

VITRIFICATION TESTING OF SIMULATED HIGH-LEVEL RADIOACTIVE WASTE FROM HANFORD

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ABSTRACT

The Hanford Waste Vitrification Plant may apply vitrification technology, being developed at Pacific Northwest Laboratory, to solidify selected Hanford waste streams prior to disposal in a federal repository. Based on the first stage of flowsheet development and laboratory testing, a reference working glass and two candidate simulated feed slurries were recommended for vitrification testing. Over 500 hours of melter testing were performed in 1985 during prototype vitrification experiments. Testing demonstrated that the slurry compositions had acceptable processing characteristics in a ceramic melter. A pre-made glass-former frit was determined to be preferred as the method of glass-former addition. Due to a high chromium content in the waste, spinel crystal formation and settling occurred in the glass tank. The nature and extent of off-gas effluents were consistent with past experiments processing slurries containing formic acid.

INTRODUCTION

As a result of nuclear activities, high-level and transuranic nuclear wastes have been generated at Hanford for over 40 years. The United States Department of Energy is currently evaluating processes within the guidelines of the National Environmental Policy Act for safely converting current and future Hanford high-level radioactive waste to a durable waste form. The liquid-fed ceramic melter (LFCM) vitrification process, developed by the Pacific Northwest Laboratory (PNL), is the leading candidate process being evaluated. Vitrification processes employing the LFCM have been selected for the Defense Waste Processing Facility (DWPF) and the West Valley Demonstration Project (WVDP).^{1,2} PNL is demonstrating remote operation of the LFCM process with the world's first pilot-scale radioactive LFCM.³ In a role similar to PNL's development and transfer of vitrification technology to the DWPF and the WVDP, PNL is using engineering- and pilot-scale vitrification systems to evaluate the proposed glass composition and flowsheet for the proposed Hanford Waste Vitrification Plant (HWVP). Rockwell Hanford Operations has the lead responsibility for the development, design, construction, and operation of the HWVP.⁴ PNL is providing the technology for the waste form and the vitrification system to be used in the HWVP.

Process development work in fiscal year 1985 concentrated on the development of reference glass and melter slurry compositions. The reference waste composition to be incorporated into a borosilicate glass matrix was a blend of two waste types: 1) the first-cycle extraction waste from the plutonium and uranium extraction (PUREX) process, neutralized current acid waste (NCAW); and 2) the transuranic waste fraction of the cladding removal waste (CRW) stream. Extensive laboratory work was conducted to develop candidate glass and slurry compositions that had acceptable physical and chemical properties. Based on laboratory results, an initial reference glass and two candidate feed slurries were recommended for LFCM testing. Two melter experiments were conducted to: 1) evaluate the processing characteristics of the simulated slurries, 2) select a method of glass-former addition, and 3) characterize the glass product and off-gas effluents. This paper presents the results of melter testing that supported the selection of the current glass and slurry compositions.

FLOWSHEET DEVELOPMENT

Prior to melter testing, significant laboratory work was conducted to develop a glass composition and subsequent suitable simulated slurry compositions. The following two sections, "Glass Design" and "Feed Formulation," describe the laboratory development work.

Glass Design

To design a glass suitable for processing in a joule-heated melter, one must consider three main properties: viscosity, electrical conductivity, and melt stability. The glass viscosity must be constant over time and should have a value of 100 Poise within a temperature range of 1075 to 1150°C. The temperature at which the viscosity is 100 Poise is called the T100P point. The permissible range of electrical conductivity of the glass melt is typically 0.18 to 0.5 (ohm·cm)⁻¹ at the T100P point in PNL-designed melters. A stable glass melt does not exhibit spontaneous oxidation shifts (reboil) or form secondary phases. Reboil occurs when multivalent elements in the glass, such as chrome and iron, exist in the melt in their highest oxidation states. A temperature change induces reactions that produce gas leading to the formation of a stable layer of glass foam on the melt surface.⁵ Generation of a foam layer creates a barrier to heat transfer between the feed pile (cold cap) and the glass, thus reducing processing efficiency. The glass melt is maintained in a slightly reduced condition to prevent reboil. The redox state of the glass is determined by measuring the ferrous-to-ferric ratio of the glass. Previous experience at PNL indicated that a ratio of 0.1 to 0.3 assured a stable melt.⁶ If required, reducing agents are added to the feed slurry. However, the glass melt must not be reduced to the point that stable metals are formed. Otherwise, highly conductive metals will deposit on the melter tank floor. The operating life of the melter could be threatened if the deposits are large enough to electrically short-circuit the current flow between the melter electrodes.

Secondary phases occur in the glass when the concentration of certain waste constituents exceed the glass solubility limit. Either crystallinity or immiscible phase separation will result. A trace amount of crystallinity is usually unavoidable due to

cooler regions in the melt tank that support crystal formation. However, this can be tolerated provided that the crystals are small, they do not tend to agglomerate, and they remain suspended by tank convection cells until they enter the melt tank discharge port. Phase separation is more serious because it can lead to the formation of a molten salt or a stable, more viscous glassy layer on the glass surface. The presence of a secondary phase is unacceptable because it will either seriously reduce the feed processing rate or it will lead to an interruption in processing. Because the secondary phase cannot be removed under normal operating conditions, secondary phases should be prevented through the proper design of the glass composition.

Through laboratory testing, coupled with the use of empirical models for waste form design, the reference glass composition, designated HW39, was formulated. At a waste loading of 25 wt%, the glass had acceptable viscosity and electrical conductivity properties. No liquid-liquid phase separation was observed in HW39 glass. However, crystallinity was detected in the as-melted and heat-treated HW39 glass due to the Cr_2O_3 concentration in the glass. The solubility of Cr_2O_3 in these borosilicate glasses was determined to be less than 0.5 wt%. HW39 glass contained 1.33 wt% Cr_2O_3 . Analysis had identified the crystals as cubic spinels (Fe-Cr-Ni) with an average size of 8 μm . Because of their small size, the crystals were expected to remain suspended by the melter tank natural convection currents. The tendency towards settling and any possible agglomeration of the crystals under actual melter processing conditions could not be adequately addressed by laboratory testing. Therefore, the impact of the crystallinity on processing could only be adequately assessed with actual melter testing.

