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Commercial LFCM Vitrification Technology

**Quarterly Progress Report
October-December 1984**

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

July 1985

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

**Pacific Northwest Laboratory
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COMMERCIAL LFCM VITRIFICATION TECHNOLOGY

QUARTERLY PROGRESS REPORT

October-December 1984

PNL--5470-1

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

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ABSTRACT

This report is the first in a series of quarterly reports compiled by the Nuclear Waste Treatment Program Office at Pacific Northwest Laboratory to document progress on commercial liquid-fed ceramic melter (LFCM) vitrification technology. Progress in the following technical subject areas during the first quarter of FY 1985 is discussed: pretreatment systems, melting process chemistry, glass development and characterization, 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 the first in a series of technical quarterly reports compiled by the Nuclear Waste Treatment Program Office (NWTPO) to describe the progress in developing, testing, applying, and documenting commercial liquid-fed ceramic melter (LFCM) vitrification technology. Activities in the first quarter of FY 1985 are summarized below:

Pretreatment Systems - The development of a reference West Valley supernatant treatment process for cesium removal is described, including data on alternative ion-exchange media.

Melting Process Chemistry - Work is in progress on West Valley high-level waste (HLW) melter feed formulations. Problems being addressed include minimizing formation of a viscous phosphate surface layer on the melt and developing techniques for redox control and measurement.

Glass Development and Characterization - Lead-iron-phosphate glass was evaluated as a possible improved glass formulation. Extensive crystallization and chemical durability lower than borosilicate glass was observed when the glass was cooled at a rate similar to that in a large canister. Rapid cooling minimizes crystallization and would result in a glass with better chemical durability than borosilicate glasses.

Feed Preparation and Transfer Systems - The results of long-term air-lift feed system testing were analyzed, and the system design appears to be adequate for West Valley requirements with a few modifications. A remotely operated model of the air displacement slurry pump was used successfully in the radioactive LFCM (RLFCM).

Melter Systems - The RLFCM was started up successfully, and shakedown tests are in progress.

Canister Filling and Handling Systems - Turntable systems for West Valley and the RLFCM have been fabricated, tested, and placed in operation.

Off-Gas Systems - An analysis of the performance of the LFCM off-gas system components during a pilot-scale ceramic melter (PSCM) test late in FY 1984 (PSCM-19) and during melter idling was completed. Decontamination factors were

determined for each system component. One component, the high-efficiency mist eliminator (HEME), malfunctioned; needed changes for improved HEME operation have been identified.

Process/Product Modeling and Control - The infrared imaging system for indicating the proportion of the melt surface covered by the cold cap was successfully tested. An electronic glass level detection system is being developed and tested.

Supporting Studies - Recent repository near-field/waste package performance literature has been reviewed, and the ranges of fractional release rates for silicate-containing groundwater in saturated and unsaturated conditions were calculated.

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INTRODUCTION

In the middle of 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 Office (NWTPO) at Pacific Northwest Laboratory (PNL).^(a) The NWTPO 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, TRUW treatment by 1996, and second-generation HLW treatment by 2000.

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

(a) Operated for DOE by Battelle Memorial Institute.

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

Progress in all program elements is reported through informal monthly status reports, formal annual reports (McElroy and Burkholder 1984; Burkholder and Rusin 1985), and formal topical reports. Recognizing both the magnitude of the first-generation HLW program element and the large number of applications currently under way, this quarterly report series was begun in FY 1985 to facilitate the transfer of LFCM vitrification technology between and among the central source (PIL) and the various user groups (the Waste Valley Demonstration Project, the Hanford Waste Vitrification Project, and the Defense Waste Processing Facility Project). Quarterly reports will be established for other program elements as the need arises. Because the emphasis of these quarterly reports is technical rather than programmatic, the reports are organized to cover technical subject areas without regard to funding sources. This quarterly is organized as follows:

- Pretreatment Systems - L. A. Bray, B. M. Wise, and T. R. Myers
- Melting Process Chemistry - D. S. Goldman
- Glass Development and Characterization - 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, M. M. Beary, G. J. Sevigny, R. W. Goles, and P. H. Hof
- Off-Gas Systems - R. W. Goles, P. A. Scott, and C. M. Anderson
- Process/Product Modeling and Control - W. L. Kuhn, S. M. Barnes, D. H. Siemens, J. M. Perez, Jr., J. H. Westsik, Jr., and L. J. Ethridge
- Supporting Studies - K. J. Schneider and R. D. Peters.

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

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PRETREATMENT SYSTEMS

L. A. Bray, B. M. Wise, and T. R. Myers

SUMMARY

A reference supernatant treatment process has been developed for West Valley Tank 8D-2 high-level waste (HLW). Alternative ion exchangers were tested but did not have the cesium capacity of IONSIV IE-96®. A pilot-scale ion-exchange column was constructed and is operational for determination of the hydraulic properties of IE-96. The performance of melter feeds may be adversely affected by the use of zeolite that has been digested with nitric acid. A small sample of Tank 8D-2 supernatant has been analyzed; the sample compares favorably with synthetic feeds used to select the reference process.

INTRODUCTION

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

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

®Registered trademark of Union Carbide Corporation, Tarrytown, New York.

cesium loading capacity of IE-96 at a feed Na/Cs mole ratio of 4,800 has been determined to be 3.7×10^{-2} moles of Cs^+ per liter of exchanger or 26 column volume (cv) equivalents of feed.

Two cesium-loaded zeolite processing scenarios were proposed. In the first, the sludge phase remaining in Tank 8D-2 would be blended with a small volume of Thorex acid waste from Tank 8D-4 and nitric acid from eluting the cesium-loaded zeolite ion exchanger. The cesium-eluted zeolite would be disposed of at onsite LLW burial grounds. In the second scenario, the Thorex acid waste, the Tank 8D-2 sludge, and the cesium-loaded zeolite (IE-96) would be directly blended for vitrification feed. This second approach would increase the amount of glass produced because of the need to accommodate the Al_2O_3 and Fe_2O_3 present in the zeolite. While not preferable, this second scenario was finally chosen because nitric acid elution of the zeolite did not remove all of the cesium from the exchanger. Adding this cesium to onsite LLW would reduce the West Valley site cesium DF from the 10^3 to 10^{-4} range to the 10^2 to 10^3 range. In addition, the acid eluate was found to contain 90 wt% of the initial Al_2O_3 - Fe_2O_3 because the zeolite partially dissolved during column elution.

TECHNICAL PROGRESS

A number of investigations have been conducted this quarter in support of the West Valley selection of the above reference pretreatment system. These investigations included:

- construction and initial testing of a pilot-scale ion-exchange column
- evaluation of an alternative ion exchanger for supernatant treatment processing
- evaluation of the acid digestion of zeolite
- analysis of actual Tank 8D-2 supernatant.

ENGINEERING-SCALE ION-EXCHANGE COLUMN TESTS

The current reference process for decontaminating Tank 8D-2 supernatant involves ion-exchange columns that will be installed in process tanks or

buildings at West Valley. To characterize the engineering aspect of these columns, a pilot-scale column similar in design to the actual column/exchanger system will be tested for hydraulic properties, flow distribution, exchanger changeout efficiency, and sensitivity to zeolite fines.

The test column installation, calibration, and initial shakedown were completed this quarter. The column is similar in design to the column proposed by West Valley, but it is smaller (diameter of 2 ft versus 3 ft; cylindrical section height of 10 ft versus 10.5 ft). The cylindrical section of the column is fabricated from Plexiglas® so that the exchange bed can be directly observed. The column top and bottom are fabricated from ASME dished heads. The vessel distribution/collector system consists of a series of Johnson screens^(a) with internal piping for the backwash distributor/service collector and inlet distributor and Johnson screens without internal piping for the backwash collector. The column installation, top fittings, and bottom fittings on the Plexiglas column are shown in Figures 1, 2, and 3.

EVALUATION OF AN ALTERNATIVE ION EXCHANGER

At the request of WVNS, PNL investigated Durasil® ion exchangers as alternatives to zeolite for decontaminating the West Valley alkaline supernatant. Durasil 10A and 210 were suggested for study; cesium loading performance, water leaching, and acid elution were evaluated. The results indicate that Durasil 10A and 210 can be expected to achieve a cesium loading of 10 to 12 cv equivalents when used to treat West Valley Tank 8D-2 supernatant. Similar experiments by the Catholic University Vitreous State Laboratories show 17 cv equivalents for Durasil 10A and 210. The West Valley reference ion exchanger (IE-96) is expected to achieve a cesium loading of 26 to 30 cv equivalents.

Samples of Durasil 10A were tested for retention of cesium using simulated West Valley alkaline supernatant. Batch relative distribution ratios (R_d) were determined for three small samples. The cesium R_d values were 11.7, 24.3, and 13.4 after a 16-h batch contact with Durasil 10A and synthetic supernatant (pH 10.4).

®Registered trademark of Rohm and Haas Company, Philadelphia, Pennsylvania.

(a) Manufactured by Johnson Division-UPO, Inc., St. Paul, Minnesota.

®Registered trademark of Duratek Corporation, Beltsville, Maryland.

FIGURE 1. Overall View of Pilot-Scale Zeolite Ion-Exchange Column

FIGURE 2. Head Fitting for Pilot-Scale Zeolite Ion-Exchange Column

FIGURE 3. Bottom of Pilot-Scale Zeolite Ion-Exchange Column

A 20-cm³ column of Durasil 10A was tested using simulated West Valley alkaline supernatant (pH 10.4) (Figure 4). The feed flow rate was 0.2 cv/h; a 50% cesium breakthrough occurred at 12.5 cv. Water washing (10 cv), sodium elution (0.1 M HNO₃), and cesium elution (3 M HNO₃) were tested based on Duratek advice. The first 2 cv of H₂O were composited (pH 10.35), and 0.5 mL (centrifuged volume) of postprecipitated silica gel was observed in the sample. Approximately 2.6% of the loaded cesium was eluted with the water wash cycle. The sodium wash removed about 71% of the loaded cesium. The 3 M HNO₃ strip solution removed the remaining 26% of the cesium. Results for Durasil 10A and IE-96 are compared in Figure 5. IE-96 has a 50% cesium breakthrough at 27.5 cv as compared with 12.5 cv for Durasil 10A.

Three loading/elution cycles were completed using the same column of Durasil 10A. West Valley alkaline supernatant feed was loaded to 50% cesium breakthrough, followed by a water wash, 3 M HNO₃ elution, and the exchanger was then reconditioned using 0.15 M sodium tetraborate. The Durasil 10A cesium capacity was reduced after each cycle as shown in Figure 6. The 50% cesium breakthrough was reduced from the initial 12.5 cv to 5 cv and 3.8 cv for the

FIGURE 4. Cesium Breakthrough Profile for Alkaline Supernatant and Durasil 10A

FIGURE 5. Comparison of Cesium Loading and H₂O Profiles for IE-96 and Durasil 10A

next two loading cycles. A postprecipitate was observed in the first fraction of water wash for each cycle. The 17-cm tall ion-exchange column lost 0.5 cm of bed height after three cycles. This loss and the observation of postprecipitated material indicate that Durasil 10A is soluble in West Valley alkaline supernatant. A 3 M HNO₃ elution profile is shown in Figure 7. The majority of the cesium was released in the first 3 cv, but the remaining cesium "tails" during the next 15 to 20 cv.

FIGURE 6. Cesium Loading Profile for Durasil 10A as a Function of Loading Cycle

FIGURE 7. Elution of Durasil 10A Using 3 M HNO₃

A sample of Durasil 210 was also tested for cesium retention using the West Valley alkaline supernatant. The 45 to 80 mesh exchanger was prepared by Duratek in the NH₄⁺-form. Duratek suggested that the cesium loading would increase if the West Valley supernatant was adjusted to pH 8 using HNO₃ and that the stability of the exchanger to OH⁻ attack would improve. No improved cesium loading was found (about 10 to 12 cv at 50% breakthrough at both pH 8.3 and pH 10.4). However, postprecipitation of silica was not observed at pH 8.3

during water washing, and exchange stability was improved. Postprecipitation of the Durasil 210 was observed at pH 10.4. Severe gassing of the exchanger was observed during initial alkaline supernatant (pH 8.3) loading of the Durasil 210. The gassing was eliminated by partially converting the Durasil 210 (NH_4^+ -form) to the Na^+ -form using 10 cv of 5 M NaNO_3 .

The results for a loading, water wash, and 3 M HNO_3 elution cycle with Durasil 210 are shown in Figure 8. The cesium loading profile shows an earlier initial breakthrough than for Durasil 10A (Figure 6, first cycle) but a similar 50% cesium loading breakthrough of 10.5 cv. A second test column with NaNO_3 -washed Durasil 210 and pH 8.3 feed (eliminating gas formation) resulted in essentially the same loading profile at 12 cv (Figure 9).

Batch relative distribution ratios were obtained for Durasil 210 at 6°C and 25°C for synthetic West Valley alkaline supernatant and for pH 10.4 and pH 8.3 feeds diluted 1:3 and 1:10. The R_d results were about 20 for pH 10.4 feed and about 10 for pH 8.3 feed (Table 1). However, this difference was not observed in the above column tests. IE-96 results are also shown in Table 1 for comparison.

Batch equilibrium tests were completed to determine the R_d of cesium-loaded Durasil 210 in contact with demineralized water at 6°C, 25°C, and 70°C. The average R_d for Durasil 210 was about 10^4 ; the average IE-96 R_d was $>10^6$ (Table 2). These results confirm the H_2O wash profiles shown in Figure 5.

CURRENT ACID FLOWSHEET DEVELOPMENT

Process requirements for preparation of a melter feed for vitrification are being evaluated. As now conceived, Tank 8D-2 sludge will first be washed with water to remove excess sodium and sulfate. The washed sludge will then be transferred from Tank 8D-2 to a concentrator and blended with Thorex acid waste and water-slurried cesium-loaded zeolite. Nitric acid may also be blended with this mixture if feed rheology or melter performance benefits would result.

