**HANFORD WASTE VITRIFICATION PROGRAM
PILOT-SCALE CERAMIC MELTER TEST 23**

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ABSTRACT

The pilot-scale ceramic melter test, run number 23, was conducted to determine the vitrification processing characteristics of simulated Hanford Waste Vitrification Plant process slurries and the integrated performance of the melter off-gas treatment system. Approximately 15,000 L of a simulated melter feed was prepared and processed to produce 7,450 kg of glass. The vitrification system, which was operated for a 351-h period, achieved an on-stream efficiency of greater than 98%. The average melter feeding rate was $57.2 \text{ L/h}\cdot\text{m}^2$ ($1.4 \text{ gal/h}\cdot\text{ft}^2$) and a glass production rate of $28.4 \text{ kg/h}\cdot\text{m}^2$ ($5.8 \text{ lb/h}\cdot\text{ft}^2$) was achieved.

The melter off-gas treatment system included a film cooler, submerged bed scrubber, demister, high-efficiency mist eliminator, preheater, and high-efficiency particulate air filter (HEPA). Evaluation of the off-gas system included the generation, nature, and capture efficiency of gross particulate, semivolatile, and noncondensable melter products. The overall system solids decontamination factor (melter, submerged bed scrubber, demister, high efficiency particulate mist eliminator) was 1×10^7 . For semivolatile cesium in particular, the system elemental mass decontamination factor was 5×10^6 .

SUMMARY

The Hanford Waste Vittrification Plant (HWVP) is being designed for the Department of Energy under the management of Westinghouse Hanford Company to immobilize pretreated radioactive high-level waste as a glass for geologic disposal. Pilot-Scale Ceramic Melter (PSCM) operation with associated feed preparation and melter off-gas systems testing is being performed by Pacific Northwest Laboratory (PNL) to provide data for design, environmental permitting, waste form qualification, and operations. The PSCM test, run number 23, was conducted to determine the integrated performance of the melter off-gas treatment system and processing characteristics of simulated HWVP process streams. Subsequent to the test, the Defense Waste Processing Facility (DWPF) melter was established as the HWVP reference melter for design. The DWPF melter uses plenum heaters and has a different melt cavity geometry from the PSCM. These differences between melters may influence the application of melt processing from the PSCM to the DWPF melter design.

Following melter feed processing for 15 days, testing was conducted for five days to obtain off-gas treatment system performance data when the melter was in a non-feeding state at idling at temperature. During the melter feeding period, steady-state conditions were maintained in the PSCM. Melter off-gas characteristics and the chemical capture efficiency of the melter off-gas treatment equipment were determined for both melter feeding and idling conditions.

Feed was started to the melter on June 6, 1988, at 1100^(a) and continued for 351 h until June 21, 1988, at 0200. The feed rate to the melter averaged between 43 and 44 L/h [$-57 \text{ L/h} \cdot \text{m}^2$ ($1.4 \text{ gal/h} \cdot \text{ft}^2$)]. The melter feed was at a nominal total oxides concentration of 500 g total oxides per liter of feed. Taking into account downtime periods when feed was not being fed to the melter, an average feed rate for the entire test of just over 41 L/h was achieved. Approximately 15,000 L of melter feed were processed, resulting in approximately 7450 kg (16,390 lb) of glass product and a glass production

(a) Hours of the day were reported according to the 24-hour clock throughout this test.

rate of $28.4 \text{ kg/h}\cdot\text{m}^2$ ($5.8 \text{ lb/h}\cdot\text{ft}^2$). With the exception of short downtime periods, due primarily to feed pump difficulties and feed line and feed nozzle plugging, the PSCM operation was very stable. The on-stream melter processing efficiency was better than 98%.

Throughout the test, melter cold cap characteristics remained consistent during feeding. Vitrification processing behavior produced by the simulated melter feed composition was very good. The slurry spread over the glass and cold cap easily without accumulating. Venting was routinely observed from the cold cap, and the cap thickness appeared to remain consistent at about 2 to 5 cm (1 to 2 in.). The cold cap characteristics were very similar to the previous HWVP tests in which melter feeds based on neutralized current acid waste (NCAW) were processed.

Melter off-gas characterization demonstrated that most melter solids losses were associated with aerosol escape. The average size distribution of melter effluent aerosols was bi-modal. The larger sized particles ($>1 \mu\text{m}$ in diameter) were predominantly non-volatiles. The small-diameter component of the aerosol consisted of semi-volatiles.

Aerosol entrainment losses were very low during steady-state melter feeding conditions. Well over half of the airborne particulate mass leaving the melter was associated with aerosols having aerodynamic diameters less than or equal to $1 \mu\text{m}$. Because of this behavior, average melter decontamination factors (DFs) for all but the most volatile feed components were found to be significantly greater than expected for a remote production facility. Semi-volatile emissions are also responsible for most melter off-gas losses during idling; however, these emissions do not place any additional functional requirements on the off-gas system. Melter-generated combustible gases do not present an off-gas flammability hazard under any of the operating conditions investigated during the test.

The submerged bed scrubber (SBS) performed both of its major off-gas functions well. As an off-gas system quencher, it successfully reduced the temperature of the off-gas stream to below 30°C and condensed 84% of the process steam. As an effluent scrubber, it essentially removed all effluent

aerosols with diameters larger than $1\text{ }\mu\text{m}$ and provided significant semi-volatile off-gas decontamination. No correlation between aerosol scrubbing efficiency and melter off-gas flow rate was observed for the range of flows tested. The overall melter DF was a very strong function of melter entrainment rates. Reentrainment of SBS scrubbing liquor and previously removed effluent was found to be an insignificant effluent source during both processing and idling. Melter idling was not found to increase effluent concentrations in the SBS exhaust. A particulate solids gradient was found to exist in the SBS tank because of insufficient agitation. It is not clear whether the solids accumulated at a sustained rate or if the gradient is a steady-state phenomenon. Although the SBS gas scrubbing capabilities have not been fully evaluated, SBS NO_x removal efficiency was ~1%. This low efficiency was due to both low NO_x concentrations and high $\text{NO}:\text{NO}_2$ ratios.

The high-efficiency mist eliminator (HEME) exhibited very high aerosol removal efficiencies under all off-gas flow and inlet water loading conditions used during PSCM-23. Definitive assessments concerning the effects of off-gas flow rate, off-gas moisture loading and idling upon HEME performance could not be made because of the variable nature of the limited data available. The HEME effectively removed all off-gas aerosols having diameters greater than $0.5\text{ }\mu\text{m}$, and reduced aerosol concentrations to values so low that the service life of high-efficiency particulate air (HEPA) filters under these conditions was estimated to exceed a service life of 1 yr. The HEME-captured effluent was effectively purged from the filter element by collection and run off of the normal SBS mist carryover (100 mg/scfm). Increases in pressure resulting from particulate buildup were not observed under any of the operating conditions of the test. The use of 15 L/h humidifying spray did cause a 50% increase in the normal operating pressure drop across the HEME filter element. Because of the high surface area of the HEME filter element and the long residence times of filter purge water, the HEME aqueous waste stream is more concentrated in semi-volatiles, halogens, sulfates, nitrates, and acidity than SBS solutions and is consequently more corrosive.

The film cooler was successfully used throughout the duration of the melter test, and no significant solids accumulations were found in the melter/SBS off-gas jumper. However, feed and glass entrainment was so low

during the present test that off-gas jumper conditions may not be totally attributable to film cooler operations. The chevron demister was found to have little effect on the SBS exhaust under normal SBS operating conditions but was quite useful in removing large quantities of water carried into the off-gas system when the SBS operation was destabilized by an inadequate tank fluid level. No operational difficulties were encountered with the HEPA filter during its limited time of evaluation during PSCM-23 testing.

Based on revisions to the reference HWVP feed, a pretreated NCAW, modification of the glass-forming frit composition was required. The revised NCAW composition, designated NCAW'87, had lower fractions of iron and aluminum and higher concentrations of sodium, zirconium, and uranium. To compensate for these changes, the glass-former frit composition had increased concentrations of silica and boron and reduced concentrations of sodium and calcium. The resulting viscosity and electrical conductivity, properties critical to melter operation, had values of 64 poise and $0.26 \text{ (ohm-cm)}^{-1}$, respectively, at the nominal melter operating temperature of 1150°C . No evidence of spinel formation in the product glass (quenched samples) was found in PSCM glass samples.

The durability of the revised glass composition, HW-39-4, was found to be comparable to the previous test glass, HW-39-2, under MCC-1 7- and 28-day leach test conditions. However, the durability of HW-39-4 glass under MCC-3 test conditions was poorer than that of the HW-39-2 glass. The HW-39-42 test glass durability met the proposed leach rate requirements for disposal.

As part of the PSCM-23 test, the method of HWVP feed simulation was revised to more realistically simulate the expected feed stream. Rather than purchase the major feed chemicals as commercially available hydroxides, a precipitation technique was established. Based on FY 1987 work at PNL and on feed preparation methodology developed at Savannah River Laboratory, the major hydroxide metals (iron, aluminum, nickel, and zirconium) were prepared from nitrates. Through neutralization and washing steps, the basic feed stock was prepared. Once received at PNL, the remaining chemicals were blended with the precipitated hydroxide slurry. The final feed slurry was found to have satisfactory feed handling properties. The apparent viscosity

and yield stress measured for PSCM-23 samples were 1/3 to 1/2 and 20X to 50X less, respectively, than 1987 laboratory samples similarly prepared.

The HWP process flowsheet includes treatment of the received feed with formic acid to improve the feed's rheological properties and provide an organic reductant for melter processing requirements. Approximately the same quantity of formic acid (10 g/L of 90 wt% formic acid) appeared to achieve an acceptable slurry rheology. However, due to a higher concentration of nitrates in the NCAW'87, additional reductant was required to achieve the slightly reducing glass melt conditions required in the melter. As a result, a total of 24.6 g/L of 90 wt% formic acid and 10 g/L of sugar were used in the melter during PSCM-23.

During treatment of the simulated slurry with formic acid (at 90°C), a stable layer of foam formed in three of the five batches of feed that were prepared. It appears that a higher level of surface turbulence prevented foam layers from being established in two of the five batches. However, once the foam layer had been established, increasing agitation of the batch did not dissipate the foam layer. In extreme cases, the addition of formic acid to the batch had to be halted for a period to allow the foam layer to dissipate.

The overall heat transfer coefficient was estimated in pilot-scale, non-prototypic equipment during the boiling/concentration of one batch of the feed slurry. A value of 88 Btu/h·ft²·°F (±50%) was calculated. Heat losses from the tank were estimated to account for less than 15% of the heat input to the tank. The measured overall heat transfer coefficient is lower than equivalent full-scale, prototypic test values measured at the Savannah River Laboratory using DWF slurry.