Feed Formulation

The HWVP melter slurry must pass through several process steps before it is delivered to the melter. The waste is first concentrated by more than a factor of five from a dilute concentration of 19 g equivalent oxides/L. Glass-forming chemicals and redox-controlling agents must then be added to make the melter feed. The melter feed contains dissolved salts and insoluble particles that must be homogenized and maintained as a homogeneous slurry until the feed reaches the melter. The chemical and rheological properties of the slurry must therefore be adjusted to assure that the slurry can be successfully blended, concentrated, agitated, and pumped. Criteria used in developing an acceptable slurry were based upon DWPF process technology and slurry property requirements. Melter feed specifications for the DWPF are shown in Table I.⁷ The objectives of these laboratory studies

TABLE I

Specifications for DWPF Melter Feed Properties

Property	Acceptable Range
Density, g/ml	1.29 to 1.46
pH	Less than 8
Concentration, wt% total solids (dried at 105°C)	40 to 50
Consistency, cP	10 to 40
Yield point, dynes/cm ²	
Range	25 to 150
Design value	80

were to: 1) define an acceptable waste simulation, 2) recommend the method of glass-former and reductant addition, and 3) specify any additives to adjust slurry rheological properties.⁸

A treatment process adopted from the DWPF flow-sheet is the addition of formic acid to the waste slurry. Used by the DWPF to recover mercury, this treatment was found to significantly improve the suspension of the waste sludge, resulting in more favorable rheological properties. The quantity of formic acid added is based upon the concentration of mono- and divalent hydroxides in the waste. The stoichiometric quantity of formic acid for the simulation is 0.29 mole/L of melter feed at 400 g total oxides/L (TO/L).

Another process adopted from the DWPF was the use of a high-pressure water-frit method of canister decontamination. The contaminated frit slurry will be used as approximately one-third of the required glass formers. The remaining glass-forming chemicals can be added either as frit or as unreacted chemicals. Unreacted chemicals that were studied included nitrates, carbonates, oxides, formates and oxalates. Based on laboratory test results, two glass-former addition cases were recommended.⁸ Both cases met rheological property criteria for melter feed. The first case required frit as the sole glass-former source. The particle size of the frit was specified in two classifications. They are: 1) the one-third fraction coming from the canister decontamination with a size distribution of -80+200 mesh (177 to 74 μm) and 2) the remaining two-thirds of the frit being -200 mesh. The smaller -200 mesh frit was more likely to remain suspended, and its use improved the feed rheological properties. The second option used unreacted chemicals as glass-formers. The particular salt combination was designed to result in acceptable slurry rheological properties and a ferrous-to-ferric ratio of the feed close to the 0.1 to 0.3 range. Both feed slurries had a TO/L content of 400 grams. Reductant was also added to assure that the glass melt achieved the proper redox state. In both cases sugar was added as the reductant. The resulting feed slurry compositions to be processed in melter experiments are shown in Tables II and III. Both compositions were tested in a five-day engineering-scale melter experiment. Based on test results, the slurry composition with superior processing characteristics was selected for verification in a long-term pilot-scale melter experiment.

ENGINEERING-SCALE EXPERIMENT

The primary objectives of the engineering-scale melter experiment were to evaluate processing characteristics of the two candidate slurries and the quality of the product glass. During the five-day experiment, the slurry compositions were evaluated at design and maximum feeding rates. Design rates are those rates that can be maintained indefinitely within the following constraints: 1) the cold-cap coverage was not to exceed 80% of the glass surface, 2) off-gas venting was to be stable with minimal surges, and 3) glass, plenum, electrode and off-gas temperatures were to be stable over time. Processing at maximum rates would achieve cold-cap coverages of up to 95% with stable glass, plenum, electrode and off-gas temperatures. Off-gas venting would be expected to have more active surging events. However, the frequency of surges could not indicate a degrading situation.

To evaluate the processing characteristics of the slurries, we evaluated cold-cap thickness, spreading ability of the slurries on the glass melt, flexibility of the cold cap, venting behavior, and the time it

TABLE II

Simulated Waste Fraction of Melter Feed Slurry^(a)

Melter Feed Slurry		Resultant Glass		
Compound ^(b)	Concentration (g/L)	Assumed Oxide	Concentration (g/L)	Glass (wt%)
Fe(OH) ₃	59.5	Fe ₂ O ₃	44.4	11.10
Al(OH) ₃	26.3	Al ₂ O ₃	17.2	4.30
NaNO ₃	13.4	Na ₂ O	10.7	2.68
Cr(OH) ₃	7.21	Cr ₂ O ₃	5.3	1.33
NaOH	3.58	ZrO ₂	2.4	0.60
Na ₂ C ₂ O ₄ ^(c)	3.37	SiO ₂	3.0	0.75
Zr(OH) ₄	3.11	NiO	2.4	0.60
SiO ₂	3.00	SO ₃	1.5	0.38
Ni(OH) ₂	3.00	La ₂ O ₃	2.2	0.55
Na ₂ SO ₄	2.32	MoO ₃	1.2	0.30
LaF ₃	2.16	Nd ₂ O ₃	2.1	0.53
Na ₂ MoO ₄ · 2H ₂ O	2.00	Cs ₂ O	1.0	0.25
Nd(OH) ₃	1.84	CeO ₂	0.7	0.18
CsOH	1.05	CuO	0.6	0.15
Ce(OH) ₃	0.79	MnO ₂	0.7	0.18
Cu(OH) ₂	0.74	BaO	0.4	0.10
Mn(OH) ₂	0.74	F ⁻	1.2	0.30
BaSO ₄	0.63	SrO	0.4	0.10
NdF ₃	0.58	Pr ₆ O ₁₁	0.4	0.10
Sr(OH) ₂	0.47	MgO	0.3	0.08
Pr(OH) ₃	0.47	CaO	0.3	0.08
La(OH) ₃	0.47	Y ₂ O ₃	0.2	0.05
NaF	0.47	Sm ₂ O ₃	0.2	0.05
Mg(OH) ₂	0.42	TOC	0.6	0.15
CaF ₂	0.42	I ⁻	0.04	0.01
Y(OH) ₃	0.26			
Sm(OH) ₃	0.21			
NaI	0.05			
SUBTOTALS	138.56 g/L		99.4 g/L	24.9%

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

(b) Prior to reaction with formic acid.

(c) TOC substitute.

took for the cold cap to melt into the bulk glass once feeding was stopped. It is evident that the tools used to evaluate how well a slurry composition behaved and processed in a melter were largely subjective. Therefore, it was important that all the operators made frequent comparative visual observations of the cold-cap condition to yield an evaluation that was as balanced as possible.

