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LFCM Vitrification Technology

Quarterly Progress Report
January-March 1986

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

September 1986

Prepared for the U.S. Department of Energy
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H. C. Burkholder and J. E. Minor, Compilers

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ABSTRACT

This report is compiled by the Nuclear Waste Treatment Program and the Hanford Waste Vitrification Program at Pacific Northwest Laboratory to document progress on liquid-fed ceramic melter (LFCM) vitrification technology. Progress in the following technical subject areas during the second quarter of FY 1986 is discussed: melting process chemistry and glass development, feed preparation and transfer systems, melter systems, canister filling and handling systems, off-gas systems, and process/product modeling and control.

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SUMMARY

This report is compiled by the Nuclear Waste Treatment Program (NWTP) and the Hanford Waste Vitrification Program (HWVP) to describe the progress in developing, testing, applying, and documenting liquid-fed ceramic melter (LFCM) vitrification technology. Activities in the second quarter of FY 1986 are summarized below:

Melting Process Chemistry and Glass Development - Laboratory procedures used for HWVP feed processing studies were evaluated, including the HWVP reference feed simulation, the methods of concentrating the simulation, and the melter feeds made with it. Two simulations were prepared and compared. One consisted of a blend of dry chemicals and a concentrated iron hydroxide slurry. The other was prepared by dissolving the desired elements in a nitric acid solution, then converting it to HWVP feed by sugar denitration, neutralization, digestion, settling, decanting and washing. The two simulations exhibit significant physical and chemical differences. Further work with actual aging waste samples is needed to determine which simulation more accurately represents the physical and chemical properties of the aging waste. The simulated wastes were concentrated by boiling, and measurements were made of the effects of processing variables on the rheology of the concentrates and on the melter feeds. While some melter-feed properties, such as yield stress and apparent viscosity, do not appear to be a function of the concentrating process used, dilatant properties in a slurry do appear to depend on the concentrating process.

Feed Preparation and Transfer Systems - Fabrication and installation of a large-scale mixing tank were completed. It will be used as the melter feed makeup tank for the pilot-scale ceramic melter system. Functional testing of a remote air-displacement slurry pump with a newly designed air-supply system was successfully completed. The test's primary objectives were to verify alignment and mechanical integrity of the pneumatically actuated valve, to mock up installation of the pump and thus verify that dimensions and clearances are sufficient for it to fit into the remote tank, and to determine the effect of cycle time and air pressure on the flow rate using the new air-supply system.

Melter Systems - Operation of the radioactive liquid-fed ceramic melter (RLFCM) in campaign/test RLFCM-7 produced a rather poor glass product. However, the constant-current manual power control worked well as the glass level was brought up to normal operating level. The control maintained temperatures reasonably stable as the melter tank resistance value shifted with the rising glass. Nonetheless, continuing erosion of the melter weight factor dip tube and deterioration of the gas system resulted in an uncontrolled discharge of glass to the receiving canister. This emphasizes the importance of the glass weight factor sensor and the need for stable melter pressure control. In the second half of the campaign, indirect indications of glass temperatures suggested that they were within the specified range. However, too many changes of the power controller set point were made to permit the control system's performance to be assessed with certainty. Evidence indicates that the slurry feed rate needs to be better controlled to control the melter cold cap.

Canister Filling and Handling Systems - The HWVP has completed a conceptual turntable design for handling canisters similar to the West Valley Demonstration Project (WVDP) turntable design. The turntable is a cylindrical enclosure located below the HWVP melter. Within the enclosure is a carousel that accommodates four canisters and rotates them into position for filling. The design provides for moving the canisters under the melter discharge, controlling spread of contamination to the process cell, controlling inleakage to the melter, weighing canisters, and detecting their glass level using a gamma-level detection system.

Off-Gas Systems - Characterization studies of melter effluent emission and off-gas system performance were conducted on B-Cell's RLFCM. Melter feed entrainment losses were found much greater than anticipated based upon past nonradioactive testing. Melter decontamination factors for both ^{90}Sr and ^{137}Cs were both a factor of 10 lower than cold-test predictions for normal feed-processing conditions. Performance of the ejector venturi quench scrubber was not consistent in all phases of RLFCM processing. Despite acceptable efficiencies during normal feed-processing conditions, the off-gas sampling data indicate a complete loss of scrubber capability during the spike-feeding

presently available, use of the EVS to control melter vacuum may have caused this loss of off-gas processing efficiency.

Process/Product Modeling and Control - A mass balance model of a hypothetical LFCM vitrification system has been developed using the SIMAN simulation language. It can model simultaneously occurring batch and continuous processes and take into account process uncertainties. The model, being used to investigate methods of controlling and predicting the product composition, can be modified readily to investigate effects of any process uncertainty on the process' ability to produce glass acceptable for disposal. A method for correlating glass dissolution rate versus composition was tested using leach rate data for several waste glass compositions, and a preliminary dependence of dissolution rate and composition was determined. Also methods were developed to relate the uncertainty in predicted glass dissolution rate with the uncertainty in predicted composition of waste glass.

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INTRODUCTION

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

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

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

- Technology Development - W. A. Ross
- Technology Testing - R. A. Brouns

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

- 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; Burkholder and Jarrett 1986), and formal topical reports. Recognizing both the magnitude of the first-generation HLW program element and the large number of applications currently under way, this quarterly report series was begun in FY 1985 to facilitate the transfer of LFCM vitrification technology between and among the central source (PNL) and the various user groups: the Waste Valley Demonstration Project (WVDP), the Hanford Waste Vitrification Program (HWVP), and the Defense Waste Processing Facility (DWPF) Project. Quarterly reports will be established for other program elements as the need arises.

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

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

- Melting Process Chemistry and Glass Development - S. O. Bates
- Feed Preparation and Transfer Systems - M. E. Peterson
- Melter Systems - J. M. Perez, Jr.
- Canister Filling and Handling Systems - D. H. Siemens and G. J. Sevigny

- Off-Gas Systems - R. W. Goles
- Process/Product Modeling and Control - W. L. Kuhn.

Each section contains summary, introduction, and technical progress subsections. This report was compiled by H. C. Burkholder and J. E. Minor and edited by J. A. Powell.

REFERENCES

Burkholder, H. C., and J. H. Jarrett, compilers. 1986. Nuclear Waste Treatment Program, Annual Report for FY 1985. PNL-5787, Pacific Northwest Laboratory, Richland, Washington.

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

McElroy, J. L., and H. C. Burkholder, compilers. 1984. Commercial Waste Treatment Program, Annual Report for FY 1983. PNL-4963, Pacific Northwest Laboratory, Richland, Washington.

MELTING PROCESS CHEMISTRY AND GLASS DEVELOPMENT

S. O. Bates, H. T. Blair, and R. K. Farnsworth

SUMMARY

Laboratory procedures used for conducting Hanford Waste Vittrification Plant (HWVP) feed processing studies were evaluated in a laboratory-scale scoping study. The study evaluated the HWVP reference feed simulation, the methods of concentrating the simulation, and the melter feeds that were made with it. Two HWVP feed simulations were prepared for comparison in the study. One consisted of a blend of dry chemicals and a concentrated iron hydroxide slurry. The other was prepared by dissolving all the desired elements in a nitric acid solution. The solution was then converted to HWVP feed by sugar denitration, neutralization, digestion, settling, decanting and washing. There were significant physical and chemical differences between the two simulations. It remains to be determined which simulation more accurately represents the physical and chemical properties of the aging waste. This can be resolved only by obtaining and characterizing more aging waste samples and samples from pre-treatment studies using actual waste.

After the simulated wastes were concentrated by boiling, measurements were made of the effects of processing variables on rheological properties of the concentrates and on the melter feeds made from them. Some melter-feed properties, such as yield stress and apparent viscosity, do not appear to be a function of the concentrating process that is used. The presence, however, of dilatant properties in a slurry appears to depend on the concentrating process. More data must be collected before these preliminary results are valid. The effects of these feed processing variables on the melting behavior of the melter feed are yet to be determined.

INTRODUCTION

The Hanford Waste Vitrification Plant program is dedicated to vitrification of defense wastes produced and stored at the Hanford Site near Richland, Washington. The objectives of the feed-processing subtask of this program for FY 1986 are to:

- Conduct laboratory-scale tests of adjustment of feed rheological properties in support of studying the effects of feed process and composition variability, optimizing melter feed, and evaluating feed processing analytical requirements.
- Document laboratory-scale testing of effects of process and waste composition variability on the rheological and redox properties of feed.
- Document engineering-scale testing of effects of process and waste composition variability on the rheological and redox properties of feed.

TECHNICAL PROGRESS

MELTER FEED PROCESSING

A laboratory-scale scoping study was performed to validate the laboratory procedures used for feed-processing studies. The study evaluated both the HWVP feed simulation and the processing steps used to prepare a melter feed for study in the laboratory. Simulations of HWVP feed are usually prepared in the laboratory by mixing dry hydroxide, nitrate, fluoride, and sulfate compounds into a concentrated ferric hydroxide slurry. This results in a slurry at a concentration between 130 and 160 g waste oxides per liter (W0/L). The real HWVP feed is expected to contain 19 g W0/L and must be concentrated by boiling before it can be charged to the melter. Melter feeds are prepared in the laboratory by treating the simulated concentrate with formic acid and then by adding dry frit. The resulting slurry has a concentration of about 500 g total oxides per liter (T0/L) and usually requires no further concentration by boiling. The concentration of the feed when the formic acid is to be added in the

HWVP has not been determined. Because the frit will be added as a slurry to the feed concentrate in the HWVP, it will be diluted. Therefore, further concentration by boiling may be required after the frit slurry is added.

The objectives of the scoping study were to determine: 1) what the initial concentration of the simulation should be, 2) how much boiling and concentrating should be done, 3) at what feed concentration the formic acid should be added, 4) whether or not the frit can be added dry, and 5) how much boiling is required after the frit is added to obtain properties that represent the real HWVP melter feed. However, the properties of the real HWVP feed and melter feed are not known. Hence, this test was conducted to compare the properties of a simulation, prepared from the reference flowsheet steps, with the properties of simulated feeds prepared using laboratory shortcuts. The properties of the laboratory simulation were compared also with those of washed synthetic B-Plant feed prepared by Rockwell from a nitric acid solution. The study was conducted according to the outline presented in Table 1.

Simulated HWVP Reference Feed

A 15-L batch of simulated HWVP reference feed, identified as HWS6, was prepared using the reference PNL procedure (Blair and McMakin 1986). Its composition is shown in Table 2. This batch was prepared at a concentration of 157 g WO/L. A portion was diluted to about 17 g WO/L (HWS6-D1) for Phases 2 and 3 of the study. Two liters of the diluted, simulated feed were placed in

TABLE 1. Outline of Scoping Study To Validate Laboratory-Scale Feed Processing Studies Methods

<u>Phase</u>	<u>Starting Material</u>	<u>Boil Down</u>	<u>Formate At</u>	<u>Frit Addition</u>	<u>Additional Processing</u>
1	HWS6	None (control)	141 g WO/L	Dry	Dilute to 500 g TO/L
2	HWS6-D1	17 → 145 g WO/L	145 g WO/L	Slurry	Boil to 500 g TO/L
3	HWS6-D1	17 → 198 g WO/L	198 g WO/L	Slurry	Boil to 500 g TO/L
4	Synthetic B-Plant	34 → 161 g WO/L	161 g WO/L	None	None

TABLE 2. Composition of Simulated HWVP Reference Feed Batch HWS6

Compound Used	g/L	Equivalent Oxide	Desired Oxide Content, wt%	Average Analytical Result, wt% ^(a)
Al(OH) ₃	39.13	Al ₂ O ₃	17.2	17.1
None	--	B ₂ O ₃	0.0	0.4
BaSO ₄	0.94	BaO	0.4	0.4
CaF ₂	0.63	CaO	0.3	0.4
Ce(OH) ₃	1.17	CeO ₂	0.7	0.5
Cr(OH) ₃	10.72	Cr ₂ O ₃	5.3	5.5
CsOH	1.57	Cs ₂ O	1.0	(b)
Cu(OH) ₂	1.10	CuO	0.6	0.6
Fe(OH) ₃	88.44	Fe ₂ O ₃	44.4	40.9
La(OH) ₃	0.70	La ₂ O ₃	2.2	2.2
LaF ₃	3.21			
None	--	Li ₂ O	0.0	0.3
Mg(OH) ₂	0.63	MgO	0.3	0.3
Mn(OH) ₂	1.10	MnO ₂	0.7	0.7
Na ₂ MoO ₄ ·2H ₂ O	2.97	MoO ₃	1.2	1.1
NaF	2.74			
Na ₂ SO ₄	3.44			
NaNO ₃	19.96	Na ₂ O	10.7	10.2
Na ₂ C ₂ O ₄	5.01			
NaOH	5.32			
Nd(OH) ₃	0.70	Nd ₂ O ₃	2.1	2.4
NdF ₃	0.86			
Ni(OH) ₂	4.46	NiO	2.4	2.3
Pr(OH) ₃	0.70	Pr ₆ O ₁₁	0.4	(b)
None	--	RuO ₂	0.6	(b)
SiO ₂	4.46	SiO ₂	3.0	2.9
Sm(OH) ₃	0.31	Sm ₂ O ₃	0.2	(b)
Sr(OH) ₂	0.70	SrO	0.4	0.4
None	--	TiO ₂	0.0	0.03
Zr(OH) ₄	4.62	ZrO ₂	2.4	2.6
Y(OH) ₃	0.39	Y ₂ O ₃	0.2	(b)

(a) Normalized to 157.1 g WO/L.