Materials testing was also performed during PSCM-23 to evaluate the performance of selected materials exposed to the simulated HWP process conditions in the PSCM and off-gas systems. Metal coupons were installed in the PSCM plenum space above the glass pool and in the SBS, both in the condensate solution and in the gas space above the solution. Alloys tested in the

melter plenum were Inconel^(a) 690, Incoloy^(a) 825, Haynes^(b) 214, Haynes 556, and Hastelloy^(c) C-276. The melter coupons exposed to feeding-only conditions resulted in measurable but slight corrosion, in general showing only tenths of a mil per year. Corrosion rates during idling-only periods were significantly higher, ranging from a few mil/yr to tens of mil/yr. The samples from combined feeding and idling periods, expected to exhibit the most severe corrosion, actually ranged between the feeding and idling rates. The INCO materials (Inconel 690 and Incoloy 825) and the Haynes 214 were most resistant to both feeding and idling conditions.

The SBS coupons (Hastelloy C-276, Alloy 20 Cb-3, and 304L-SS) showed very little corrosion during the melter run. Differences in the vapor space and submerged corrosion rates were measurable, tenths of a mil/yr in the vapor space compared to hundredths of a mil/yr in the solution. Although any of the three materials tested would appear adequate for the SBS service based on these results, it is probable that more corrosive conditions could exist elsewhere in the SBS other than where the coupons were located for this test.

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- (a) Inconel and Incoloy are tradenames of Huntington Alloys Inc., Huntington, West Virginia.
 - (b) Haynes is a company name of the Cabot Corporation, Kokomo, Indiana.
 - (c) Hastelloy is a tradename of Union Carbide Corporation, New York, New York.

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ABBREVIATIONS AND ACRONYMS

AOD	Advanced Conceptual Design
DAS	Data Acquisition System
DF	Decontamination Factor
DM	Demister
DOE	Department of Energy
DWPF	Defense Waste Processing Facility
EVS	Ejector/Venturi Scrubber
FC	Film Cooler
HEME	High-Efficiency Mist Eliminator
HEPA	High-Efficiency Particulate Air
HLW	High-Level Waste
HWP	Hanford Waste Vitrification Plant
IRC	Inner Refractory Cooling
LFCM	Liquid-Fed Ceramic Melter
LOI	Letter of Instruction
MFT	Melter Feed Tank
MOG	Melter Off-Gas
NCAW	Neutralized Current Acid Waste
PNL	Pacific Northwest Laboratory
PSCM	Pilot-Scale Ceramic Melter
SBS	Submerged Bed Scrubber
SGM	Scale-Glass Melter
SHT	Slurry Hold Tank
SRAT	Slurry Receipt and Adjustment Tank
SRL	Savannah River Laboratory
TO	Total Oxide
TCC	Total Organic Carbon
WHC	Westinghouse Hanford Company
WVDP	West Valley Demonstration Project

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1.0 INTRODUCTION

The Hanford Waste Vitrification Plant (HWVP) is being designed to immobilize pretreated radioactive high-level waste (HLW) as glass for geologic disposal. The pretreated HLW is concentrated and then chemically adjusted with formic acid and/or sugar for melter feed rheology and melter glass redox control. After addition of the glass forming chemicals (frit) and final concentration adjustment, the feed is transferred to the melter for conversion to a molten glass (vitrification). The molten glass is poured into canisters for solidification and containment. The melter off-gas (MOG) is treated for hazardous particulate, noxious gases, and water removal. Integrated testing of these process steps provide information for process and equipment design, waste form qualification, process operating specifications, and safety and environmental considerations.

The pilot-scale ceramic melter (PSCM) together with the associated feed preparation and MOG treatment systems at the Pacific Northwest Laboratory (PNL) are used to generate technical process and equipment data. Testing data are used in the HWVP implementation of existing vitrification technology developed at PNL, the Savannah River Laboratory (SRL), and the West Valley Demonstration Project (WVDP). Subsequent to the test, the Defense Waste Processing Facility (DWPF) melter was established at the HWVP reference melter for design. The DWPF melter uses plenum heaters and has a different melt cavity geometry from the PSCM. These differences between melters may influence the application of melt processing from the PSCM to the DWPF melter design.

The PSCM-23 test was performed to establish acceptable operating parameters and expected efficiencies of the reference off-gas equipment under operating conditions to support plant design and environmental permitting. The integrated operation of MOG components will provide a reliable system design. Activities to accomplish these issues are:

- Melter Testing - Perform a 20-day PSCM test to provide melter variability and processing variability data.

- Off-Gas System - Operate the PSCM off-gas system with prototypic components during the FY 1988 PSCM run to collect needed performance data to demonstrate the integrated performance of off-gas components to be used in the HWVP and to establish off-gas component system decontamination factors (DFs).
- Materials Evaluation - Place coupons in PSCM melter and melter off-gas system during the scheduled PSCM run to assess corrosion rates in the PSCM.
- Feed Processing - Support PSCM run and perform pilot-scale testing of the feed preparation process. Evaluate mixing, heat transfer, and foaming during feed concentration and forming operations.
- Waste Form Development - Support PSCM run.

This document reports the results of the PSCM-23 test by first providing the testing conclusions and recommendations (Section 2.0) and defining the test objectives (Section 3.0). The approach used in performing the test to meet the objectives (Section 4.0) and the major pieces of equipment used in conducting the test (Section 5.0) are then described. Operational highlights of the test run are summarized (Section 6.0). The run results and analyses are then presented:

- glass formulation (Section 7.0)
- feed preparation (Section 8.0)
- melter processing (Section 9.0)
- melter off-gas processing (Section 10.0)
- materials evaluation (Section 11.0)

2.0 CONCLUSIONS AND RECOMMENDATIONS

2.1 CONCLUSIONS

The following conclusions can be made from the results and analyses of the PSCM-23 test program.

2.1.1 Glass Formulation

- The HW-39-4 glass composition has the required viscosity, electrical conductivity, and phase behavior to be processable within joule-heated ceramic melters.
- The HW-39-4 frit is commercially producible.
- The durability of the HW-39-4 glass is comparable to HW-39-2 glass under MCC-1(a) test conditions up to 28 days. The durability of HW-39-4 under MCC-3(b) test conditions is measurably less than that of HW-39-2. This result is not expected based on the similarities between the two glasses. The HW-39-4 test glass durability does meet the proposed leach rate requirements for disposal.
- Formating the PSCM-23 simulated HWP feed up to levels as high as 40 mL formic acid/L slurry was not sufficient to produce a glass with a detectable ferrous-to-ferric ratio. Additional reductant, such as sugar, will be required for the case of a high nitrate concentration in the HWP feed.

2.1.2 Feed Preparation

- Significant foaming was observed during the formic acid treatment in three of the five PSCM-23 feed batches that were prepared. Increased surface motion had a positive effect on minimizing foaming. However, the degree of surface turbulence cannot be quantified to conclude whether the current full-scale equipment design will be sufficient to minimize foam accumulation. The increased time required for formic acid treatment and/or the need to use antifoaming agents may have an impact on HWP operation.
- The precipitated feed formulation has acceptable handling characteristics but is rheologically dissimilar to previous feed slurries that were prepared on a laboratory scale.

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- (a) MCC-1P Static Leach Test Method. 1983. Available from the Materials Characterization Center, Pacific Northwest Laboratory, Richland, Washington.
- (b) MCC-3S Agitated Powder Leach Test Method. 1984. Available from the Materials Characterization Center, Pacific Northwest Laboratory, Richland, Washington.

- Although the tank dimensions and steam coil configurations of the bench-scale and pilot-scale feed preparation tanks differed, the values for overall heat transfer coefficient during concentration of simulated HWP feed were comparable. The measured pilot-scale test boiling heat transfer coefficient ($88 \text{ Btu/h}\cdot\text{ft}^2\cdot^\circ\text{F}$) is significantly lower than the value used for equipment design at the Defense Waste Processing Facility (DWPF) ($120 \text{ Btu/h}\cdot\text{ft}^2\cdot^\circ\text{F}$).

2.1.3 Melter Processing

- The nominal PSCM processing rate of $57 \text{ L/h}\cdot\text{m}^2$ ($1.4 \text{ gal/h}\cdot\text{ft}^2$) that was established during PSCM-23 is 27% higher than that specified in the HWP reference processing rate of $45 \text{ L/h}\cdot\text{m}^2$ ($1.1 \text{ gal/h}\cdot\text{ft}^2$).
- The nominal PSCM glass production rate that was achieved, $28.4 \text{ kg/h}\cdot\text{m}^2$ ($5.8 \text{ lb/h}\cdot\text{ft}^2$), is 58% higher than the HWP design criteria.
- The processing characteristics of the NCAW'87 and frit melter feed slurry were very good. The slurry exhibited good spreading characteristics over the glass surface and formed a thin flexible cold cap 2 to 5 cm thick.
- The operation of the air-displacement slurry feed pump was very good. There were no indications of degrading performance. Instances of feed system plugging that did occur were due to oversized feed particles that lodged in the feed line or feed nozzle.
- No further instances of plugging in the feed nozzle occurred after the 0.95-cm-ID nozzle was replaced by a nominal 2.54-cm-ID feed nozzle.

2.1.4 Melter Off-Gas Treatment

Melter-generated combustible gases do not present an off-gas flammability hazard under any of the conditions tested during PSCM-23.

Melter idling emissions do not place any special functional demands on the off-gas system.

- The SBS adequately performed both quenching and aerosol scrubbing functions. This equipment condensed 84% of the process steam and efficiently removed aerosols having diameters $>1 \mu\text{m}$.
- SBS aerosol scrubbing performance was not affected by the range of flows used during PSCM-23, and SBS reentrainment losses were found to be an insignificant effluent source.
- SBS NO_x scrubbing efficiency was -1% due to low NO_x concentrations and high $\text{NO}:\text{NO}_2$ ratios.

- The chevron demister removed very little entrained water during normal processing conditions. However, it was very effective in abating scrub fluid carryover during unstable SBS operation.
- High DFs for the high-efficiency mist eliminator (HEME) aerosol were achieved throughout PSCM-23 testing. The mass median diameter of aerosols exiting the HEME was always found to be $\leq 0.5 \mu\text{m}$.
- Aerosol influent concentrations in the high-efficiency particulate air (HEPA) filter were very low in PSCM-23. A similar condition in the HWVP may mean that a handling dose limitation from ^{137}Cs accumulation, rather than a pressure-drop limitation resulting from aerosol accumulation, will dictate replacement of the HEPA filter.
- HWVP MOG treatment system HEPA filter service life is projected to exceed the one-year design life requirement.