FIGURE 8. Cesium Breakthrough Profile for Alkaline Supernatant and Durasil 210

As part of this study, IE-96 zeolite was digested with HNO₃ acid to determine acid requirements and melter performance. To determine the acid leaching requirements, three tests were conducted using 10 M HNO₃ at 25°C or 70°C and 5 M HNO₃ at 25°C; 10 cv of acid were used to leach the IE-96 zeolite. The acid

FIGURE 9. Cesium Breakthrough Profile for Alkaline Supernatant at pH 8.3 and pH 10.4

was passed through the column of zeolite at 0.5 cv/h. The initial zeolite weight was determined to be 740 g/L of exchanger. The final weight ranged from 488 to 529 g/L (29 to 34 wt% lost) after acid digestion.

The undigested and final quantities of digested zeolite were analyzed for oxide content (Table 3). The results show that 10 M acid is more efficient at elevated temperatures in removing iron from the zeolite structure. About

TABLE 1. Cesium Batch Distribution Values for Durasil 210 and IE-96^(a)

Dilution	Cesium R_d , Durasil 210			
	6°C		25°C	
	pH 8.3	pH 10.4	pH 8.3	pH 10.4
1:1	18.9	19.9	6.6	21.4
1:3	59.6	94.5	26.4	87.2
1:10	147.3	290.0	109.8	249.7

Dilution	Cesium R_d , IE-96			
	6°C		25°C	
	pH 8.3	pH 10.4	pH 8.3	pH 10.4
1:1	50.7	62.5	39.5	43.8
1:3	231	232	123	151
1:10	980	986	455	362

(a) Conditions: 45 to 80 mesh, HN_4^+ -form, H_2O -washed Durasil 210.

TABLE 2. Cesium Distribution Between Loaded Exchangers and H_2O as a Function of Temperature^(a)

Temperature, °C	Distribution Coefficient, R_d	
	IE-96	Durasil 210
6	--	7.4×10^4
25	3×10^6	1.7×10^4
40	$>1 \times 10^6$	--
70	4×10^6	4.6×10^3
120	7×10^6	--

(a) Conditions: 16-h contact.

TABLE 3. Analysis of IE-96 Exchanger with HNO_3 Digestion^(a)

Oxide, wt% ^(b)	Standard	5 M HNO_3 , 25°C	10 M HNO_3 , 25°C	10 M HNO_3 , 70°C
Al_2O_3	15.4	2.4	2.35	1.4
B_2O_3	0.1	0.6	--	--
BaO	0.1	0.02	0.02	0.01
CaO	1.3	0.39	0.40	0.39
Fe_2O_3	3.3	2.0	1.8	0.23
MgO	0.6	0.24	0.19	--
Na_2O	6.8	0.48	0.29	0.27
SiO_2	60.1	82.2	82.6	85.4
SrO	0.04	0.02	0.02	0.02
TiO_2	0.26	0.26	0.31	0.23
Other	1	1	1	1
H_2O	11	11	11	11
Final weight, g/L	740	514	529	488

(a) Conditions: 10 cv HNO_3 at 0.5 cv/h; initial IE-96 = 740 g/L.

(b) Adjusted results to 11 wt% H_2O .

0.2 wt% and 2 wt% Fe_2O_3 remained in the silica structure after elution with 10 M HNO_3 at 70°C and 25°C, as compared with 3.3 wt% Fe_2O_3 in the undigested exchanger. The eluate analyses showed that 15 to 20 moles of HNO_3 are required per liter of IE-96 for maximum Fe, Ca, Al, and Na removal.

Zeolite resulting from the 10 M HNO_3 -70°C column acid digestion test was blended into a melter feed and tested in a laboratory-scale crucible to determine melting performance. When compared with undigested zeolite feeds, the melting performance was poor.

ANALYSIS OF WEST VALLEY TANK 8D-2 SUPERNATANT

About 25 mL of Tank 8D-2 alkaline supernatant was sent to PNL after cesium decontamination in the West Valley hot cells using a PNL-fabricated ion-exchange column containing 30 mL IE-95. The decontaminated sample (cesium DF of about 10^6) is being used to obtain a variety of analytical data. A cation

analysis using inductively coupled argon plasma spectroscopy (ICP) is shown in Table 4. Density and viscosity values for synthetic and actual alkaline supernatant are compared in Table 5 for four temperatures. The sodium and specific gravity values indicate that the West Valley supernatant had concentrated in the tank by evaporation based on previous sampling results. The viscosity data for actual and synthetic supernatant are in good agreement (Figure 10).

TABLE 4. Analysis of West Valley Alkaline Supernatant by ICP

<u>Element</u>	<u>Concentration, mg/L</u>	<u>M/L</u>
Al	(5)(a)	--
B	65	0.006
Ca	(2)	--
Ce	(8)	--
Cr	680	0.013
Fe	(2)	--
K	5100	0.13
Mg	(1)	--
Mo	210	0.002
Na	196,640	8.55
Nd	(5)	--
P	240	0.008
Rh	(7)	--
Si	80	0.003
Te	(5)	--
Zn	(1)	--

(a) Parentheses indicate approaching detection limits.

TABLE 5. Physical Property Measurements for Synthetic and Actual West Valley Alkaline Supernatant

Temperature, °C		Viscosity, Cp		Density, g/mL	
Synthetic	Actual	Synthetic	Actual	Synthetic	Actual
6.5	6.5	6.58	7.15	1.33	1.40
25	25	4.32	3.38	1.32	1.39
40	40	2.70	2.34	1.31	1.38
85	65	1.27	1.29	1.275	1.36

Viscosity and Density of NaNO_3 at 25°C

NaNO_3 , M	Viscosity, Cp	Density, g/mL
3	1.129	1.159
5	1.539	1.255
7	2.159	1.366

CONCLUSIONS AND RECOMMENDATIONS

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

- Alternative ion exchangers (Durasil 210 and 10A) were tested for cesium recovery from West Valley alkaline supernatant as compared with the reference exchanger (IE-96) and were found to have no cesium capacity advantage.
- A pilot-scale ion-exchange column was constructed; IE-96 zeolite will be tested next quarter.
- Zeolite IE-96 was digested with nitric acid to determine acid requirements and resulting melter performance when the zeolite was blended with West Valley sludge. About 15 to 20 moles of HNO_3 were required per liter of IE-96 for maximum cation removal. When compared with undigested zeolite added to the melter feeds, the melting performance for digested zeolite was poor.

FIGURE 10. Viscosity of Synthetic and Actual West Valley Supernatant with Temperature

REFERENCES

Bray, L. A., et al. 1982. Experimental Data Developed to Support the Selection of a Treatment Process for West Valley Alkaline Supernatant. PNL-4969, Pacific Northwest Laboratory, Richland, Washington.

MELTING PROCESS CHEMISTRY

D. S. Goldman

SUMMARY

A nitrated feed formulation has been developed for West Valley high-level waste (HLW). This formulation melts efficiently; however, a viscous surface layer tends to form on the resulting glass due to phosphate phase separation. Potential solutions to this problem are being investigated. Redox control of the glass-making process is essential to minimize melt foaming and metal formation. Procedures for redox control and measurement are being developed.

INTRODUCTION

The objective of this work is to design a feed formulation that can be processed in the liquid-fed ceramic melter (LFCM) at an acceptable rate and that will produce an acceptable glass product. The oxide composition and properties of the glass product will be prescribed by the glass formulation design. The feed includes simulated HLW, glass-forming chemicals, and ion-exchange material. Glass-forming chemicals and other chemicals used for redox control are selected to maximize melting performance and minimize problems due to foaming, metal precipitation, and other adverse phase separation.

The technical approach involves a close interaction among feed formulation, glass composition, and waste processing work concurrently conducted at Pacific Northwest Laboratory (PNL). Hence, a glass composition is being developed to provide the appropriate high-temperature (viscosity, electrical conductivity) and low-temperature (elemental release rate, crystallization rate) properties. Nitrate chemicals representing the waste fraction and nitrate glass formers 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 0.4. Then, the melting rate of this feed is determined using the bottom-heated crucible test in the laboratory to measure 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 melter testing in the experimental-scale ceramic melter (ECM). The ECM test is used to corroborate the laboratory findings and evaluate if melting problems would occur over a longer time frame in a more continuous melting environment. If problems occur, further glass composition or feed formulation work is conducted in the laboratory. A successful ECM test leads to the development of a run plan for an extended test in the pilot-scale ceramic melter (PSCM).

TECHNICAL PROGRESS

The main objectives of work conducted in the first quarter of FY 1985 were to optimize the melting efficiency of West Valley WV183 feed and to develop the means to measure and control redox in the melting process. Progress on these objectives is described below.

MELTING RATE

The nitrated WV183 feed formulation includes a waste loading of 23%, 30 column volume (cv) equivalents of IE-96 zeolite, and sulfate at a concentration that will lead to 0.7 wt% SO_3 in the glass (Table 1). Sodium tetraborate is used to supply all of the needed boron. The remaining sodium that is required is added as sodium oxalate in order to efficiently include carbon into the feed for redox purposes. An additional 58 g/L of sugar is added to the feed to produce glass with a ferrous/ferric ratio between 0.1 and 0.4, which reduces foaming and minimizes metal precipitation.

The melting rate of this feed in the laboratory test was extremely high; complete cold cap burnoff occurred in about 3 to 4 min. Some of this improvement was due to the presence of sulfate. For comparison, PSCM-16 feed, representing the earlier working glass composition, took about 6 min for cold cap burnoff; in PSCM-7, Savannah River feed had a burnoff time of about 6 min. Thus, from these measurements, it does not appear that the presence of zeolite in the WV183 formulation was adversely affecting melting behavior. A low

TABLE 1. WV183 Glass/Feed Formulation

Feed		Glass	
Compound	g/L	Oxide	wt%
$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	157.81	SiO_2	44.6
$\text{FePO}_4 \cdot 2\text{H}_2\text{O}$	24.06	B_2O_3	15.5
NaNO_3	8.98	Na_2O	14.7
$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	12.58	CaO	0.7
CsNO_3	0.48	Fe_2O_3	12.3
RuO_2	0.28	Al_2O_3	2.4
RhO_2	0.03	Others	9.8
$\text{Zr}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	12.75		
$\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	4.83		
$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	6.16		
Didymium solution(a)	14.67		
Y_2O_3	0.06		
$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	14.60		
KNO_3	0.56		
$\text{Ba}(\text{NO}_3)_2$	0.33		
Na_2SO_4	0.85		
NaCl	0.11		
$\text{Sr}(\text{NO}_3)_2$	0.21		
$\text{Ce}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	1.69		
$\text{Ca}(\text{NO}_3)_2$	5.86		
$\text{Na}_2\text{C}_2\text{O}_4$	45.24		
$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	148.85		
SiO_2	132.04		
IE-96	40.55		
Sugar	58.00		

(a) Rare-earth mix, primarily La, Nd.

concentration of sugar (30 g/L) led to a thick, impermeable cold cap in the laboratory and the ECM with poor melting performance, which demonstrated the need for redox control not only for foaming but also for melting.

Several other feed formulation variations were evaluated in the laboratory. Acid-leached zeolite (mostly silica) was used with nitrate glass formers in a WV183 feed. When redox was readjusted for this feed using sugar, the melting rate deteriorated. In another experiment, the zeolite was replaced with 10 cv equivalents of the glass-based ion-exchange material, Durasil 210. Again, redox was adjusted with sugar. Poorer melting behavior was observed, and a significant cold cap was still present after 5 min. In another experiment, the oxalate was replaced with sodium nitrate and additional sugar was used to maintain redox conditions. Extremely poor melting behavior was observed; a thick, impermeable cold cap rose out of the crucible. Thus, multiple reducing agents appear to be required for acceptable cold cap behavior. The best melting behavior observed was with the nitrated feed formulation containing the IE-96 zeolite, sodium oxalate, and between 50 and 60 g/L of sugar.

SCUM FORMATION

"Scum" refers to any layer on the surface of the melt that has different properties than the bulk glass. In the case of West Valley glass, the scum that forms tends to be enriched in phosphate phases. The 10-day PSCM-19 experiment with WV182 glass with a calcium content of about 3% CaO was strongly and adversely affected by a calcium phosphate phase separation problem. The surface material from the melter was sampled, sectioned, polished, and analyzed by electron microscopy with energy-dispersive x-ray analysis. A calcium/rare-earth/phosphate phase (rare-earth elements are used to simulate uranium and thorium) coated residual silica grains in the cold cap. Similar results were noted earlier in sections of WV182 glass made in laboratory crucibles. The phosphate appears to form due to liquid-liquid immiscibility at the cooler temperatures found in the surface layer near 1000°C. In the laboratory crucible, phosphate was not found at higher temperatures. The calcium phosphate is shapeless, suggestive of liquid immiscibility. Given sufficient time,

dendritic crystals can form that interlock and strongly increase the viscosity of the bulk melt, as found in laboratory viscosity tests. Dendritic phosphate was not observed in the PSCM-19 scum. Rather, the poor melting behavior appears to arise from the chemical insulation of the remaining silica grains by the phosphate. No evidence of aluminum, iron, or calcium was found in the silica grains, which makes it unlikely that these grains were originally IE-95 zeolite.

Based on the PSCM-19 analyses, efforts began to reduce the calcium content in the glass by replacing the IE-95 with IE-96 zeolite and eliminating the calcium nitrate glass former to arrive at the WV183 composition. This composition resulted in 0.7 wt% CaO in the glass, 0.5% of which comes from the waste and 0.2% from the IE-96. Again, laboratory crucible tests showed that when the redox conditions were optimized, the feed melted rapidly. It appears that the laboratory test was of such short duration that it primarily evaluated cold cap burnoff behavior. Problems associated with scum formation were not readily seen in the test since these processes often take time to accumulate. Thus, the concern was that at the lower calcium content in WV183 the scum may appear but it may take longer to form. For this reason, longer ECM experiments were planned.