(b) No analysis.

two vessels (A and B) and boiled down to a volume of about 850 mL each. Then the volume in each vessel was increased to 2 L again by adding more diluted feed. As boiling continued, samples were taken from Vessel A of both the concentrate and the condensate for characterization. At a concentration of 200 g WO/L, solids began to accumulate on the sides of the vessels and on the agitator shafts. At this point, the feed was considered at maximum concentration and the formic acid treatment was required to improve the physical properties of the slurry. The contents of the two vessels were then blended, sampled, and divided to create Batches C and D. Batch C was diluted to 145 g WO/L that is a concentration typical of laboratory-prepared simulations. The results of the characterizations are presented in Table 3, and the rheological properties are presented as a function of concentration in Figures 1, 2, and 3.

The plots show that the density of the slurry is a linear function of the concentration. The rheological properties, however, respond to increasing concentration much differently. Between concentrations of 110 g WO/L and about 180 g WO/L, the yield stress and apparent viscosity increase exponentially with increasing concentration. It is in this concentration range that simulated

TABLE 3. Properties of HWS6-D1 During Concentration Phase

Slurry Property	Batch and Boiling Cycle Number								
	A-1	A-2	A-3	A-4	A-5	B-1	A-5+B-1	C-1	D-1
Total Oxides, g/L	45.9	84.0	90.7	109.2	209.5	217.1	211.1	145.1	197.7
Total Oxides, wt%	4.4	7.8	8.6	10.0	17.8	18.2	18.0	12.8	16.9
Total Solids, wt%	6.1	9.7	10.8	12.4	22.1	22.8	22.5	16.1	21.0
Density, g/mL	1.05	1.06	1.08	1.09	1.18	1.19	1.17	1.13	1.17
pH	11.3	11.2	11.0	11.3	--	--	11.4	11.3	11.1
Apparent Viscosity at 183 s ⁻¹ , cP	2.6	9.8	14.8	12.7	--	--	279.0	40.1	198.0
Yield Stress, dyne/cm ²	1.0	7.7	9.7	10.7	--	--	421.0	38.6	290.0

FIGURE 1. Changes in Density of HWS6-D1 as the Concentration Is Increased

HWVP feed was usually prepared and studies were performed on many process variables. When conducting studies in this range, it must be remembered that small changes in concentration result in nonlinear, large changes in rheological properties of the simulated HWVP reference feed.

The rheograms prepared at each step of the concentration process show the slurries are yield-pseudoplastic fluids at all concentrations. Correctness of those rheograms for the more dilute (less than 50 g WO/L) slurries is questionable because some particles settled out of the samples before the rheograms were completed.

FIGURE 2. Changes in Yield Stress of HWS6-D1 as the Concentration Is Increased

FIGURE 3. Changes of Apparent Viscosity of HWS6-D1 as the Concentration Is Increased

A sample of the particles that settled in the simulated HWVP feed when it was diluted was analyzed by x-ray diffraction analysis. The particles were large enough that they could be separated into four color groups with the aid of a microscope. The black/brown flakes were the inverse spinel Fe_3O_4 . The green crystals were $\text{Al}(\text{OH})_3$ and LaF_3 . The white particles were Gibbsite

[Al(OH)₃], and the lavender/pink particles were NdF₃. The presence of the relatively large spinel particles is of particular interest because they could act as seeds for spinel phase nucleation and growth in the melt. These particles of Fe₃O₄ can be removed from HWVP feed simulation with a magnet. Doing so should be considered when melter runs are being performed to study spinel phase separation unless similar particles are found in samples of real Hanford waste.

The control batch (F-1) was prepared by diluting the master batch of simulated HWVP feed (HWS6) from a concentration of 157 g WO/L to 141 g WO/L so that it would be similar to batch C-1. Each of the three batches, C-1, D-1, and F-1, were then treated with a stoichiometric amount of formic acid (0.092 g HCOOH/g WO). Following the acid treatment, the batches were again characterized. The results are presented in Table 4 so that the control batch can be compared to the boiled down batches and the effects of the forming treatment can be seen.

These data were also plotted along with some data developed in 1985 as part of the formic acid treatment studies as shown in Figures 4 and 5. The differences in the response of rheological properties to the addition of formic

TABLE 4. Properties of Simulated HWVP Feed Concentrates Before and After Treatment with Formic Acid

Slurry Property	Batch Number					
	C-1	C-2	D-1	D-2	F-1	F-2
Formic Acid Addition	Before	After	Before	After	Before	After
Total Oxides, g/L	145	151	198	216	141	152
Total Oxides, wt%	12.8	13.4	16.9	18.2	12.8	13.3
Total Solids, wt%	16.1	17.3	21.0	23.5	16.1	17.4
Density, g/mL	1.13	1.13	1.17	1.19	1.10	1.14
pH	11.3	6.4	11.1	6.9	11.8	6.8
Apparent Viscosity at 183 s ⁻¹ , cP	40.1	33.7	198	176	51.7	36.9
Yield Stress, dyne/cm ²	38.6	42.5	290	239	69.5	46.3

FIGURE 4. Effects of Formic Acid Addition on the Apparent Viscosity of Simulated HWVP Feed Concentrates

FIGURE 5. Effects of Formic Acid Addition on the Yield Stress of Simulated HWVP Feed Concentrates

acid at concentrations of 140 g W0/L and 190 g W0/L emphasize the consequences of the exponential relationship between the rheological properties and the concentration that were discussed previously.

Filled-in points represent data from samples that were not boiled; open points designate data from boiled samples. As observed before, boiling lowers both the apparent viscosity and yield stress of simulated feed that has not been treated with formic acid. Formic acid treatment appears to have less effect on the rheological properties of boiled slurry than on those of unboiled slurry. In either case the end results are similar, which confirms the conclusion reported last quarter that boiling the melter feed had little effect on the yield stress and apparent viscosity at concentrations below 550 g T0/L. The increased yield stress of Batch C after formic acid addition is not considered significant because it is within measurement variance.

Rheograms of each batch were prepared following the formic acid addition. Treating the slurries with formic acid makes little difference in the shape of the plots. The slurries remain yield-pseudoplastic.

After the three batches of simulated HWVP feed made from HWS6 were treated with formic acid, they were allowed to age from 4 to 10 days as shown in Table 5. Aging after treatment with formic acid results in rheological property changes ranging from 0 to 12%. Such changes are not likely to have much effect on the process operations.

Just after the rheological properties were measured for aging effects, frit was added to the simulated waste concentrates. Dry frit and an amount of

TABLE 5. Rheological Properties of HWS6 Concentrate Treated with Formic Acid Before and After Aging

Slurry Properties	Sample Numbers					
	C-2	C-3	D-2	D-3	F-2	F-3
Date Measured	2/13/86	2/24/86	2/13/86	2/24/86	2/20/86	2/24/86
Apparent Viscosity at 183 s ⁻¹ , cP	33.7	35.8	176	190	36.9	36.9
Yield Stress, dyne/cm ²	42.5	48.3	239	264.6	46.3	48.3

formic acid equal to 1 wt% of the frit were added to the control Batch F to produce melter feed Batch F-4, shown in Table 6. Frit slurries were added to Batches C and D to produce Batches C-4 and D-4, also shown in Table 6. One frit slurry contained 60 wt% -80/+200 mesh frit HW39, and the other slurry contained 30 wt% frit. Both frit slurries contained formic acid equal to 1 wt% of the mass of frit in the slurry. One-third of the required frit was added to the waste concentrate as the 30 wt% slurry and two-thirds was added as the 60 wt% slurry. Frit was added until the ratio of waste oxides to glass-forming oxides was 1:3. Table 6 presents the properties of the resulting melter feeds. Because the batches were not at the desired 500 g T0/L, each batch was boiled to increase concentrations. A calculation error resulted in the concentrations beyond the target values. The resulting concentrations and rheological properties of each batch are presented in Table 6 as Batches C-6, D-6, and F-5.

These data are plotted in Figures 6 and 7 together with those presented last quarter. All the data fall within the same ranges except the F-4 and the C-6 yield stress. The results of F-4 are most puzzling because F-4 is the control batch that should have most resembled the earlier data. The C and D batches are those prepared by concentrating HWS6-D1 from 17 g W0/L by boiling. These results suggest that the concentration history of the simulated waste has no significant effect on melter feed rheological properties.

The rheogram for melter feed F-5 is presented in Figure 8. Each batch becomes yield-dilatant/rheopectic at the maximum concentration evaluated. However, because each batch is at a different concentration and because rheological properties vary so with concentration changes at these levels, conclusions are difficult to make. Batches D-6 and F-5 have the most similar concentrations. The control batch, F-5, is more dilatant and has lower apparent viscosity and yield-stress values. Whether or not these differences are significant is not clear from these data. Further evaluations will be performed to clarify the relationship between processing variables and rheological properties.

TABLE 6. Properties of Melter Feeds Made with Simulated HWVP Feed Concentrates as Concentrations Were Increased by Boiling

Slurry Properties	Sample Numbers							
	C-4	C-5	C-6	D-4	D-5	D-6	F-4	F-5
Date Measured	2/25/86	3/12/86	3/14/86	2/25/86	3/17/86	3/18/86	2/25/86	3/18/86
Total Oxides, g/L	318.52	456.53	618.63	379.40	452.79	547.81	456.27	540.61
Total Oxides, wt%	26.32	35.12	42.66	30.84	35.21	40.29	35.37	39.75
Total Solids, wt%	28.59	38.13	49.02	33.45	37.39	43.13	39.63	42.31
Density, g/mL	1.21	1.30	1.45	1.23	1.31	1.36	1.29	1.36
pH	4.6	6.9	6.1	5.0	6.3	6.5	4.8	7.46
Apparent Viscosity, cP								
at 183 s ⁻¹	7.4	27.7	154.6	15.0	22.2	63.3	58.1	42.2
at 323 s ⁻¹	(a)	17.5	100.9	(a)	14.4	44.8	(a)	36.4
at 468 s ⁻¹	(a)	13.6	82.6	(a)	10.5	37.1	(a)	42.1
Yield Stress, dynes/cm ²	6.8	29.0	260.8	14.5	24.6	77.2	64.0	61.8

(a) Not analyzed.

FIGURE 6. Current Results Compared with Previous Apparent Viscosity Data for Melter Feed Concentrations

Synthetic B-Plant Feed

Rockwell provided PNL with about 20 L of synthetic B-Plant feed from a batch that had been prepared by dissolving all the chemicals representing the waste components in nitric acid. The solution was then denitrated with sugar, neutralized with sodium hydroxide, and digested by boiling. At PNL the supernatant was decanted, and the residual slurry was washed with 15 times its volume of deionized water. The wash supernatant was decanted after settling for 48 hr. The residual slurry was believed to be representative of HWVP feed. It had a concentration of 34.2 g WO/L, which is more than the 19 g WO/L projected for the HWVP feed.

FIGURE 7. Current Results Compared with Previous Yield Stress Data for Melter Feed Concentrations

FIGURE 8. Rheogram for Test Batch F-5 Showing Dilatant Properties

A mass balance of the decanting and washing cycles for the synthetic B-Plant feed supplied by Rockwell was completed. This mass balance was used in determining the effect of the decanting and washing cycles on various elements present in the slurry. The mass balance was performed by first using the recorded weights and densities of the various residues and supernatants produced during the decanting and washing cycle to determine the volume of the residues and supernatants from each cycle. These volumes were then applied to the compositional analyses to arrive at the elemental-oxide mass balances. Table 7 shows the mass balance for seven stages of residues and supernatants that occurred during the washing of the synthetic B-Plant feed.

TABLE 7. Mass Balance from Synthetic B-Plant Feed Washing Test

Slurry Weights and Volumes	Slurry B-1	1st Dec. B-3	2nd Dec. B-4	Unwashed Sludge B-2	1st Wash B-6	2nd Wash B-5	Washed Sludge B-7
Grams	19,128 ± 1	13,795.6 ± 0.8	1480.3 ± 0.2	3852.2 ± 0.2	42,342 ± 2	521.9 ± 0.2	3711.0 ± 0.2
Density, g/mL	1.17 ± 0.005	1.16 ± 0.005	1.17 ± 0.005	1.24 ± 0.005	1.01 ± 0.005	1.01 ± 0.005	1.05 ± 0.005
Volume, L	16.35 ± 0.07	11.89 ± 0.05	1.265 ± 0.006	3.11 ± 0.01	41.9 ± 0.2	0.517 ± 0.003	3.53 ± 0.02
<u>Oxide Balance, grams</u>							
Al ₂ O ₃	295 ± 2	200 ± 1	21.1 ± 0.2	64.6 ± 0.4	45.8 ± 0.4	0.580 ± 0.006	14.61 ± 0.09
B ₂ O ₃		0.34 ± 0.06					
BaO	0.51 ± 0.09			0.52 ± 0.02			0.51 ± 0.02
CaO	0.53 ± 0.09	0.16 ± 0.08	0.012 ± 0.006	0.051 ± 0.02			0.49 ± 0.02
CeO ₂							0.33 ± 0.02
CO ₂ O ₃		0.23 ± 0.06					
Cr ₂ O ₃	1.28 ± 0.09	0.109 ± 0.007	0.027 ± 0.007	1.31 ± 0.02			1.24 ± 0.02
CuO	0.57 ± 0.10		0.0099 ± 0.0007	0.49 ± 0.02			0.50 ± 0.02
Fe ₂ O ₃	38.9 ± 0.2	0.23 ± 0.06	0.041 ± 0.007	39.0 ± 0.3	0.21 ± 0.02	0.0081 ± 0.0003	37.7 ± 0.4
La ₂ O ₃				0.14 ± 0.01			0.18 ± 0.02
Li ₂ O	0.25 ± 0.07	0.050 ± 0.006	0.0053 ± 0.0007				0.04 ± 0.02
MgO							0.47 ± 0.02
MnO ₂	0.36 ± 0.09	0.018 ± 0.005	0.0020 ± 0.0005	0.42 ± 0.02			0.41 ± 0.02
MoO ₃	4.8 ± 0.1	3.69 ± 0.08	0.383 ± 0.008	1.06 ± 0.02	0.70 ± 0.02	0.0084 ± 0.0003	0.08 ± 0.02
Na ₂ O	1659 ± 8	1195 ± 6	125.7 ± 0.6	328 ± 1	276 ± 2	3.49 ± 0.02	26.9 ± 0.1
Nd ₂ O ₃							0.08 ± 0.01
NiO	24.0 ± 2		0.0107 ± 0.007	23.9 ± 0.1			22.9 ± 0.1
P ₂ O ₅	1.73 ± 0.09						
Sb ₂ O ₃	2.11 ± 0.09						
SiO ₂							0.21 ± 0.02
SrO	0.68 ± 0.09	0.021 ± 0.005	0.0026 ± 0.0007	0.67 ± 0.02			0.64 ± 0.02
TiO ₂							0.008 ± 0.002
ZrO	2.66 ± 0.09	1.2 ± 0.6	0.110 ± 0.007	2.07 ± 0.02			1.68 ± 0.03

Initial evaluation of the mass balance showed numerous inconsistencies, with losses in total fluid volume and numerous gains and losses in total element-oxides during the two cycles. A determination of the precision behind each fluid volume and element-oxide mass balance was made to evaluate the significance of these inconsistencies. This precision is also shown in Table 7. Precision measurements do indicate some significance in the losses

and gains. These may be attributed to volumetric losses due to numerous container transfers and to unperceived inaccuracies in instrumental precision.