2.1.5 Materials Evaluation

- Five candidate materials (Inconel 690, Incoloy 825, Haynes 214, Haynes 556, and Hastelloy C-276) were exposed in the melter plenum throughout the run. The coupons exposed to melter feeding-only conditions resulted in measurable but slight corrosion, in general showing only tenths of a mil per year. Corrosion rates during idling-only periods were significantly higher, ranging from a few mils per year to tens of mils per year.
- Three candidate materials (Hastelloy C-276, Carpenter Alloy 20 Cb-3, and 304L Stainless Steel) were tested in the SBS during the course of the melter run. Coupons placed in the SBS showed very little corrosion during the melter run, ranging from hundredths to tenths of a mil per year.
- Localized corrosion was not evident on any of the plenum or SBS samples. The corrosion of the test samples can only be classified as uniform.

2.2 RECOMMENDATIONS

Based on the PSCM-23 test program results and analyses, the following recommendations are made.

2.2.1 Glass Formulation

- Investigations are recommended to determine why HW-39-4 glass was less durable than HW-39-2 glass under MCC-3 conditions.

a

2.2.2 Feed Preparation

- A boiling heat transfer coefficient of $88 \text{ Btu/h}\cdot\text{ft}^2\cdot^\circ\text{F}$ was demonstrated during PSCM-23. Compared with existing SRL data, this would be a low design value for concentration operations in the slurry receipt and adjustment tank (SRAT). Full-scale feed preparation tests are planned to verify values for HWVP design.

2.2.3 Melter Processing

- Although the PSCM process rate was significantly higher than the current HWVP reference process rate, the current criteria of $45 \text{ L/h}\cdot\text{m}^2$ ($1.1 \text{ gal/h}\cdot\text{ft}^2$) should be retained until radioactive NCAW characterization can establish that the simulated feeds are sufficiently similar in process properties to give good confidence in the PSCM results.
- An HWVP glass production rate of $22.5 \text{ kg/h}\cdot\text{m}^2$ ($4.6 \text{ lb/h}\cdot\text{ft}^2$), based on $45 \text{ L/h}\cdot\text{m}^2$ and 500 g-oxide/L-slurry, should be used as the HWVP design criteria.
- The air displacement slurry (ADS) pump should receive serious consideration as the HWVP melter feed pump. Its consistently good performance at PNL (nonradioactive and radioactive) and at the WVDP, demonstrated flow rate control, and long-term durability are well documented. It is expected to require fewer remote connections and interlocks, provide greater process control and less water dilution, and require less maintenance compared with the current reference system. Equipment disposal and waste water treatment costs are also expected to be significantly less.
- A large-diameter feed nozzle should be tested in subsequent PSCM tests to determine if it will be reliable over longer operating periods. In association with this change, a mechanical means to clear solids deposits from the nozzle should be evaluated. Otherwise, HWVP downtime attributed to remote feed nozzle removal and cleaning/replacement could be significant.
- The glass pouring tests showed that glass could be poured outside the reference HWVP canister opening (4.5 in. I.D.) at pouring rates above 500 lb/h. Because process fluctuations could result in pour rates higher than 500 lb/h, as large a canister opening as is practical is recommended.
- An air flow rate of 2 to 4 scfh should be used for glass discharge from the melter to achieve a glass flow rate of 500 lb/h in batch glass pours.
- A 3-in. riser diameter in the HWVP melter overflow section is recommended instead of the 2-in. riser used in the PSCM to accommodate the longer riser length and to minimize glass flow resistance

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so that the melter glass inventory can be reduced as much and as quickly as possible in the event of a melter failure or planned decommissioning.

- Glass sampling of the melter pour stream should be performed within the canister or canister throat to prevent the potential of pouring glass contacting and sticking to the side of the glass discharge nozzle.
- The canister should be maintained under the melter pour opening for at least 15 minutes after terminating the last canister fill pour (turning off the air) to prevent lingering dripping glass from falling on the canister or turntable top.
- An up-sloped glass pour trough should be considered for the HWVP melter to minimize and shorten the glass dripping period after terminating the pour.

2.2.4 Melter Off-Gas Treatment

- The MOG treatment system decontamination factors recommended for HWVP design are included in Table 10.26.
- The primary off-gas line should have a minimum gas velocity of 50 ft/s to minimize the accumulation of solids in the melter off-gas line. A lower gas velocity may be acceptable but cannot be recommended until data are obtained.
- A heat transfer coefficient of 150 Btu/h·ft²·°F should be used for the heat removal coils in the SBS solution.
- The HWVP SBS should be designed based on a face velocity of 90 ft/min in the bed to minimize equipment size and still provide good particulate scrubbing.
- A demister should be placed on the SBS vessel gas outlet to prevent significant liquid and solids entrainment during SBS upset operating conditions.
- It is not expected that a water spray flush is needed for HEME-collected solids removal (provided by normal operation). However, a large deluge spray nozzle should be installed to allow batch cleaning capability.
- The HEME should be sized for a superficial gas velocity of 10 ft/min to provide good particulate performance and allow for possible increases in system inleakage.

2.2.5 Materials Evaluation

- The results of the melter plenum coupon tests support previous HWVP and SRL results that the INCO materials (Inconel 690 and Incoloy 825) and the Haynes 214 are suitable candidate materials for plenum and off-gas line high-temperature service.

3.0 OBJECTIVES

The PSCM-23 test program objectives were:

1) Glass Formulation

- Conduct pre-run laboratory crucible melt evaluations to determine requirements for formic acid and sugar addition to adjust the redox state of the glass.
- Provide new glass formulation for the NCAW 87 compositions.
- Verify glass formulation using nitrate precipitated melter feed.

2) Feed Preparation

- Evaluate processing a melter feed slurry produced from the precipitation of metal nitrates to metal hydroxides.
- Perform analyses of feed processing requirements to establish reductant treatment requirements.
- Characterize mixing, foaming, formic acid addition rate, and heat transfer conditions in small-scale feed preparation equipment.
- Test melter feed processing at limits of feed specification for nitrates.

3) Melter Processing

- Establish and maintain steady-state operating conditions in the melter for the duration of off-gas treatment system sampling.
- Evaluate the nominal processing characteristics of simulated melter feed.

4) Off-Gas Processing

- Characterize the steady-state performance of the PSCM off-gas treatment system. Test conditions will include:
 - Operate HEME at base case conditions
 - Operate HEME without a water spray
 - Operate HEME at the different noncondensable gas rate
 - Operate the PSCM in an idling (non-feeding) mode.

- Evaluate extent of solid deposits in the melter off-gas line jumper and SBS inlet pipe.
- Evaluate liquid entrainment from the SBS and HEME.

5) Materials Evaluation

- Evaluate the performance of selected materials exposed to simulated HWVP process conditions in the melter and off-gas systems.

A set of related secondary objectives were performed for the PSCM-23 test program:

1) Glass Formulation

- Characterize the quality of melter glass and cold cap samples, and identify surface phase compositions.

2) Feed Preparation

- Characterize the physical and chemical properties of the PSCM-23 feed samples generated during feed preparation.

3) Melter Processing

- Characterize the glass pouring characteristics of the PSCM pour trough as a function of bulk glass and overflow section temperatures and pour rate.
- Compile a concise process and mass balance flowsheet to support HWVP design activities.
- Evaluate the thermocouple placed in the trough block as 1) a means by which to control the overflow section heaters, 2) an accurate measure of the glass temperature during pouring periods, and 3) a means to detect slight glass discharges that might otherwise go undetected.
- Determine if plenum, refractory, and electrode temperature data can significantly aid in the monitoring of the melter process in a backup or secondary function.

4.0 TEST APPROACH

Previous melter tests conducted in support of the HWVP have been directed at evaluating the processing characteristics of a particular melter feed composition and establishing associated operating parameters. Typically, these evaluations required that a test be divided into segments in which a melter feed component was varied and the overall system response was monitored. Although operation of the melter was continuous during these tests, the duration of each segment was determined by the time required to establish the processing characteristics associated with a change and, in many cases, steady-state operation of the entire system was not maintained for a significant period. While this type of operation was sufficient to satisfy melter processing-related objectives, time between melter variable changes was not sufficient to generate a relationship between melter operation and the performance of the associated off-gas treatment system.

To characterize the performance of the off-gas treatment system in the PSCM-23 test, melter process changes were minimized for the duration of the integrated off-gas treatment system evaluation. The operating philosophy during the test was to establish a feed rate that generated a cold cap that covered approximately 80% of the melt surface and was not excessively thick. Limiting the cold cap coverage allowed processing flexibility. Large deviations in processing parameters were avoided, and realistic operating conditions were maintained.

Following an initial startup period, steady-state operation of the melter was established. Once off-gas stream sampling was initiated, changes in melter control parameters were held to a minimum. Key parameters in the operation of the melter included average glass temperature, plenum temperature, feed rate, melter pressure, and cold cap characteristics. Steady-state operation required that the values of these parameters were stable and relatively constant. Changes in melter control, such as adjusting the electrode power controller, were instituted only if process conditions fell outside the ranges established as operational constraints.

During the PSCM-23 test, the MOG treatment system was operated under four separate conditions. For **each** condition, the integrated performance of the system was established by measuring the MOG composition before and after each piece of off-gas equipment. Sampling procedures, equipment, and schedule are presented in Section 11.0.

The reference HWP off-gas treatment system configured during the PSCM-23 test was recommended by the project architect-engineer, **Fluor** Daniel, Inc., and is based on the WDP design. The system consisted of the melter film cooler, a submerged bed scrubber (SBS), a chevron demister, a high-efficiency mist eliminator (HEME), a preheater, and a **HEPA** filter. The **HEPA** and associated preheater were included in the system configuration only for a portion of the test. Because of limitations in the PSCM off-gas system blower capacity it was not possible to utilize the **HEPA** filter and preheater during the portion of the test when a higher air injection rate was used and still maintain the PSCM under a slight vacuum.

The four operating conditions for the MOG treatment system tested during the PSCM-23 test were the following (nominal):

<u>Test Condition</u>	<u>Melter Condition</u>	<u>Day</u>	<u>Air Flow at Film Cooler Outlet, scfm</u>	<u>HEME Water Flush Rate, L/h</u>
Reference	Steady State	1-7	110	0
High Air Flow	Steady State	7-12	170	0
HEME Flushing	Steady State	13-16	170	15
Melter Idling	Idling	17-20	100	0

The melter was operated at a steady-state feeding condition to maintain a cold cap coverage of approximately 80% of the melt surface area. This condition resulted in an average melter feed rate of 43 L/h (57 L/h·m²). Temperature of the glass was maintained at 1150°C ± 25°C. Glass generated during the test was batch poured into 55-gal drums using an airlift procedure. Approximately 100 kg of glass were poured per batch at an average rate of 150 kg/h (330 lb/h) using an air flow rate of 2 scfm. The effect of air

flow rate and glass overflow trough temperatures on glass flow rates and the ability of the glass to consistently pour through a 11.4-cm (4.25-in.) canister neck was evaluated.