A two-day ECM test of the low-calcium WV183 formulation verified the laboratory results. With a low sugar content (30 g/L), a thick, impermeable cold cap formed that had a tendency to bridge across the melt surface. However, a subsequent one-day ECM test with the recommended sugar concentration (58 g/L) processed extremely well at 2.5 L/h with no deterioration in melting rate over time and no evidence of scum formation during processing. This melting rate is higher than that of PSCM-16 feed in the ECM (2 L/h). These ECM results are consistent with the laboratory findings. However, a scum did form on the ECM melt surface after idling. Later ECM testing was affected by redox control problems, but the tendency to generate scum was clearly indicated. It is important to note that scum did not form on PSCM-16 glass, which had a lower concentration of rare-earth simulants and the same amount of phosphate as WV183 but lacked calcium. The contribution of the rare-earth elements to the scum formation is being investigated.

The above results raise several important issues. First, it may be possible to provide a West Valley feed formulation that processes acceptably while the melter is actively operated. However, this formulation may not be acceptable if the glass forms a surface scum during periods of idling. Scum may occur as long as calcium or rare-earth elements and phosphorus coexist in the glass. This makes it even more important to obtain accurate estimates of calcium concentration in the waste and to be concerned with calcium variability anticipated over the lifetime of the project. Chemical means must be explored to determine if the phase separation tendency can be minimized, although the glass composition is already highly constrained due to property requirements. Only a few tenths of a weight percent difference in calcium, rare earths, and phosphorus are indicated between the ECM scum and the exit glass. This finding suggests that any amount of calcium may be sufficient to induce scum formation and that mechanical means (bubblers) or higher temperatures may have to be used in the melter during idling.

Second, the calcium phosphate contains a significant portion of the rare-earth elements that are used to simulate uranium and thorium. It therefore becomes important to ensure that the observed scum formation is not enhanced by the use of these rare-earth elements. Similar concerns exist with regard to characterizing the melting behavior of simulated waste using commercially available nitrated chemicals in place of hydroxide sludge that has been nitrated.

Third, the above results and concerns strongly suggest that calcium should be eliminated from the formulations considered for the Federal Republic of Germany (FRG) project since these formulations contain phosphate.

MOSSBAUER SPECTROSCOPY

The ferrous/ferric ratio can be readily measured in simulated or radioactive glasses using wet chemical procedures. Even though this analysis can be quickly and accurately performed on 20 mg or less of glass powder, it still involves delicate manipulations with glassware, which will be difficult if the sample has to be analyzed in a hot cell environment. Mossbauer spectroscopy is currently being evaluated both at PNL and Savannah River Laboratory (SRL) as an

alternative means to measure ferrous/ferric ratios in these glasses. Once the sample is prepared (for example, into a disk in powdered form), further analyst involvement is almost eliminated. Mossbauer spectroscopy is a nuclear resonance technique that uses gamma radiation from a moving cobalt-57 source. The radiation passes through the sample and is detected with a proportional counter. Ferrous and ferric ions absorb this radiation at different resonance conditions and thus generate a spectrum that can be mathematically analyzed to provide a ferrous/ferric ratio.

Mossbauer work on simulated waste glass has been completed by correlating the Mossbauer and wet chemical data. It was found that the area ratios of the ferrous and ferric peaks determined from the Mossbauer spectra lead to a ferrous-to-total iron ratio that is 1.2 greater than the value determined by wet chemistry. This correlation is linear (correlation coefficient $> .99$) and involves a variety of glass compositions, including some where iron is the only multivalent ion and others that contain additional multivalent species. This result suggests that the wet chemical procedure is not subject to potential interferences from these ions during acid digestion. The type of surrounding atmosphere (oxidizing versus inert) during digestion was tested at the 99% confidence level and did not affect the wet chemical results. These results support the validity of the wet chemical data and suggest that the bias lies with the common assumption that area ratios lead directly to concentration ratios from the Mossbauer method. It was found that the linear correlation could only be achieved if each Mossbauer spectrum was statistically optimized for the peak line shape using a composite Gaussian plus Lorentzian function. Most Mossbauer studies arbitrarily use a 100% Lorentzian line shape in their fitting procedure and assume that the area ratios directly represent the concentration ratios.

The Mossbauer technique described above generally requires at least 6 to 8 h to acquire spectral data with acceptable signal/noise characteristics for mathematical analysis. To provide the shorter feedback time envisioned for process control, a more rapid means to acquire the Mossbauer data was sought. It was found that the entire spectral region did not have to be sampled. Rather, if three spectral locations were sampled (for example, points

representing the ferrous and ferric peaks and the background), a linear calibration with wet chemical data could be achieved. Since this would reduce the number of spectral locations collected from 1024 to 3, spectra could potentially be collected in a matter of minutes. Adding faster electronics to the commercial spectrometer would further increase the rapidity of the technique.

Based on these results, the manufacturer has modified the instrument and plans to market the new spectrometer. PNL plans to purchase the first of these instruments for development with radioactive glasses in the 300 Area. The spectrometer currently being used for nonradioactive experiments will also be upgraded to have this capability. Since the new features will be software-controlled with a microcomputer, the analyst will only have to place the sample in front of the detector and press the start button; the computer will complete the experiment and output the ferrous/ferric ratio of the sample using the calibrations described above. These advancements were presented at the "Industrial Applications of the Mossbauer Effect" symposium at the International Chemical Congress of the Pacific Basin Societies in December 1984.

The next level of this study will be to evaluate problems that may arise during the analysis of radioactive samples. This work may involve a different type of detector and evaluation of shielding requirements and will also depend on sample preparation constraints imposed by the hot cell environment.

Initial work to provide space and shielding for this spectrometer in one of the 324 Building hot cells has begun. This area will receive major emphasis in FY 1985. Interest in the PNL technique and results has been expressed by the analytical group at Savannah River; increased interaction is expected throughout the year.

CONCLUSIONS AND RECOMMENDATIONS

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

- A nitrated feed formulation for WV183 glass has been developed and shown in the laboratory to have a high melting efficiency; this formulation has been demonstrated in a one-day ECM test.
- Including the IE-96 zeolite is not considered to have an adverse impact on melting performance.
- Optimized melting performance and cold cap behavior can be achieved only under proper redox conditions.
- Even at the reduced calcium content in WV183 (0.7 wt% CaO), phosphate phase separation still occurred and a viscous scum formed on the melt surface when the melter was idling. The contribution of the rare-earth elements has yet to be determined.
- Advancements have been made in the use of Mossbauer spectroscopy as a means to rapidly measure the ferrous/ferric ratio in glass for redox control. These techniques are ready to be tested with radioactive glass.

Based on these conclusions, the following recommendations are made:

- It must be ascertained whether scum will form if any calcium or rare-earth elements are present in the glass and if chemical means are available to reduce its rate of formation. If not, mechanical means (bubblers) or higher temperatures may have to be used while the melter is idling.
- Rare-earth elements are used in nonradioactive testing as substitutes for the uranium and thorium expected in the waste. It should be ascertained whether the presence of these actinides affects melting behavior and phosphate formation.
- Measurements of the calcium and rare-earth concentrations in West Valley waste should be further refined.

GLASS DEVELOPMENT AND CHARACTERIZATION

L. A. Chick

SUMMARY

The lead-iron-phosphate (Pb-Fe-P) glass developed at Oak Ridge National Laboratory (ORNL) for immobilization of high-level waste (HLW) was evaluated for its potential as a second-generation waste form. Severe crystallization resulting in substantially reduced chemical durability would result if this glass were poured into large canisters as is currently done with borosilicate glass. Resulting cesium leach rates would be orders of magnitude greater than those from borosilicate glass. The vitreous lead-iron-phosphate glass does appear to have substantially better chemical durability than borosilicate glass, however; thus, it may be a viable candidate composition for rapidly cooled beads or marbles embedded in a metal matrix.

INTRODUCTION

Glass development and characterization primarily involve development of the oxide compositions of nuclear waste glasses through laboratory testing of glass melts and solidified glass samples. Given a specific waste composition that is intended for vitrification, designing the glass oxide composition based on crucible-scale test results is the first of several interacting steps that lead to the final recommendation of a melter feed composition. The entire design process is diagrammed in Figure 1.

Nuclear waste glass compositions must have acceptable high-temperature properties for efficient melter performance and acceptable product properties for storage, transportation, and repository disposal. Key high-temperature properties for processing in currently designed joule-heated ceramic melters are:

- viscosity - The glass should reach 100 poise viscosity between 1070°C and 1150°C.

*Rework may also be required after earlier development steps.

FIGURE 1. Glass/Feed Development Flowsheet

- electrical conductivity - Approximately 0.1 to $0.5 \text{ (ohm-cm)}^{-1}$ is generally required.
- crystallinity - The glass should not undergo significant crystallization and subsequent settling and sludge formation at temperatures above about 900°C .
- phase separation - Significant amounts of phases such as alkali-molybdate or alkali-sulfate should not form on the molten glass surface.

The key product property is chemical durability. Other product properties--such as resistance to radiation damage, mechanical strength, and resistance to gas generation during transportation fires--are important but are either insensitive to glass composition changes or are nearly always within acceptable limits for otherwise viable glasses. Specifications for chemical durability of waste glass as determined by laboratory tests have not yet been established. Existing regulations pertain to radionuclide releases from the controlled zone of the repository. The most prudent current strategy for glass development is

to assume that the chemical durability (as measured by laboratory tests) should be as high as possible within the limits imposed by the high-temperature processing properties.

Economics must also be considered when developing nuclear waste products and processes. Key factors are the waste content in the glass product (waste loading) and the melting behavior of the feed. The waste loading determines the quantity of glass to be produced and transported and may influence the size of the repository required for final disposal. Melting efficiency impacts the plant size and the throughput.

Crystallization is often the condition that limits waste loadings in the glass. Formation of dense phases in the melt and subsequent settling can result in the build-up of a sludge layer on the melter floor. This sludge tends to form in cooler portions of the melter or during idling of the melter at lower temperatures. Over long periods of time, plugging of the melter could occur. Extensive crystal formation throughout the bulk of the glass melt would cause a drastic increase in viscosity and electrical conductivity. In the extreme case, the melter would have to be shut down, still containing the crystalline materials, and replaced. Crystallization of the final product during canister cooling is of concern only if it significantly degrades leaching performance. Crystal ingrowth could cause microcracking of the glass, increasing the surface area available for leaching. Radionuclide releases could also be increased if the crystal contained large amounts of radionuclides and was easily dissolved in water. However, leaching studies on deliberately crystallized samples of borosilicate glasses have not indicated drastic effects on chemical durability.

TECHNICAL PROGRESS

Sales and Boatner at ORNL have developed a Pb-Fe-P HLW glass composition that they claim is a promising new waste form for both commercial and defense HLW because it has "several distinct advantages" over the current reference borosilicate (B-Si) HLW glasses (Sales and Boatner 1984a, b). Specific features include:

- The Pb-Fe-P glass corrosion rate at 90°C is about 1000 times less than that for B-Si glasses.
- The Pb-Fe-P glass has a low viscosity between 800°C and 1000°C and can therefore be produced at a temperature that is 100 to 250°C lower than that required for B-Si glasses.
- The Pb-Fe-P glass has the ability to melt the elements found in both commercial and defense HLW.
- The Pb-Fe-P glass "can be processed using a technology similar to that developed for borosilicate glass nuclear waste forms."

Preliminary testing of Pb-Fe-P glasses at PNL included melting, devitrification, and chemical durability studies. In summary, these studies have indicated that:

- At 1000°C, the Pb-Fe-P melts adequately dissolved typical HLW compositions. Lower melting temperatures did not produce totally vitreous samples.
- Leach releases at 90°C of vitreous Pb-Fe-P samples that were rapidly quenched from the melt were roughly 100 times less than for B-Si glass under dilute conditions (MCC-1) and 10 to 100 times less than for B-Si glass under more saturated conditions (MCC-3).
- When the Pb-Fe-P glass was cooled in a manner that mimics the centerline thermal history of glass near the center of a large canister (the centerline heat treatment or CHT), the resulting material was extensively crystallized.
- Leach releases at 90°C for this CHT material were much greater than for the rapidly cooled vitreous samples. In particular, cesium release was more than 100 times higher than that from B-Si glass.
- The melt viscosity and electrical resistivity were within reasonable ranges for joule-heated electric melting of the Pb-Fe-P glass between 900°C and 1000°C but increased rapidly below 900°C due to crystallization.

Based on these results, the Pb-Fe-P glass might represent an improved waste form if produced as rapidly cooled marbles embedded in a metal matrix (Nelson, Nesbitt, and Slate 1981). Significantly improved chemical durability could be expected from such a waste form. However, the Pb-Fe-P glass cannot be considered a viable candidate for pouring into large canisters as is currently done with borosilicate glasses. Furthermore, the potential for rapid crystallization in the melter tank if electrode power were lost for even a brief period raises some doubts as to the viability of using joule heating. External resistance heating, such as is used in the PAMELA process (Harmon and Lakey 1982; Heimerl 1979), may be more appropriate for producing Pb-Fe-P glass marbles.

In early testing of the Pb-Fe-P glass, melts prepared at 900°C and 950°C contained 15 wt% Hanford and West Valley wastes. Since the Pb-Fe-P glass has a higher density than typical borosilicate glasses, the lower weight-basis waste loading (15 wt%) was roughly equivalent in volume reduction to 25 to 30 wt% waste in borosilicate glasses. These melting temperatures did not result in totally vitreous products; aluminum oxide and transition metal phosphates remained in crystalline states in the quenched products. Subsequent testing was performed using Savannah River HLW-containing glasses melted at 1000°C; the composition and sample preparation procedures described by Sales and Boatner (1984b) were closely followed. In the PNL work, uranium oxide was replaced with cerium and neodymium oxide (nonradioactive substitutes). The glass was melted at 1000°C for 2 h, poured into a 5/8 x 5/8-in. steel bar mold, and annealed for 2 h at 475°C. The resulting glass was essentially totally vitreous; the analyzed composition of the glass is presented in Table 1.