Table 8 shows the percentage of the original amount of oxides left in the combined decant supernatant, combined wash supernatant, and leftover residue samples. Because of imprecision in the mass balances, they are reported in percentage ranges instead of exact percentages. Although some ranges are wide, they do give a good qualitative analysis as to which elements are being washed out of solution. The results shown in Table 8 yield the following conclusions:

- The elements Al, Mo, and Na washed almost completely out of the feed.
- The element Zr only partially washed out of the feed (35%).
- The elements Ba, Ca, Cr, Cu, Fe, Mn, Ni, and Sr remain in the sludge.

Of particular interest is the retention of chromium in the sludge residue because this is opposite the results for the recent aging waste tank sample reported by Rockwell that showed most of the chromium in the supernatant. The reasons for these differences need to be addressed to ensure that the simulation is prepared correctly.

TABLE 8. Percentage Breakdown of Oxides in Decant, Wash and Sludge Residue

<u>Oxide</u>	<u>In Decanted Supernatant, wt%</u>	<u>Washed Out, wt%</u>	<u>Remaining In Washed Sludge, wt%</u>
Al ₂ O ₃	74-76	15-16	5
BaO	0-17	0-8	82-100
CaO	0-13	0-13	76-100
Cr ₂ O ₃	0-11	0-8	89-100
CuO	0-26	0-2	72-100
Fe ₂ O ₃	~1	~1	95-98
MnO ₂	0-9	0-2	87-100
MoO ₃	81-85	14-16	1-2
Na ₂ O	79-80	17	2
NiO	0-1	1-6	94-97
SrO	0-16	0-12	81-100
ZrO ₂	19-26	12-17	60-67

The decanting and washing of the synthetic B-Plant feed resulted in a synthetic HWVP feed at a concentration of 34 g WO/L. The composition of this feed is presented in Table 9 and is compared to the compositions of the HWVP reference feed and the PNL simulation HWS6. Significant differences are present in the amounts of Al, Cr, Fe, Na, Ni, and rare earths. We do not know what effects these differences have on the rheological properties of the feed because the component-variables study has not yet been performed. We do know that the excess Na and Ni would have an impact on the glass product if frit HW39 were used and on the formic acid treatment because they are two of the elements that form formates.

TABLE 9. Composition of Washed Synthetic B-Plant Feed Compared to Simulated HWVP Feed Batch HWS6 and the Reference Composition

Component	Reference Amount, wt%	HWS6 Analyzed Amount, wt%	Synthetic Feed Analyzed Amount, wt%	Comparison of Synthetic Feed to Reference, %
Al ₂ O ₃	17.2	17.1	12.9	75
B ₂ O ₃	0.0	0.4	--	--
BaO	0.4	0.4	0.44	110
CaO	0.3	0.4	0.41	137
CeO ₂	0.7	0.5	0.26	37
Cr ₂ O ₃	5.3	5.5	1.02	19
CuO	0.6	0.6	0.41	68
Fe ₂ O ₃	44.4	40.9	31.3	70
La ₂ O ₃	2.2	2.2	0.15	7
Li ₂ O	0.0	0.03	0.03	--
MgO	0.3	0.3	0.38	127
MnO ₂	0.7	0.7	0.32	46
MoO ₃	1.2	1.1	0.06	5
Na ₂ O	10.7	10.2	22.3	208
Nd ₂ O ₃	2.1	2.4	0.09	4
NiO	2.4	2.3	18.9	788
SiO ₂	3.0	2.9	0.18	6
SrO	0.4	0.4	0.53	132
TiO ₂	0.0	0.03	--	00
ZrO ₂	2.4	2.6	1.37	57

Rheograms were produced by the viscometer from a sample of this washed synthetic B-Plant feed and from a sample of HWS6 that was diluted to 34.2 g WO/L. The washed synthetic B-Plant feed appears to be a Bingham fluid while the dilute HWS6 is pseudoplastic and has no yield stress. Solids settle out of the dilute HWS6 while the washed synthetic B-Plant feed appears to be a colloidal suspension.

Particle size distributions for the washed synthetic B-Plant feed residue and three PNL simulated HWVP feed samples were measured. The three PNL samples evaluated were C-2, D-1 and D-2. Gaussian particle size distributions of the four slurry samples are shown in Figures 9 through 12. They were made using instrumental particle analysis that evaluates particle size distribution from 1.5 to 67.5 μm . There is concern, however, that there may be particles larger than 67.5 μm . To better quantify the amount of particles that may exist above 44 μm , sieving analysis of some of the dried slurry will be performed.

Comparison of Figures 9 through 12 shows little difference in particle size distribution resulting from concentration of and formic acid addition to the feed. Although there is some difference between the HWS6 mockup and the synthetic B-Plant feed, it is smaller than expected.

The washed synthetic B-Plant feed was boiled to increase the concentration from 34 g WO/L to 161 g WO/L. At 161.2 g WO/L, accumulations of crusted material became so thick on vessel walls and the agitator shaft that further concentrating was considered impractical without treatment with formic acid.

The physical properties of the synthetic feed were measured frequently as it was concentrated. The results are presented in Table 10 and plotted in Figures 13, 14, and 15 along with the curves from the corresponding Figures 1, 2, and 3 for comparison. Sample E-7 was taken from the batch in the evening following a day of boiling. Sample E-8 was taken from the same batch the following morning after the batch had cooled overnight under constant agitation. Aging has an obvious but opposite effect on the apparent viscosity and yield stress. To eliminate the aging effect as a variable in this study, samples were taken and analyzed as soon as a day of boiling was completed. Rheological properties measured for archive samples must be interpreted with proper consideration for the aging effect.

FIGURE 9. Particle Size Distribution for HWS6 at 151 g WO/L With Formic Acid Added

FIGURE 10. Particle Size Distribution for HWS6 at 198 g WO/L Without Formic Acid

FIGURE 11. Particle Size Distribution for HWS6 at 216 g T0/L With Formic Acid Added

FIGURE 12. Particle Size Distribution for Washed Synthetic B-Plant Feed at 34 g W0/L Without Formic Acid

TABLE 10. Properties of Synthetic B-Plant Feed as Concentration Was Increased by Boiling

Slurry Properties	Sample Number											
	E-0	E-1	E-2	E-3	E-4	E-5	E-6	E-7	E-8	E-9	E-10	E-11
Date measured	1/23/86	2/21/86	2/21/86	2/24/86	2/26/86	2/26/86	2/26/86	2/26/86	2/27/86	2/27/86	3/3/86	3/3/86
Total oxides, g/L	33.9-34.2	53.1	81.5	53.6	65.8	69.3	74.0	89.2	91.0	104.7	134.4	161.2
Total oxides, wt%	3.29	5.00	7.55	5.11	6.15	6.41	6.85	8.18	8.35	9.43	11.79	13.89
Total solids, wt%	4.70	6.85	10.36	7.04	8.63	8.99	9.65	11.53	11.7	13.01	16.42	19.37
Density, g/mL	1.05	1.06	1.08	1.05	1.07	1.08	1.08	1.09	1.09	1.11	1.14	1.16
pH	12.6	12.7	12.7	12.6	12.7	12.6	12.6	12.7	12.8	12.8	12.8	12.8
Apparent viscosity, cP												
at 183 s ⁻¹	3.5	4.4	26.9	5.7	8.2	8.0	13.0	43.7	26.9	60.7	115.6	264.8
at 323 s ⁻¹	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)	82.5	191.4
at 468 s ⁻¹	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)	71.8	157.9
Yield stress, dynes/cm ²	2.4	2.1	8.2	3.9	2.2	1.9	2.9	4.8	30.9	7.7	118.8	473.3

(a) Not analyzed.

FIGURE 13. Changes in Density of Synthetic B-Plant Feed as the Concentration Is Increased

FIGURE 14. Changes in Yield Stress of Synthetic B-Plant Feed as the Concentration Is Increased

FIGURE 15. Changes in Apparent Viscosity of Synthetic B-Plant Feed as the Concentration Is Increased

The slope of the density versus concentration plot is greater for the synthetic B-Plant feed than for the HWS6 simulation. This may be due to the excessive nickel content. No calculations were performed to confirm this speculation.

Both the plot of the yield stress and the apparent viscosity versus concentration begin to turn upward at lower concentrations than the HWS6 simulation did. Thus greater yield stresses and apparent viscosities were measured with the synthetic B-Plant concentrate for a given concentration than with the HWS6.

Even greater differences in the rheological properties of the B-Plant feed and the HWS6 simulation can be seen by comparing the rheograms for each. The rheograms for Batches E-0 to E-5 show a Bingham-type fluid rather than a yield-pseudoplastic fluid. Then in the rheogram for E-6, yield-pseudoplastic behavior starts to appear with the yield stress increasing with time. Finally, in the rheograms for E-10 (Figure 16) and E-11 yield-dilatant/rheopectic behavior appears that results in continuously increasing apparent viscosity and high yield stresses. Particles are not likely to settle in this slurry, but agitators will have difficulty running in it, and it may not flow in small-diameter pipes.

The differences between the rheological properties of synthetic B-Plant feed and HWS6 are probably not due to their different ratios of elements. They are more likely due to the ionic concentrations and particle morphologic differences between the two simulations. Which rheological behavior most accurately represents the real HWVP feed properties is not presently known. However, the synthetic B-Plant feed was prepared using a more representative method and is therefore assumed to be a more authentic representation.

After the synthetic B-Plant feed was concentrated as much as considered practical, it was treated with the usual amount of formic acid. This was not the stoichiometric amount because of the excess sodium and nickel in the feed, but it was the reference amount. Interpretation of the results is complicated by several factors. Comparing rheological properties (Table 11) of the batch before forming (E-11) with those of the batch following addition of the

FIGURE 16. Rheogram for Test Batch E-10 Showing Yield-Dilatant/
Rheoplectic Properties

formic acid (E-12) shows that the apparent viscosity at a shear rate of 183 s^{-1} increased by 200 cP and the yield stress decreased by only 29 dynes/cm. There is, however, an aging factor that must be considered, which cannot be quantified at this time. The properties of E-11 were measured 1/2 hr after boiling had ceased, while the properties of E-12 were measured 16 hr after boiling had ceased. Both samples were continuously agitated and were at the same temperature. Also note that the concentration increased by 20 g W/O/L during the forming process, and recall how much the rheological properties change with changes in concentration at these levels. Sample E-13 was taken and measured after the batch had been boiled with full reflux and then cooled for 1/2 hr to reproduce the same conditions that produced the E-11 data. The rheograms for

TABLE 11. Properties of Synthetic B-Plant Feed Concentrate
During Treatment With Formic Acid

Slurry Properties	Sample Number			
	E-12	E-13	E-14	E-15
Amount HCOOH Added, g	5.86	0.0	6.36	0.0
Sample Treatment	Cooled 16 hr	Reheated and Cooled 1/2 hr	Dried	Reslurried
Date Measured	3/6/86	3/7/86	3/10/86	3/10/86
Total Oxides, g/L	182.0	(a)	(a)	(a)
Total Oxides, wt%	15.42	(a)	20.88	14.58
Total Solids, wt%	22.54	(a)	31.59	22.11
Density, g/mL	1.18	(a)	(a)	(a)
pH	11.4	11.31	(a)	6.85
Apparent viscosity, cP				
at 183 s ⁻¹	464.5	(a)	(a)	83.1
at 323 s ⁻¹	281.1	(a)	(a)	53.4
at 468 s ⁻¹	183.7	(a)	(a)	41.2
Yield stress, dynes/cm ²	444.4	405.7	(a)	101.4

(a) Not analyzed.

E-12 and E-13 show more clearly the effects of adding formic acid on the rheology. The dilatant/rheopectic behavior of E-11 is gone from sample E-12, but E-13 is still dilatant.

Formic acid was added to the batch using the reference procedure until the pH became the same as that of control batch F-2. This was done to see what effects forming all the materials that react with the acid would have on the rheology. After all the acid was added, the batch was boiled for 2 hr as usual to complete the reactions. It turned to a dry solid before the 2-hr boil was

completed. The dry cake was reslurried with water, and sample E-15 was characterized. E-15 has a rheology similar to that of the PNL simulation that has been concentrated and formatted. This is most likely due to the conversion of iron hydroxide to iron oxide when the material went dry. Evidence of this conversion was seen in the appearance of small black flakes in the dry material that resemble the Fe_3O_4 in the iron hydroxide used to prepare the PNL simulations. This conversion cannot be reversed by adding water; therefore, no further work with this batch is planned.