The melter feed processed during this test was a simulated HWVP composition consisting of pretreated neutralized current acid waste (NCAW) and a premade glass-forming frit. The basis for the waste oxide composition was the FY 1987 HWVP feed pretreatment specifications for NCAW. Based on this composition, a nonradioactive waste oxide composition was determined. The chemicals used to batch the melter feed and the associated glass oxide composition are presented in Table 4.1.

The major constituents of the melter feed, $\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$, $\text{Zr}(\text{OH})_4$, and $\text{Ni}(\text{OH})_2$, were supplied by an off-site vendor in a blended slurry form that was to be prepared using the procedure outlined in Figure 4.1. However, because of excessively slow settling rates, the settle/decant procedure was replaced by a filtration procedure. The remaining melter feed components were combined with the mixed hydroxide slurry and a compositional analysis was performed. Based on the results of this analysis, adjustments were made as needed to reach the target composition. The feed was then heated to between 90°C and 95°C, and 24.6 g of 90 wt% formic acid was added per liter of melter feed slurry. Following completion of the formic acid treatment, the temperature of the feed was increased to approximately 100°C and held there for 2 h to ensure that all chemical reactions had reached equilibrium.

The amount of additional reductant (formic acid and sugar) required to adjust the $\text{Fe}^{+2}/\text{Fe}^{+3}$ ratio to the desired value was established during preparation of the melter feed (see Section 8.0). For the PSCM-22 test, 10.2 g/L of 90 wt% formic acid per liter of melter feed was used to establish an average $\text{Fe}^{+2}/\text{Fe}^{+3}$ ratio of 0.015 in the glass. The average $\text{Fe}^{+2}/\text{Fe}^{+3}$ ratio of the PSCM-23 glass was 0.055 and was obtained by adding 24.6 g/L of 90 wt% formic acid and 10 g/L sugar to the feed during preparation.

TABLE 4.1. PSCM-23 Melter Feed Composition

Chemicals Used^(a) In Makeup	Concentration, g/L	Assumed State After Reaction	Concentration, g/L	Glass Concentration, wt% (b)
Al(OH) ₃	18.11	Al ₂ O ₃	11.84	2.36
H ₃ BO ₃	0.23	B ₂ O ₃	0.13	0.03
BaSO ₄	0.80	BaO	0.53	0.10
CaHPO ₄ *H ₂ O	1.21	CaO	0.39	0.08
Ce(OH) ₃	0.87	Ce ₂ O ₃	0.79	0.16
Cr(NO ₃) ₃ *9H ₂ O	2.06	Cr ₂ O ₃	0.66	0.13
CsNO ₃	1.09	Cs ₂ O	0.79	0.16
CuSO ₄ *5H ₂ O	2.47	CuO	0.79	0.16
Fe(OH) ₃	49.31	Fe ₂ O ₃	36.85	7.36
LaF ₃	1.97	La ₂ O ₃	6.44	1.29
La/Nd(NO ₃) ₃ *6H ₂ O	17.25	MgO	0.46	0.09
MgSO ₄	1.23	MnO ₂	0.79	0.16
Mg(NO ₃) ₂ *6H ₂ O	0.30	MoO ₃	1.58	0.31
Mn(NO ₃) ₂ *4H ₂ O	2.27	Na ₂ O	23.03	4.60
MoO ₃	1.58	Nd ₂ O ₃	3.35	0.67
NaCl	0.63	NiO	3.03	0.61
Na ₂ Cr ₂ O ₇ *2H ₂ O	0.53	P ₂ O ₅	0.53	0.10
Na ₂ C ₂ O ₄	13.95	Pr ₆ O ₁₁	0.53	0.10
NaF	0.79	SiO ₂	5.26	1.05
NaNO ₃	19.58	Sm ₂ O ₃	0.26	0.05
NaOH	10.46	SrO	0.53	0.10
Na ₂ HPO ₄ *7H ₂ O	0.10	Y ₂ O ₃	0.26	0.05
Na ₂ SO ₄	0.65	ZnO	2.50	0.50
NdF ₃	2.02	ZrO ₂	19.74	3.94
Ni(OH) ₂	3.76	F	1.24	0.30
Pr(OH) ₃	0.59	Cl	0.56	0.08
SiO ₂	5.26	SO ₃	2.25	0.45
Sm(OH) ₃	0.30	NO ₃	35.0 ^(c)	--
Sr(NO ₃) ₂	1.07	TOC	2.50 ^(c)	--
Y(OH) ₃	0.33			
ZnO	2.50			
Zr(OH) ₄	25.51			
Subtotals:	188.8 g/L		125.2 g/L	25.0 wt%
<u>HU-39-4 Frit Composition^(d)</u>		SiO ₂	262.50	52.50
		B ₂ O ₃	52.50	10.50
		Na ₂ O	33.75	6.75
		Li ₂ O	18.75	3.75
		CaO	3.75	0.75
		MgO	3.75	0.75
		Subtotals	375.0 g/L	75.0 wt%
		TOTALS	500.2 g/L	100.0 wt%
<u>Reductant Added</u>		HCOOH ^(e)	28.8 g/L ^(f)	
		Sugar	10.0 g/L	

(a) Prior to formic acid treatment.

(b) Values **assume** no volatility Losses.

(c) Value is not included in **subtotal** values.

(d) Size distribution of frit was **-80/+200** mesh with a maximum of 10 **wt%** -200 mesh.

(e) Value given is for a 90 **wt%** solution of HCOH

(f) Value includes 90 **wt%** HCOH added with frit, equivalent to 1 **wt%** of frit added, or 4.2 g/L.

FIGURE 4.1. Procedure for the Preparation of Hydroxides from Nitrates

were housed in a separate stainless steel thermowell. The glass and plenum thermowells were placed in 10-cm (4-in.) flanges located next to the feed port.

Current and voltage transformers, coupled with interface modules, were used to monitor electrode power, current, voltage, and resistance during the test. Pressure in the melter was maintained using an analog process controller and a diaphragm-operated valve located just upstream of the HEPA pre-heater in the off-gas line. A pressure transducer, placed in the emergency off-gas vent, monitored the pressure in the plenum space of the melter. The signals generated by these pieces of equipment were fed to the data acquisition system (DAS) and chart recorders for storage. In addition, a glass level detection system, consisting of a set of bubblers that measured glass weight factor and specific gravity, was used for the initial 7 days of the test.

During the test, melter feed was transferred from the MFT to the melter through a 0.78-cm (0.31-in.) I.D. feed line connected to a water-cooled feed nozzle. Both a Moyno® progressive cavity and an air displacement slurry (ADS) pump were used during PSCM-23. Each of the pumps was used for an approximately equal amount of time. Details of the ADS pump development and operation have been reported previously (Peterson, Perez, and Blair 1986).

The instantaneous feed rate was determined using a magnetic flowmeter. The signal from the flowmeter was sent to the data acquisition system (DAS), and the feed rate was monitored on the computer display. In addition, the computer calculated an average feed rate, which was also displayed by the DAS, and maintained a record of the total amount of feed processed during the test.

Glass produced during the test was periodically airlifted from the melter into 55 gallon drums. The quality of the stream associated with glass pours was assessed by the consistency in which the stream passed through an 11.4-cm (4.5-in.) ring placed in the opening of the receiving drum. Temperatures in the overflow section were monitored by Type K thermocouples,

* Moyno is a registered tradename of Robbin & Myers, Springfield, Ohio.

located in the trough, face, and trough block. Glass pour rate was established by monitoring the initial and final weight of the receiving drum and the time of the pour.

5.3 OFF-GAS TREATMENT SYSTEM

The steam, gases, and airborne effluent generated by the liquid-fed ceramic melter (LFCM) waste solidification process are exhausted through and treated by a melter off-gas processing system. For PSCM-23, this system was composed of a film cooler (FC), a submerged bed scrubber (SBS), a chevron demister (DM), a high-efficiency mist eliminator (HEME), an off-gas heater, a HEPA filter, a blower, and interconnecting piping. The arrangement of these components is illustrated in Figure 5.1, and a functional description of each active component is given below. The sampling equipment used to characterize off-gas system performance is described in Section 10.

5.3.1 Film Cooler

An air driven film cooler forms the plenum exhaust port in the lid of the melter. The function of the film cooler, shown in Figure 5.4, is to maintain a clear and unobstructed pipe between the melter and the SBS. Air is injected through radial slots to cool the melter exhaust stream to 350°C (below the softening point of glass) and to increase the off-gas stream velocities. The off-gas stream velocities were maintained above 45 ft/s to minimize particulate deposition.

5.3.2 Submersed Bed Scrubber

The PSCM-23 primary MOG system scrubber is the SBS (see Figure 5.5). The SBS is a packed bed submerged in a vessel in which melter off gas enters the bottom of the bed. The gas buoyancy and off-gas vacuum cause the SBS fluid to circulate through the bed. This recirculating fluid transfers heat from the hot melter exhaust and provides for gas scrubbing and cleaning of the bed. These processes are schematically illustrated in Figure 5.5. In operation, the process exhaust is concurrently contacted and cooled by the scrubbing liquor in the SBS bed. The MOG steam condensate continuously overflows into a collection tank. Cooling coils are located along the outer

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5.0 EQUIPMENT DESCRIPTION

The PSCM-23 test was conducted in the Engineering Development Laboratory of the 324 Building. The major pieces of equipment used in melter feed preparation and storage, vitrification, and off-gas treatment are described in this section. The integrated melter test system is shown schematically in Figure 5.1.

5.1 FEED PREPARATION AND STORAGE

Two stainless steel process tanks, with similar dimensions and agitation systems were used to prepare feed for the PSCM-23 test. These tanks are located in the Chemical Makeup Room of the 324 Building and have a diameter of 165 cm (65 in.), a total height of 147 cm (58 in.), and a capacity of approximately 3000 L (790 gal). Agitation in both tanks is provided by two 91-cm-(36-in.-) diameter impellers powered by a 7.5-hp motor coupled with a variable speed controller. The top impeller is a 45° pitched blade and the bottom impeller is a four-bladed paddle. Heating of the feed is accomplished with an internal steam coil constructed of nominal 1-in. diameter stainless steel pipe. The total heat transfer area of the coil is approximately 2.7 m² (28.9 ft²), and the maximum steam pressure for the system is 100 psig. For this test, formic acid was introduced under the surface (~50 cm under surface) of the feed. Temperature of the feed was monitored using a Type K thermocouple and a chart recorder.