The vitreous glass was subjected to a heat treatment designed to simulate the cooling curve for glass near the center of a large-scale canister. This canister centerline heat treatment (CHT) is calculated based on the melting temperature of the Pb-Fe-P glass and an approximation of canister heat loss derived from thermocouple data on pilot-scale ceramic melter (PSCM) canisters. The calculation scheme is discussed in more detail in Chick et al. (1984). Since the thermocouple data were for borosilicate glass, the actual cooling

TABLE 1. Analyzed Bulk Composition of PNL Version of Pb-Fe-P Glass with 15 wt% SRL Waste

<u>Oxide</u>	<u>wt%</u>
PbO	51.5
Fe ₂ O ₃	8.9
P ₂ O ₅	31.8
Al ₂ O ₃	1.5
MnO ₂	2.1
NiO	0.95
SiO ₂	0.60
CaO	0.58
SrO	0.13
CeO ₂	0.19
Nd ₂ O ₃	0.40
Na ₂ O	1.2
Cs ₂ O	0.09
SO ₃	0.2
	<u>100.1</u>

rates for the Pb-Fe-P glass may be slightly different. The following heat treatment was used on the Pb-Fe-P samples: soak at 1000°C for 1 h and then cool the samples at the following rates.

<u>Cool From, °C</u>	<u>Down To, °C</u>	<u>Rate, °C/h</u>
1000	950	31
950	750	20
750	600	13
600	450	7
450	350	4

The resulting product was almost totally crystallized to the point that it was difficult to locate the residual glass phase in micrographs (see Figure 2). Areas that crystallized first were composed of densely packed fine grains. The regions that cooled more slowly, from which Figure 2 is taken, contained much

FIGURE 2. Optical Micrograph of CHT Pb-Fe-P Glass

larger grains (up to 3 mm long) as well as large voids. To better understand the CHT material, isothermal heat treatments were performed by heating the premelted samples at a constant temperature for 24 h. These anneals covered the temperature range from 550 to 1000°C in 50°C increments. Thin sections of these samples were examined optically; extensive crystallization occurred between 600°C and 800°C, producing morphologies similar to those of the CHT material. Less-extensive crystallization occurred at 550°C and in the higher range from 850 to 950°C. Very few crystals were observed in the 1000°C sample.

Scanning electron microscope (SEM) studies using energy-dispersive x-ray analysis (EDX) indicate that the crystals produced in the CHT and the 600 to 800°C anneals are lead-phosphates with varying amounts of iron, nickel, and

manganese. The phases produced at 550°C and from 850 to 950°C are aluminum-iron phosphates. These phases are also present in the CHT material. X-ray diffraction patterns of the CHT materials are extremely complex and have not yet been fully interpreted. Initial findings indicate that the major lead-phosphate-transition metal phase has a triclinic structure.

Leach results shown in Tables 2 and 3 include those from the 28-day MCC-1 test (monolith under relatively dilute conditions) and the 28-day MCC-3 test (powder under relatively concentrated conditions). For MCC-1, the CHT material was partitioned into predominately fine-grained and coarse-grained portions. Most of the release data for the vitreous Pb-Fe-P samples were below detection limits in the MCC-1 test (Table 2). If Pb and P releases are assumed to represent the glass matrix behavior (such as the Si and B releases do for borosilicate glass), then it can be said that the vitreous Pb-Fe-P matrix will leach 50

TABLE 2. Comparison of ARM-1, Pb-Fe-P Quenched, and Pb-Fe-P Heat-Treated Glasses^(a,b)

Element	ARM-1	Pb-Fe-P Glass		
	Borosilicate Glass	Vitreous	Small-Grained CHT	Large-Grained CHT
Si	9.5	<0.9 ^(c)	<0.2	<0.2
B	11	NP ^(d)	NP	NP
Pb	NP	0.14	0.093	0.17
P	<4	0.23	9.2	11
Na	11	<0.3	30	39
Li	11	NP	NP	NP
Ca	6.2	<0.7	3.1	5.1
Sr	5.8	<0.3	<1	<2
Al	8.7	<0.5	<0.2	0.64
Fe	NP	2.8	0.12	0.19
Cs	11	<12	2500	3200
Final pH	8.9	5.2	5.1	5.1

(a) All values are in units of normalized mass release (g/m^2).

(b) Test conditions: MCC-1; 90°C; 28 days; deionized water; $\text{SA/V} = 10 \text{ m}^{-1}$.

(c) Values preceded by < were less than the ICP detection limit.

(d) NP - not present in glass.

TABLE 3. Comparison of ARM-1, Pb-Fe-P Quenched, and Pb-Fe-P Heat-Treated Glasses

Element	ARM-1 30-Day Borosilicate Glass	Pb-Fe-P Glass	
		28-Day Vitreous	28-Day Composite
Si	0.39	0.14	<0.003 ^(c)
B	0.79	NP ^(d)	NP
Pb	NP	0.004	0.0026
P	0.52	0.058	0.43
Na	0.82	0.12	1.3
Li	1.2	NP	NP
Ca	0.00074	0.11	0.28
Sr	0.0016	0.065	0.074
Al	0.18	<0.003	<0.003
Fe	NP	0.00079	<0.0004
Cs	0.10	0.14	61
Final pH	11	4.0	3.8

(a) All values are in units of normalized mass release (g/m^2).

(b) Test conditions: MCC-3; 28 days; 90°C; 4 g -100+200 mesh powder in 40 mL deionized water; SA/V = 1120 m^{-1} .

(c) Values preceded by < were less than the ICP detection limit.

(d) NP - not present in glass.

to 100 times more slowly than the ARM-1 matrix. However, both fractions of the CHT material leached P, Na, Ca, and especially Cs much more rapidly. The MCC-3 data in Table 3 exhibit similar patterns.

It is evident that P, Na, Ca, Al, and particularly Cs have been partitioned into highly leachable phases during the heat treatment. SEM micrographs and EDX spectra of the Cs-containing phase are shown in Figure 3. The Cs phase is rich in Si and tends to be found on the boundaries of those Al-Fe-P crystals in shrinkage voids. Although the Al-Fe-P crystals are distributed throughout the material, cesium was only found attached to those crystals located in voids, which would explain the enhanced leachability of Cs in the CHT material.

FIGURE 3. SEM Micrographs of Central Area of CHT Devitrified Pb-Fe-P Specimen. Area A is the major phase, a lead-transition metal phosphate; Area B is a resin-filled shrinkage void; Area C (enlarged in right-hand photograph) shows the aluminum-iron-phosphate phase (gray) with the cesium silicate phase (white) on its surface.

The Cs was partitioned into a relatively soluble composition and was located in voids that are readily invaded by water. The Na- and Ca-containing phases have not yet been found.

Viscosity and electrical conductivity data for the Pb-Fe-P glass melt are illustrated in Figure 4. The effects of crystallization on these properties are strongly indicated by rapid changes at temperatures below about 900°C. As the melt cools and begins to crystallize, the viscosity increases sharply and the electrical conductivity decreases rapidly. Although the melt properties are probably acceptable for joule-heated melting from 900 to 1000°C, these data suggest that such melting may be inadvisable for Pb-Fe-P glass. For example, if electrode power were lost for a long enough period that the melt cooled to 800°C, the resulting crystalline mass would probably not be conductive enough

FIGURE 4. Viscosity and Electrical Conductivity of Pb-Fe-P Glass Melt

to allow restarting using the joule-heating electrodes. Pot melting or a continuous process using external resistance heating or induction heating would be more appropriate for the Pb-Fe-P glass.

CONCLUSIONS

The following conclusions can be drawn from the work reported:

- At 1000°C, the Pb-Fe-P melts adequately dissolved typical HLW compositions. Lower melting temperatures did not produce totally vitreous samples.

- Leach releases at 90°C of vitreous Pb-Fe-P samples that were rapidly quenched from the melt were roughly 100 times less than for borosilicate glass under dilute conditions and 10 to 100 times less than for borosilicate glass under more saturated conditions.
- When the Pb-Fe-P glass was cooled in a manner that mimics the thermal history of glass near the centerline of a large canister, the resulting material was extensively crystallized. Leach releases at 90°C for this material were much greater than for the rapidly cooled vitreous samples. In particular, cesium release was more than 100 times higher than that from borosilicate glass.
- The melt viscosity and electrical resistivity were within reasonable ranges for joule-heated electric melting of the Pb-Fe-P glass between 900°C and 1000°C but increased rapidly below 900°C due to crystallization.

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FEED PREPARATION AND TRANSFER SYSTEMS

H. T. Blair

SUMMARY

Long-term testing and demonstration of the two-stage air-lift design selected by West Valley Nuclear Services (WVNS) as best satisfying their vitrification process requirements were completed. As a result, several design and operational changes were recommended. With these changes, the air-lift design is considered adequate for WVNS requirements.

A remote model of the air displacement slurry (ADS) pump was installed in the radioactive liquid-fed ceramic melter (RLFCM) testing facility and successfully used during two nonradioactive runs and the first radioactive test. A fully remote ADS pump design was prepared and transmitted to WVNS for final review. The output of the pump varies directly with the head in the feed tank. A siphon break in the feed line was required to obtain consistent rate control in the nonradioactive demonstrations.

Test plans and other preparations were completed to start evaluation of tank and agitator designs, sampler performance, and slurry level and specific gravity measuring instruments. The tests are designed to confirm existing design correlations or to determine other correlations.

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 liquid HLW.

Activities and results of the work being performed at PNL to support development, design, selection, and operation of the feed preparation and transfer systems are discussed. During FY 1984 and continuing into the first quarter of FY 1985, melter feed systems using two kinds of pumps were being evaluated in a test loop for extended periods using simulated melter feeds. One pump is a two-stage air lift selected by WVNS as the melter feed pump best satisfying their requirements. The other pump is an ADS pump with a two-way pneumatic-activated valve selected for use in the RLFCM test and as a backup pump in the West Valley process.

TECHNICAL PROGRESS

The air-lift feed system used for long-term testing and for the melter demonstration made for WVNS in the pilot-scale ceramic melter (PSCM) during August 1984 (PSCM-19) is shown in Figure 1. The conclusion from this testing was that the full-scale West Valley air-lift pump design would be adequate with the following design changes:

- The diameter of the second-stage liquid supply line should be reduced from 3/4 in. to 1/2 in. to increase the fluid velocity in the line.
- Full-cone spray nozzles should be placed in the head pots as shown in Figure 1 to allow periodic washing of the insides of the pots to dissipate foam and prevent solids buildup.
- Operational procedures should include a daily water flush of the foot piece air orifices to prevent solids accumulations that could cause plugging.

Further testing of the air-lift feed system was suspended during the first quarter of FY 1985.

The prototype ADS pump that was demonstrated during FY 1984 (Burkholder and Rusin 1985) was used as a basis for a fully remote ADS pump design prepared for WVNS. The design reviews were completed at PNL early in December 1984, and the revised drawings were transmitted to WVNS for final review.

FIGURE 1. Air Lift Feed System for Long-Term Test Stand

Another remote version of the ADS pump was fabricated and installed in the RLFCM testing facility. The pump was successfully used during two nonradioactive runs and the first radioactive run. The RLFCM feed pump uses the MICON as a controller instead of a dedicated microprocessor as the prototype did, but the results appear to be the same.

During the PSCM-19 run, the prototype ADS pump was used to charge 1364 L of a simulated West Valley feed that included nitric acid and ground zeolite to the PSCM. At first, the pump did not deliver slurry to the melter at a consistent rate. It was determined that the relative elevations of the feed tank and the melter and the negative pressure in the melter were combining to create a siphon. After a siphon break was installed at the apex of the feed line, the ADS pump operated satisfactorily for the duration of the run at an average rate of 30 L/h. The pump rate varied about 15% with an inlet head change from 50 to 20 in. This variance could be compensated for by adjusting the pump control parameters.

In addition to the pump design and testing that are being done for specific applications, more generic studies are being conducted in the areas of tank and agitator design, sampler performance, and slurry level and specific gravity measurement. The objectives of these studies are to:

- Confirm existing design correlations or identify where the correlations do not apply to the unique properties of melter feeds and establish the necessary correlations.
- Establish performance tolerances so that their influence on the process quality control scheme can be determined.
- Prepare a large-scale prototype processing system design using the verified correlations and performance parameters.

A test plan was prepared to evaluate agitator and tank designs using a bench-scale mixing apparatus. The following variables will be evaluated: agitator speed; agitator position in the tank; type and size of agitator blades; number, size, and position of baffles in the tank; and the shape of the tank. Cooling coil designs will also be evaluated in the bench-scale apparatus. In conjunction with this testing, a tank sampler, which uses a steam jet to draw a

sample from the tank through a sample vial and recirculate it to the tank, will be tested to determine if representative samples are collected.

A test plan was prepared and approved for the evaluation of two systems that measure the specific gravity and the slurry level in a process tank. Because the slurries tend to plug conventional bubbler tubes, sensors that use metal diaphragms to seal the ends of the tubes will be tested. Both systems were installed, and testing has started with one of the systems.

CONCLUSIONS

- Testing of the two-stage air-lift pump designed for WVNS requirements was completed, and the design appears to be adequate.
- The ADS pump was designed for a fully remote application, and a prototype was successfully operated in a radioactive demonstration.
- Further modifications to the ADS pump are necessary to achieve consistent output control.

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MELTER SYSTEMS

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SUMMARY

The initial startup of the radioactive liquid-fed ceramic melter (RLFCM) was successful. Three short shakedown experiments produced a total of 34 kg of glass. The melter air-lift glass discharge system operated without fault. Glass foaming appeared to be related to the initial introduction of feed at the beginning of two of these initial experiments; decreasing the electrode voltage quickly returned the system to normal operating conditions.

Testing with simulated high-level waste (HLW) has focused on small non-radioactive melter testing to evaluate the effect of modifications to the West Valley melter feed composition. The objective is to determine the relationship between the feed components and the formation of an immiscible crystal phase on the glass melt surface. This phase is predominated by the presence of calcium/rare-earth/phosphate crystals. To date, the results have shown that the reduction in calcium alone is not adequate to prevent the crystal phase formation.