CONCLUSIONS

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

- Simulated HWVP reference feed can be concentrated by boiling it to between 160 and 200 g WO/L before formic acid must be added to prevent caking.
- Yield stress and apparent viscosity of simulated HWVP reference feeds increase exponentially with increasing concentration. The rate of increase varies with the way the simulation is prepared.
- Boiling a PNL simulation to a concentration of 150 g WO/L from 17 g WO/L produces rheological properties after addition of formic acid that are much like those of a simulation prepared by blending chemicals at a concentration of 150 g WO/L and treating it with formic acid.
- The yield stress and apparent viscosity of melter feeds prepared with the PNL simulation all fall in the same envelope no matter what concentration process is used. However, whether the fluid is Bingham, yield-pseudoplastic, or yield-dilatant/rheopectic does seem to be a function of the concentration history. The details of this relationship were not discovered in this study.
- Most of the Al, Mo, and Na are washed out of synthetic B-Plant feed while the Ba, Ca, Cr, Cu, Fe, Mn, Ni, and Sr remain in the sludge.

- Although the PNL simulation and synthetic B-Plant feed have similar particle-size distributions, they differ rheologically. Which rheological behavior most accurately represents the real HWVP feed properties is not known at this time. However, the synthetic B-Plant feed has a preparation more like that of the real waste and is therefore assumed to be a more authentic simulation.

REFERENCES

Blair, H. T., and A. H. McMakin. 1986. Modifying the Rheological Properties of Melter Feed for the Hanford Waste Vittrification Plant. PNL-SA-13365, Pacific Northwest Laboratory, Richland, Washington.

FEED PREPARATION AND TRANSFER SYSTEMS

M. E. Peterson

SUMMARY

The Pacific Northwest Laboratory (PNL) topical report Evaluation and Testing of Metering Pumps for High-Level Nuclear Waste Slurries has been cleared by DOE for publication. It documents the selection of an air-displacement slurry pump and an air-lift pump as candidate pumps for metering slurry to the ceramic melter. Both pumps were subjected to extensive long-term tests. The air-displacement slurry pump operated well in both acidic and alkaline slurries and is the recommended pump.

The PNL topical report Design of a Mixing System for Simulated High-Level Nuclear Waste Melter Feed Slurries has been published and distributed. It documents the results of bench-scale experiments used to assess the effects of several independent variables on homogeneity in the mixing tank. These results were scaled up and used in designing the large-scale mixing tank.

Fabrication and installation of a large-scale mixing tank were completed. This tank will be used as the melter feed makeup tank for the pilot-scale ceramic melter system.

The functional testing of a remote air-displacement slurry pump with a newly designed air-supply system was successfully completed. The test's primary objectives were to verify the alignment and mechanical integrity of the pneumatically actuated valve, to mock up the installation of the pump and thus verify that the dimensions and clearances are sufficient for it to fit into the remote tank, and to determine the effect of cycle time and air pressure on the flow rate using the new air-supply system.

INTRODUCTION

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

Activities and results of the work being performed at PNL to support the development, design, selection, and operation of the feed preparation and transfer systems are discussed. During FY 1986, specific activities concerning feed preparation and transfer systems have included:

- evaluation of the resuspension of simulated melter feed slurries in pipes
- bench-scale testing to determine the design of heat-transfer equipment (jacket or coils) for the slurry feed makeup tanks
- selection of the sampler, level detector, and transfer pump for the large-scale mixing tank
- radioactive demonstration of melter feed transfer equipment in support of radioactive demonstration of the liquid-fed ceramic melter
- installation and functional testing of a full-scale melter feed-slurry mixing tank complete with agitator.

TECHNICAL PROGRESS

TESTING AND EVALUATION OF METERING PUMPS

The transfer of information among the various HLW treatment programs, including the nonradioactive and radioactive testing, requires that the work conducted and results obtained by each program be well-documented. The PNL

topical report Evaluation and Testing of Metering Pumps for High-Level Nuclear Waste Slurries (PNL-5851) has been prepared for clearance and is summarized below.

The metering pump system that delivers HLLW slurry to a melter is an integral subsystem of the vitrification process. The pump used to feed slurry to the melter must satisfy many unique requirements because of the slurry's chemical, physical and radiological properties. Moreover, the requirement for fully remote operation and maintenance places special constraints on its design.

The process of selecting a pump for this application began with a technical review of pumps typically used for slurry applications. The design and operating characteristics of numerous pumps were evaluated against established criteria. Two pumps, an air-displacement slurry (ADS) pump and an air-lift pump, were selected for further development at PNL. Development was conducted under the Nuclear Waste Treatment Program, with later development of the ADS pump performed under the Hanford Waste Vitrification Program.

In the development activity, from FY 1983 to FY 1985 the two pumps were evaluated in long-term performance tests using simulated melter feed slurries. Throughout this period, the designs of both pumps were modified to better adapt them for this application. Final reference designs were developed for both the ADS pump and the air-lift pump. Successful operation of the final reference designs has demonstrated the feasibility of both. A fully remote design of the ADS pump has been developed and is currently undergoing testing at the West Valley Demonstration Project (Peterson et al. 1985).

The simulated slurries used in the pump tests have been tailored to produce an acceptable glass product based on site-specific HLLW chemical and physical properties. Slurries prepared to simulate the waste-glass compositions for two different sites were used. One slurry type evolved from glass development for a defense waste stored at Hanford in Washington State. The second slurry evolved from glass development for a commercial waste currently stored at the West Valley Demonstration Project Site in New York State. As development of acceptable glass compositions has continued for each, the slurry compositions have also evolved. At the time of each pump test, the

then-current composition was used. While these compositions are no longer considered the reference for these sites, their rheological properties are sufficiently representative of typical HLLW slurries and cover the normal range of both alkaline and acidic mixtures. The slurries tested demonstrated well the pump's ability to perform in this application.

Results of ADS Pump Tests

Five designs of the ADS pump were tested and evaluated. The initial four designs proved the operating concept of the ADS pump. Weaknesses in the ADS pump system were identified and were eliminated in later designs. The final, reference design was subjected to 3700 hr of continuous testing. Flow rates ranging from 10 to 185 L/hr were achieved; however, flow rates below 20 L/hr were unstable. The effects of air pressure and cycle time on the pump flow rate were determined. Degradations of the set-point flow rate were monitored and consequently signaled the need to water-flush the lines of any solid deposits. The slurry flow rate from the pump was found to be affected only slightly by the tank head. Because the chamber was gravity-filled, the pump chamber would not fill with a consistent volume of slurry at low tank heads. The flow rate from the pump was found to degrade at heads less than 1.0 psi. Increasing the fill-time compensated for the low tank head, allowing a stable feed rate to be maintained.

After 3700 hr of operation, the pump was disassembled. The major components were weighed and measured to determine the corrosion/erosion effects of the slurry on the pump. Wear of the valve, seats, and drive mechanism had occurred; however, wear was not significant and pump operation was not affected. A service life beyond 6 months can be expected for the main pump body, based on the rate of wear observed.

Results of Air-Lift Pump Tests

The initial design for the air-lift pump was based on existing published design data, mostly for water and salt solutions. Before 1983, work at PNL with air-lift pumps to transfer a slurry having 40 wt% solids had established the pump system's practicality. The initial air-lift designs were two-stage pilot-scale pumps designed to lift slurry at rates of 20 to 75 L/hr. These

early designs incorporated advances by West German researchers who were also developing the air-lift pump for transferring slurry to a ceramic melter. Early testing resulted in many design changes, particularly in air injection, headpot configuration, and second-stage liquid supply line. This test phase also established the importance of adequate flushing capabilities to prevent deposits in the air-injection points and to allow flushing of lift lines and headpots.

A full-scale air-lift pump was designed and tested as a final demonstration of its capabilities. The system demonstrated design rates of 35 to 175 L/hr and pumped an estimated 124,726 L of slurry during the 1067-hr test period. One period of 782 hr of continuous operation was achieved. As testing progressed, preventive maintenance steps were instituted to improve pump performance. Air-injection footpieces, headpots and first-stage demister pad were water-flushed daily with a small amount of water. Furthermore, the second-stage lift rate was increased to 175 L/hr for 5 min each day to re-entrain any solids that may have settled in the second-stage liquid supply line.

No plugging or other operational problems occurred with the first-stage system. After daily flush procedures were started, only one failure of the second-stage lift occurred. The plug occurred in the second-stage liquid supply line due to settled solids but was easily removed by backflushing the line with water.

Testing the air-lift pump showed that its simplicity makes it attractive for use in radioactive environments. Slurries containing up to 40 wt% solids were tested and successfully pumped continuously for over a month. It was apparent, however, that adequate flushing capabilities were necessary, thus somewhat complicating the air-lift pump design for remote use.

Comparison of the ADS and Air-Lift Pumps

The ADS pump was operated successfully using both alkaline and acidic slurries and showed that a service life beyond 6 months can be expected. Operation of the air-lift pump, however, was affected both by the type of slurry tested and by solids in the slurry. Alkaline slurries caused deposits

to cake in the air-liquid interface zones. Acidic slurries had poor air-disengaging characteristics in the headpots that led to flooding of the pots with a stable foam. Best results were achieved with a neutral slurry. However, a daily flush procedure was required to remove solid buildups at the air-injection points.

The extensive test program has established that both the air-displacement slurry pump and the air-lift pump can pump solids-containing slurries at low flow rates. However, application of the air-lift pump is constrained by the slurry type being considered. Furthermore, its simple design is complicated by the need for valves and services for periodic flushing and to ensure that pump-line plugs can be removed. The air-displacement pump operation is not sensitive to slurry type and has minimal flushing requirements. Therefore, the air-displacement slurry pump is preferred over the air-lift pump for this application.

DESIGN OF A MIXING SYSTEM

The PNL topical report Design of a Mixing System for Simulated High-Level Nuclear Waste Melter Feed Slurries (PNL-5745) has been published. This report documents the results of bench-scale experiments used to assess the effects of a number of independent variables on the degree of homogeneity in the mixing tank. These results were scaled up and used in the design of the large-scale mixing tank.

Equipment Installation

During FY 1985 bench-scale mixing experiments were conducted. One goal of these was to select a reference prototype mixing system for large-scale verification tests. After selection of the reference, the fabrication drawings were prepared for a large-scale mixing tank that incorporates the geometric features necessary to properly mix simulated melter feed slurries. Fabrication and installation of this tank have been completed. The tank is 9 ft in diameter and 11 ft in height. The total height of the mixing tank was set at 11 ft to allow for 2 ft of freeboard above the maximum liquid level. The tank has a

flat bottom and is equipped with four equally spaced wall baffles. This tank will be used as the melter feed makeup tank for the pilot-scale ceramic melter experiments.

REMOTE ADS PUMP DEMONSTRATION

Functional testing of a remote ADS pump with a newly designed air-supply system was successfully completed. The primary objectives of the test were to verify the alignment and mechanical integrity of the pneumatically actuated valve, mock up the installation of the pump to verify that the dimensions and clearances are sufficient for it to fit into the remote tank, and determine the effect of cycle time and air pressure on the flow rate using the newly designed air-supply system. The results of the functional testing are summarized below.

Pneumatically Actuated Valve

Verification of the alignment and operation of the pneumatically actuated valve was required. On first examination of the valve, alignment and seating were not adequate. The drive rod was binding at the flange interface. When the pump was dismantled, galling was observed on the sections of the drive rod that extended through the flange, guide rings, and rocker arm. A slight amount of warpage was also detected in the rod. The drive rod was trued and the shaft diameter, at the points where galling occurred, was decreased slightly with the use of fine sandpaper. The pump was reassembled and no further difficulties were detected. The pump chamber was pressurized to 15 psig, and after 1 min no signs of pressure decrease occurred.

Dimensional Verification

A check was completed on the ADS pump to ensure that it would accurately fit on the Tank-131 flange. This pump, seen as a backup for the ADS pump currently in B-Cell, will be stored until it is needed there. A dimensional check was performed, and all measurements were within dimensional tolerances. The pump was installed in its prefabricated jig, and no modifications were necessary.

Pump Calibration

Calibration of the ADS pump using the newly designed air-supply system was the prime objective of this test. B-Cell conditions were simulated as close as realistically possible (i.e., heights and piping diameter sizes were duplicated, but actual piping lengths were not). It was judged that the areas not duplicated were not critical parameters and that their overall effect on results would be negligible. The pump was calibrated at two air pressures (8.6 psig and 7.8 psig). Flow rates between 0 and 128 L/hr were achieved (Figure 1). Before the pump was calibrated, the fitting located on the feed line immediately above the pump chamber was welded shut. This was done to preclude any leakage through the fitting in case the nitric content in the feed damaged the fitting packing.

Optimally, the operating pressure to use is the smallest at which flow can be maintained. Under this condition, the flow rate is better controlled and the time with no flow in the line is minimized. During this experiment it was

FIGURE 1. ADS Pump Calibration

determined that 7.8 psig represented the optimum pressure. Greater control of the flow rate at the lower flow rates was possible. A maximum of 15 sec with no flow in the line was observed, and only at flow rates below 5 L/hr. Above this rate, flow would degrade to a steady dribble, but did not completely stop.

The final portion of this test was to operate the pump over a minimum 3-day period. The ADS pump was operated for more than 5 days with only one period of 10 min when the pump was shut off to allow reaming of the headpot drain line. (The feed line terminated in a headpot representing the height of the RLFCM. From there it was allowed to gravity-drain back to the feed tank.) The pump never quit operating.