Equipment Description

The engineering-scale experiment was performed in PNL's high bay ceramic melter (HBCM), which is shown in Fig. 1. The glass tank has an exposed glass surface of 0.25 m², which is 1/10 scale of the proposed HWVP melter. The slurry processing capacity of the HBCM is in the range of 15 to 20 L/h. The melter front and back walls slope from 40.6 cm apart at the

glass overflow level to 31.8 cm apart along the floor. During operation, the normal glass depth is 21.6 cm. The resulting melt volume is approximately 55 L (138 kg at a glass density of 2.5 kg/L). Two Inconel-690[®] electrodes on opposing walls provide an electrical current through the glass melt to achieve the joule-heating effect.

Glass generated during the experiment was periodically transferred from the melt tank up a discharge riser using an air-lift bubbler. Air was bubbled into the riser causing the air/glass mixture to rise into the overflow section discharge trough. The glass flowed down the trough and off the face block into receiving drums.

Operating Procedures

During the experiment, the use of operating constraints assured consistency of operation by providing guidance for the operation of the melter system. Some of the important operating constraints follow.

- The melter is to be operated at an average bulk glass temperature of 1150°C ± 50°C.
- Electrode temperatures are to be maintained below 1000°C.
- Melter vacuum is to be maintained at 12.7 cm WC.
- The overflow section temperature is to be maintained at 1075°C ± 25°C.

Data generated during the experiment was continuously recorded on strip and multipoint recorders. Also, to aid in data analysis and provide added monitoring and recording capabilities, the data points were also monitored by a Hewlett-Packard 3497A data acquisition and control system, interfaced with a HP9836 desk-top computer.

Throughout the experiment, samples of the feed and off-gas scrub solution were sampled every two hours for post-test analysis. In addition, glass samples were obtained during every pouring event. Cold-cap samples were taken at the end of processing each slurry to be analyzed for compositional segregation and for evidence of crystals or unreacted carbon.

Test Results

Experimental results are summarized in Table IV. The waste+frit feed slurry case was processed for 72 h, 24 h longer than the waste+frit+salts case. The first 24 h of feeding to the melter allowed the melter to equilibrate from an idling mode to an operating mode. Results of only the final 48 h of the waste+frit case are relevant.

Melter operating conditions were similar during both phases of the experiment. Throughout the experiment the operators faithfully followed the operating constraints. The operating bulk glass temperature was 1150 to 1200°C for the majority of the experiment. The 20°C higher average off-gas temperature for the waste+frit+salts case was indicative of the lower processing rates achieved with this slurry composition. Both feeds pumped well with no feed-related problems. The glass melt was stable throughout the experiment because no foaming of the melt occurred. The ferrous-to-ferric ratio of the glass melt was 0.04 during the first three days, when the waste+frit

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TABLE III

Glass-Forming Fraction in Melter Feed Slurry

Glass Formers		Resultant Glass		
Compound	Concentration (g/L)	Oxide Form	Concentration (g/L)	Glass (wt%)
<u>Case 1: 100% Frit</u>				
HW39 Frit ^(a)	300.0	SiO ₂	201.8	50.44
		B ₂ O ₃	38.2	9.56
		Na ₂ O	30.8	7.69
		Li ₂ O	15.0	3.75
		CaO	11.2	2.81
		MgO	3.0	0.75
SUBTOTALS	300.0 g/L		300.0 g/L	75.0%
<u>Case 2: 1/3 Frit; 2/3 Unreacted Chemicals</u>				
HW39 Frit ^(b)	100.0	SiO ₂	201.8	50.44
SiO ₂	134.4	B ₂ O ₃	38.2	9.56
NaCHO ₂	20.0	Na ₂ O	30.8	7.69
Na ₂ B ₄ O ₇ · 10H ₂ O	69.9	Li ₂ O	15.0	3.75
LiCHO ₂ · H ₂ O	46.9	CaO	11.2	2.81
Mg(NO ₃) ₂ · 6H ₂ O	12.8	MgO	3.0	0.75
Ca(NO ₃) ₂ · 4H ₂ O	31.6			
SUBTOTALS	425.6 g/L		300.0 g/L	75.0%

(a) HW39 frit size distribution as follows: 1/3 to be -80+200 mesh
2/3 to be -200 mesh.

(b) HW39 frit size distribution as follows: -80+200 mesh.

slurry was processed. Although below the pre-run target range of 0.1 to 0.3, the melt was sufficiently reduced to prevent any reboil occurrences. The ferrous-to-ferric ratio over the last two days of the experiment steadily rose to a range of 0.2 to 0.3.

The overall performance of the waste+frit slurry was very good. Feed rates up to 14 L/h (56 L/h·m²) were achieved. Design rates ranged from 10 to 12 L/h (40 to 48 L/h·m²) for most of the two-day period. The cold cap was very flexible, and numerous vents were visible in and around the cold cap. This indicated that decomposition gases could readily escape from within and beneath the cold cap. The cold cap was 2.5 to 5 cm thick. The cold-cap coverage during feeding was 50-80% of the melt surface.

Processing the waste+frit+salts slurry resulted in substantially lower feeding rates. The design feed rate was only 8 L/h (32 L/h·m²). The maximum rate established was 8.9 L/h (35.6 L/h·m²). This rate was maintained over a 12-h period with a cold-cap coverage that approached 100%. The cold cap produced by this feed tended to be thicker and more rigid. At 2.5 to 7.5 cm thick, the cap displayed very little flexibility or venting action. Cold-cap coverage ranged from 70% to as high as 100% for short periods. Due to a lack of visible venting, the cold cap was presumed porous and therefore more insulating, resulting in lower heat transfer rates. The insulating properties of the thick cold cap seemed to limit the feed rate, contributing to the overall poor performance of this slurry composition.

Glass samples obtained during the 5d experiment were evaluated for viscosity, electrical conductivity, and composition. The viscosity and electrical-conductivity curves as functions of temperature were very close to laboratory results. The T100P temperature of the melter glass was 1095°C, compared to 1124°C in the laboratory glass. The slopes of the melter and laboratory glass viscosity curves were similar, but the curves were offset approximately 30°C lower. An electrical conductivity value of 0.30 (ohm·cm)⁻¹ was obtained for both the melter and the laboratory glasses at a temperature of 1150°C. The conductivity-versus-temperature curves were nearly identical.