Following completion of formic acid addition and heat treatment, the slurry was transferred to the slurry hold tank (SHT) located in the High-Bay Annex of the 324 Building for storage during the run. This tank is 3.4 m (11 ft) in height, 2.7 m (9 ft) in diameter, and has a nominal capacity of 16,500 L. The tank is equipped with load cells to assist in tank level determination. Agitation is supplied by a 10 hp motor, a variable speed controller, and two 82.3-cm- (32.4-in.-) diameter impellers. The upper impeller is a 45° pitched blade and the lower is a four-bladed paddle.

During the test, melter feed was transferred from the SHT to the melter feed tank (MFT) as needed. The MFT is 140 cm (55 in.) in diameter, 165 cm

FIGURE 5.1. PSCM Process Flowsheet

(65 in.) in height, and has a nominal capacity of approximately 2100 L (550 gal). The agitator is equipped with a single high-efficiency impeller, a 3.5-hp motor, and a variable speed controller.

5.2 PILOT-SCALE CERAMIC MELTER SYSTEM

The PSOM system consists of the melter and equipment associated with the delivery of feed and the discharge of glass. A cut away view of the melter is presented in Figure 5.2.

FIGURE 5.2. The Pilot-Scale Ceramic Melter

The melt cavity of the PSCM measures 74 cm by 102 cm (29 in. by 40 in.) with an exposed glass surface area of 0.76 m^2 (8.2 ft^2). Operating at a nominal vacuum of 12.7 cm (5.0 in.) W.C., the melter has a glass depth of 38 cm (15 in.) and a volume of 288 L. Based on a density of 2.5 kg/L, this volume corresponds to an inventory of 720 kg (1584 lb) of glass. The plenum space height above the glass is 60 cm (24 in.). The melter lid is a one-piece unit which covers both the melt cavity and the overflow section.

The locations of specific instrumentation for the PSCM-23 test are shown in Figure 5.3. Seven Type K thermocouples, placed in an Inconel 690 thermowell, were used to monitor glass temperatures in the melter cavity. Three Type K thermocouples, used to measure temperatures within the plenum space,

FIGURE 5.3. Instrument Locations for PSCM-23

FIGURE 5.4. PSCM Film Cooler

portion of the vessel to maintain a constant liquid temperature. Buoyancy effects maintain the fluid recirculation, so no external pump is needed. Not requiring a pump is a significant operational advantage because the scrubbing liquor is abrasive and usually corrosive. However, the pressure drop through the bed is high, being established by the submergence of the inlet pipe. The submergence for PSCM-23 was 32 in. The SBS specifications and operating conditions are provided in Table 5.1.

5.3.3 Chevron Demister

Scrub solution carryover from an SBS can be quite large; consequently, a chevron demisting device was installed to reduce the liquid-phase aerosol loading of the SBS process exhaust stream. The chevron demister principle method for removing water droplets from the exhaust stream is by causing the

FIGURE 5.5 Submerged Bed Scrubber

TABLE 5.1. Submerged Bed Scrubber Design Specifications and Operating Conditions

SBS Design Specifications		
Bed Diameter	20 in.	
Bed Height	24 in.	
Bed Packing	3/8 in. dia. Ceramic Spheres	
Water Depth to Bed Bottom	31 in.	
Tank Diameter	3 ft	
Bed Cross-Sectional Area	1.98 ft ²	
Skirt Depth	10 in.	
Heat Transfer Area	43 ft ²	
SBS Operating Conditions		
	Condition I	Condition II
Inlet Gas Temperature	190°C	125°C
Outlet Gas Temperature	35°C	35°C
Mid Bed Temperature	45°C	35°C
Noncondensible Gas Flow Rate	110 scfm	170 scfm
Superficial Air Velocity	1 ft/s	1.5 ft/s

droplets to impact on corrugated plates. The impaction method of droplet removal works well for droplets larger than 3 μm but less well on submicron droplets. The chevron demister shown in Figure 5.6 was located at the outlet of the SBS to collect the larger fluid droplets entrained in the SBS outlet gas stream.

The manufacturer design specifications and actual operating conditions for the demister used during PSCM-23 are shown below:

solution carry over under upset conditions. A higher efficiency is not required and it would be more likely to become plugged.

5.3.4 High-Efficiency Mist Eliminator

The combined effect of the SBS and demister is to quench the off-gas stream and to remove large diameter (>1 μm) condensed phase aerosols by impaction. The HEME is used as a high-efficiency filtration device to remove the aerosolized matter penetrating the previous, low-efficiency MOG system components. The HEME is designed to remove submicron particles. HEME fiber (depth) filters were originally developed to remove acid or caustic fumes and are commercially available with either fiberglass or polypropylene batt. Like HEPA filters, these devices can efficiently remove airborne submicron matter, but unlike HEPAs, they can be operated wet, allowing simultaneous removal of both liquid and solid aerosols. Since HEMEs can be operated wet, a continuous water spray has often been employed to wash down and cleanse filter elements of accumulated debris, thus extending the service life of the filter. The HEME, used during PSCM-23, was configured as shown in Figure 5.7 so that it could be irrigated and drained. The manufacturer design specifications and actual operating conditions for the HEME used during PSCM-23 are shown below:

HEME Design Specifications:

Outside Surface Area	20.4 ft^2
Inside Surface Area	11.5 ft^2
Outside Diameter	24 in.
Packing Thickness/Fiber Diameter	
Inside Layer	0.5 in./30 μm
Outside Layer	2.5 in./8 μm
Height	6.5 ft.
Efficiency for Particles >1 μm	99.9%

HEME Operating Conditions:

Gas Temperature	26°C
Gas Superficial Velocity	6.7 - 9.8 ft/min

Superficial Gas Velocity, 9.6 to 15 ft/min
 Outside Surface Area, 20.4 ft²
 inside Surface Area, 11.5 ft²
 Outside Diameter, 24 in.

FIGURE 5.7. High-Efficiency Mist Eliminator

HEME Operating Conditions: (contd)

Gas Flow Rate	7.4 - 12 lb/min
Gas Pressure	0.9 atm
Gas Density	0.067 - 0.07 lb/ft ³
Water Content	
With Water Spray Off	0.002-0.004 lb water/lb dry air
With Water Spray On	0.03 - 0.05 lb water/lb dry air

5.3.5 HEPA Filter Heater

An electric heater (shell with heating element bars) was used in front of the HEPA filter during PSCM-23 to ensure that the HEPA filter stayed dry. The HEPA must stay dry to be an effective final barrier to particulate effluents penetrating previous melter off-gas clean-up equipment. The heater used during the PSCM-23 experiment was an 7.5 kW electric tube heater with an on/off control. The heater maintained an exit off-gas temperature at least 20°C higher than the inlet temperature. The average energy required to heat the off gas 20°C at 170 scfm was calculated to be about 2 kW.

5.3.6 HEPA Filter

A Flanders 12 in. x 12 in. x 11-1/2 in. HEPA filter was used for the PSCM-23 experiment. The filter has a baffle design with an actual surface area of 62 ft². The filter was rated at 210 ACFM with a pressure drop of 1 in. WC. The rated efficiency of the filter was greater than 99.97% for particles $\geq 0.3 \mu\text{m}$ in diameter. The HEPA filter pressure drop was measured across the housing and averaged 2 in. WC for the entire experiment.

6.0 OPERATIONAL HIGHLIGHTS

The PSCM-23 test consisted of approximately 15 days of melter feeding. During operation, simulated HWP melter feed was processed under nominal conditions, and the integrated performance of the off-gas treatment system was characterized. Following completion of processing, the melter was placed in an idling mode, and characterization of the off-gas treatment system was continued for an additional 5 days. A chronology of PSCM operational testing is shown in Figure 6.1.

6.1 FEED AND GLASS HIGHLIGHTS

A total of five batches of simulated feed were prepared for the PSCM-23 test. Three of the batches were completed and transferred to the SHT prior to the initiation of the test. A final composition analysis was performed; sugar, frit, and additional formic acid (equivalent to 1 wt% of the frit) were added; and the resulting melter feed was diluted to a concentration of 500 g total oxide (TO) per liter. The fourth batch of NAW 87 was transferred to the SHT on the third day of the test (after 83 h of operation). The fifth batch was prepared during the test and transferred to the SHT on the 10th day (250 h). Both batches were analyzed and makeups completed prior to transfer for melter feeding. Approximately 15,000 L (3,960 gal) of melter feed were prepared and processed during the test.

During the test, melter feed was transferred from the SHT to the MFT approximately every 24 h, and samples of the feed were collected from the MFT every 8 h. Physical property data, including wt% total solids, wt% TO, and g-TO/L, were obtained during operation from samples collected at 48-h intervals. Following completion of the test, six samples were sent for compositional analysis in addition to wt% TO and g-TO/L. A summary of the wt% TO data is presented in Figure 6.2. There is no explanation for the -10% drop in oxide content at the 200-h point in the run. There was no indication in the run log to indicate an accidental dilution of the MFT contents. Dropout of frit was encountered during the final transfer of feed from the SHT to the MFT resulting in the decreased wt% TO values shown by the last two data points in Figure 6.2.

FIGURE 6.1 PSCM-23 Melter/Off-Gas Treatment Operations Chronology

FIGURE 6.2. Total Oxide Concentration of PSCM-23 Melter Feed Samples

During the last feed transfer, the pump failed midway through the operation, and the melter feed was left unagitated (tank level was below the bottom impeller) for approximately 6 h while the pump was repaired. The wt% TO of the samples collected at 335 and 343 h, as well as the compositional analysis of the final sample verified that this MFT feed was not representative of the target composition. Therefore, information obtained from these samples was not included in average values reported for physical properties and composition.