CONCLUSIONS

- The ADS pump is preferred over the air-lift pump for metering the mixture of HLW and glass-formers to the ceramic melter because of its superior operation in both acidic and alkaline slurries and its minimal flushing requirements.
- The remote ADS pump was found to operate optimally at an air pressure of 7.8 psig.
- The large-scale mixing tank that has been fabricated and installed incorporates the geometric features necessary to properly mix simulated melter feed slurries and will be used for the pilot-scale ceramic melter experiments.

REFERENCES

Peterson, M. E., et al. 1985. "Adaptation of an Air Displacement Slurry Pump for Remote Service." In the Transactions of the American Nuclear Society Winter Meeting, pp. 584-585, American Nuclear Society, LaGrange, Illinois.

Peterson, M. E., D. McCarthy and K. D. Muhlstein. 1986. Design of a Mixing System for Simulated High-Level Nuclear Waste Melter Feed Slurries. PNL-5745, Pacific Northwest Laboratory, Richland, Washington.

MELTER SYSTEMS

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

SUMMARY

RLFCM-7, the first of three campaigns to fill a total of 30 canisters with vitrified high-level radioactive waste for the Federal Republic of Germany's storage experiments at the Asse Salt Mine facility, was started. Although operation of the melter system was reasonable, accumulations of solids in the off-gas system caused problems that forced the temporary suspension of the campaign.

INTRODUCTION

The primary objective of the melter operation is to control the heat input to the melter tank such that the viscosity of the glass is maintained at about 100 poise; this is normally defined for each glass composition by a glass temperature range. The plan for this campaign specified an average bulk-glass temperature at $1150^{\circ}\text{C} \pm 25^{\circ}\text{C}$. At lower glass viscosities (higher temperatures) the corrosivity of the glass for the melter tank refractory lining, the discharge throat, and for glass tank-sensing devices increases. The release of volatile components from the glass into the off-gas system also increases somewhat. At higher glass viscosities (lower temperatures) the slurry vitrification rate decreases, discharging the glass from the melter becomes more difficult, and problems of roping, stringing and devitrification in the receiving canister increase.

The heat input to the melter is controlled by regulating the electrical voltage that is applied by a silicon-controlled rectifier (SCR) controller to the two melting electrodes. The heat input to the melter is the product of the electrode volts and amps and is expressed in kilowatts. When this particular

SCR controller is operated in its manual mode, the electrode current is maintained constant and the electrode voltage is adjusted as the melter-tank resistance fluctuates. When the SCR is operated in its automatic mode, the present controller configuration maintains the melter-tank resistance value constant with electrode voltage adjustments and resultant electrode current changes. The melter tank's electrical resistance is generally an inverse function of the average glass temperature, and is used here to maintain the average glass temperature within the specified temperature range. Feed-composition changes and glass-level changes in the melter tank shift the relationship slightly between the melter tank's electrical resistance and the average glass temperature.

The secondary objective of the melter operation is to maintain an optimum cold-cap coverage in the melter tank. A maximum coverage of the molten glass surface of 85% has somewhat arbitrarily been established as optimum. Higher coverages tend to inhibit release of vitrification gases from underneath the feed pile, resulting in sporadic high off-gas evolutions, and complete coverage generally leads to cold-cap bridging and its consequences. High cold-cap coverages generally are caused by excessive slurry feed rates or by low glass temperatures. Low coverages are very stable, but also are very inefficient and tend to increase the release of volatile components from the glass to the off-gas system. Low cold-cap coverages are generally caused by very low feed rates.

Without visual access to the glass surface inside the RLFCM melter tank, the operating condition of the melter (glass temperatures, cold-cap coverage, foaming tendencies, feed rate stability, etc.) must be deduced from the indications of sensing devices positioned within the melting cavity, and on the services supplied to the melter.

Various sensors are used to indicate the melter operating parameters continuously. These include thermocouple arrays to indicate temperatures of glass and plenum, discharge throat, and melter tank refractory, a pneumatic dip-tube assembly to indicate the quantity of glass and the specific gravity in the melter tank and the pressure in the melter plenum. Electrical transducers

indicate electrode voltage, current and power values, the melter tank electrical resistance values, and the discharge section heater voltage and current values.

TECHNICAL PROGRESS

RADIOACTIVE TESTING

RLFCM-5 and -6, completed last quarter, were the last of a series of shakedown experiments using radioactive feed slurries that were intended to reveal the operational characteristics of the RLFCM and its ancillary systems and to identify any hardware improvements that could enhance operation.

RLFCM-7, -8 and -9 are extended experiments, or campaigns, intended to fill 30 canisters with vitrified high activity-level radioactive waste for the Federal Republic of Germany's (FRG) high activity level storage experiments at the German Asse Salt Mines facility. Each of these campaigns will fill ten FRG canisters, with the glass formulation for each campaign differing in radiation activity and decay heat content.

RLFCM-6 was terminated by reducing the inventory in the melter tank to a minimum (7.25 in. or about 96 liters) in preparation for the first part of RLFCM-7, which was a spiking operation designed to bring the glass composition in the melter up to the feed composition specifications for the first FRG campaign. Spiking was started on 1-20-86 and continued until 1-25-86, when the slurry feed to the melter was shut down because of accumulations of solids in the off-gas system. The solids buildup in the off-gas lines increased the off-gas flow restrictions, reducing the ability of the melter vacuum control system to maintain a negative pressure in the melter. Periodic positive pressurization spikes caused undesirable glass discharges from the melter.

RLFCM-7 was restarted on 1-31-86 and continued until 2-5-86, when the slurry feed to the melter was shut down because of loss of the discharge section heaters, damaged by a pressure spike-induced glass discharge on 2-2-86. This uncontrolled glass discharge was caused by a foaming incident that upset the normal cold-cap stability and resulted in an unusually high discharge rate of glass from the melter. This high discharge rate and the low viscosity of

the melter glass caused the glass stream leaving the discharge trough tip to arch over the edge of the raised discharge tube in the floor of the discharge section and fill the bottom of the discharge section with about 2 in. of molten glass. This covered the bottom ends of the Zones 2 and 3 heaters with about an inch of molten glass and anchored them firmly as the glass cooled slightly. When the sample port was opened to sample the next controlled glass transfer, the heaters were unable to adjust to their subsequent dimensional changes as they cooled slightly, and they broke.

Discussion

Without visual access to the glass surface inside the remotely operated RLFCM melter tank, the operating condition of the melter (glass temperatures, cold-cap coverage, foaming tendencies, feed rate stability, etc.) must be deduced from the indications of sensing devices positioned within the melting cavity, and on the services supplied to the melter.

Various sensors are used to indicate the melter operating parameters continuously. These include thermocouple arrays to indicate temperatures of the melter glass and plenum spaces, the discharge throat, and the melter tank refractories, and a pneumatic dip-tube assembly to indicate the quantity of glass in the melter and its specific gravity and the pressure in the melter plenum. Electrical transducers indicate electrode voltage, current and power values, the melter tank electrical resistance values, and the discharge section heater voltage and current values.

During the experiments RLFCM-5 and -6, and before the RLFCM-7 campaign was started, it became obvious that the specific gravity and weight factor dip tubes were becoming shorter. This proved true when the dip tube assembly was replaced with a spare unit after the RLFCM-7 spiking operation. Both dip tubes had been eroded away by the purge air bubbles rising along the side of the dip tubes. As a result, no accurate melter tank weight factor or specific gravity data were available during the spiking operation.

Also during RLFCM-5 and -6, it became apparent that the lower portion of the melter tank thermowell had been dissolved away. Thus measurements by thermocouples below the normal glass level (at the 3, 6, 9, 12, and 15-in. levels)

were unreliable. The 34-in.-level plenum thermocouple had failed some time previously for an undetermined reason, leaving only the 18-in. level thermocouple indicating reasonable melter tank temperature values. With the normal melter vacuum of 5-in. water column, the 18-in. level thermocouple is located in, or slightly above, the glass surface during idling or the cold cap during slurry feeding. In addition, during earlier shakedown experiments, it was observed that the thermocouple monitoring the cold-face temperature of the melter tank refractory liner at the 6-in. level was consistently about 100°C colder than the glass temperature indication at the 6-in. level.

Because of the very low glass level (7.25 in.) at the beginning of the RLFCM-7 spiking operation, it would have been awkward to use the melter electrode power control resistive feedback control system. Accordingly, during the spiking operation the power control system was shifted to manual control (constant current for the RLFCM's SCR voltage regulator). Thus the glass temperature was estimated from the 6-in. level refractory cold-face temperature indications and from the lower discharge-riser temperature indications. Operation of the melter on manual control was uneventful, although a constant-power configured SCR voltage regulator would have been more appropriate.

After the spiking was completed, the melter was operated mostly on automatic control, using the electrical resistance of the melter tank as feedback to the controller. This system generally performed quite well. However, without any direct indication of glass temperatures, and knowing the resistive feedback system's tendency to increase glass temperature briefly following a glass discharge from the melter, an operator made several unwarranted shifts to manual control. These shifts caused more process instability during transfer of the glass to the canister than would have occurred if automatic control had been used throughout the glass transfer.

CONCLUSIONS

Batch glass transfers from the melter generally result in rapidly increased melter resistance values because of the rapidly decreased cross-sectional area of the electrical current path through the glass. The constant-resistance power

control system interprets these, and any other resistance value increases, as a glass temperature decrease. Hence, following a glass transfer from the melter, the resistive feedback electrode power control system increases the power to the melter proportionally to the magnitude of the resistance increase, resulting in a glass temperature increase. Because of the speed of the typical glass transfer, the resistance change is essentially a step function; this, combined with the 3 to 4 hr time constant of the temperature control system, generally results in a power surge lasting 2 to 3 hr, with possibly some overshoot of the resistance set point. However, the temperatures rarely exceed their upper limit value unless they were already near their upper limit at the start of glass transfer. Generally, if left alone, the resistive feedback power control system can handle glass transfers without excessive glass temperature excursions. This emphasizes the importance of minimizing interference in the operation of the power control system.

The cold cap's stability is generally controlled by that of the slurry feed rate. However, if the power control system is left in its automatic resistive feedback mode and set point adjustments are minimized, it appears that certain attributes of the cold cap can be interpreted from the 18-in.-level glass temperature indications.

CANISTER FILLING AND HANDLING SYSTEMS

D. H. Siemens and G. J. Seigny

SUMMARY

The Hanford Waste Vitrification Plant (HWVP) has completed a conceptual turntable design for handling canisters that is similar to the West Valley Demonstration Project (WVDP) turntable design. Other designs and modifications were considered. This design describes the systems chosen based on current technology.

The turntable is a cylindrical enclosure, 10 ft in diameter, located below the HWVP melter. Inside the enclosure is a carousel that holds four canisters and is used to rotate them into position for filling. The turntable accommodates canisters 10 ft tall and 2 ft in diameter. The design provides for moving the canisters under the melter discharge, controlling spread of contamination to the process cell, controlling inleakage to the melter, weighing canisters, and detecting their glass level using a gamma-level detection system.

INTRODUCTION

The objectives of this work are to develop and demonstrate systems for positioning canisters under the ceramic melter overflow; sealing the canisters to the melter overflow; monitoring the glass level in the canister during filling; sealing and leak-testing the filled canisters. A turntable, used to position the canister under the melter, is enclosed in a tank 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 glass level in the canister during filling. Two canister-handling systems have been fabricated and tested. Both systems are currently installed in their respective locations, where extensive operational testing will be conducted.

TECHNICAL PROGRESS

The following sections discuss the conceptual design for the HWVP turntable (shown in Figure 1).

SHELL AND FRAME ENCLOSURE

The fixed turntable shell surrounds the rotating carousel and, in conjunction with the supporting frame, provides the structural support and containment for the carousel system. The turntable shell is connected to the melter discharge chamber to receive glass from the melter and to vent the turntable. Venting the turntable shell through the melter overflow chamber makes it unnecessary to couple each canister directly to the melter. The vent will also draw the turntable inleakage up through the glass-receiving port and thus minimize the possibility of contaminated vapors depositing in the turntable. The sealed shell will minimize the spread of contamination from the melter/turntable system to the process cell.

The turntable shell has a cooling jacket to remove the heat from the canister filled with molten glass. The molten glass contains considerable thermal heat plus radioactive decay heat.

The flanged lid of the turntable is remotely removable to allow canisters to be retrieved if the carousel system cannot be moved by the turntable drive system. Incorporating the flanged lid instead of a welded lid will allow increased air inleakage, but the small increase in air flow will not adversely affect the overall turntable operation or melter pouring operation.

CAROUSEL

The carousel is a structure containing four metal cylinders, called thimbles, for carrying canisters around the turntable and positioning them beneath the melter glass discharge port. The thimble support beams have wheels on one side that ride on a rail attached to the turntable shell. On the other side the support beams are hinged to a central support column. Inside each thimble is a removable liner into which the canisters are directly placed. The liners allow for cleanup of accidentally spilled glass. The center column

FIGURE 1. Hanford Waste Vitrification Plant Turntable

rests on a bearing in the bottom of the turntable and is supported by a bearing at the top of the turntable. The carousel is rotated by an electric motor and gear reduction unit connected to the carousel's center column.

The drive unit is mounted atop the turntable shell and away from the center. The melter/turntable coupling does not leave enough room to locate the drive directly over the center column. Therefore, the drive system is located away from the center of the turntable and connected to the center column by an extension unit. The extension unit is a set of gears and a chain for power transmission.

The carousel has cams of different heights located by each thimble so that thimbles positioned under the glass discharge can be identified. The cams are used in combination with a linear variable differential transducer (LVDT) that detects them and signals the control system.