INTRODUCTION

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

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

RLFCM Initial Startup

The initial startup of the RLFCM was accomplished using two spiral-cut silicon carbide radiant electric heaters (I^2R SGR-41x24x2-1/8 units), rated at 11.2 kW each. These heaters were inserted into the melter tank plenum space through two nozzles in the melter tank lid and were powered from the discharge section Zone 1 heater circuit. The melter tank plenum temperature and the melter discharge section temperature were increased from ambient to 850°C over a period of six days to minimize the possibility of thermal-stress-induced refractory fracturing. Before the melter was installed in its in-cell location, the free water associated with the castable refractories and the water-based cements that were used to fabricate the melter tank were driven out of the containment vessel during a 30-day "curing" procedure. During this procedure, the melter plenum and discharge section temperatures reached 750°C.

To minimize the heat loss from the melter during the startup procedure, the melter tank was filled up to the shoulders of the electrodes (19 in. above the floor of the melter) with broken pieces of PSCM-16 glass, ranging in size from slivers to chunks up to 4 in. in diameter. After six days, the surface temperature of the cullet charge was about 730°C and the two startup heaters were delivering a total of 20 kW (about 88% of their recommended maximum output).

With the application of the maximum system voltage to the electrodes (352 V ac), a current flow of 7 amps between the electrodes was detected, indicating that electrical contact between the electrodes and the cullet had

been established and that electrical conduction through the cullet had been realized. At this point, the electrical resistance of the current path through the surface cullet was approximately 50 ohms. Within 6 min, the electrical resistance of this current path had dropped to 8 ohms, and 14.7 kW of heat was being released along the current path. About 60 min after the power was initially applied to the electrodes, the electrode current flow was held at 50 amps by reducing the electrode voltage, thus minimizing the probability of electrode damage from an excessive current density because of the limited electrical contact between the electrodes and the cullet charge at this point. About 17 h after power was initially applied to the electrodes, the electrode voltage control was shifted from a manual operation to an automatic control system that utilized the electrical resistance of the melter tank as a feedback value. Four days after power was initially applied to the electrodes, the melter reached steady-state conditions, the startup heaters were removed, and the power circuit was returned to the Zone 1 heaters.

The melter tank was filled to its normal operating level by dumping buckets of cullet into the melter tank through a funnel inserted in the feed nozzle in the melter lid. About 16 h were required to fill the melter tank.

RLFCM Shakedown Experiments

Three short RLFCM experiments were completed to confirm the operability of the facility. The first two experiments utilized a nonradioactive feed slurry and lasted for a total of 38 h. The last experiment used a radioactive feed slurry and lasted for 2-1/2 h. The three experiments successfully demonstrated the operability of the RLFCM facility and, at the same time, clarified the need for improvements in the feed delivery and off-gas treatment systems.

During the three initial experiments, 34 kg of glass were produced. This glass was subsequently air lifted out of the melter and into the receiving canister. The normal path for glass leaving the melter tank through the K-3 discharge throat block is first through the upward-inclined 3-in. diameter throat off the melter floor, then into a vertical 2-in. diameter riser tube, and finally overflowing into the 2-in. diameter downward-inclined discharge trough and a freefall from the discharge trough lip into the receiving canister. Normally as a slurry feed is added to the melter, the glass level rises

in the melter tank and in the riser tube until it reaches the overflow point and flows down the discharge trough. With very low slurry feed rates, the glass stream leaving the discharge lip is so thin that it cools and solidifies before it reaches the receiving canister. This thin stream tends to fill the discharge tube and canister neck with glass filaments or "hair" that can eventually cause a complete blockage. To avoid these glass filaments, the glass is normally discharged intermittently at high rates.

Air-Lift Glass Discharge System

For the RLFCM, a 3/4-in. diameter heavy-walled Inconel 690 tube inserted deep into the glass in the vertical riser tube (through a nozzle in the melter lid) becomes a very efficient air-lift pump when purged with a low airflow. This tube can pump glass out of the melter tank at a high enough rate so that the temperature of the glass in the receiving canister is only 50 to 100°C lower than the average melter tank temperature.

The RLFCM glass air-lift pump performed quite well during the initial shakedown experiments, pumping at about 0.5 L/min with an airflow rate of 3 scfm at a pressure of 20 in H₂O. No calibration of discharge rate versus airflow rate has been established. Glass drainage from the Inconel 690 discharge trough lip lasted about 2 min after the air-lift flow was terminated.

Remote Sensors

The RLFCM has one view port, specifically designed to view the top of the discharge tube to confirm that it is not obstructed and that the glass is free falling from the discharge trough lip through the discharge tube. Since no view ports were provided for viewing the inside of the melter tank, the status of the tank must be determined by interpreting the remote sensing devices that monitor the tank and its contents. Three instrument systems were used during the three initial RLFCM experiments: 1) the melter tank resistance value; 2) the melter tank temperature probe; and 3) the molten glass weight factor, specific gravity, and liquid level indicating systems.

The melter tank resistance value is calculated by a transducer that accepts the output of two other transducers that monitor the electrode voltage and current. A six-thermocouple bundle inserted in a vertical thermowell

monitors the vertical temperature distribution in the melter tank from a point 3 in. above the melter floor to a point 3-1/2 in. above the normal glass level immediately in front of the melter tank discharge throat. The active portions of the thermocouples are spaced 3 in. apart. The molten glass weight factor and specific gravity values are monitored with a conventional pneumatic dip tube and differential pressure system. The molten glass level is determined by a computer calculation based on the weight factor and specific gravity measurements.

Glass Foaming

On three separate occasions during the initial RLFCM experiments, process upsets were indicated by the instrument systems. These indications were strongly suggestive of a reboil-type glass foaming condition. The first indication of this condition was always seen as a sharp increase in the melter tank electrical resistance. With the resistive feedback electrode voltage control system in place, this increased electrical resistance implied a decrease in the melter temperature and resulted in an increase in the electrode voltage, which provoked additional foaming, and an accelerated increase in the electrical resistance. As the foaming progressed, the molten glass specific gravity dropped, indicating the lower density of the foamy glass. Glass temperatures increased simultaneously at all glass levels as the increased electrode voltage increased the power dissipated in the melter tank. Plenum temperature increases at the 15- and 18-in. levels, slightly lagging the tank resistance and specific gravity changes, suggested a rise in the glass surface level as the foaming progressed. The computer-calculated glass surface level confirmed this suggested level rise. By turning the electrode voltage down to its minimum (bias) value, the melter tank resistance, the molten glass specific gravity, and the molten glass liquid level values quickly returned to normal, again strongly suggesting that the process upsets were reboil-type foaming incidents.

Data Acquisition and Display System

Figure 1 typifies part of the still-developing RLFCM data acquisition and display system (DADS). A total of 208 analog sensors are sampled once every

FIGURE 1. Typical Computer-Generated On-Line Data Display

5 s for a period of 5 min (60 samples) once every 15 min. The average and standard deviation values of each of these 60 sample groups are calculated, converted into engineering units, and stored on disk immediately after Sample 60 has been taken. The 5-min sampling periods bracket the hour and quarter-hour periods, and the sampling time for the average and standard deviation values is recorded as the even hour and quarter-hour values. Immediately after the average and standard deviation values have been transferred to disk and tape storage, calculated values based on one or more of the average analog values just recorded are determined. These calculated values are termed "pseudo sensors," and they are also stored on disk and magnetic tape without standard deviation values. Space has been allotted for 42 pseudo sensor values.

Random access space has been allotted on the disk for 400 sets of average analog sensor values and their standard deviation values and for 42 pseudo sensor values. This space wraps around; the last data values overlay data values determined 400 scans previously. Thus, the disk maintains the last four days of data for the 250 analog and pseudo sensors.

A plotting routine, drawing on the data stored on disk, enables an operator to display both the averaged analog sensor values and the calculated pseudo sensor values plotted versus the sampling time. The operator can specify the y-axis limiting values and the tick mark intervals; but the x-axis remains fixed at 100 h with minor tick marks every hour, major tick marks at 00:00 h, and the date if a sample was taken at 12:00 h. Five plots can be made at a time, with one, two, or three plots per page, all with an identical x-axis.

The data are stored on magnetic tape and are primarily intended for archive use; however, since the data have the same format as those stored on disk, they can be used as a source of operational data for periods in excess of the four-day limit of the random access disk storage data. This feature is ideal for long-range studies such as the degradation of the electrode power connector blocks, the degradation of the melter tank liner, or shifting temperature distributions within the melter refractories. Currently, a 10-in. reel of magnetic tape lasts about 13 days.

NONRADIOACTIVE TESTING

Nonradioactive process development work involving the LFCM continued during the first quarter of FY 1985. ECM experiments were performed to evaluate the processibility of West Valley waste and glass former melter feed simulations. The ECM is a small test melter used to perform preliminary scoping studies to evaluate slurry processing characteristics (Figure 2). The melt cavity has an exposed melt surface of 0.054 m^2 and an operating depth of 15.2 cm. The resulting glass inventory is about 8.2 L. Under normal operating conditions, the glass melt is maintained at a bulk glass temperature of 1150°C . Slurry processing rates of up to 3 L/h can be achieved with some slurries. During operation, glass is periodically transferred from the melt tank to a receiving canister via a glass riser and overflow trough. Glass enters the

FIGURE 2. Experimental-Scale Ceramic Melter

riser through a port in the melt tank side wall at the tank floor level. Glass discharge is assisted by an air-lift lance in the riser that bubbles air into the riser glass. The difference in apparent density of the glass/air mixture to the glass in the melt tank causes the glass in the riser to move up the riser and into the pour trough. The glass flows down the pour trough and into the receiving canister.

Three experiments were conducted in the ECM during the first quarter of FY 1985 to evaluate modifications to the basic West Valley glass composition.

Testing in FY 1984 with the West Valley composition demonstrated that glass foaming could be measurably prevented by using carbon reductants. However, the combination of phosphate, alkaline earth, and rare-earth elements in the composition resulted in the formation of an immiscible phase. This phase was concentrated on the melt surface and inhibited heat transfer, causing a reduced achievable feed rate. In addition, the immiscible material was very stable; it has remained on the melt surface after four months of melter idling.

Two 24-h experiments were performed in the ECM in November 1984. The feed compositions contained less calcium than the FY 1984 West Valley composition (Table 1). To do this, calcium was eliminated as a glass former and reduced still further by using a modified zeolite ion-exchange additive with reduced calcium. The tests were designated ECM-85-1 and ECM-85-2, indicating that they were the first and second ECM tests in FY 1985. Carbon reductant was added to the two slurries as sodium oxalate and as commercial sugar. ECM-85-1 had a carbon loading of 6 wt%; ECM-85-2, 9 wt%.

The stable processing rate during ECM-85-2 was 1.5 L/h, which is similar to the processing rate of the previous West Valley composition fed during FY 1984. The cold cap was characterized as rigid with very little venting. The cap did appear to melt readily, indicating that the slow processing rates could be due to poor contact with the melt glass. Poor contact would result in reduced heat transfer to the cold cap. The poor contact was due to the formation of an immiscible crystalline phase. Although reducing the calcium content in the composition did reduce the rate at which the immiscible phase formed, the crystals still formed.

In the second ECM experiment, the carbon content was increased from 6 wt% to 9 wt%. One objective of this test was to verify whether crystal formation was a function of the reducing conditions in the melt. Prior to ECM-85-2, the glass in the ECM was replaced with an earlier West Valley glass that did not contain calcium. The ECM was flushed to remove the immiscible glassy phase that had formed on the glass surface. The results from ECM-85-1 had indicated that the presence of the higher calcium content in the melter tank glass at the start of the test could have contributed to the poor performance during the test.

TABLE 1. West Valley Simulated Slurry Composition

Waste		Assumed Oxide	
Compound	g/L	Compound	g/L
$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	158.01	Fe_2O_3	41.51
$\text{FePO}_4 \cdot 2\text{H}_2\text{O}$	24.06	P_2O_5	9.14
NaNO_3	8.94	Na_2O	3.64
$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	12.53	Cr_2O_3	2.38
CsNO_3	0.48	Cs_2O_3	0.35
RuO_2	---	RuO_2	---
RhO_2	---	RhO_2	---
$\text{ZrO}(\text{NO}_3)$	12.75	ZrO_2	5.88
$\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	4.85	MnO_2	1.68
$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	6.15	NiO	1.58
Lanthanum/neodymium	14.64	RE_2O_3	10.26
Y_2O_3	0.07	Y_2O_3	0.07
$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	14.71	Al_2O_3	2.00
KNO_3	0.60	K_2O	0.28
$\text{Ba}(\text{NO}_3)_2$	0.36	BaO	0.21
---	---	B_2O_3	0.04
Na_2SO_4	0.87	SO_3	0.49
$\text{Sr}(\text{NO}_3)_2$	0.22	SrO	0.11
$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	1.70	CeO_2	0.60
NaCl	0.11	---	---
$\text{Ca}(\text{NO}_3)_2$	5.84	CaO	1.75
Subtotal	266.9		82.0

ECM-85-1

Glass Formers		Assumed Oxide	
Compound	g/L	Compound	g/L
SiO_2	132.09	SiO_2	132.09
$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	148.88	B_2O_3	54.36
$\text{Na}_2\text{C}_2\text{O}_4$	45.23	Na_2O	45.12
$\text{C}_6\text{H}_{12}\text{O}_6$	30.00		

TABLE 1. (contd)

ECM-85-2

Glass Formers		Assumed Oxide	
Compound	g/L	Compound	g/L
SiO ₂	132.09	SiO ₂	132.09
Na ₂ B ₄ O ₇ • 10H ₂ O	148.88	B ₂ O ₃	54.36
Na ₂ C ₂ O ₄	45.23	Na ₂ O	45.12
Na ₂ SO ₄	1.99	SO ₃	3.53
C ₆ H ₁₂ O ₆	58.00		

The processing characteristics during ECM-85-2 were better than those in ECM-85-1. The stable feeding rate was 2.5 L/h, which was 67% higher than the rate maintained during ECM-85-1. The cold cap appeared to have the same rigid characteristics during both tests; however, active venting and flexing were observed in ECM-85-2. The cold cap remained relatively thin with little tendency to either build vertically or bridge solidly to the melter tank walls. The heat transfer to the cap from the glass melt was definitely improved over ECM-85-1. The formation of the immiscible phase was not as apparent during the test or the post-test sampling. However, after the test, the phase was visible. The main conclusion of this experiment was that processing characteristics were improved. Longer term testing would be required to determine if a gradual accumulation of crystals would occur over longer processing times or if the rate of crystal formation could be balanced by the glass production rate.