Glass samples from the two parts of the test had approximately the same quantity of crystalline material as was observed in the laboratory, approximately 1-4 vol%. The crystalline phase material in both the laboratory glass and the bulk melter glass was a Fe-Cr-Ni cubic spinel. The crystal size range in the melter glass was similar to the spinel size range seen in laboratory glasses, 5-20 μm. However, the crystals agglomerated to an average diameter of 50 μm with a maximum size of 80 μm. Compositional analyses of glass samples indicated 5-10 wt% lower chrome oxide concentrations than those reported from feed analyses. Apparently, the order-of-magnitude increase in crystal size led to a significant amount of settling in the melter. Samples of the cold cap that were analyzed contained the cubic spinel in the already agglomerated state. Therefore, some or all of the spinel crystal agglomeration occurred in the cold-cap

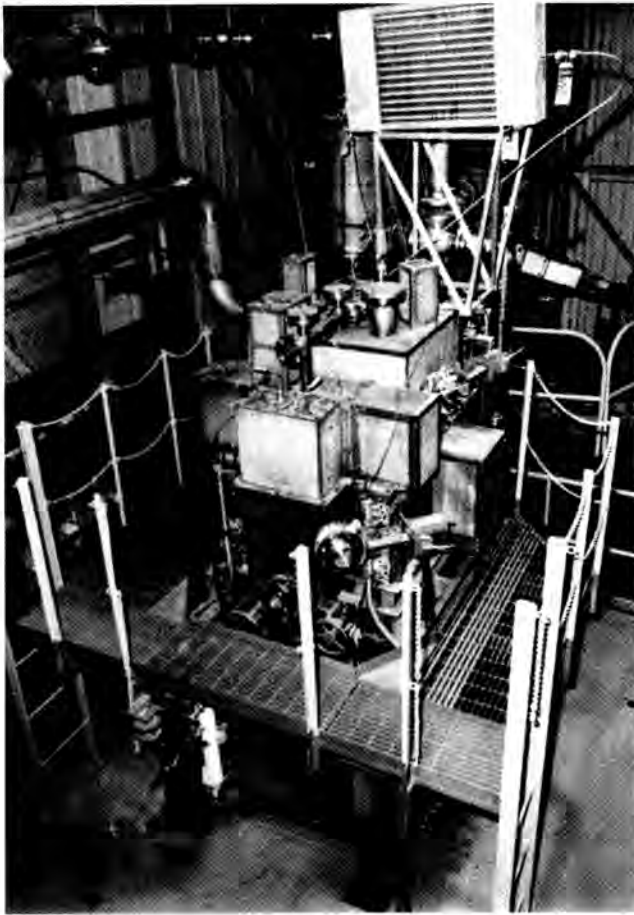


Fig. 1. High bay ceramic melter.

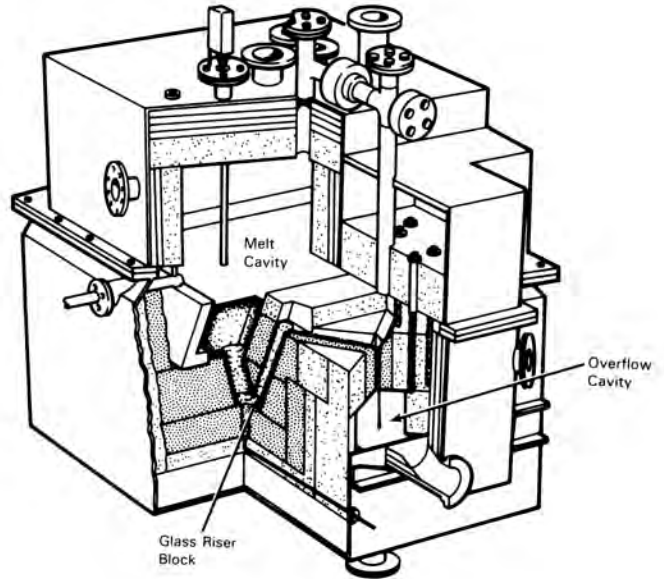


TABLE IV

Summary Data of HBCM Experiment

Summary Item	Slurry Type	
	Waste+Frit	Waste+Frit+Salts
Test Period, h	71.6	47.75
On-Line Efficiency, %	91	100
Slurry Oxide Loading, g/L	396	365
Total Slurry Processed, L	687	407
Est. Glass Produced, kg	272	149
Avg. Feed Rate, L/h ^(a)	10.5	8.5
Avg. Bulk Glass Temperature, °C	1150-1200	1150-1200
Avg. Off-Gas Temperature, °C (measured at Venturi)	425	445

(a) Based on actual feeding time and total slurry processed.

region. Because the laboratory tests did not duplicate the time-temperature conditions existing in the cold cap, it is understandable that agglomerations of the spinels were not observed in the laboratory.

Based on the results of this HBCM experiment, the long-term, pilot-scale experiment was planned. The candidate slurry that included frit as the sole glass-former source was selected for further testing based on its superior performance during the HBCM experiment. In addition, a ferrous-to-ferric ratio as low

as 0.1 was adequate for glass melt stability. One of the objectives was to continue to characterize the potential for spinel crystals to form, agglomerate, and settle to the melt-tank floor.

PILOT-SCALE EXPERIMENT

The purpose of the pilot-scale ceramic melter (PSCM) experiment was to evaluate the processing and product quality of the proposed feed and glass compositions on a pilot scale under long-term operating

conditions. The objectives included evaluation of the slurry processing characteristics in the melter, the melt stability through redox control by addition of reductants to the feed, off-gas equipment performance, and continued evaluation of the existence and impact of crystals in the bulk glass. The slurry composition was as shown in Tables II and III. In addition, 9.2 g/L of formic acid were added during the waste forming process, and 3 g/L of formic acid were added to each 300 g/L of frit to aid frit suspension per the DWPF flowsheet.⁷ The processing evaluation was similar to the ESCM experiment in identifying cold-cap thickness, spreading ability of the slurry, and cold-cap venting and flexibility.

The experiment was divided into three segments. During the first part of the experiment the feed slurry would be processed at a ferrous-to-ferric ratio of 0.1. Laboratory tests had determined that 3.5 g/L of sugar should be added to the feed slurry to achieve this state of redox. Once steady state was achieved (we allowed 72 h), the slurry was tested in the melter for an additional 120 h to obtain feeding rate and off-gas system performance data. At the end of this period the feeding was interrupted to allow changing over to feeding slurry without the added sugar reductant. Eight days of testing were conducted to evaluate the processing characteristics without the added reductant; specifically, whether the melt would remain stable or reboil would occur at various processing rates (design maximum and overfeeding). Performance evaluations of off-gas equipment were continued during this period.