VENTING

A connecting vent line 2 in. in diameter maintains the turntable at essentially the same vacuum as the melter. The vent line is connected at the top of the activated melter overflow chamber and to the top of the melter plenum. The line provides for equalizing the pressure between the melt cavity and the turntable so that the glass level in the melter is not affected by changes in melter pressure. If a melter pressure surge occurs, the vent line prevents glass from being poured inadvertently into the turntable. The vent allows air inleakage from the overflow chamber lid and the turntable to pass to the melt cavity and into the melter off-gas system. The direction of air flow up through the glass discharge port helps prevent contaminated particles from reaching the turntable and the glass canisters. As too much air inleakage through the turntable may affect the glass pour stream, air inleakage is minimized in the turntable construction and melter coupling design. Air inleakage through the overflow chamber lid or the heater seals will not affect the pour stream as long as the overflow chamber is kept hot.

The vent line pipe was sized at 2 in. in diameter to maintain the gas velocity in the jumper and thus prevent particle collection at the design air inleakage rate of 15 scfm. A larger line would not only require more room,

but would also need a higher air-flow rate to prevent particle deposits. The larger air flow would make it difficult to maintain the overflow temperature at 1100°C.

CANISTER INSTALLATION AND REMOVAL

Canisters are removed from and inserted into the turntable via the canister access port (Figure 2), which prevents excessive air inleakage during canister changeout that would impede melter and off-gas equipment operations. During normal melter operation the cover is not used frequently because a canister is removed and a new one inserted only once every 36 hr.

The canister access port is a combination of two seals used to seal the turntable during different periods. The first seal is a water trough around

FIGURE 2. Turntable Access Port and Seal Assembly

the access port and the outer cover. This cover, which resembles an inverted bucket, slides into the trough of water to ensure an airtight seal. The outer cover is used to disengage the inner cover from the turntable liner by resting on one side of a rocker arm and thus raising the inner seal device. The inner cover is two concentric cylinders connected at the top with a metal doughnut. The outer cylinder rests on the rocker arm in the water trough. When the outer cover is lifted, the inner cover falls in place. The outer cylinder provides a water seal between the turntable and the cell. The inner cylinder rests atop the turntable liner. The bottom of the inner cylinder makes a seal with the top of the liner. This provides a seal between the turntable and the access port, leaving the access port and the liner open to the cell. The inner cover allows canisters to be removed and inserted into the turntable while minimizing air inleakage. The inner cover is lifted off the liner by the outer cover when not in use so as to prevent its interfering with turntable rotation.

DUAL OVERFLOW ACCOMMODATION

The melter has been designed with a primary glass discharge chamber and a backup chamber in case the first chamber becomes blocked or otherwise inoperative. The turntable has been designed to accept glass from either chamber without repositioning the turntable.

MELTER/TURNTABLE BELLOWS SEAL

The turntable ports under the melter glass discharge chambers are sealed to the melter with double-walled metal bellows that are inflated with air to provide a force against the sealing surfaces. A metal "E" seal on the top of the bellows provides a good seal between them and the melter. The bellows and associated parts are all metal to withstand the high temperature and radiation in the area. The bellows seal is part of a unit that can be remotely removed from the turntable and replaced while the melter is idling. The removable melter discharge insert and holding mechanism is part of the bellows assembly and is described in the following section.

MELTER DISCHARGE INSERT

The melter discharge insert is an inverted cone section used in the interface area between the melter and the turntable. The discharge insert can be removed through the turntable and is used to contain glass that may build up between the overflow pour tip and the top of the turntable. Glass may build up in this region because of a deflected glass stream or severe nesting or coning of glass in the canister. The discharge cone allows for the removal of this obstruction with remote devices.

The discharge insert is installed in the turntable bellows seal device; it is put into place by loading it and the handling equipment into the turntable canister access port. The carousel is rotated so that the insert is directly beneath the melter discharge. When the turntable is in position, the insert is raised by an air cylinder that is part of the handling equipment. When the air cylinder is retracted, the insert is held in place by a set of self-locking cams attached to the bellows assembly.

The discharge insert can be removed by using the same handling equipment with a removal tool placed on top. The removal tool unlocks the cams holding the insert and forces the insert out of the melter discharge port. Since the discharge insert is inserted into the melter but held in place by the bellows assembly attached to the turntable, the insert must be removed before the turntable can be moved from under the turntable. The discharge insert, locking cams, and bellows assembly are shown in Figure 3.

DRIVE MOTOR SYSTEM

The drive motor system is a reversible electric motor connected to a 3600:1 gear reduction unit. The electric motor is reversible so that the discharge cone handling equipment can be used properly. The discharge cone-handling equipment needs to be rotated back, opposite to the way it is rotated in. This is done to prevent the air lines from being wrapped around the center post of the turntable. The gear-reduction unit is an index drive or Geneva gear that provides a dead spot in the gearing so that the carousel will stop

FIGURE 3. Melter/Turntable Bellows Seal and Melter Discharge Insert Assembly

accurately at 90° intervals. The index drive allows the carousel to pause while the position indicator signals the control system to stop the electric motor.

GLASS-LEVEL DETECTION

Two methods are used to determine the level of glass in canisters inside the turntable. First the canisters are weighed continuously while under the melter discharge chambers. The turntable thimbles are supported by the center column and the rail on the side of the turntable. Incorporated in the rail are mechanical arms that transmit the weight on the rail to a load cell located just outside the turntable enclosure. The load cell detects the weight on the mechanical arm that can be related to the glass weight in the canister. From the glass weight the glass level can be determined in the canister if it fills

evenly. The second glass-level detection system is needed to ensure that the glass is filling evenly and to provide a backup to the weighing system.

The second method determines the glass level by using a vertical array of collimated gamma detectors that are positioned in the cell wall directly in line with a radiation source and the glass canisters under the glass discharge port. The gamma detectors determine the glass level by the attenuation of the signal from the remote radiation source and from the radiation in the canisters.

TURNTABLE INSTALLATION AND REMOVAL

The turntable assembly can be installed and removed without turning off the melter power. The turntable is mounted on wheels so that it can be rolled in or out from under the melter. The wheels roll on a track to guide the turntable into the proper position under the melter. The design for turntable movement will be completed during advanced conceptual design and may involve a scissor-type mechanism that can be operated by an impact wrench. This type of mechanism was tested at PNL (Siemens et al. 1985) and appears to operate satisfactorily. Other alternatives would include a remote motor and drive system.

INSTALLATION OF THE BELLWS SEAL

The entire bellows seal assembly is attached to the turntable shell by a remote flange and studs. To couple the turntable shell to the melter, the turntable is rolled under the melter overflow chamber with the bellows assembly bolted in place. After the bellows assembly is bolted in place, a jumper is attached to the bellows air inlet nozzle and the bellows are inflated with air. When inflated with air, the bellows flange lifts ~1 in. and forces the "E" seal against the underside of the flange on the melter discharge chamber. The bellows are protected by both inner and outer skirts.

THIMBLE LINER REPLACEMENT

The thimble liner is a replaceable metal cylinder that collects any glass spilled during melter operation. It can be replaced remotely by using a specially designed spreader bar. The spreader bar is suspended from a rotatable

crane hook and lowered into the canister access port. The spreader bar is lowered to the top of the liner, is raised slightly and is then rotated into position. In this position, the ears on the liner are engaged and the liner can be lifted out. Overhead viewing is required for this operation.

LOAD CELL REPLACEMENT

The load cell is attached to a remote flange on the turntable. An electrical jumper is connected to the load cell. A female PUREX connector is part of the remote flange and load cell assembly. The load cell can be replaced by removing the electrical jumper and unbolting the remote flange that holds the PUREX connector and the load cell.

INSTALLATION OF THE INDEX DRIVE UNIT

The index drive unit with a reversible motor was designed for HWVP hot cell use based on experience gained from testing at PNL and West Valley Nuclear Services. The unit is installed by hanging the drive unit assembly from the crane with a temporary power lead attached and then lowering the output shaft into place. The temporary power connection allows the square output shaft to be rotated before it is installed to align it properly with the square hole that accepts the shaft. The square holes have close tolerances that require very careful alignment of the output shaft.

INSTALLATION OF THE CAROUSEL POSITION INDICATOR

The carousel position indicator, a linear variable differential transmitter (LVDT), is built into one end of a jumper. The jumper has a PUREX head at one end and an electrical head at the other. The 3-in. PUREX connector holding the LVDT connects directly to the top of the turntable above the rail that supports the canister thimbles. The LVDT has an extension rod that projects from the PUREX connector and contacts the cams on the carousel. These cams signal the canister thimbles' position and identification.

CONCLUSIONS

The conceptual turntable design developed for HWVP effectively provides the following services:

- positions the canisters accurately under the melter discharge chambers
- controls the spread of radioactive contamination in the melter cell
- limits the amount of air leaking into the melter
- determines the glass level in the canister being filled with glass
- determines the weight of the glass in the canister.

REFERENCE

Siemens, D. H., et al. 1985. High-Level Radioactive Waste Vitrification Process Equipment Component Testing. PNL-5394, Pacific Northwest Laboratory, Richland, Washington.

OFF-GAS SYSTEMS

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SUMMARY

Characterization studies of melter effluent emission and off-gas system performance have been conducted on B-Cell's radioactive liquid-fed ceramic melter (RLFCM) during the production of isotopic heat sources for the Federal Republic of Germany. Melter feed entrainment losses were found to be much greater than anticipated based upon past nonradioactive testing experience. Melter decontamination factors (DF) for both ^{90}Sr and ^{137}Cs were both a factor of 10 lower than cold-test predictions for normal feed-processing conditions.

The performance of the RLFCM's ejector venturi quench scrubber was not consistent through all phases of RLFCM processing. Although measured scrubbing efficiencies were quite acceptable during normal feed-processing conditions, the off-gas sampling data indicate a complete loss of ejector venturi scrubber (EVS) capability during the spike-feeding phase of the RLFCM processing campaign. No definite explanation for this operational inconsistency is presently available; however, use of the EVS to control melter vacuum may have caused this loss of off-gas processing efficiency.

INTRODUCTION

Characterization studies of effluent emission and off-gas performance 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 emission characteristics of PNL's RLFCM and the performance of its exhaust system quench scrubber--an ejector venturi scrubber--was completed during the second quarter of FY 1986. The basis of this evaluation was the first part of the RLFCM-7 processing campaign, which is designed to produce ten isotopic heat sources for the Federal Republic of Germany. Specifically these heat sources are canisters of RLFCM-produced glass, each of which contains 210 kCi of ^{137}Cs and 160 kCi of ^{90}Sr . Two separate processing phases were evaluated during RLFCM-7. To quickly bring up melter glass activity to design levels, the melter first processed highly concentrated ^{137}Cs - and ^{90}Sr -loaded feed. Once the desired glass loading of these isotopes was achieved, melter feeding resumed with cesium and strontium concentrations reduced by 67%. Off-gas samples were collected during both of these processing modes as is discussed below.

MELTER AND OFF-GAS SYSTEM PERFORMANCE

Melter emission and off-gas component performance is commonly expressed in terms of a unitless decontamination factor, or DF. By definition, a feed-component DF is the ratio of the rate at which that particular component enters a device to the rate at which it exits. Consequently, melter DFs are related to the process efficiency $(1-1/\text{DF})$ of the liquid-fed melter 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 RLFCM-7 melter and venturi scrubber DF performance data for the two processing modes studied. Also given in this

TABLE 1. Melter and Off-Gas System Decontamination Factors

Element	Spike Feeding DF				Normal Processing DF			
	Melter		Venturi		Melter		Venturi	
	RLRCM-7	PSCM-20	RLRCM-7	PSCM-20	RLRCM-7	PSCM-20	RLRCM-7	PSCM-20
Al	36	2,600	1.2	20	53	1,900	17	110
B	23	27	3	7	12	55	89	2
Ba	25	700	1	15	28	1,800	14	35
Ca	20	270	1.2	12	14	150	10	32
Cr	5	52	1	29	8	280	2	5
Cs	28	22	1	4	10	140	3	2
Fe	61	2,300	1	5	--	2,800	--	100
La	55	4,300	1	19	110	1,500	--	720
Li	34	--	1.1	--	--	--	--	--
Mg	21	680	1.2	18	17	290	11	100
Mn	52	1,500	1	24	21	1,300	70	96
Mo	20	--	1	--	--	--	4	--
Na	25	130	1.2	7	30	370	9	4
Nd	61	3,100	1.1	49	190	1,800	--	460
Ni	66	1,700	1	10	100	1,800	--	33
Ru	11	330	1	6	--	--	--	2
Si	40	1,700	1.7	6	590	1,400	7	19
Sr	50	500	1	22	130	1,200	72	44
Ti	65	--	1.2	--	--	1,800	--	--
Zn	53	--	1	--	11	--	--	--
Zr	--	14,000	--	--	4	33,000	--	--
Total	30	100	1	2.5	50	640	5	2.4

table for comparison are average results derived from a previously completed cold test, PSCM-20, which provide baseline data and performance expectations for subsequent RLFCM operations.

Melter

During spike feeding, gross feed entrainment was the primary mechanism for losses of melter off-gas system effluent. This is clearly illustrated by the fact that nearly all feed components exhibited similar DFs, which were about the same as the total overall melter DF value of 30. To put it another way, during RLFCM-7, gross feed entrainment was as important a loss mechanism as volatilization in determining overall melter effluent losses. Of the off-gas effluents characterized, only ruthenium, which can be strongly evolved as a gas during LFCM processing, exhibited enhanced melter emission rates.

The high rate of effluent loss due to process exhaust feed entrainment is not typical of the melter, as the PSCM-20 comparative data in Table 1 illustrate. Normally the melter feed component DFs for volatile and semivolatile components differ markedly from those of nonvolatile constituents. This was the case during PSCM-20 but is clearly not true for the RLFCM-7 spike-feeding campaign. Since cesium losses from the melter usually are dominated by a volatilization/condensation mechanism, the increase in entrainment losses did not significantly influence the melter's cesium DF during spike-feeding, as is shown in Table 1. Strontium losses, however, were a factor of 10 higher than expected based on previous cold-testing data.