The results of compositional analyses performed on five melter feed samples taken during the test are presented in Table 6.1. In general, the composition of the melter feed was consistent throughout the test and approximated the target composition for a majority of the individual feed components. A total of five samples taken during glass pours were also sent for compositional analysis. The results of these analyses, as well as

TABLE 6.1. Oxide Composition of Melter Feed Samples Taken During the PSCM-23 Test

Oxide	Individual Sample Compositions, g Oxides/L ^(a)					Average	Standard Deviation	Target
A1203	11.64	12.07	12.38	12.83	12.87	12.36	0.46	11.84
8203	48.62	50.23	51.20	53.13	50.56	50.75	1.46	52.63
BaO	0.49	0.50	0.52	0.54	0.52	0.52	0.02	0.53
CaO	4.21	4.32	4.43	4.56	4.46	4.40	0.12	4.14
CeO ₂	0.61	0.68	0.70	0.70	0.74	0.69	0.04	0.79
Cr ₂ O ₃	0.67	0.69	0.70	0.72	0.72	0.70	0.02	0.66
Cs ₂ O	0.81	0.84	0.83	0.85	0.85	0.83	0.02	0.79
CuO	0.74	0.75	0.81	0.79	0.78	0.77	0.03	0.79
Fe ₂ O ₃	32.31	33.17	34.03	35.17	34.60	33.86	1.02	36.85
La ₂ O ₃	6.06	6.27	6.38	6.53	6.39	6.33	0.16	6.44
Li ₂ O	17.33	17.78	18.21	18.97	17.91	18.04	0.54	18.75
MgO	3.95	4.13	4.21	4.31	4.25	4.17	0.13	4.21
MnO ₂	0.85	0.89	0.89	0.92	0.92	0.89	0.02	0.79
MoO ₃	1.50	1.56	1.59	1.64	1.61	1.58	0.05	1.58
Na ₂ O	53.92	53.78	55.40	56.21	55.40	54.94	0.94	56.78
Nd ₂ O ₃	2.68	3.14	2.99	3.09	2.85	2.95	0.17	3.35
NiO	2.75	2.85	2.96	2.98	2.95	2.90	0.09	3.03
P ₂ O ₅ (b)	0.53	0.53	0.53	0.53	0.53	0.53	0.00	0.53
Pr ₆ O ₁₁ (b)	0.53	0.53	0.53	0.53	0.53	0.53	0.00	0.53
SiO ₂	252.42	260.98	275.95	275.95	269.53	266.97	9.12	267.76
Sm ₂ O ₃ (b)	0.26	0.26	0.26	0.26	0.26	0.26	0.00	0.26
SrO	0.52	0.53	0.53	0.56	0.54	0.54	0.01	0.53
Y ₂ O ₃	0.27	0.28	0.28	0.29	0.28	0.28	0.01	0.26
ZnO ₂	2.32	2.38	2.44	2.51	2.49	2.43	0.07	2.50
ZrO ₂	18.37	18.51	18.91	19.45	19.05	18.86	0.39	19.74
Cl	0.58	0.59	0.55	0.54	0.55	0.56	0.02	0.38
F	1.23	1.33	0.61	1.22	1.16	1.11	0.26	1.50
SO ₄	0.98	0.98	1.00	0.99	1.00	0.99	0.01	2.70
NO ₃ (d)	<u>35</u>	<u>36</u>	<u>37</u>	<u>37</u>	<u>37</u>	<u>36.4</u>	<u>0.8</u>	<u>35.0</u>
Total ^(c)	478.6	496.3	518.4	515.9	507.9	503.4	14.6	500.6

(a) Samples were collected after 23, 71, 119, 167, and 263 h of operation.

(b) Analyses did not include these compounds. Values reported are target values.

(c) Total oxide concentration value was determined by oxide burn.

(d) Concentration of NO₃ is not included in total oxide value.

Fe²⁺/Fe³⁺ ratio determinations, are presented in Table 6.2. Again, the steady-state composition of glass during the test was consistent and approximated the target composition.

6.2 MELTER/OFF-GAS TREATMENT

Major changes in operational parameters during the first 15 days of the test were limited to the off-gas treatment system. The test during melter feeding, divided into three segments based on these changes, is summarized in Figure 6.1 and Table 6.3. During the first segment, the HEME was operated

TABLE 6.2. Composition of Melter Glass Samples Taken During the PSCM-23 Test

Oxide	Individual Sample Compositions, wt% Oxides ^(a)					Average ^(c)	Standard Deviation	Corrected Average ^(d)	Target
Al ₂ O ₃	2.69	2.52	2.52	2.64	2.55	2.58	0.07	2.68	2.36
B ₂ O ₃	9.98	9.94	10.00	9.74	9.90	9.91	0.09	10.29	10.53
BaO	0.09	0.10	0.10	0.11	0.10	0.10	0.01	0.10	0.10
CaO	1.12	0.90	0.87	0.87	0.88	0.93	0.10	0.97	0.83
CeO ₂	0.15	0.16	0.15	0.17	0.17	0.16	0.01	0.17	0.16
Cl	--	--	--	--	--	0.08 ^(e)	--	0.08 ^(e)	0.08
Cr ₂ O ₃	0.15	0.16	0.16	0.17	0.16	0.16	0.01	0.16	0.13
Cs ₂ O	0.16	0.17	0.16	0.18	0.16	0.17	0.01	0.17	0.16
CuO	0.13	0.15	0.15	0.16	0.15	0.15	0.01	0.15	0.16
F	--	--	--	--	--	0.20 ^(e)	--	0.20 ^(e)	0.20
Fe ₂ O ₃	7.03	6.74	6.71	7.01	6.78	6.85	0.14	7.11	7.36
La ₂ O ₃	1.13	1.26	1.26	1.33	1.29	1.25	0.07	1.30	1.29
Li ₂ O	3.48	3.52	3.54	3.45	3.44	3.49	0.04	3.62	3.75
MgO	0.86	0.83	0.82	0.82	0.83	0.83	0.02	0.86	0.84
MnO ₂	0.17	0.18	0.17	0.19	0.18	0.18	0.01	0.19	0.16
MoO ₃	0.28	0.31	0.31	0.32	0.30	0.30	0.02	0.32	0.31
Na ₂ O	9.92	10.20	10.20	10.40	10.30	10.20	0.16	10.59	11.35
Nd ₂ O ₃	0.53	0.60	0.60	0.61	0.56	0.58	0.03	0.60	0.67
NiO	0.52	0.58	0.58	0.60	0.60	0.58	0.03	0.60	0.61
P ₂ O ₅ (b)	0.10	0.10	0.10	0.10	0.10	0.10	0.00	0.10	0.10
Pr ₆ O ₁₁ (b)	0.10	0.10	0.10	0.10	0.10	0.10	0.00	0.10	0.10
SiO ₂	52.80	52.40	52.40	51.20	52.30	52.22	0.54	54.20	53.55
Sm ₂ O ₃ (b)	0.05	0.05	0.05	0.05	0.05	0.05	0.00	0.05	0.05
SO ₄	--	--	--	--	--	0.17 ^(e)	--	0.17 ^(e)	0.17
SrO	0.09	0.10	0.10	0.11	0.11	0.10	0.01	0.11	0.10
Y ₂ O ₃	0.05	0.06	0.06	0.06	0.06	0.05	0.00	0.06	0.05
ZnO	0.43	0.48	0.48	0.51	0.49	0.48	0.03	0.50	0.50
ZrO ₂	3.08	3.56	3.62	3.82	3.76	3.57	0.26	3.71	3.94
Total	95.09	95.15	95.20	94.69	95.33	95.09	0.22	99.16	99.16
Fe ²⁺ /Fe ³⁺	0.045	0.045	0.055	0.049	0.056	0.050	0.005		

- (a) Samples were collected after 72, 142, 216, 287, and 334 h of operation. **Values** total to less than 100% because of trace impurities and error induced.
- (b) Analyses did not include these **compounds**. Values reported are target values.
- (c) Average values are of individual samples given to left.
- (d) Corrected average reflects normalizing as-determined average to 99.16 **wt%** to be on the same basis as the reported target values.
- (e) Cl, F, and SO₄ were not analyzed. **Values** reported are estimated based on off-gas losses.

without water spray to establish the performance of the system under nominal reference conditions. After 166 h of operation, the film cooler air flow was increased from 40 scfm to 80 scfm, while the HEME continued to be operated without spray. These conditions were maintained for 96 h. In the third segment of the test, a **water/air** spray to the HEME was established. The water spray rate during this segment was approximately 15 L/h, and the air pressure was 30 psig. The duration of the third segment was 89 h.

Following completion of melter feeding operation, the characterization of the off-gas treatment system continued for approximately 5 days to

TABLE 6.3. PSCM-23 Processing Summary

Test Duration:

HEVE no spray/low MOG rate	166 h
HEVE no spray/high MOG rate	96 h
HEVE with spray/high MOG rate	89 h
Total Processing	351 h
Idling	126 h
Total Test	471 h

Process Efficiency:	98%
Total Feed Processed:	15,000 L
Total Glass Generated:	7,450 kg
Average Feed Concentration: (a)	493.8 $\pm$ 22.3 g TO/L
	37.4 $\pm$ 1.3 wt% TO
	43.0 $\pm$ 1.4 wt% $\pm$ total solids

Reductant Added:

Formic Acid (90 wt%)	28.8 g/L (b)
Sugar	10 g/L
Average Glass Fe ⁺² /Fe ⁺³ :	0.050 $\pm$ 0.005

-
- (a) Physical property data obtained from melter feed samples taken during the test. Average and standard deviation calculations did not include values from the final two samples taken.
- (b) Value includes 4.2 g/L 90 wt% formic acid added with the frit.

establish the performance of the system under typical melter idling conditions. During this portion of the test, the HEVE was operated without spray and the film cooler air flow rate was 100 scfm.

The primary feed pump for the PSCM-23 test was a Moyno progressive cavity pump. In previous PSCM tests, the Moyno has been used as a backup for the ADS and has been operated for periods of weeks without failure. During the PSCM-23 test, however, excessive erosion between the stator and the rotor caused the pump to fail on two occasions. Initially, the Moyno was equipped with a butyl rubber stator. After approximately 73 h of operation, the pump was unable to deliver the required feed rate while operating at full speed. The pump was removed from service and the stator was replaced with one made of Buna N. Once placed back online, the Moyno operated for approximately 102 h before failing. The Moyno failed again due to erosion of the stator material. The cause of the excessive wear to the Moyno stator experienced

during this test cannot be explained at this time. During periods of the test when the Moyno was out of service, the ADS pump was used. This pump operated well during 176 h of operation with no incidences of plugging in the pump chamber being observed.

The majority of downtime during the test was associated with plugs in the feed delivery system (see Table 6.4). Frit tended to accumulate in the **feedline** just above the feed nozzle. On the average, these accumulations occurred a little more than once per ^(a)24-h period and were generally removed by flushing the **feedline** with water. However, the feed pump had to be stopped occasionally to remove an obstruction from the **feedline** or the feed nozzle by inserting a reamer rod into the top of ^(b)the feed nozzle or disconnecting the feed line from the feed nozzle.

Before the start of the test, a glass level detection system was installed in the PSCM. This system consisted of two bubbler tubes constructed from 1.3-cm (0.5-in.) nominal 0.5-in. diameter schedule 80 **stainless steel pipe (304L)** and was used to determine the specific gravity and weight factor of the glass in the melter. Using this information, the glass level in the **melter** was calculated.

During the test, the operators used the level measurement, along with visual observations, to project when the glass should be poured. The system performed well during the initial part of the test, predicting when the glass should be poured within approximately 0.25 h. The operation of the system began to deteriorate after 96 h of operation, and the system failed after 167 h because the stainless steel bubbler tubes submerged in the glass corroded.

(a) Water usage estimated to be <1L per flush operation.

(b) The feed line joins the feed nozzle at a **45°** angle. A vertical tube section extends above this y-junction to allow nozzle access for cleaning the feed tube.