Equipment Description

The PSCM and associated support equipment are shown in Fig. 2. The glass tank has an exposed glass surface of 0.73 m² which is almost 1/3-scale. The

melt tank is rectangular with dimensions of 69 cm wide by 104 cm between the two electrodes. At a normal glass overflow depth of 37 cm the melt volume is 270 L. The electrodes are single 5-cm thick Inconel-690 plates with 5-cm thick feet that extend 13 cm into the melt. The feet cause the electrical current flux to be skewed slightly towards the floor of the melt tank. The additional heating helps to prevent spinel sludge formation from occurring.⁹

The glass is discharged from the tank through a 7.6-cm riser port located near the melter floor in the center of the refractory wall. Glass from the melter can be discharged continuously or in batches via an air-lift bubbler. Glass flows from the riser, down the discharge trough and off the face block. The glass product is received in either 55-gal drums or instrumented canisters. The overflow glass discharge section is maintained at 1000 to 1100°C by six spiral, bayonet-type silicon carbide heating elements.

The plenum space vacuum is maintained at 12.7 cm WC by the off-gas system. This system consists of a film cooler (located in the melter off-gas lid nozzle), ejector venturi scrubber (EVS), packed-column, steam-atomized scrubber (SAS), and a high-efficiency mist eliminator (HEME). The operation of these systems is presented in references 10 and 11 and so will not be described here.

Operating Procedures

Operating constraints for this experiment were similar to those in the HBCM experiment. Additional constraints were as follows.

- During attainment and operation at design processing rates, the plenum temperature did not drop below 275°C ± 25°C.

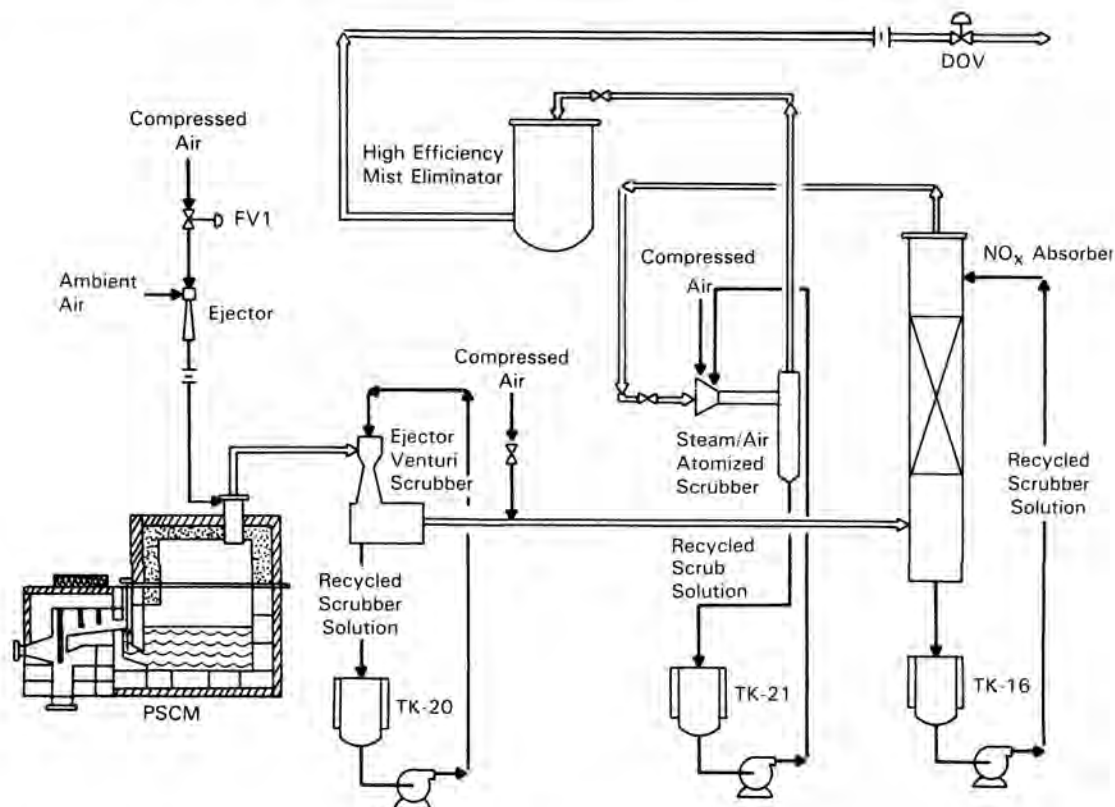


Fig. 2. PSCM and associated off-gas treatment equipment.

- During operation at maximum rates, the plenum temperature did not drop below $225^{\circ}\text{C} \pm 25^{\circ}\text{C}$.

Data generated during the experiment was continuously recorded on strip and multipoint recorders. In addition, the Hewlett-Packard data acquisition system was again used to monitor and store data.

Samples of the feed and off-gas scrub solution were routinely sampled every two hours for analysis. In addition, glass samples were obtained during every pouring event, and cold-cap and glass tank samples were also taken.

Test Results

The PSCM experiment successfully processed ~16,000 L of simulated melter feed slurry. The test duration was 384 h, during which time ~6250 kg of glass product were produced. The following three sections, "Processing Characteristics," "Off-Gas System Performance," and "Spinel Crystal Settling," present and discuss the PSCM test results.

Processing Characteristics

A summary of the experiment is provided in Table V. The periods of testing using slurry without sugar and when sugar was added are shown separately. It is obvious from the data that the slurry processed at a higher rate when sugar was not present in the melter feed.

The operational control parameters of the experiment are plotted in Figs. 3 and 4. The plenum temperature operated between 200 and 400°C throughout the test period. The changes in temperature correspond to changes in melt surface coverage. The average glass temperature was maintained within operational constraints for the majority of the experiment. For short periods the indicated temperature surpassed 1200°C ; however, they do not appear in the averaged data plotted in Figs. 3 and 4. Values for the average bulk glass temperature and electrode power throughout the experiment were unsteady. This was due to the Inconel-690 crystal settling boat that was placed near the thermowell and electrode foot on the melt tank floor prior to the experiment. Once processing began and the electrode current was increased, partial shorting of the current apparently occurred. As a result, the electrode power readings fluctuated and

required constant adjustment. It is also theorized that localized heating of the glass in the area of the thermowell occurred, resulting in high temperature indications that were not representative of the bulk of the glass.