Melter performance during normal RLFCM-7 feed processing was much poorer than had been achieved during the analogous PSCM-20 cold-testing experiment. RLFCM feed-component DFs are mostly a factor of ~10 less than had been achieved then. There appear to have been slightly less feed-entrainment losses during normal processing than were observed during earlier spike feeding; however, overall loss rates were still much higher than previous testing would have predicted. Specifically, isotopic losses of both ^{90}Sr and ^{137}Cs exceeded expectations by an order of magnitude during normal feed processing. This finding is further corroborated by the buildup of activity of ^{137}Cs in the EVS scrub

liquor. The steady-state concentration of this isotope achieved during normal feed processing indicated a melter cesium DF of 10, which agrees with the off-gas sampling data in Table 1.

Ejector Venturi Scrubber

The behavior of the RLFCM's quench scrubber during RLFCM processing of FRG waste was ambiguous. During spike feeding, the performance of the EVS was so poor overall that it is thought the scrubber may not have functioned during the beginning phases of RLFCM-7. Since melter entrainment losses during spike feeding were quite high, one would expect a rather high EVS scrubbing efficiency rather than an imperceptibly low one. The use of scrubbing liquor flow to control melter vacuum may have been responsible for the loss of EVS off-gas processing performance; however, any explanation offered now for this inexplicable result would be highly speculative.

In contrast to the spike-feeding behavior, EVS performance during normal melter feed processing was higher, overall, than was achieved under cold simulation testing. More importantly, greater cesium and strontium DFs were achieved during RLFCM-7 than during the analogous phase of the PSCM-20 experiment. From the limited off-gas data that exist, it appears that the EVS performed well within design expectations during routine melter processing conditions.

PROCESS/PRODUCT MODELING AND CONTROL

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SUMMARY

A mass balance model of a hypothetical LFCM vitrification system has been developed using the SIMAN simulation language. Two important features of the model are its ability 1) to model simultaneously occurring batch and continuous processes and 2) to take into account uncertainties in the process. The model is being used to investigate methods of controlling and predicting the product glass composition from an LFCM vitrification system. The glass composition is expected to fluctuate with time because of process uncertainties such as batch-to-batch variations in the waste composition, sampling and analytical errors, and errors in measuring tank levels and in adding glass formers. Given these uncertainties, the ability to control vitrification (i.e., to add the correct amount of glass formers) depends strongly on the waste-sampling strategy, and the ability to predict glass composition depends strongly on the feed-sampling strategy. The mass balance model can be readily modified to investigate the effects of any process uncertainty on the process' ability to produce glass that is acceptable for disposal.

An approach is presented here for correlating glass dissolution rate versus composition. The method is tested using leach rate data for several waste glass compositions in both fresh water and brines. With this information, a preliminary dependence of dissolution rate and composition is determined. Additionally, methods are developed for relating the uncertainty in predicted glass dissolution rate with the uncertainty in predicted composition of waste glass. The limitations of the method, as imposed by the available data on composition versus leach rate, are identified and recommendations on future efforts are included in the section on conclusions.

INTRODUCTION

The Nuclear Waste Treatment Program (NWTP) is a participant in the Waste Acceptance Process (WAP) convened by the DOE to ensure that waste forms produced by existing and future producers will be acceptable for disposal in licensed high-level waste repositories. Consequently, the NWTP needs to define and implement a technical approach for addressing, evaluating, and meeting waste acceptance specifications.

A technical approach has been outlined that calls for development of product and process models as means for relating product quality to process measurements. Work on a product model has been supported to the extent necessary to understand the significance of results from process modeling, but the NWTP emphasizes development of process models because of their generality, as opposed to product models, which are more specific to particular waste-form producers. The process model is divided into a mass balance model and a thermal model of the canister as it fills with glass and cools. The thermal model is mathematically sophisticated, but conceptually is simply a heat-transfer model for the canister/turntable system as glass is poured and cools. This section describes work done to develop and validate the process and product models.

TECHNICAL PROGRESS

MASS BALANCE MODELING/PROCESS MODELING

A mass balance model has been developed primarily to support waste-form qualification activities within the NWTP. The model is implemented using the SIMAN simulation language because SIMAN offers dynamic simulation modeling capabilities that enable incorporation of uncertainties (stochastic variables) and batch-wise processes (discrete events) into a model otherwise described by a system of differential and state equations. This is important because an understanding of the propagation of uncertainties through the batch-operated LFCM vitrification system is essential to development and demonstration of waste-form qualification technology.

The hypothetical LFCM vitrification system modeled consists of five tanks: a waste batching tank, i.e., the receipt and lag storage tank (RLST); two slurry mix evaporator (SME) tanks (glass formers are added to the second); a melter feed tank; and a melter. A flow diagram of the system is shown in Figure 1. Seven components are considered in the system: decay heat-producing compounds in the waste, other constituents in the waste, sodium oxide (Na_2O), boron oxide (B_2O_3), silicon dioxide (SiO_2), other glass formers, and water. All components are considered to be oxides at every point in the system (i.e., conversion of hydroxides, nitrates, etc., to oxides is not taken into account).

FIGURE 1. Flow Diagram of LFCM Vittrification System

Melter decontamination factors for all components except water are assumed to be infinity (an off-gas system is not included in the model). All tanks in the system are considered to be ideally mixed.

An objective in operating the hypothetical system is to achieve a certain loading of both decay heat and boron in the glass (assuming that boron controls key glass quality and processability properties). To simultaneously control these two parameters, two glass formers are used: one rich and the other lean in boron. A control algorithm to determine how much of each glass former should be added to each batch of waste (based on upstream sampling) has been developed and incorporated into the model. Control of glass-former addition is necessitated by inherent batch-to-batch fluctuations in incoming waste composition. Precise control is impossible, however, due to sampling error, error in measuring levels in tanks, and error in makeup and addition of glass formers.

Sampling error includes two components: sample-to-sample variation (when duplicate samples are taken at the same time) and sample analytical error. These two sources of error allow the user to investigate how well glass composition can be controlled or predicted based on the number of samples taken and/or the number of analytical determinations performed on each sample.

All uncertainties in the mass balance model are treated stochastically. This is done by taking advantage of internal subroutines in SIMAN that generate random numbers and use these to randomly sample distributions that the user has defined. Only normal distributions are currently specified in the model. The following uncertainties are presently included in the model:

- 5% relative standard deviation (RSD) in batch-to-batch waste composition
- 4 to 6% RSD in sampling and analytical errors (depending on the species)
- 1% RSD in tank level measurement (1% of full-scale reading)

- 0.2% RSD in the amount of glass formers added relative to what the control algorithm prescribes
- 2% RSD in the time between batch canister pours.

When the mass balance model is executed, the concentration of each constituent in each tank versus time is calculated by simultaneous solution of the differential and state equations that describe the system (these are mass balance equations for ideally mixed tanks). The equations are solved using a Runge-Kutta-Fehlberg numerical differentiation algorithm that is part of the SIMAN subprogram library. The values obtained from solving these equations are taken to be the "true" concentrations in the system. Apparent concentrations differ from the true concentrations because they have sampling and analytical errors imposed on them. "Predicted" concentrations in the system are calculated by taking the apparent concentrations and plugging them into the same set of equations used to calculate the true concentrations. Doing this propagates the apparent concentrations at the sampling points through the system in the same way that the true concentrations are propagated.

The mass balance model has been exercised many times to provide data for analysis by PNL statisticians. The purpose of the runs has been to investigate the effect of different sampling strategies on the ability to control and predict the composition of the glass being produced. The difference between the true composition and the target composition is a measure of how well the process was controlled. Likewise, the difference between the predicted composition and the true composition is a measure of how well the glass composition was predicted.

The sampling strategies investigated so far are as follows:

- Case 1: 1 sample and 1 analysis of both the waste and the feed.
- Case 2: 1 sample and 1 analysis of the waste, 5 samples and 5 analyses of each sample of the feed.

Case 3: 5 samples and 5 analyses of each sample of the waste, 1 sample and 1 analysis of the feed.

Case 4: 5 samples and 5 analyses of each sample of both the waste and the feed.

Results from these runs are summarized in Tables 1 and 2; values were based on the simulation of 40,000 hr of operation of the vitrification system. Table 1 shows that the ability to control the glass composition is affected

TABLE 1. Comparison of the True and Target Glass Composition

Component	Case 1		Case 2		Case 3		Case 4	
	AAD ^(a)	MAD ^(b)	AAD	MAD	AAD	MAD	AAD	MAD
Heat	3.6	19.0	3.8	14.5	1.4	6.9	1.6	6.2
Other Waste	4.8	23.5	5.2	21.2	3.1	13.6	3.4	13.4
Na ₂ O	2.4	12.4	2.6	10.6	1.5	6.5	1.6	6.4
B ₂ O ₃	1.2	6.4	1.1	5.5	0.5	2.3	0.6	2.9
SiO ₂	2.3	12.2	2.6	10.4	1.5	6.7	1.6	6.2

(a) AAD is the average absolute difference between the true and target glass compositions represented as a percent of the target composition.

(b) MAD is the maximum absolute difference between the true and target glass compositions represented as a percent of the target composition.

TABLE 2. Comparison of the True and Predicted Glass Composition

Component	Case 1		Case 2		Case 3		Case 4	
	AAD ^(a)	MAD ^(b)	AAD	MAD	AAD	MAD	AAD	MAD
Heat	3.1	16.4	1.2	5.7	2.8	11.5	1.0	4.3
Other Waste	2.0	10.8	0.8	3.5	2.3	10.1	0.8	3.4
Na ₂ O	2.8	12.4	0.8	4.3	2.3	11.5	0.8	3.8
B ₂ O ₃	2.4	12.3	0.8	3.2	2.5	10.1	0.8	3.7
SiO ₂	1.4	6.9	0.5	2.1	1.6	5.8	0.5	3.8

(a) AAD is the average absolute difference between the true and target glass compositions represented as a percent of the target composition.

(b) MAD is the maximum absolute difference between the true and target glass compositions represented as a percent of the target composition.

primarily by the waste sampling strategy, and Table 2 shows that the ability to predict the glass composition is affected primarily by the feed-sampling strategy. This is exactly what was expected since the amount of glass formers added is based on the apparent composition of the waste, and the predicted glass composition is based on the apparent composition of the feed.

A second objective of executing the mass balance model was to investigate the possibilities of applying process control charting to operation of the vitrification system. Among other things, process control charting provides an objective, statistically-based method of distinguishing between normal process fluctuations and true process upsets. Control charting can be used to determine when the process has deviated enough from steady-state conditions to warrant corrective action.

A more complete description of the mass balance modeling activities undertaken during the January-March 1986 quarter will appear in a May 1986 milestone report on a demonstration of waste form qualification technology. A second May 1986 milestone report will be dedicated to the application of process control charting to the operation of a LFCM vitrification system.

STATISTICAL QUALITY CONTROL

Application of the theory of statistical quality control (SQC) to the melter process was examined. SQC techniques are widely used in industry to monitor the quality level of a product and to increase understanding of the variables that influence the process. Because these techniques are standard in industrial practice, they could easily enhance demonstration of the quality of the glass to the public.

The melter process is unlike many processes where the observations over time are independent of one another. Sequential samples from the tanks along the melter process are correlated because of the heels left over in each tank after completing a tank transfer. The normal application of SQC assumes independent observations. Appropriate methods for applying SQC to correlated data were examined and developed.

These methods were applied to data simulated from the modeling program described above. SQC was applied to the SME samples. The ability of these methods to detect shifts in the boron composition of the feed was examined for various SME and RLST sampling schemes and is summarized in Table 3. Table 3 shows the average number of observations (ARL) plotted on a control chart after a process shift before detecting an out-of-control point. Note that by using five replicates of feed samples and five replicates of analyses of samples, a 10% change in the boron concentration can be detected after 10 points plotted on a control chart, in this simulation.

Using data from the simulation, a comparison of the true glass composition coming from the melter and the predicted glass composition based on feed samples was begun. A bug in the simulation program was detected by examining plots of the simulated data. The bug has been corrected, and the comparison of the true and predicted glass composition is being reexamined (the results presented in Tables 1 and 2 were obtained after the bug was corrected). The correlation of sequential observations inflates the variance estimates of the differences between true and predicted values. This problem is still being evaluated.

PRODUCT MODEL DEVELOPMENT

It has long been known that the chemical durability of glass is affected by its composition. Establishing this dependence for purposes of quality control is important since waste-form manufacturers have primary control over glass composition. An approach is presented here for correlating glass dissolution rate with composition. The method is tested using leach rate data for several waste glass compositions in both fresh water and brines. With this information, a preliminary dependence of dissolution rate on composition is determined. Additionally, methods are developed for relating the uncertainty in predicted glass dissolution rate to the uncertainty in predicted composition of waste glass. The limitations of the method, as imposed by the available data on composition versus leach rate, are identified and recommendations on future efforts are included in the "Conclusions" section.