The third test, ECM-85-3, was a three-day test performed to verify the data and hypotheses from ECM-85-2. In this test, 115 L of slurry was processed at an average rate of 1.7 L/h. Melter test parameters were similar to those of the previous tests. The glass temperature was maintained at an average of 1160°C. Processing rates were comparable to those for ECM-85-1. The immiscible glassy phase became visible within the first day of the test. The processing rate dropped 36% in comparison to the one-day ECM-85-2 test due to the presence of the immiscible phase. The physical appearance of the cold cap was similar to that observed in ECM-85-2. The cap readily fluxed and did not tend

to build up; but, due to the slow processing rate, the cap material accumulated more easily and some bridging did occur. Post-test analysis of the slurry and the glass verified that there were no compositional differences that could be attributed to the different results. The slurries were compositionally correct, but some variation in the reducing strength was found. This discrepancy is interesting in that additional slurry that was prepared for ECM-85-2 was used at the beginning of ECM-85-3. The fact that the reducing strength of this feed changed with time was not anticipated. Additional analysis of the results is continuing.

CONCLUSIONS

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

- With the relatively straightforward RLFCM startup experience, the restart of a cold melter should not be a problem.
- With appropriate air-lift calibration experiments, the RLFCM air-lift system may be suitable for precisely filling receiving canisters.
- The startup procedures for the RLFCM experiments must be redesigned to minimize initial foaming tendencies.
- The usefulness of the DADS has been demonstrated, and every effort should be made to expand the on-line data reduction programming and to develop programs for examining archive data.
- Small melter testing with West Valley simulated slurry compositions has shown that the presence of an immiscible calcium-bearing crystal phase that forms on the melt surface during processing cannot be attributed just to the presence of calcium in the flowsheet.

CANISTER FILLING AND HANDLING SYSTEMS

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SUMMARY

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

INTRODUCTION

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

TECHNICAL PROGRESS

FUNCTIONAL TESTS OF WVDP TURNTABLE

The WVDP turntable and melter are illustrated in Figure 1. The turntable is used to position the canisters under the dual discharges of the melter. It also provides isolation of the canister from the cell atmosphere during the fill/cool cycle and provides for controlled cooldown of the filled canisters.

FIGURE 1. West Valley Melter and Turntable Assembly

Design and fabrication of the turntable were completed in early November 1984. After preliminary functional tests were performed on the turntable, it was shipped to West Valley in late November 1984. A summary of the test results is presented below.

The operation of all turntable features, with the exception of the turntable drive, was demonstrated. The load cell and a transducer that indicates canister location were both checked out. The load cell and the transducer are not intrinsic to the turntable design, and each is attached to the turntable with a Purex connector.

The rotating mechanism was checked with three canisters loaded with concrete to simulate glass-filled canisters. During this phase of testing, the clutch, which is rated at 11,000 in.-lb, was found to be undersized for the load. The clutch was replaced with a 25,000-in.-lb unit prior to shipment to West Valley. Efforts to reduce the rolling friction by reducing the length of the thrust pin that supports the canister during weighing was unsuccessful. The inertial torque or breakaway torque required to turn the turntable carousel loaded and unloaded is illustrated in Figure 2. Additional measurements were made with an empty turntable and with the carousel loaded with three canisters.

A linear variable displacement transducer indicates where the four canister holders (A, B, C, and D) are loaded in the course of a complete revolution of the carousel, i.e., at the primary pour spout, secondary pour spout, cooling position, or canister access port. The transducer successfully indicated the location of each of the four canister holders as the carousel turned. A functional checkout of the transducer as an electronic switch for stopping carousel movement when a canister is aligned for a glass pour or empty canister placement in the carousel was never completed. However, canister alignment was observed to coincide well with the pause in carousel movement and the "in alignment signal" from the transducer. Physical measurements were not made because of difficulties with the drive unit.

The load cell was calibrated once by adding steel shot to an empty canister located under the primary melter pour spout. The load cell response was adequate for process control but lacked in sensitivity. Lubrication and an

FIGURE 2. Torque Required to Move Carousel at Rest

alignment check are recommended and should result in improvement. The load cell, without any adjustment, will indicate a 50-lb incremental addition in the weight of a canister filling with glass. Simulation of the heat resulting from filling and cooling glass canisters was not a parameter in any of the tests.

Air inleakage was measured with the turntable completely sealed, with the lid on the canister access port in place, and in a not so tightly sealed condition with the lid on the canister access port removed and the secondary seal dropped into position. Inleakage at 3.5 in. H_2O was measured at 15 scfm. Bolts on the turntable lid were torqued to 100 ft-lb. In a final check, the containment integrity of the turntable was determined by measuring the air

inleakage rate at various levels. The criterion for these measurements was 15 scfm, a value that can be satisfied by operating at vacuum levels typical of the vessels in Hanford radiochemical plants.

RLFCM CANISTER HANDLING TURNTABLE

The canister handling turntable provides physical movement and positioning of the canisters underneath the RLFCM for canister filling and initial cooldown of the thermally hot canisters. The dunnage that supports the turntable also provides support for the RLFCM.

Turntable Design Description

The canister turntable (Figure 3) consists of a three-position motor-driven carousel that is located inside a containment vessel. The carousel consists of three containment pods equally spaced around a center axis. The carousel rotates around the center shaft supported by two bearings located at the top and bottom of the shaft. The normal rotational direction of the turntable is clockwise, although it can rotate in either direction. The top of the shaft extends out of the containment vessel through a bearing seal retainer. The turntable positioning motor is coupled to a hole on top of the shaft.

The three containment vessel pods each contain removable thimbles that are used to position various canister sizes. The thimble system can accept canisters up to 40.7 cm (16 in.) in diameter and 2.64 m (8 ft 8 in.) long. In addition to providing containment of the canister, these thimbles also collect any glass shards that fall from the discharge trough.

The turntable containment vessel is fabricated from 304L stainless steel plate. The walls are 0.47 cm (3/16 in.) thick, the floor is 0.95 cm (3/8 in.) thick, and the overall dimensions of the tank are 2.83 m (9 ft 3-3/4 in.) tall and 1.93 m (6 ft 4-1/8 in.) in diameter. The turntable containment vessel is equipped with: 1) dip legs to measure any liquid that could collect in the tank; 2) a dip leg for jetting out that solution; and 3) six thermocouples. The thermocouples, arranged three to a set, are located at opposing sides of the turntable: three are located near the canister filling position and three are located near the canister cooling position. The thermocouples in each set

FIGURE 3. Cutaway View of the RLFCM Canister Handling Turntable

are positioned near the top, bottom, and middle of the turntable wall. Each set of thermocouples is located within a blister connected to the tank. A window at the bottom of each thermowell allows contact between the thermowell and the inside of the containment vessel.

The carousel is positioned and centered underneath the melter overflow by two methods. The primary positioning method consists of using a cam attached to the carousel drive system in combination with a potentiometer-indicating system. This system, once calibrated, limits the movement of the carousel to 120° with each activation of the drive motor. The second method consists of using a cobalt source and detector to ensure that the canisters are in the current position.

Turntable Melter Seals

The turntable has two primary openings: one for replacement of canisters, and the other for mating the RLFCM and the canister handling turntable. Each of these connections is provided with a vacuum seal.

The seal cover concept for moving canisters into and out of the turntable is shown in Figure 4. The canister removal seal uses a 24-in. deep water seal to maintain vacuum in the canister handling turntable during normal operation. The seal consists of four basic parts: 1) a water seal trough, which is an integral part of the turntable cover; 2) a removable lid; 3) a floating inner seal; and 4) a cam-positioning system for moving the inner seal. During normal operation, the removable lid, which is weighted by a lead-filled circular block, is in place; and a vacuum seal of up to 24 in. H₂O is provided by the water seal. In the canister port closed position, the weighted lid also lifts up via a cam interlock of the inner seal so that the carousel is free to rotate. Access to the turntable is achieved by removing the weighted lid, which allows the inner seal to fall. In the port open position, the inner seal and the top of the canister thimble mate and provide a temporary seal that minimizes the air inleakage into the canister handling turntable and, subsequently, air leakage into the vitrification system.

A second turntable seal is used to mate the turntable to the RLFCM (Figure 5). The metal seal is comprised of three basic parts: 1) a metal

FIGURE 4. Canister Removal Port Positions

reservoir; 2) a lip that extends down from the RLFCM containment vessel; and 3) the seal material, which is a low-melting-point alloy (150°C), such as Woods metal. This seal concept was chosen because it is possible to make or break the seal remotely. To make the seal, the metal seal is positioned and bolted to the turntable. Low-melting alloy bars are placed in the steam-traced sealing trough. The liquid metal bars melt and fill the sealing trough. The bars are fed to the sealing trough until a sufficient mass has been fed to

FIGURE 5. Melter/Turntable Discharge Port

achieve a predetermined seal depth. Next, the steam service is discontinued and the seal metal is allowed to solidify, forming a high-integrity seal.

During normal vitrification operations, the temperature of the area around the seal may exceed the melting point of the sealing alloy. To prevent remelting of the seal, cooling air can be applied to the trough seal through the same tubes that were used to provide steam. The cooling of the seal metal will maintain the seal integrity.

Turntable Canister Positioner

The turntable canister positioner was tested to ensure its accuracy in lining the canisters up concentrically with both the canister access/removal and melter discharge ports with the carousel rotating in both clockwise and counterclockwise directions. The time required for the carousel to turn one-half of a revolution at the maximum speed was an average of 1 min 18 s, with an average 33-s pause with the canister positioned in the ports. The positioner was accurate enough to allow easy removal and installation of the thimbles, canister, and discharge cone equipment.

Torque Required to Rotate Turntable

Initially, the torque required to rotate the turntable carousel was 130 ft-lb with all three thimbles in place and no canisters and 200 ft-lb with two empty canisters in place. After modification of the lower bearing seal on the main shaft of the carousel, the average torque required for rotation was reduced to 60 to 70 ft-lb with three full canisters (each weighing an average of 1270 lb). The available torque is 917 ft-lb before the drive clutch disengages.

Airtightness of Turntable Seals

The turntable air inleakage was measured under a vacuum of 5 in. H₂O and with the access port cover on; the inleakage rate was 1.2 scfm. During the test, the hole below the melter discharge was covered with a rubber gasket, and the block connectors were sealed with tape. The water seal was filled to a WF of 12 in. when there was no vacuum on the turntable. The water seal WF drops 2.5 in. when 5 in. of vacuum is applied to the turntable. When the water seal WF (with no vacuum applied) is greater than one-half the maximum turntable vacuum expected, the water seal will function properly. The low inleakage rate will be maintained when the vacuum is started up. The low inleakage rate of 1.2 scfm is acceptable.

The inner cover seal in the access port was not tested for inleakage because the E-seal, which attaches to the bottom of the inner cover, was not available. The E-seal cannot be built under the current load specifications.

REMOTE TESTS/CANISTER ACCESS PORT COVER

Initially, the access port cover would not lower into position without manually shaking it back and forth. After the turntable was leveled, the cover slid down more easily and no shaking was required. The access port cover was removed and installed on the turntable with a vacuum of 5 in. H₂O. When it is removed, the vacuum increases in the area confined by the thimble, inner cover, and the main cover. The vacuum increases until it sucks air through the water seal or pulls water into the turntable. This effect can be minimized by removing the turntable outer cover at the lowest crane setting and by limiting the water height in the water seal to 6 in. A ball valve for venting was added to the outer cover and will be part of the operating procedure so the vacuum inside can be relieved after the inner cover falls into place. If venting is not performed when the access port cover is installed, the area between the inner cover can become pressurized and water can be pushed out of the water seal. The same procedure will be used for removing the outer cover and will also minimize the depressurization. The main cover should always be installed and removed at the slowest crane setting.

LFM CANISTER LEVEL/TURNTABLE POSITIONING SYSTEM

The design of the RLFCM provides for a glass canister turntable consisting of a three-position motor-driven carousel located within a containment vessel. This containment vessel is coupled directly to the overflow section of the RLFCM and, as such, provides a vacuum seal for the melter. Since the canisters are totally contained within the turntable enclosure, remote contactless microprocessor-controlled methods have been developed to establish the elevation and extent of canister glass fill as well as turntable positioning of the canister beneath the RLFCM.

The glass level detection system is composed of a translatable in-cell gamma ray source, out-of-cell gamma ray detection/analysis equipment, and a microprocessor controller/interpreter. The physical arrangement of the in-cell and out-of-cell components is illustrated in Figure 6. Functionally, the microprocessor sequentially positions the gamma ray transmission source adjacent to 11 fixed out-of-cell detectors with the melter canister interposed. At

FIGURE 6. Canister Level/Turntable Positioning System Layout

each detector elevation, a 1-min count is automatically initiated; the resulting counting rate is transferred to the microprocessor where the value is compared with a previously established background rate. This comparison serves to establish both the presence of the glass level and the extent of canister cross-sectional fill. The level detection systems also independently searches for the presence of the canister glass level based on changes in ^{137}Cs activity in the field of view of the 11 stationary detectors. If radioactive glass is being produced, complementary glass level information will be displayed based on both the ^{60}Co transmission source and ^{137}Cs loading in the glass. The functional interactions between the various components making up the canister level detection system are illustrated in Figure 7.

FIGURE 7. Canister Level Detection System

Correct positioning of canisters beneath the overflow section of the RLFCM is similarly verified by radioactive sources fixed to the periphery of the turntable carousel. A single fixed out-of-cell detector, with the field-of-view restricting collimator, provides all the necessary data for the microprocessor to establish absolute turntable positioning as well as canister melter alignment to a ± 0.3 -cm tolerance. The components making up the turntable positioning system and their functional interactions are illustrated in Figure 8.