TABLE 6.4. Summary of PSCM Feeding Interruptions

<u>Date</u>	<u>Time Off</u>	<u>Time On</u>	<u>Problem/Cause</u>	<u>Response/Comments</u>
6/08/88	1333	1337	Feed stoppage (line plugged).	Feed line was flushed to the melter and out the ball valve (with the feed line capped). Also cleaned out the feed nozzle and Y-junction at feed nozzle. Flushing did not produce any large particles or improve the feed rate.
6/09/88	1130	1134	Feed stoppage.	Switched to the ADS pump from the Moyno.
6/10/88	0729	NA	Feed stoppage.	Air pressure to pump chamber was increased for 3 min to flush feed line, then returned pressure to 7.5 psig.
6/10/88	0800	0820	Feed stoppage.	Feed on and off for ≈25 min. Line plugs were suspected. Pressure was increased temporarily and then reduced. Feed line was also water flushed.
6/10/88	1300	NA	Feed stopped momentarily .	Increased pressure to feed chamber to 15 psig until plug cleared.
6/10/88	1330	1338	Feed line plugged.	Increased air pressure to 15 psig and tried water flush. Neither method cleared the line. A solid plug of feed was found in the Y-junction at the feed nozzle. The feed nozzle was also cleaned out.
6/10/88	2000	NA	Feed off.	Flushed line with water to the melter . Feed rate jumped to ~150 L/h due to back pressure, then dropped to 0 L/h again. Dismantled the feed line to clear plug. Plug suspected in the ADS pump. Switched to Moyno pump .
6/10/88	2110	NA	Feed off.	Moyno pump was turned off. Making noises.
6/10/88	2115	NA	65 minutes	turned on ADS again. Feed rate shot up over 100, then plugged up again. Lines dismantled to clear plug.
6/10/88	2143	NA		Tried to start feed with ADS pump . Feed rate climbed to over 100, then stopped.
		2215	Feed on.	Moyno on and pumping feed to melter.
6/11/88		0030		ADS feed pump back in use.
6/12/88	2040	2055	Feed line plugged (buildup of frit at the Y-junction at the feed nozzle).	Switched to Moyno, line still plugged. Cleaned out feed line section between pump and melter. A buildup in line near valve (near feed nozzle) was cleared out. Switched back to ADS pump .
6/14/88	1500		Feed line plugged up.	Flushed with water and increased feed rate for a few minutes.
6/16/88	0127	NA	Lost feed.	Flushed the feed line .

TABLE 6.4. (contd)

<u>Date</u>	<u>Time Off</u>	<u>Time On</u>	<u>Problem/Cause</u>	<u>Response/Comments</u>
6/16/88	0145	0330	Feed off (ADS pump).	Switched to Moyno. Deadheaded, tripped the breaker. Flushed both pumps, tried to flush feed line. Tried to rear nozzle with rod--unsuccessful. Removed feed nozzle and used a drill to remove the plug. Hooked the feed line back up and found it was plugged. Forced water through to remove buildup.
6/16/88	0402	0413	Feed off--plug.	Switched to Moyno pump.
6/17/88	0102	0107	Maintenance procedure (precautionary).	Broke line to inlet of feed pump and added water flush for approximately 5 min.
6/18/88	0230	0330	Lost feed.	Feed nozzle was replaced. Insulated 3/8" feed nozzle was plugged solid.
6/20/88	0530	NA	Lost feed momentarily (perhaps for 3 minutes).	
6/20/88	0945	0950	Feed rate declining.	Moyno pump turned off. ADS pump piped in and turned on.
6/20/88	2252	2358	Feed stoppage.	Lost flow on ADS. Moyno on line.
6/21/88	0030	0035	Turned feed off to PSCM to sample cold cap. End of feeding portion of PSCM-23.	Switched back to ADS pump.

7.0 GLASS FORMULATION

A glass/frit composition was formulated for the updated neutralized current acid waste (NCAW 87) composition. The composition modification was necessary because of differences between the updated NCAW composition (NCAW 87) and the previous NCAW composition (NCAW 84). The differences affected the glass processing properties, such as viscosity, when using the associated NCAW 84 glass frit. The major differences between the two waste compositions (Table 7.1) are lower concentrations of Fe_2O_3 , Al_2O_3 , and Cr_2O_3 , and the higher concentrations of Na_2O , ZrO_2 , and CdO in NCAW 87. Formated melter feed samples were tested to determine reductant adjustments needed for the PSCM-23 feed to achieve a slightly reduced redox state within the glass melt. The redox state is determined by the quantitative ratio of Fe^{+2} to Fe^{+3} and is controlled to be between 0.005 (detection limits) and 0.3. The glass $\text{Fe}^{+2}/\text{Fe}^{+3}$ ratio in the melter must be maintained within these limits to prevent glass foaming (low value) and sludge formation (upper value). Samples of glass, cold cap, and surface phases generated during the test were obtained and analyzed to determine the quality of the glass.

7.1 TEST APPROACH

7.1.1 Glass Formulation

Glass formulation for the PSCM-23 test was based on the glass/melt viscosity, electrical conductivity, and limited phase behavior properties. Subsequent glass leaching tests were also performed on the HW-39-4 test glass to assess product durability. The resultant glass/frit composition is designated HW-39-4. The compositions of NCAW 87, the HW-39-4 frit, and resulting HW-39-4 glass are presented in Table 7.2 along with the former reference glass/frit, HW-39-2.

7.1.2 Formated Feed Redox Adjustment

Various amounts of formic acid and sugar were added to HWVP feed samples. Following the addition of frit, the melter feed samples were melted in laboratory crucibles. The resulting glasses were then analyzed to determine the $\text{Fe}^{+2}/\text{Fe}^{+3}$ ratio. Glass samples were produced from formated waste

TABLE 7.1. Comparison of Oxide Compositions of NCAW 84 and NCAW 87

<u>Oxide</u>	<u>NCAW 87 Normalized Waste</u>	<u>Reference NCAW 84 Waste</u>
Fe2O3	28.0	46.3
Na2O	17.5	11.1
ZrO2	15.0	2.50
Al2O3	9.0	17.9
SiO2	4.0	3.09
NiO	2.30	2.47
La2O3	2.50	2.29
Nd2O3	2.00	1.79
SO3	1.80	1.54
F	1.20	1.24
MoO3	1.20	1.24
U3O8	4.70	0.62
CeO2	0.60	0.62
Cs2O	0.60	0.62
CuO	0.60	0.62
MnO2	0.60	0.62
RuO2	0.60	0.62
Cr2O3	0.50	0.56
BaO	0.40	0.43
Pr6O11	0.40	0.37
SrO	0.40	0.37
Tc2O7	0.40	0.37
CaO	0.30	0.31
MgO	0.20	0.25
PdO	0.20	0.19
Rb2O	0.20	0.25
Rh2O3	0.20	0.19
Sm2O3	0.20	0.19
Y2O3	0.20	0.19
B2O3	0.10	0.00
BeO	0.10	0.06
NpO2	0.10	0.12
TeO2	0.10	0.12
K2O	0.05	0.00
PbO2	0.05	0.00
SeO2	0.03	0.03
Am2O3	0.02	0.02
CdO	3.00	0.02
Eu2O3	0.02	0.02
P2O5	0.40	0.02
PuO2	0.02	0.02
SnO2	0.02	0.02
Ag2O	0.01	0.01
Gd2O3	0.01	0.01
Nb2O5	0.01	0.01
Pm2O3	0.01	0.01
Ta2O5	0.01	0.01
TiO2	0.01	0.01
	100.00	100.00

with sugar additions by adding the required amount of frit and vitrifying the resulting slurry feed using a bottom-heated crucible technique. At 10-min intervals, additional aliquots of slurry were added until ~50 g of glass were produced. After melting, the crucible was removed from the furnace and

TABLE 7.2. Comparison of Oxide Compositions of NCAW 87, HW-39-4 Frit, HW-39-4 Glass, HW-39-2 Frit, and HW-39-2 Glass

Oxide	NCAW 87 wt% Oxide	Substituted Waste, wt% Oxide	HW-39-4 Frit wt% Oxide	HW-39-4 Glass wt% Oxide	HW-39-2 Glass wt% Oxide	HW-39-2 Frit wt% Oxide
SiO ₂	4.00	4.11	70.00	53.53	51.22	67.25
B ₂ O ₃	0.10	0.10	14.00	10.53	9.56	12.75
Na ₂ O	17.5	18.0	9.00	11.25	10.52	10.25
Li ₂ O	0.00	0.0	5.00	3.75	3.75	5.00
CaO	0.30	0.31	1.00	0.83	2.89	3.75
MgO	0.20	0.37	1.00	0.84	0.84	1.00
Fe ₂ O ₃	28.0	28.8	--	7.19	11.79	--
ZrO ₂	15.0	15.4	--	3.85	0.63	--
Al ₂ O ₃	9.0	9.3	--	2.31	4.56	--
NiO	2.30	2.36	--	0.59	0.63	--
La ₂ O ₃	2.50	2.57	--	0.64	0.58	--
Nd ₂ O ₃	2.00	5.07	--	1.27	0.53	--
SO ₃	1.80	1.85	--	0.46	0.39	--
F	1.20	1.23	--	0.31	0.31	--
MoO ₃	1.20	1.23	--	0.31	0.31	--
U ₃ O ₈	4.70	SUB Nd	--	--	--	--
CeO ₂	0.60	0.62	--	0.15	0.16	--
Cs ₂ O	0.60	0.62	--	0.15	0.16	--
CuO	0.60	0.62	--	0.15	0.16	--
MnO ₂	0.60	0.62	--	0.15	0.16	--
RuO ₂	0.60	0.62	--	0.15	0.16	--
Cr ₂ O ₃	0.50	0.51	--	0.13	0.14	--
BaO	0.40	0.41	--	0.10	0.11	--
Pr ₆ O ₁₁	0.40	0.41	--	0.10	0.09	--
SrO	0.40	0.41	--	0.10	0.09	--
Tc ₂ O ₇	0.40	DEL	--	--	--	--
PdO	0.20	0.21	--	0.05	0.05	--
Rb ₂ O	0.20	0.21	--	0.05	0.06	--
Rh ₂ O ₃	0.20	0.21	--	0.05	0.05	--
Sm ₂ O ₃	0.20	0.21	--	0.05	0.05	--
Y ₂ O ₃	0.20	0.21	--	0.05	0.05	--
BeO	0.10	SUB Mg	--	--	--	--
NpO ₂	0.10	DEL	--	--	--	--
TeO ₂	0.10	DEL	--	--	--	--
K ₂ O	0.05	DEL	--	--	--	--
PbO ₂	0.05	DEL	--	--	--	--
SeO ₂	0.03	DEL	--	--	--	--
Am ₂ O ₃	0.02	DEL	--	--	--	--
CdO	3.00	3.08	--	0.77	--	--
Eu ₂ O ₃	0.02	SUB Nd	--	--	--	--
P ₂ O ₅	0.40	0.41	--	0.10	--	--
PuO ₂	0.02	DEL	--	--	--	--
SnO ₂	0.04	DEL	--	--	--	--
Ag ₂ O	0.01	DEL	--	--	--	--
Gd ₂ O ₃	0.01	DEL	--	--	--	--
Nb ₂ O ₅	0.01	DEL	--	--	--	--
Pm ₂ O ₃	0.10	SUB Nd	--	--	--	--
Ta ₂ O ₅	0.03	DEL	--	--	--	--
TiO ₂	0.01	DEL	--	--	--	--
	100.0	100.0	100.0	100.0	100.0	100

air-quenched. Upon cooling, the glass sample was broken from the crucible, powdered, and sent for $\text{Fe}^{+2}/\text{Fe}^{+3}$ analysis. This same technique was used previously for the PSCM-22 melter test (Nakaoka et al. 1986).

