estimate to ensure that all actual costs were considered. The process is assumed to be continuously monitored by two full-time operators in an "ABCD" shift schedule. A dedicated radiation protection technician is also assumed to be necessary 24 h/day. The estimate allows for a day shift supervisory engineer, a transport crew, and staff for routine maintenance. A travel allowance is also assumed. In addition, a significant allowance is made for nonroutine maintenance (materials and labor) to replace processing equipment. The allowance is based on 33% of the capital investment of the melter, which requires replacement every 3 years, and 10% of the remaining capital items, which have a minimum 10-year operating life. The nonroutine maintenance factor should not be confused with capital recovery. The factor simply keeps the system in new condition. With the nonroutine maintenance factor, the entire system can be expected to be competitive with the longest term solidification systems (i.e., 30 years).

MEVS costs were compared with current practices by evaluating the entire "cradle to grave" waste management costs. The most common form of treatment presently used is to concentrate the wet wastes by evaporation and solidify the concentrated liquids, resins, and sludges by cementation. The cemented wastes are deposited in 55-gal drums or metal liners capable of holding 5.4 m^3 (190 ft^3). The cementation process actually increases the evaporated waste volume by a factor of 1.3, which also increases transportation and disposal costs. Total waste management costs from the evaporator through burial have

been quoted by plant operators at \$155 to \$350/ft³ for concentrated liquids and from \$300 to \$350/ft³ for resin slurries. These costs are for contracted services.

Disposal costs for cementation and MEVS are compared in Table 1 in dollars per cubic foot of wet wastes before solidification. The MEVS operational cost is the annual operating cost divided by the annual waste processing volume. The MEVS processing cost also includes an allowance for full capital recovery and a 20% rate of return on investment. Transportation and burial costs are based on a cost breakdown given by Jacobs et al. (1984).

MEVS costs/ft³ for transportation and burial are lower because of the high volume reduction factor. Fewer casks are needed and less volume at the burial site is required. The analysis assumes one cask per shipment and 190 ft³ of cement in each cask. Only 14 drums of glass can be transported in one cask, each containing 5.7 ft³ of glass (75% full) for a total of 80 ft³. Nevertheless, because of the volume reduction factor, cost savings are realized for cask rental. Cost savings are more pronounced for the remaining disposal costs.

Utility Assessment

One of the objectives of this program was to obtain an assessment of nuclear electrical utility interests in the volume reduction service that MEVS would provide. The utility assessment provided some very encouraging findings on how the utilities perceive the adaptability of the MEVS to their present and near-term plans for radioactive waste disposal. There appears to be a great deal of uncertainty as to the status of national disposal sites after January 1, 1986. According to the Low-Level Radioactive Waste Policy Act of 1980, each state will assume responsibility for wastes generated within its borders (Moore 1985). States currently operating national waste disposal sites may close them or put severe restrictions on acceptance of wastes as of January 1986 unless regional agreements for LLW are in place. Present indications are that the current national sites may remain open for another 4 years. Nevertheless, increasing burial costs are resulting in increased emphasis on volume reduction for onsite storage and/or disposal at national or regional burial sites.

TABLE 1. Comparison of Disposal Costs for Cementation and the Mobile Encapsulation and Volume Reduction System (MEVS)

	Disposal Costs, \$/ft ³ (a)		
		MEVS	
	Cementation(b)	Resins	Concentrated Liquids
<u>Processing:</u>			
Operations	121	111	60
Capital recovery and return on investment	(c)	68	25
<u>Transportation:</u>			
Transport, truck rental, and loading	20	3	14
Cask rental	86	15	60
<u>Disposal:</u>			
Burial	24	2	8
Radiation surcharge	9	4	4
Curie surcharge	13	13	13
Weight surcharge	9	1	3
Perpetuity escrow fund	4	<1	1
Disposal and business license tax	9	1	3
Approximate totals	\$300/ft ³	\$220/ft ³	\$190/ft ³

(a) January 1985 dollars.

(b) Resins or concentrated liquids.

(c) Included in operations costs.

Although response to the transportable self-contained process approach was positive, the utilities do not appear to be willing to commit capital or to hire more operating staff for radwaste treatment at this time. Contracted services for radwaste treatment appear to appeal to the utility managers. It allows them flexibility, an essential for adapting radwaste volume reduction processes to the utilities at this time.

Another desirable feature of the process was the self-contained approach, which requires minimal interfaces and services from the nuclear power plant. The diesel generators, which provide operating and backup power for the melter and off-gas system, met with good response. Most utilities do not have spare 1200 A, 480 V buses to operate the system.

Off-gas cleanup prior to release was also essential for utility acceptance. The off-gas system allows the utilities to exhaust directly from the process trailer or to tie in with the plant stack to maintain a single exhaust point on the plant site.

During the utility assessment, it became apparent that the assumption that ion-exchange resins can be fed to the melter as a pumped slurry needs to be reevaluated. Most resins are currently dewatered. It is more sensible to feed the resins to the melter as wet dewatered solids than to reslurry the resins, which would create additional condensate. The glass former feeder located on the top of the process trailer could be adapted to feed wet solids.

The disposal of the condensate produced from the vitrification of wet wastes also needs to be reconsidered. The preconceptual design calls for a resin column decontamination of the condensate prior to discharge. The resins can then be recycled to the melter for full incorporation of radionuclides. However, the presence of sulfonate groups in ion-exchange resins will produce a dilute sulfate/sulfite scrub solution. It is not yet known what the sulfur concentration will be in the scrubber solution or whether the sulfur will impact the removal efficiency of the resin column. The uncertainty lies in the degree of solubility of sulfates in the glass, which is normally limited to 0.5 to 1.0 wt%. As discussed previously, verification tests are necessary to answer technical questions such as these and provide information for definitive

design. Also, the acceptable release concentrations of sulfates for chemical waste disposal at a reactor facility need to be investigated.

Overall, the response of the utility representatives was quite positive. The representatives are not satisfied with the present state of commercially available technology for radwaste volume reduction and stabilization. The costs presented for the MEVS service in most cases provided an economic incentive for the MEVS. The overall response of the utilities was that if the reported costs are true then indeed the MEVS will fill LLW treatment needs and should be supported for commercial development.

CONCLUSIONS

It is concluded that potential second-generation waste forms that require processing temperatures up to 1400°C should be processable in a joule-heated ceramic melter. Some melter system components will require replacement with materials having higher temperature capabilities, and others may require more frequent replacement than for processing borosilicate glass at lower temperatures.

The MEVS has been preconceptually designed to fill a basic need for treatment of slurries, sludges, and ion-exchange resins in preparation for disposal. Provided the economics presented in this paper are representative of actual costs, it appears that electrical utility companies with nuclear power plants would be interested in a transportable volume reduction and stabilization service of this type. Utility representatives have indicated that presently available processes do not adequately fulfill their waste management needs. The economics presented in this report have been estimated on a conservative basis. When considering the total costs of disposal, which include processing, transportation, and burial, the costs for MEVS are about two-thirds of the costs of commonly used techniques.

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APPENDIX

ACRONYMS AND ABBREVIATIONS

APPENDIX

ACRONYMS AND ABBREVIATIONS

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

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

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

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