All components of the canister level/turntable positioning system were integrated in the 324 Building during this reporting period. All of these components, including the in-cell sensors, have been shown to be operational. The source positioner has been exercised, and empirically determined preset values have been established for all 11 level positions. The correspondence between the alignment of the canister and melter and that of the turntable sources and the out-of-cell turntable positioning detector have been verified. Total functionality of the system has been established.

FIGURE 8. Turntable Positioning System

CONCLUSIONS

The following conclusions can be drawn from the work performed to date:

- The enclosed turntable appears to be a viable method for positioning the canister and for sealing the canister to the melter.
- Both gamma ray detection and load cell weighing appear to be viable methods for monitoring canister filling.

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OFF-GAS SYSTEMS

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SUMMARY

Melter emissions and off-gas system performance studies have been conducted to evaluate the reference West Valley Nuclear Services (WVNS) liquid-fed ceramic melter (LFCM) processing system. The overall system decontamination factors (DFs) established during testing were lower than expected primarily because of a malfunctioning high-efficiency mist eliminator (HEME). Post-test melter emission rate studies have indicated that idling melters do not present an inordinate effluent burden to the off-gas system.

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

TECHNICAL PROGRESS

An empirical evaluation of the reference WVNS LFCM processing system was completed during the last quarter. The basis of this evaluation was the 240-n PSCM-19 melter test conducted during the last quarter of FY 1984. The melter

off-gas system supporting this test was a scaled representation of the WVNS reference design that included an off-gas film cooler, a submerged bed scrubber (SBS), and a HEME. Consequently, the melter and off-gas system performance evaluation conducted for PSCM-19 provides the criteria for establishing the adequacy of the WVNS plant design to meet regulatory radiological emission guidelines.

FILM COOLER

A film cooler was installed in the PSCM to reduce the tendency of entrained particles to deposit on the wall of the off-gas jumper. This device introduces a boundary layer of cool air on the inside wall of the pipe, which effectively cools molten glass fragments below the softening point and prevents small particles from being deposited. The device was designed to be similar in function to the film cooler developed at Savannah River Laboratory (SRL). The PSCM-19 experiment demonstrated its effectiveness in preventing solids accumulation. Some solids did deposit in the film cooler but were quite friable and easily removed. The pattern of solids deposition indicated that the air injection rate may have been too high, causing separation of the boundary layer from the pipe wall. Melter vacuum was controlled directly by the rate of film cooler injection air and was a marked improvement over previous systems in controlling pressure during melter surges.

MELTER AND OFF-GAS SYSTEM PERFORMANCE

Melter emission and off-gas component performance is commonly expressed in terms of a unitless DF. By definition, a feed component DF is the ratio of the rate at which that particular feed component enters a device to the rate at which it exits. Consequently, melter DFs are related to the liquid-fed melter process efficiencies ($1 - 1/DF$) for converting feed components into a borosilicate glass. Similarly, the DFs associated with off-gas system components are measures of their scrubbing efficiencies for various airborne effluents. Table 1 presents averaged PSCM-19 melter and off-gas system DF performance data for representative off-gas effluent species.

TABLE 1. Melter and Off-Gas System Performance

Element	Average Decontamination Factor			
	Melter	SBS	HEME	Overall
B	47	1300	51	3.1×10^6
Ce	370	--	--	--
Cs	97	6	19	1.1×10^4
Fe	300	2700	33	2.7×10^7
La	340	1000	56	1.9×10^7
Nd	380	1500	--	--
Ru	29	16	23	1.1×10^4
Si	520	8000	19	7.9×10^7
Sr	430	1300	44	2.5×10^7
Zr	970	850	24	2.0×10^7
Total	380	30	3.9	4.4×10^4

Melter

The melter DFs listed in Table 1 are quite reasonable and comparable to results obtained from previous WVNS tests. However, higher average DFs for ruthenium were obtained during the present test due to the presence of reductant in the melter feed, which suppressed gaseous effluent losses of this element. The average melter Cs DF is quite respectable, although its variability throughout the test was quite large (from 27 to 280).

Submerged Bed Scrubber

The scrubbing performance of the SBS was apparently unaffected by the high flow (125 scfm) noncondensing off-gas operating conditions associated with PSCM-19 (Table 1). Overall SBS DFs obtained during PSCM-19 were greater than those observed during previous WVNS-sponsored tests, including PSCM-9, which utilized a venturi ejector quench scrubber. The aerosols capable of penetrating the SBS were found to have a mass median diameter of $<0.5 \mu\text{m}$, which is in good agreement with previously obtained venturi ejector results.

High-Efficiency Mist Eliminator

The off-gas performance of the HEME was inadequate (Table 1). The low DFs associated with this device are due to effluent breakthrough resulting from a wet filter element. Apparently, the dew point of the filtered gas was not maintained below the ambient conditions of the HEME, which resulted in solution penetration of the filter. These results underscore the fact that, although a HEME is a passive device, a good deal of processing care and control is required to achieve adequate operational performance. If dew point control is not desirable, HEME filtration can effectively be carried out using a water spray that continually washes the filter element in a countercurrent direction to the flow. However, one of these two operating modes must be adopted if the HEME is to perform any useful off-gas function.

Since the HEME element collects particles from the off-gas stream, it will eventually become plugged with excess solids. The element used in the PSCM off-gas system has not been changed since it was originally installed. Pressure drop data will be used to predict its life, but the change in recorded drop has not yet been measurable; therefore, no maximum estimate is yet available. During the PSCM-19 experiment, the pressure drop through the HEME showed no relationship to run duration, indicating that the solids accumulation was not appreciable. Analysis of backwashing samples showed that the element was cleaned of soluble material in less than 10 min. Following the experiment, the element fibers were found to be high in iron and chromium.

LFCM OFF-GAS SYSTEM PERFORMANCE ASSESSMENT

The average overall melter off-gas system DFs listed in Table 1 are below expectations primarily because of the solution-breached HEME. If WVNS plant stack emissions at the point of injection are to conform to uncontrolled area release guidelines, design performance specifications of the HEME need to be realized or additional off-gas processing equipment will be required.

A hydrosonic scrubber is a high-efficiency device that could potentially enhance LFCM off-gas system DFs. Very limited data are available involving the use of hydrosonic scrubbers in LFCM applications. LFCM off-gas testing of this device has been almost exclusively conducted by SRL, although PNL has had some

limited experience. SRL off-gas design provides for two cascaded hydrosonic devices directly downstream of the LFCM venturi ejector quench scrubber. Consequently, most of the LFCM scrubbing performance data associated with this device involve the tandem, cascaded system, which is designed to meet a Defense Waste Processing Facility-required DF of 50 for Cs aerosols. PNL performance data were obtained from a single unit located downstream of the SBS quench scrubber. Representative data obtained from both laboratories are presented in Table 2. Interlaboratory comparison of single-stage hydrosonic DFs agree quite well. However, the important comparison to be made is between single- and dual-stage operational performance data. The efficiency of the first scrubber does not impair or degrade the Cs or total DF performance of the second in a cascaded system. Furthermore, the data in Table 2 suggest that the hydrosonic scrubbing system can provide significant process control of submicron LFCM-generated aerosols. Although a single hydrosonic unit does not provide extremely high DFs, it may serve to increase DFs of subsequent processing equipment.

PNL has conducted parametric tests on the hydrosonic scrubber to help determine the most efficient water and air injection rates. These data are

TABLE 2. Hydrosonic Scrubber Performance

<u>Element</u>	<u>Aerosol Decontamination Factor</u>		
	<u>SRL (a)</u>		
	<u>Dual</u>	<u>Single</u>	<u>PNL</u>
B	--	--	23
Cs	61	7.2	4.9
Fe	--	--	9.2
Sr	3	5.2	5
Zr	--	--	3.2
Total	47	9	12

(a) See Colven (1983).

important for studies that compare the performance of the hydrosonic scrubber with that of the HEME. Only limited data were collected, but the general relationship showed that an increase in the water rate slightly decreased collection of aerosols while an increase in air injection significantly improved performance. The collection efficiency should peak for each of these parameters; more testing will be necessary to define the best operating point.

IDLING EMISSION

To assess the impact of melter off-gas idling emissions on the overall melter source term, off-gas effluent emission rates were studied for 14 days after the conclusion of PSCM-19. The results of these studies show that idling emission rates never exceed nominal operational rates that occur during normal melter feeding. Consequently, an idling melter does not present an inordinate effluent burden to the off-gas system.

CONCLUSIONS

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

- The performance of the off-gas system used in PSCM-19 was evaluated; overall DFs were lower than expected due to a malfunctioning HEME.
- It does not appear that a melter in the idling mode would overburden the off-gas system.

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PROCESS/PRODUCT MODELING AND CONTROL

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SUMMARY

The infrared imaging system was successfully tested. The images generated by this system provide improved differentiation between the feed slurry and the cold cap, permitting better estimates of the cold cap area. Under simulated liquid-fed ceramic melter (LFCM) conditions, the glass level monitor indications were accurate to 3 mm. In addition, it appears that the system can recognize that second phases are present in the glass surface.

The work on process control algorithms is continuing; process data from 10 pilot-scale ceramic melter (PSCM) runs were recorded on magnetic tape. These data are being used to study glass temperatures as a function of melter operating conditions. The data qualitatively agree with a computer code used to model convective currents. Attempts to quantify the intensity and scale of the turbulence for comparison with computer predictions will be made.

Analysis of West Valley PSCM-19 feed samples indicated large fluctuations in B_2O_3 concentrations. Sampling techniques, tank mixing, analytical techniques, component solubility, feed makeup materials are being investigated to explain these fluctuations.

INTRODUCTION

The purpose of this work is to develop correlations and models that can be used in the future to 1) adapt LFCM technology to a new high-level waste (HLW) composition and processing rate and 2) operate the adapted LFCM process. 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 regression 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 correlation to determine if the correlation is adequate. If it is 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

Progress on process control instrument development, process control algorithms, and product quality control is discussed below.

MELTER PROCESS CONTROL INSTRUMENT DEVELOPMENT

Several instrumentation concepts are being developed for use in remote melters. The instrumentation packages must allow the operators to monitor the performance of the melter and detect the onset of conditions that could lead to process upsets. These conditions include excessive surface glass foaming, molten salt phase separation from the glass, accumulation of the slurry feed in the melter, and formation of a rigid crust of feed materials or an immiscible phase over the entire glass surface.

Melter Viewing Systems

A melter imaging system has been tested that allows remote viewing of the melter cavity (Figure 1). The optics for this system are contained in the periscope portion of the assembly, which extends into the melting cavity. The camera is located above the melter where additional shielding can be provided, if necessary.

FIGURE 1. Melter Imaging System

The camera assembly is air cooled to prevent lens distortion or damage from the temperature changes that are caused by cycling the melter from operating conditions to idling and back. This cooling requires about 18 scfm of airflow to maintain the operating temperatures between 60°C and 130°C. The airflow is divided into two circuits; one that cools the camera and most of the optics and one that cools the last lens of the wide-angle lens assembly. This arrangement produces a cooling airflow into the melter of less than 2 scfm, which is adequate to prevent feed spatters from entering the orifice and obstructing the field of view. The remaining cooling air is exhausted outside the melter vessel. Because the periscope is cooled, volatile glass can condense on exposed surfaces. It has been shown that a steam jet directed at the lens aperture will remove these condensates.

This system uses a high-resolution camera and vidicon (imaging) tube that have been very resistant to gamma radiation damage. Tests at SRL have shown that this model will survive cumulative gamma exposure of more than 5×10^7 rads (Heckendorn 1983). The camera and periscope design have been tested in a melter for more than 1200 h.

This camera system was recently adapted to generate infrared-based pictures of the melter. The infrared images are created by filtering the light

that enters the camera to remove wavelengths shorter than about $0.7 \mu\text{m}$. The two primary advantages of this system are: 1) the images are directly related to the temperature and the emissivity of melter features and 2) high-resolution images can be generated in the low-light conditions typical in operating melters.

The infrared signal from the camera is processed to convert the black-and-white picture into an eight-color display. The color bands represent various temperature ranges inside the melter; thus, both quantitative and qualitative information is obtained. The melter images are also recorded on video tape for future reference and data reduction.

The images generated by the infrared system improve differentiation between the feed slurry and the dried feed crust, and the percentage of the glass surface area that is covered by the crust can be estimated. The resolution of this system under extremely low-light conditions (melting cavity features are usually not discernible to the naked eye) is better than the camera design used previously.

Glass Level Monitor

An electronic monitoring system is being developed to determine the glass level in the melter (Figure 2). The system requires only two Inconel conductors inside the melter. The capabilities of this system may also include determination of the thickness of the glass foam layer and detection of the molten salt phase separation.

The electronic level monitoring system determines the position of the glass surface by measuring the time required for an electric pulse to travel along a conductor entering the glass from above and be reflected by the glass surface interface back to the source. This technique--time domain reflectometry (TDR)--is conceptually similar to wave-guided radar. The output from this system includes the glass depth and a trace indicating the impedance of the conductor along its length.

The time required for the pulse to be reflected from the glass is a function of the position of the glass surface and the dielectric constant of the media surrounding the conductors. The shape of the impedance ratio trace is

FIGURE 2. Electronic Glass Level Monitoring System

also indicative of the physical conditions present at the glass surface. For example, if a glass foam layer is present, the impedance of the material between the two Inconel sensor rods would be higher than the impedance of the glass only; therefore, the reflected pulse would be weaker than for only glass, indicated by the slope of the impedance ratio curve. Similarly, for a molten salt layer, the impedance would be lower than that of glass only and the slope of the impedance ratio curve would be higher. Typical impedance traces for these cases are shown in Figure 3.

Tests with this instrument under simulated conditions have shown that the liquid level can be determined to within 3 mm. It appears that the system can recognize that second phases are present at the glass surface; however, further testing is required to quantify these results.

FIGURE 3. Impedance Ratio Curves from Glass Level Monitor

Cold Cap Stability Sensor

A pneumatic cold cap stability sensor has been developed to increase the feed crust monitoring capability using differential pressure cells and dip tubes (Figure 4). The glass level, the glass specific gravity, and the pressures at the 1-in. and 2-in. levels are recorded and plotted; the pressure at the 1-in. level is defined as the stability sensor.