A plot of feed rate versus time is shown in Fig. 5. Each data point represents a 6-h average rate. Startup of the melter lasted three days with the feed rate being maintained at an average value of 32 L/h. The cold cap coverage of the glass surface ranged from 60-75%, with good flexibility and venting. Based on visual observations, cold-cap thickness ranged from 2.5 to 5.0 cm. Plenum temperatures remained high (greater than 300°C). Following startup, a design feed rate was established at 37 L/h ($51 \text{ L/h}\cdot\text{m}^2$) and maintained for 120 h. Feed rates greater than 40 L/h were maintained during this time for periods of 6-12 h. However, these rates could not be maintained based upon the operating constraints. The maximum feed rate was established at 41 L/h ($56 \text{ L/h}\cdot\text{m}^2$) during the final 18 h prior to switching over the feed slurry containing no sugar. Cold-cap thickness ranged from 4.0 to 6.0 cm for the design-rate period and from 5.0 to 6.5 cm for the maximum-feed-rate period.

After 186 h of operation, feed to the melter was stopped and the cold cap was allowed to melt. The feed tank was recharged with slurry feed that did not contain sugar. This slurry was processed for 198 h, including an 18-h restart period to allow for re-establishing steady-state conditions. The average feed rate during the startup period was 36 L/h. A design feed rate of 45 L/h ($62 \text{ L/h}\cdot\text{m}^2$) was sustained for 96 h. The maximum rate established and maintained was 53 L/h ($73 \text{ L/h}\cdot\text{m}^2$) over a 78-h period. Processing characteristics for the feed with and without sugar were similar except for achievable processing rates where the feed without sugar was 22 to 29% higher. The cold cap was very thin and flexible. Vents were numerous, and the glass surface near the cold cap was active, even vigorous at times.

Results of the HBCM experiment indicated that a design feed rate of $48 \text{ L/h}\cdot\text{m}^2$ was possible. A design rate of $51 \text{ L/h}\cdot\text{m}^2$ was reached with the feed containing sugar. Therefore, the HBCM, which processed a slurry containing sugar, and PSCM experiments showed good agreement in the processing rate of the simulated feed. The glass melt was stable during the entire

TABLE V

Summary Data of PSCM Experiment

Item	Test Period	
	Slurry With Sugar	Slurry Without Sugar
Test Period, h	186	198
On-Line Efficiency, %	99	99
Slurry Oxide Loading, g/L	389	381
Total Slurry Processed, L	6737	9213
Est. Glass Produced, kg ^(a)	2621	3510
Design Feed Rate, L/h ($\text{L/h}\cdot\text{m}^2$)	37 (51)	45 (62)
Max. Feed Rate, L/h ($\text{L/h}\cdot\text{m}^2$)	41 (56)	53 (73)
Ferrous-to-Ferric Ratio		
Feed Slurry	0.104	0.002
Glass	0.160	0.015

(a) Based on reported total slurry processed and slurry oxide loading values.

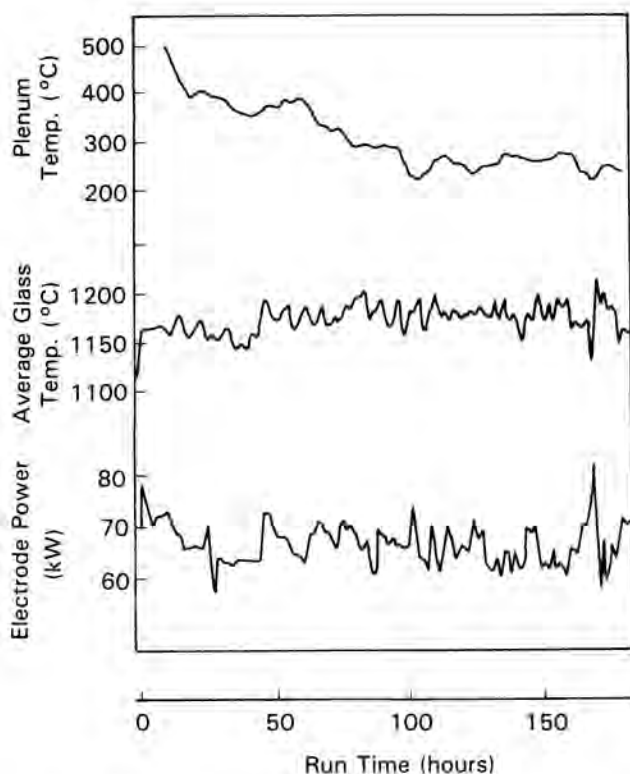


Fig. 3. Operational control parameters for the first 200 h of the PSCM experiment.

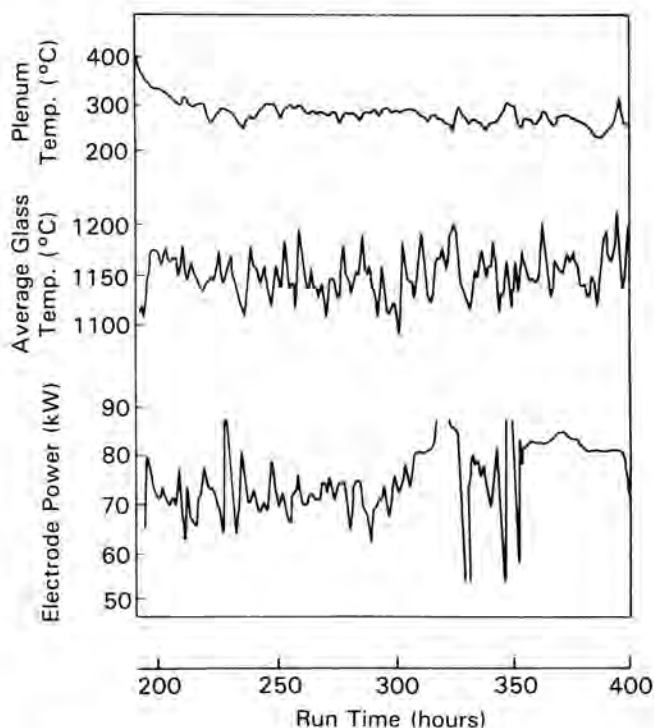


Fig. 4. Operational control parameters for the final 200 h of the PSCM experiment.

experiment, even under only very slightly reducing conditions. Even though no sugar was added to the feed during the second half of the experiment, the ferrous-to-ferric ratio remained greater than zero. The forming step used in feed preparation, along

with formic acid added with the frit-addition step, added sufficient carbon to maintain the slurry composition in a reducing condition. Based upon melter stability and the higher processing rates obtained without sugar, a minimal ferrous-to-ferric ratio (less than 0.1) is desired.