TABLE 3. Average Run Lengths (ARLs) for Boron

RLST		Target Value	Process Shift	NS(a)	NA(b)	ARLI(c)	ARLM(d)
Samples	Analyses						
1	1	0.02917	0.0025	1	1	>20	>20
1	1	0.02917	0.0025	1	3	>20	>20
1	1	0.02917	0.0025	3	1	>20	15
1	1	0.02917	0.0025	3	3	>20	17
1	1	0.02917	0.0050	1	1	12	4
1	1	0.02917	0.0050	1	3	7	3
1	1	0.02917	0.0050	3	1	4	2
1	1	0.02917	0.0050	3	3	4	2
1	1	0.02917	0.0100	1	1	1	1
1	1	0.02917	0.0100	1	3	1	1
1	1	0.02917	0.0100	3	1	1	1
1	1	0.02917	0.0100	3	3	1	1
5	5	0.02917	0.0025	1	1	>20	10
5	5	0.02917	0.0025	1	3	>20	7
5	5	0.02917	0.0025	3	1	16	5
5	5	0.02917	0.0025	3	3	12	5
5	5	0.02917	0.0050	1	1	5	2
5	5	0.02917	0.0050	1	3	3	1
5	5	0.02917	0.0050	3	1	2	1
5	5	0.02917	0.0050	3	3	1	1
5	5	0.02917	0.0100	1	1	1	1
5	5	0.02917	0.0100	1	3	1	1
5	5	0.02917	0.0100	3	1	1	1
5	5	0.02917	0.0100	3	3	1	1

- (a) NS is the number of samples obtained from each SME batch.
 (b) NA is the number of analyses performed per SME sample.
 (c) ARLI is the average run length for the individual SME batch control chart. The large values are not very accurate since this was based on a simulation of only 1000 RLST/SME batches.
 (d) ARLM is the average run length for the control chart on RLST/SME batch averages. Large values are not accurate because they are based on a simulation of only 1000 batches. It should be noted that the ARLM refers to the number of RLST/SME batch averages, not SME batches.

The approach adopted here is based on the work of A. Paul (1977), who correlated glass chemical durability with composition via thermodynamic stability of the glass constituents. Later, Plodinec et al. (1983) applied this method to evaluation of nuclear waste glasses and several simple glasses. Accordingly, glasses are treated as a composite solid of individual silicate and/or

oxide phases. The free energies of aqueous dissolution reactions are calculated for these phases, and this provides an indicator of glass durability. It should be understood that this method has no rigorous thermodynamic or kinetic basis since 1) the thermodynamic state of a vitreous phase cannot be defined, and 2) kinetic mechanisms are not identified. The procedure, however, is useful in correlating the effect of compositional variations on glass durability.

It is assumed that the driving force for these individual reactions is determined according to their free energy, which is calculated as follows:

$$G = RT \ln Q + G^\circ \quad (1)$$

where $Q = \prod_i a_i v_i$ is the ratio of the activities of the products and reactants, where a_i is the activity of a product or reactant, and v_i is the associated stoichiometric coefficient.

The free-energy data is to be correlated with glass dissolution rates. Most leach tests are performed in fixed volumes of water, and the dissolution rate generally is found to decrease with time. This trend is associated with "saturation" effects. In a repository, it is expected that slow mass transfer rates away from the waste package will result in similar saturation. Therefore, such leach tests provide useful information about the behavior of glass in repositories. The rates used for correlating the free energy data are those obtained at "saturated" or near-saturated leachate conditions from these static tests. Grambow (1985) attributes this final rate to the residual affinity of the dissolution of the glass. Final dissolution rates for various glasses that have been studied at PNL are given in Table 4. The rates are derived from changes in the concentration of soluble species dissolved from the glass, such as sodium, boron, and lithium. The glass designated WV205R is a version of WV205 that was formed under reducing conditions.

The composite free energy of the glass dissolution reaction is assumed to be represented by the mole-fraction weighted sum of the individual free energies of reactions (Equation 1) of the glass constituents:

$$G = \sum n_i (RT \ln(Q_i) + G_i^\circ) \quad (2)$$

TABLE 4. Dissolution Rates and Free Energies for Waste Glasses

	<u>SRL-165</u>	<u>WV205</u>	<u>WV205R</u>	<u>ATM-9</u>
Dissolution Rate at 90°C, g-glass/m ² day	0.016	0.035	0.25	0.01
Standard Free Energy of Glass at 90°C (G°), kcal/mole	-5.5	-6.4	-7.7	-4.9

where n_i is the mole fraction of glass constituents. Grambow (1985) reported that dissolution rate should depend on free energy according to:

$$\ln(\text{Rate}) = A' - B G \quad (3)$$

where A' and B are constants at a fixed temperature, and G is obtained from Equation 2. It is difficult to rigorously calculate G in this case since the activities of the dissolved products and reactants are not known with sufficient accuracy. However, rearrangement of Equation 2 is possible such that the dependent variable involves only the standard free energies. Expanding Equation 3 with Equation 2 results in:

$$\ln(\text{Rate}) = A' - B \sum n_i RT \ln(Q_i) - B \sum n_i G^\circ \quad (4)$$

Combining the terms A' and $B \sum n_i RT \ln(Q_i)$ into a new "constant" A results in:

$$\ln(\text{Rate}) = A - B G^\circ \quad (5)$$

where G° is the standard free energy of hydration of the glass and is given by $\sum n_i G_i^\circ$. By combining the solution activity term into a constant, Equation 5 implies that the free energy contribution of the aqueous solution activities for all glasses is the same. Although not rigorously correct, such an approximation may be reasonable, considering that the leach solutions are nearly saturated in many of the dissolved species.

The standard free energies for the glasses, calculated without the activity term, are shown in Table 4. The free energy data was taken from Plodinec et al. (1983) and extrapolated to 90°C using the Van't Hoff equation. A plot according to dissolution rate is given in Figure 2. Following Equation 5, a regression analysis was used to fit a straight line through the four data, resulting in the following values for the parameters A and B:

$$A = -10.43 \pm 0.8$$

$$B = 1.15 \pm 0.13.$$

Equation 5, with these coefficients, is thus the resulting empirical correlation between the final dissolution rate of nuclear waste glasses at 90°C and their composition.

FIGURE 2. Dependence of Final Dissolution Rate at 90°C on Standard Free Energy of Hydration

Sensitivity of Dissolution Rate to Variations in Composition

With the above correlation, the glass composition can now be related to dissolution rate. The overall objective, however, is to understand how changes in composition (due to variations in vitrification process) will affect this dissolution rate. Uncertainties associated with the process can be propagated through to a variation in leach rate of the glass. Using statistical propagation-of-error methods, the error in Equation 5 is given by the following relation:

$$\sigma_{\ln R} = \left[\left(\frac{\partial \ln R}{\partial A} \sigma_A \right)^2 + \left(\frac{\partial \ln R}{\partial B} \sigma_B \right)^2 + \left(\frac{\partial \ln R}{\partial G} \sigma_G \right)^2 + 2 \operatorname{cov}(A, B) \frac{\partial \ln R}{\partial A} \frac{\partial \ln R}{\partial B} \right]^{1/2} \quad (6)$$

where σ_A^2 , σ_B^2 , σ_G^2 represent the error in A, B, and G° , respectively. Carrying out the differentiation in Equation 6 yields:

$$\sigma_R = [\sigma_A^2 - 2G \operatorname{cov}(A, B) + (G^\circ \sigma_B)^2 + (B \sigma_G)^2]^{1/2} \quad (7)$$

The error in the free-energy σ_G depends on errors in free energies of individual glass components and also on errors in composition. Assuming that component free energies are known exactly and, further, that mole fractions can be varied independently result in the following simplified relation for σ_G :

$$\sigma_G = f [\sum (G_i^\circ \sigma_{ni})^2]^{1/2} \quad (8)$$

where σ_{ni} is the error in mole fraction of individual components and we assume for convenience that the component comparisons are not correlated. If it is assumed that all mole fractions of glass constituents are known to within the same fractional limit f , then substituting $\sigma_{ni} = fn_i$ into Equation 8 results in:

$$\sigma_G = f [\sum (n_i G_i^\circ)^2]^{1/2} \quad (9)$$

Of interest is the sensitivity of the error term for the predicted glass dissolution rate (Equation 6) on the composition error factor f . To carry out the analysis numerically, a value of $G^\circ = -6.39$ kcal/mole is selected, corresponding to the oxidized form of the glass WV205 from Table 4. Using the available composition and standard free-energy data, the term $[\sum(n_i G_i^\circ)^2]^{1/2}$ in Equation 9 becomes 6.89 kcal/mole. The regression analysis done above resulted in values of $\sigma_A = 0.8$ and $\sigma_B = 0.13$, and $\text{cov}(A,B) = 0.102$. Equation 6 becomes:

$$\sigma_{\ln R} = [0.026 + 62.8 f^2]^{1/2} \quad (10)$$

According to Equation 10, $\sigma_{\ln R}$ is not significantly affected until f reaches values greater than 0.02. This means that relative uncertainties in composition of less than 2% will not have a significant impact on glass dissolution rates, assuming that glass dissolves according to the correlation given by Equation 5. The results of the process simulations performed by the Technology Testing subtask indicate that process variations (excluding upsets) are expected to result in compositional uncertainties on the order of 1 to 5% (f values on the order of 0.01 to 0.05) if the assumed standard deviations for process operations are correct.

VALIDATION OF A THERMAL CODE

Additional attempts were made this quarter to conduct thermal computations to compare with temperatures measured during the filling and cooling of the 24-in. canister filled during operation of the pilot-scale ceramic melter. It was realized last quarter that a problem lies within the TEMPEST heat transfer code being used to implement the model; this problem is requiring the attention of the group who developed the code. Though several errors have been uncovered and corrected, the problem remains unsolved. Consideration is being given to postponing this computation until completion of the TEMPEST code development activities described below. These activities include modifying TEMPEST to eliminate many of the operational problems that have been experienced, including this one.

TEMPEST DEVELOPMENT

This effort is just getting under way, as work began in early March. The scope of work and the quality assurance aspects of this effort were documented. All work will be traceable, orderly tracking of computer versions will be accomplished with the software utility UPDATE, and internal testing will be reported.

Additionally, a literature search concerning software applicable for this project was conducted. Several pieces of software have been ordered. Plans for the next quarter include obtaining the latest version (N) of TEMPEST, studying the implicit fluid mechanics option, and developing a small test problem (analogous to the 24-in. canister problem discussed above). This will be followed by installation of the implicit fluids capability into the code and the start of model testing.

GLASS CRACKING

Work is proceeding on a PNL document that describes past studies of cracking of glass in a canister. Most of the review comments have been incorporated into the report. Further analysis of the data has also led to incorporation of transient thermal stresses into the model in addition to locked-in stresses for the prediction of cracking in canisters subjected to changes in the cooling environment. This appears to have eliminated many previous inconsistencies in interpretation of the data.

A regression analysis was performed to determine a "best line" for the correlation of cracking versus temperature differences. The resulting regression line was almost identical to the line originally drawn; at the 95% confidence level, the uncertainty of the slope of the model line is $\pm 17\%$.

The above developments have required rewriting portions of the report. This will be completed in April, whereupon final editing will commence with preparation of a draft for clearance in May.

CONCLUSIONS

1. A mass balance model of a hypothetical LFCM vitrification system has been developed using the SIMAN simulation language.
2. The mass balance model can be readily modified to investigate the effects of any process uncertainty on the ability to control or predict the product glass composition in an LFCM vitrification system.
3. Given sufficient replication of feed samples taken and of chemical analyses done on the samples, a 10% shift in the boron concentration--i.e., caused by some process shift--could be detected after 10 boron feed compositions are plotted on a process control chart, in the simulation of an LFCM process described above.
4. Analysis of the dependence of glass dissolution rate on glass composition has shown how composition and dissolution rate can be correlated, and how uncertainties in composition due to the vitrification process can influence dissolution rate.
5. Data used to demonstrate the waste form qualification methodology came from previously conducted experiments not aimed at this purpose; thus the numerical results are not applicable to any specific vitrification process or waste form. The analysis does indicate that consideration of the free energies of hydration of glass constituents may provide a reasonable framework for correlating glass dissolution rate and composition.
6. Future efforts to improve and validate this approach are needed. The following work is indicated:
 - Leach tests should emphasize determination of glass dissolution rate in solutions saturated with dissolution products.
 - Tests are needed on a range of glass compositions (about a target composition).
 - More precise information on solution activities is needed so that the solution portion of the free energy equation can be used.

7. A regression analysis of data on canister cracking versus temperature differences during cooling provided a linear correlation with a relative standard deviation in the slope of $\pm 17\%$.

REFERENCES

Grambow, B. 1985. "A General Rate Equation for Nuclear Waste Glass Corrosion." Mat. Res. Soc. Symp. Proc. 18:15, Materials Research Society, Pittsburgh, Pennsylvania.

Paul, A. 1977. "Chemical Durability of Glasses; A Thermodynamic Approach." J. Mat. Sci. 12:2246.

Plodinec, M. J., et al. 1983. "Thermodynamic Approach to Prediction of the Stability of Proposed Radwaste Glasses." Advances in Ceramics, Vol. 8, G. G. Wicks and W. A. Ross, ed., American Ceramic Society, Columbus, Ohio.

APPENDIX

ACRONYMS AND ABBREVIATIONS

ADS - air displacement slurry (pump)
°C - degree Celsius
cm - centimeter
cP - centipoise
DF - decontamination factor
DOE - U.S. Department of Energy
DWPF - Defense Waste Processing Facility
EVS - ejector venturi scrubber
FRG - Federal Republic of Germany
g - gram
hr - hour
HLLW - high-level liquid waste
HLW - high-level waste
HWS - Hanford waste simulation
HWVP - Hanford Waste Vittrification Program
kCi - kilocuries
L - liter
LFCM - liquid-fed ceramic melter
LVDT - linear variable differential transducer
mL - milliliter
NWTP - Nuclear Waste Treatment Program
PNL - Pacific Northwest Laboratory, Richland, Washington
RLFCM - radioactive liquid-fed ceramic melter
RLST - receipt and lag storage tank
RSD - relative standard deviation
s - second
SCR - silicon-controlled rectifier
SME - slurry mix evaporator
TO/L - total oxides per liter
TRUW - transuranic waste
wt% - weight percent
WO/L - waste oxides per liter
WVDP - West Valley Demonstration Project

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