The feed crust stability sensor is an excellent indicator of periods of overfeeding. During these periods, the crust appears to enlarge and begins to bridge along the melter walls, which tends to restrict the flow of decomposition gases from below the crust. The additional pressure exerted by these gases is recorded by the stability sensor as a higher backpressure in the dip tube (Figure 5). The initial portion of the stability sensor chart (Figure 5) indicates uniformly increasing dip tube pressures as the glass level rises between batch transfers. The rapid pressure fluctuation characteristics of overfeeding conditions are obvious in the last portion of the chart. Researchers at SRL have reported similar findings (SRL 1984).

FIGURE 4. Crust Stability Sensing System

FIGURE 5. Output from Crust Stability Sensing System Showing Nominal and Overfeeding Behavior

PROCESS CONTROL ALGORITHMS

Algorithms are being developed for LFCM process control, based on available and developing process instrumentation; tests will be conducted to validate these algorithms. Initial activities included examination of PSCM run data to determine if and how existing process instrumentation can be correlated with observed melter phenomena (cold cap coverage, pressurization, and foaming).

Process data were recorded on magnetic tape during PSCM Runs 4 through 9, 11, 15, 16, 17, and 19. Data from Runs 4, 5, 6, 8, 9, 11, and 16 are available for immediate examination. The recorded data include: refractory, cooling fluid, off-gas, and plenum temperatures; feed rates; off-gas pressures; and canister weights. Glass, off-gas, and plenum temperatures; feed rates, and electrode potential, current, and power are of primary interest with respect to melter control. Initially, these parameters are being evaluated as a function of time.

Glass temperatures 1.5 in. and 9 in. above the floor of the melter during PSCM-11 are plotted in Figures 6 and 7. Both the temperatures as recorded every 5 min and the 1-h moving average of those temperatures are illustrated. The temperatures observed at the 1.5-in. level show three sharp spikes, corresponding to three glass air lifts, and one broad temperature peak associated with foaming in the glass. Other than these large changes, the temperature curve at this level is relatively smooth.

Temperatures at the 9-in. level are more than 100°C higher and much more erratic than those observed at the 1.5-in. level. The temperature peak associated with glass foaming is still evident and can be identified at all thermocouple levels (1.5, 3, 6, 9, 12, 15, and 18 in. above the melter floor). However, the three temperature spikes observed at the 1.5-in. level during air lifting of the glass are not identifiable at the 6-in. level or above.

These observations qualitatively agree with a computer code that modeled convective currents in the melter. The model predicted a relatively cool, quiescent layer of glass near the melter refractories and a hotter, turbulent region in the remainder of the melter. The thermocouple at the 1.5-in. level is apparently in the relatively cool region. During PSCM-11, the thermowell was near the riser/overflow entrance; as glass was air lifted from the melter, the hotter glass was drawn into the cooler region near the riser/overflow entrance, causing the observed temperature spikes. The thermocouple at the 9-in. level was in the hotter region and, therefore, shows large temperature fluctuations. An attempt will be made to quantify the intensity and scale of the turbulence and compare the values with the computer predictions.

FIGURE 6. Glass Temperatures Observed at the 1.5-in. Level During PSCM-11

FIGURE 7. Glass Temperatures Observed at the 9-in. Level During PSCM-11

Foaming can be detected with the thermocouple located in the glass; but, at this time, it cannot be predicted using temperature data. Glass temperatures tend to increase during the foaming event, although the increase may not be as evident as at the 1.5-in. level (Figure 6). Thermocouples at the 15- and 18-in. levels, which are typically above the glass level, measure the large temperature increases as the foam rises to these levels.

WEST VALLEY/PRODUCT QUALITY CONTROL

The West Valley PSCM-19 feed samples were analyzed by inductively coupled plasma spectroscopy (ICP) for all major and minor constituents. The B_2O_3 , SiO_2 , and Na_2O concentrations are shown in Figure 8. The following areas are being investigated to explain the fluctuations: sampling techniques, tank mixing, analytical techniques, component solubility, and materials used for feed makeup.

During PSCM-19, a large quantity of feed was made that contained most of the necessary constituents. As needed, small batches (about 1000 L) were made by adding one or more of the following: sugar, nitric acid, sodium borate, sodium oxalate, or cerium oxide. These small batch mixtures added more chances for error. Although sodium was added to each small batch, its concentration did not fluctuate as extensively as boron. This behavior may be due to the mixing of the tank before the sampling or to the difference in solubility between boron and sodium.

The compositional analysis of the glass samples taken from the canister filled during PSCM-19 will be compared with the feed sample analysis. This type of comparison will help describe the mixing that occurs in the glass tank.

CONCLUSIONS

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

- The improved images from the infrared imaging system permit better estimates of the surface area covered by the crust.

FIGURE 8. B₂O₃, Na₂O, and SiO₂ Concentrations in PSCM-19 Feed Samples

- Under simulated LFCM conditions, the glass level monitor indications were accurate to 3 mm; in addition, the system appears to recognize that additional phases are present at the glass surface.
- The cold cap stability sensors are excellent indicators of overfeeding conditions.
- PSCM glass temperature data and computer code predictions used to model convective currents within the melter qualitatively agree.
- Large fluctuations in B₂O₃ concentrations were found in West Valley PSCM-19 feed samples.

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SUPPORTING STUDIES

K. J. Schneider and R. D. Peters

SUMMARY

Improvements have been made in the methodology used for predicting near-field repository release rates from borosilicate glass cylinders. The long-term glass log dissolution rate in silicate-containing groundwaters of a flooded repository are estimated at 3×10^{-5} to 1.4×10^{-4} fraction per year. Assuming silicate saturation in the groundwater, the dissolution rate in the water-limited conditions of a repository in unsaturated host rock is conservatively estimated at between 5×10^{-6} and 2×10^{-4} fraction per year. A preliminary evaluation of the effects of time-distributed failure of overpacks has been conducted and indicates that this may not be an important factor in limiting peak release rates from the total population of glass waste forms. This effect is a result of the slow degradation rate of glass compared with that expected of overpacks.

• 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, and documentation of vitrification technology and plans for specific applications.

TECHNICAL PROGRESS

Progress on the borosilicate glass performance evaluation is presented below.

BOROSILICATE GLASS PERFORMANCE EVALUATION

The objective of this evaluation was to provide a performance analysis of borosilicate glass as a high-level waste (HLW) form through the waste management steps of vitrification, storage, transportation, and disposal. The disposal analysis considered repositories in basalt, granite, tuff, and salt. Performance criteria are those of the Environmental Protection Agency (40 CFR 191), the U.S. Nuclear Regulatory Commission (10 CFR 60), and doses to future generations. Performance was also compared with existing regulations for the steps of solidification, interim storage, and transportation. Disposal was emphasized in this work because of the long-term certainties and because of the difficulty in implementing corrective action, if necessary, after repository closure. The first draft of a report was issued in FY 1983, and comments were received in FY 1984. During the first quarter of FY 1985, improvements were made in the methodology used for predicting release rates from the borosilicate glass to the near-field.

Glass Dissolution in Silicate-Containing Water

The dissolution of borosilicate glass in silicate-containing waters was reevaluated, and an improved estimate of waste glass dissolution rates at the high-silica groundwater conditions of a water-saturated repository was obtained. The data of Strachan (1982) and Pederson et al. (1982), who performed batch leach tests on PNL glass 76-68, were examined. Time versus cumulative boron release data at 90°C were fit to an exponential functional form that was then time-differentiated to yield glass dissolution or leach rates. The lowest rates correspond to the longest dissolution times and/or the highest aqueous concentrations of silicate. Because of the scatter of data associated with the low rates of glass degradation, upper and lower estimates were obtained for the leach rate when silica concentrations exceed 70 mg/L. The lower and higher rates for PNL glass 76-68 degradation at these high aqueous silica concentrations were 0.034 and 0.16 g/m²-day, respectively. For a cylinder of glass 0.3 m diameter by 3 m long (assuming no available surface area due to fractures), these rates correspond to average fractional dissolution rates of 3×10^{-5} to 1.4×10^{-4} per year. The release rates of the minority of radionuclides with high solubilities (such as isotopes of Ra and

Cs) would be expected to fall within this estimated range. Release rates of radionuclides with low solubilities would be below this range and would be controlled by their respective solubilities and/or flow rates.

An estimate of the glass leaching rate in the unsaturated water conditions of a tuff repository has been calculated. The basis for the calculation method is that disposed borosilicate glass dissolves at the rate that its silica is dissolved and transported away from the waste package. This approach is prompted by observations from experiments, as discussed above, where the glass leach rate slows drastically as silicate becomes more concentrated in solution. It has been conservatively estimated that individual waste packages disposed in a Yucca Mountain repository can be exposed to between 5 and 208 L/yr of unsaturated tuff groundwater (Oversby 1983; Aines 1984); the higher estimate is an extreme upper-bound. Our analysis conservatively assumes that this groundwater, which at 90°C normally contains 40 mg Si/L, becomes saturated with respect to amorphous silica (solubility of 140 mg Si/L at 90°C) because of contact with the waste glass. The difference in silica concentration between this saturation limit and that of the fresh tuff groundwater provides the driving force for dissolution of silica for the resultant fractional release rate F:

$$F = \frac{V(C_s - C_b)}{mM_g}$$

where V = the groundwater volumetric flow rate (5 to 208 L/yr)

C_s = the solubility of amorphous silica

C_b = the concentration of silica in pristine groundwater

m = the mass fraction of silica in the glass (0.19 g-Si/g-glass)

M_g = the mass of glass per waste package (500 kg).

With these values, low and high fractional release rates (corresponding to the low and high flow rates) of 5×10^{-6} and 2×10^{-4} are obtained for the degradation rate of borosilicate waste glass in tuff.

Effect of Partial Failure of Overpack

Corrosion and failure of overpack materials is a prerequisite to release of radionuclides from waste glass. Previous analyses conducted in this program have assumed that all packages fail simultaneously; in reality, the population in the repository will fail over a period of time. A sensitivity analysis was performed to determine the effect that time-distributed package failures has on release of radionuclides from the overall population of packages.

The Weibull distribution has been proposed by Chu and Axness (1983) to represent the time dependence of cumulative failures of waste packages in the repository. Because of the lack of corrosion and lifetime data on waste package designs, the required input parameters for a Weibull model (which is usually constructed by empirical fitting of lifetime data) or any type of complex representation are not yet available. The approach taken here is to assume a constant failure rate and thus a linear cumulative distribution function.

The relationship between two characteristic times has been examined: the time (T_L) it takes to "leach out" a radionuclide from a waste form (assuming it is freely exposed as if the overpack and canister have corroded away) and the time required for failure of all packages in the repository (T_F). It is assumed that both the numerical rate of package failures and the leach rate of a given radionuclide are constant with time, given by the inverses of T_F and T_L , respectively. It was found that the maximum fraction of packages that contribute to release of a given nuclide is less than the total number of packages only when leach time is less than overpack failure time ($T_L < T_F$). If leach time is greater than failure time ($T_L > T_F$), then the maximum number of packages contributing at the same time is equivalent to the number of packages in the repository. If packages are nominally designed to last 1000 years (in accordance with NRC 10 CFR 60), then the failure time for all packages will probably be longer than this, perhaps up to 10,000 years. The glass degradation rates calculated above for the saturated repository correspond to leach times of 7,000 to 33,000 years; thus, this preliminary calculation suggests

that T_L is greater than T_F for nuclides incorporated into glass. In this case, the delay due to a distribution of overpack failures will not reduce the peak release rate, relative to the case of simultaneous failure.

CONCLUSIONS

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

- Long-term borosilicate glass log dissolution rates in silica-containing ground waters are estimated to be from 3×10^{-5} to 1.4×10^{-4} fraction/year.
- Long-term borosilicate glass log dissolution rates in unsaturated host rock are estimated to be from 5×10^{-6} to 2×10^{-4} fraction/year.
- Preliminary analyses indicate that the effects of time-distributed failure of overpacks/canisters in a repository may not be an important factor in limiting the peak release rates from the total population of glass waste forms.

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APPENDIX

ACRONYMS AND ABBREVIATIONS

APPENDIX

ACRONYMS AND ABBREVIATIONS

ADS - air displacement slurry (pump)
Al - aluminum
B - boron
Ba - barium
Ca - calcium
Ce - cerium
cm - centimeter
Cr - chromium
Cs - cesium
CTS - component test stand
cv - column volume
DF - decontamination factor
DOE - U.S. Department of Energy
ECM - experimental-scale ceramic melter
Fe - iron
FRG - Federal Republic of Germany
ft - feet
FY - fiscal year
g - gram
h - hour
H - hydrogen
HEME - high-efficiency mist eliminator
HLW - high-level waste
ICP - inductively coupled plasma (spectroscopy)
in. - inches
K - potassium
kg - kilogram
L - liter
LFCM - liquid-fed ceramic melter
LLW - low-level waste
M - molar
mg - milligram
Mg - magnesium
mL - milliliter
mm - millimeter
Mo - molybdenum
N - nitrogen
Na - sodium
Nd - neodymium
NWTPO - Nuclear Waste Treatment Program Office
O - oxygen
ORNL - Oak Ridge National Laboratory, Oak Ridge, Tennessee
P - phosphorus

Pb-Fe-P - lead-iron-phosphate (glass)
PNL - Pacific Northwest Laboratory, Richland, Washington
PSCM - pilot-scale ceramic melter
R_d - relative distribution ratio
Rh - rhodium
RLFCM - radioactive liquid-fed ceramic melter
S - sulfur
SBS - submerged bed scrubber
scfm - standard cubic feet per minute
Si - silicon
Sr - strontium
SRL - Savannah River Laboratory, Aiken, South Carolina
TDR - time domain reflectometry
Te - tellurium
Ti - titanium
TRUW - transuranic waste
wt% - weight percent
WVDP - West Valley Demonstration Project
WVNS - West Valley Nuclear Services
yr - year
Zn - zinc

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