Off-Gas System Performance

Effluent sampling was performed to characterize volatile and particulate releases from the PSCM and the scrubbing efficiencies of the off-gas equipment. Operational off-gas performance characteristics of the ejector venturi scrubber (EVS) and high-efficiency mist eliminator (HEME) were obtained throughout the experiment as were melter effluent emission characteristics. The performance of the steam-atomized scrubber (SAS) was evaluated during the last two days of testing. However, when not operating, the off-gas stream still passed through the SAS. The HEME was operated with and without a co-current water spray wash.

Feeds containing the formate anion are capable of producing significant concentrations of H_2 and CO. Previous PNL melter tests involving SRL-formated feeds have shown relative production rates of CO_2 , H_2 and CO to be 1, 0.5 and 0.1, respectively.¹² The relative production ratios of CO_2 , H_2 and CO observed during this experiment were 1, 0.1 and less than 0.1, respectively. The presence of highly oxidizing NO_x gases in the melter exhaust may have been responsible for reducing the net off-gas yield of hydrogen produced.

Melter gas-phase losses to the off-gas system were only significant for the elements B, C, N, S, and the halogens, which all readily form volatile acidic gases. This data is consistent with previous testing.¹² The presence of sugar had no effect upon melter volatility. The halogen feed components had the ability to penetrate all off-gas processing equipment studied.

Because effluent gas-phase losses were limited to B, C, N, S, and the halogens, most melter off-gas system losses were associated with aerosol emission. Off-gas equipment performance can be measured in terms of decontamination factors (DFs). A DF is the ratio of the gas-stream mass rate of a component exiting a device to the mass rate of that component entering the device. Therefore, the larger a DF is, the more efficient the device. The average feed component DFs established for the melter, EVS, HEME, and the SAS throughout the experiment are summarized in Table VI.

The melter performance in terms of DF was quite consistent and reasonable. The very low cesium (Cs) DF is associated with the presence of formate anion and is strikingly similar to previous PSCM data obtained during the processing of formated SRL feeds.¹² Formated feeds appear exceptionally effective in promoting the Cs volatilization/condensation process in the melter plenum. As a result, they have been responsible for the lowest recorded melter Cs DFs measured at PNL. It should be noted that the sugar component of the feed had no apparent influence upon Cs or, for that matter, overall melter losses.

Like the halogens, sulfur exhibited a very low average melter DF of 1.8. The additional formic acid added with the frit addition (3 g/L of melter feed) may have been responsible for promoting higher volatile loss rates of sulfur than those that occurred during the HBCM experiment.

The total melter DF for Ru was determined only during one day when it was added directly to the

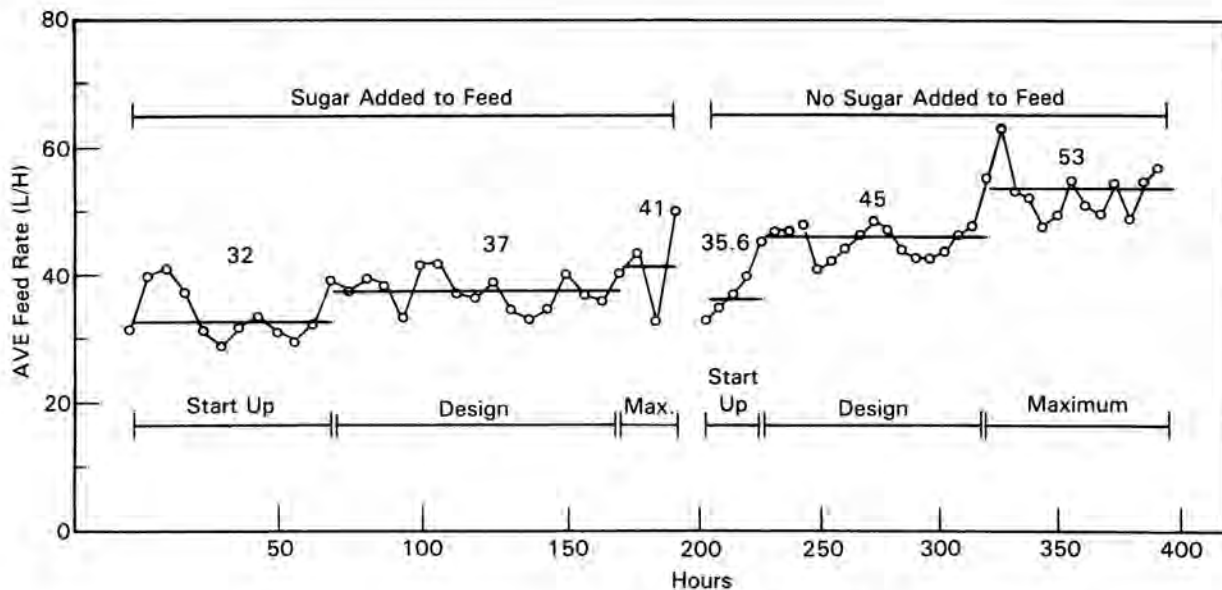


Fig. 5. Plot of feed rate versus time of the PSCM experiment.

TABLE VI

Average Elemental Decontamination Factors for the Melter and Off-Gas System

Element	Melter	EVS	HEME	SAS
Al	750.0	32.0	10.0	4.5
B	63.0	11.0	7.5	6.2
Ba	190.0	290.0	8.7	7.3
Ca	730.0	160.0	3.0	5.9
Ce	450.0	--	--	--
Cl	1.3	6.2	14.0	4.9
Cr	180.0	14.0	16.0	5.3
Cs	14.0	1.4	19.0	4.3
Cu	250.0	7.2	16.0	7.3
F	3.2	14.0	6.1	3.5
Fe	260.0	92.0	44.0	6.1
I	1.3	--	--	--
La	610.0	440.0	--	--
Li	500.0	2.6	19.0	5.0
Mg	630.0	94.0	1.0	1.2
Mn	300.0	220.0	36.0	5.5
Mo	57.0	1.6	19.0	4.8
Na	260.0	2.1	17.0	5.0
Nd	290.0	190.0	--	--
Ni	2100.0	3.7	64.0	6.1
Ru	42.0	1.4	32.0	4.8
S	1.8	4.3	18.0	2.3
Si	780.0	59.0	--	1.1
Sr	230.0	260.0	6.2	11.0
Ti	250.0	970.0	41.0	18.0
Zn	160.0	19.0	3.9	1.4
Zr	420.0	670.0	25.0	8.8
Total	180.0	5.0	5.6	1.7

melter feed tank. Its relatively low DF of 42 is indicative of an initial volatilization mechanism; however, its subsequent conversion to an aerosol is quite prompt because all detected Ru melter off-gas system emissions were confined to the aerosol sample fraction.

The performance of the EVS was quite predictable. This type of scrubber is a low-efficiency device that is only designed to deal with large-diameter aerosols. As a result, EVS elemental DFs should be direct measures of the mass mean diameters of the aerosols responsible for individual feed component

losses. The low aerosol DFs are probably attributable to the fact that a film cooler device was used upstream of the EVS. Because the film cooler used a noncondensable gas (air) as sweep gas, the dilution of the off gas by the air upstream of the EVS resulted in reduced contacting and a resultant lower scrubbing efficiency. Steam collapse of the off-gas during EVS quenching was also significantly reduced or eliminated by film cooler operations that may have contributed to the poor performance.

Because most aerosols penetrating the EVS are submicron, they all exhibited essentially the same HEME DFs. Effluents with volatilized components exhibited lower-than-average DFs. The variability associated with the HEME results is a reflection of analytical uncertainties at or near detector limits. The Cs DFs recorded during this experiment were a factor of ~3 higher than has been observed during previous PSCM testing. These DFs, however, remain a factor of 3 below HEME design expectations. The reason for deficient performance may involve solution breaching of the filter element. Use of a water spray at the HEME inlet did not impact the HEME DFs. However, the mist carryover from the packed tower probably introduced as much moisture as did the 16-ml/min water spray when used. Only dry operation of the HEME has been successful in producing acceptable HEME performance (DF=50) at PNL.¹¹

The SAS elemental DFs observed during the experiment were mostly lower on the average than values recorded for the HEME. Moreover, the DFs observed are not strongly element-dependent, which suggests that most aerosols penetrating the EVS are submicron. The single-stage Cs DFs observed during the experiment were an order of magnitude lower than design values of 50 for a dual-cascade SAS system.¹⁰ If one optimistically assumed that the combined DF associated with cascaded SASs is the square of single-stage performance, the Cs DF for this test would have been ~20, which is significantly less than has been recorded at SRL.¹³

Spinel Crystal Settling

The extent of spinel settling was studied using glass samples and mass balance calculations. Glass samples were obtained from the settling boat, bulk

glass tank samples and overflow product glass. The glass collection boat had two chambers. The first chamber was covered after eight days of testing. The second chamber could not be covered at the end of the experiment due to a failed guide rod, and the data was lost. A cross-section sample of the boat glass was obtained and examined optically and by scanning electron microscopy/energy-dispersive x-ray (SEM/EDX) analysis. The top 2 cm of the glass sample had only a very few agglomerated crystals. This glass had a Cr_2O_3 content of 0.52 wt%, which is approximately the solubility limit of Cr_2O_3 in HW39 glass. The Cr_2O_3 concentration in the bottom 2.5 cm of the sample was 18.3 wt%. The crystal phase was estimated to be 19 vol%. The crystals were again agglomerated and had crystal diameters up to 80 μm .

The bulk tank glass samples provided a vertical core of the tank glass composition. The samples contained a significant amount of crystalline material. In all but the bottom 1.8 cm of the core, the amount and types of crystalline material resembled the phases observed in the output glass. The bottom 1.8 cm of the core contained a settled layer of material of much greater density than that of the upper portion of the core.

Evaluation of the day-to-day feed and glass analyses indicated that while the average feed content of Cr_2O_3 was 1.30 wt%, the average glass Cr_2O_3 content was only 1.18 wt%. Of this 9.2% difference, analytical error was estimated to account for ~4%. Therefore, ~5%, or 4.6 kg, of the Cr_2O_3 remained in the melter. Assuming a 19 vol% of crystals, based upon the boat analyses, the sludge thickness formed during the experiment would be ~1 cm.

Mass balance, melter core samples, and settling boat analyses indicate that a measurable amount of settling of chrome spinels occurred during melter processing of the HWVP composition. It is not known whether the layer will reach a steady-state thickness due to melter convection currents or continue to accumulate over time. Based on the measured and calculated thicknesses of spinels by the three methods mentioned, settling can be expected to continue in stagnant regions. In the well-mixed areas of the tank the extent of settling cannot be quantified without further study. Should settling continue under long-term processing conditions, the operational life of the melter could be unacceptably shortened. Rockwell Hanford Operations currently has an active program of tank sampling and characterization. Should the present level of chrome be verified, work will need to be initiated to identify solutions to the spinel settling problem through either modification of the glass composition or melter tank design.

CONCLUSIONS

Nonradioactive vitrification testing during two experiments has studied the processing characteristics of the slurry composition anticipated to be solidified in the Hanford Waste Vitrification Plant. Initial testing identified that glass formers should be added to the waste fraction as a frit to obtain optimum processing characteristics of the slurry. Subsequent testing on a pilot scale confirmed the acceptable processing characteristics. The forming process used in feed preparation added sufficient carbon to maintain the glass melt in a slightly reduced condition. This resulted in a stable glass melt that was insensitive to reboil induced by temperature change.

A significant amount of agglomerated chrome spinel crystals was formed during processing because the chrome content in the waste exceeds the glass solubility limit. As a result, some settling of the spinels occurred, resulting in approximately a 5% retention of chrome oxide in the melter tank. Under long-term processing conditions, if settling were to continue, the operating life of the melter could be shortened. Efforts are underway by Rockwell Hanford to verify the chrome content in the waste. Should the present chrome content be verified, work will need to be initiated to identify solutions through modification of the glass composition or possibly glass tank design.

Melter off-gas losses were found to be consistent with previous experimental processing of formated slurries. Ruthenium volatility loss from the melter was only 2% due to the reducing conditions of the melt. Off-gas scrubbing efficiencies of the high-efficiency mist eliminator and the steam atomized scrubber were a factor of 3 and 10, respectively, below design expectations. The impact of this data on the current equipment flowsheet is being evaluated.

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