7.1.3 Characterization of PSCM-23 Glass Product Samples

Melter samples of glass, cold cap, and surface phases taken during and immediately after the melter test were analyzed to compare preliminary laboratory physical properties and establish the existence of any crystalline or salt phases. Analyses included melt viscosity, electrical conductivity, surface phases composition, and crystal phase characterization.

7.2 TEST ANALYSES

7.2.1 Glass Formulation

Melter operation requires the temperature at which the glass melt has a viscosity of 100 poise (T100P) to be between 1070 and 1150°C. In the glass industry, melting of glasses at economically adequate rates ordinarily proceeds at the T100P (Chick et al. 1984; Babcock 1977; Stanek 1977). The maximum design electrode and maximum nominal melter operating temperature is 1200°C based on melter materials properties. Therefore, the nominal glass operating temperature was set 50°C lower as a safety factor. A high glass viscosity that occurs at lower operating temperatures can also cause problems with glass pouring, such as stringing or nesting of glass filaments. The lower limit of 1070°C is to ensure that the melt is not too fluid when heated to operating temperatures, which may result in excessive glass penetration into the refractories. The T100P of the HW-39-4 glass has been determined to be 1106°C $\pm$ 10°C. The viscosity curve for HW-39-4 is shown in Figure 7.1 along with that of HW-39-2 and a PSCM-23 glass sample for comparison. The viscosity was stable with respect to time.

The electrical conductivity of the glass melt at 1150°C is required to be between 0.18 and 0.50 (ohm-cm)⁻¹ by melter design criteria. The electrical conductivity at 1150°C (E1150) of HW-39-4 is 0.26 $\pm$ 0.02 (ohm-cm)⁻¹. The electrical conductivity curve for the HW-39-4 is shown in Figure 7.2 along with that of HW-39-2 and a PSCM-23 glass sample for comparison.

FIGURE 7.1. Viscosity Curves for HWVP Glasses HW-39-2, HW-39-4, and PSCM-23 (HW-39-4)

The phase behavior of laboratory-prepared glass samples was evaluated by optical and SEM/EDAX analyses of thin sections of quenched and heat-treated glass. The gross devitrification behavior of the HW-39-4 glass was evaluated by subjecting the glass to a 900°C 3-day isothermal anneal and a simulated canister heat-treatment. In the quenched and isothermal heat-treated laboratory development test glass, the only crystalline phases present were the oxide and metallic phases of noble metals i.e., ruthenium, rhodium, and palladium (which were expected because of the negligible solubility of the noble metals). In the simulated canister heat-treated glass, small amounts of nickel-iron-chrome spinel crystals, $(\text{Ni,Fe})(\text{Fe,Cr})_2\text{O}_4$, were also observed (estimated ≤ 5 wt%). No crystalline phases were observed in PSCM-23 melter glass samples that were inspected optically. There was also no indication of

FIGURE 7.2. Electrical Conductivity Curves for HWVP Glasses
HW-39-2, HW-39-4, and PSCM-23 (HW-39-4)

any significant sludge (crystalline phase) accumulation in the PSCM tank when the tank bottom was probed after the run. At this time, no product specifications exist on the amount of crystallinity that may exist in the production canisters transported to a federally licensed repository. Based on these evaluations, the phase behavior of the HW-39-4 is judged to be acceptable.

To determine if the HW-39-4 frit composition could be produced commercially, the melting behavior of the frit alone was evaluated. Carbonate and oxide components of the frit were found to melt very well at 1150°C. Therefore, commercial frit producers should have no problem producing this frit composition.

The HW-39-4 laboratory glass was tested for 7 and 28 days using MCC-1 and MCC-3 leaching procedures. Tests were run in duplicate. The test

results are summarized in Tables 7.3 and 7.4 for the MCC-1 tests, and Tables 7.5 through 7.8 for the MCC-3 tests. Leach testing results for HW-39-2 glass are presented for comparison. To compare the relative durability of different glasses, elemental glass components that do not precipitate after being released from the glass should be compared. Such elements include boron, and to a slightly lesser degree, alkalies such as lithium and sodium.

In the 7- and 28-day MCC-1 test, the normalized boron releases for the HW-39-4 and HW-39-2 glasses were found to be similar, with slightly higher releases from HW-39-4 in the 28-day test. Both of these glasses were below the proposed tuff geologic repository boron limit of 28 g/m^2 for a 28-day MCC-1 test.

The results from the MCC-3 tests were significantly different. The MCC-3 leach test is very similar to the MCC-1 test procedure with two exceptions: the glass is in a powdered form, and glass powder and leachant are agitated by rotating the container. The elemental leachate concentrations from MCC-3 tests approximate long-term extrapolation of MCC-1 test results and assess the glass dissolution properties when glass components may be saturated in the leachant.

In the 7-day MCC-3 tests, the normalized boron release from HW-39-4 was ~5 times higher than the normalized boron release from HW-39-2. In the 28-day MCC-3 tests, the normalized boron release was ~8 times higher. The reason for this significant increase of glass dissolution under MCC-3 conditions is not clear. The final pH for the HW-39-4 leachant was slightly lower than for HW-39-2; generally, the higher the pH the greater the dissolution of the glass. The differences in the two glass compositions do not suggest any large change in durability. Calculating the free energies of hydration for the two glasses using a DWPF (Plodinec et al. 1984) model, indicated that the HW-39-4 glass should be more durable than the HW-39-2 glass.

TABLE 7.3. Comparison of Normalized Releases from HWVP Glasses HW-39-4 and HW-39-2 in 7-Day MCC-1 Leach Testing. Conditions: MCC-1 in DIW, SA/V = 10^{-1} , 90°C.

<u>Element</u>	<u>Normalized Elemental Release, g/m²</u>	
	<u>HW-39-4</u>	<u>HW-39-2</u>
Si	7.93	8.10
B	9.83	9.88
Li	9.84	9.93
Na	9.79	9.51
Ca	2.97	6.25
Mo	9.70	9.30
Sr	2.84	5.57
Al	6.88	7.40
Fe	0.16	0.00
Cs	12.73	13.66
Final pH	9.24	9.52

TABLE 7.4. Comparison of Normalized Releases from HWVP Glasses HW-39-4 and HW-39-2 in 28-Day MCC-1 Leach Testing. Conditions: MCC-1 in DIW, SA/V = 10^{-1} , 90°C.

<u>Element</u>	<u>Normalized Elemental Release, g/m²</u>		<u>Draft Specifications^(a)</u>
	<u>HW-39-4</u>	<u>HW-39-2</u>	
Si	13.34	11.20	28
B	19.31	14.83	28
Li	16.50	15.01	
Na	15.95	13.54	28
Ca	0.23	7.23	
Mo	16.74	13.94	
Sr	0.89	5.72	
Al	9.61	9.11	
Fe	0.22	0.00	
Cs	20.68	16.22	28
Final pH	9.41	9.32	

(a) Draft "Waste Acceptance Preliminary Specifications for the Defense Waste Processing Facility. High-Level Waste Form," Revision 1, 06R/B-8, April 1988. The U-238 was not in the test glass so that its leach rate could be measured. The leach specification is for Cs-137 instead of total Cs as indicated in Table 7.4.

TABLE 7.5. Comparison of Normalized Releases from HWVP Glasses in 7-Day MCC-3 Leach Testing with 0.45- μm Filtrate. Conditions: MCC-3 in DIW, 7 days, SA/V = 2000 m^{-1} , 90°C.

<u>Element</u>	<u>Normalized Elemental Release, g/m^2</u>	
	<u>HW-39-4</u>	<u>HW-39-2</u>
Si	0.60	0.21
B	2.19	0.44
Li	1.81	0.49
Na	1.58	0.40
Ca	0.02	0.04
Sr	0.02	0.03
Al	0.04	0.12
Fe	0.18	<0.01
Mg	0.39	0.25
Cs	0.21	0.13
Final pH	10.18	10.38

TABLE 7.6. Comparison of Normalized Releases from HWVP Glasses in 7-Day MCC-3 Leach Testing with 18-Angstrom Filtrate. Conditions: MCC-3 in DIW, SA/V = 2000 m^{-1} , 90°C.

<u>Element</u>	<u>Normalized Elemental Release, g/m^2</u>	
	<u>HW-39-4</u>	<u>HW-39-2</u>
Si	0.52	0.20
B	2.19	0.45
Li	1.75	0.47
Na	1.54	0.39
Ca	0.01	<0.01
Sr	<0.01	<0.01
Al	0.01	0.04
Fe	0.15	<0.01
Mg	<0.01	<0.01
Cs	0.17	0.05
Final pH	10.18	10.38

TABLE 7.7. Comparison of Normalized Releases from HWVP Glasses in 28-Day MCC-3 Leach Testing with 0.45- μm Filtrate. Conditions: MCC-3 in DIW, SA/V = 2000 m^{-1} , 90°C.

<u>Element</u>	<u>Normalized Elemental Release, g/m^2</u>	
	<u>HW-39-4</u>	<u>HW-39-2</u>
Si	0.64	0.25
B	4.29	0.53
Li	2.90	0.62
Na	2.74	0.52
Ca	0.01	0.07
Sr	<0.01	0.05
Al	<0.01	0.17
Fe	0.04	<0.01
Mg	0.08	0.36
Cs	0.19	0.23
Final pH	10.41	10.55

TABLE 7.8. Comparison of Normalized Releases from HWVP Glasses in 28-Day MCC-3 Leach Testing with 18-Angstrom Filtrate. Conditions: MCC-3 in DIW, SA/V = 2000 m^{-1} , 90°C.

<u>Element</u>	<u>Normalized Elemental Release, g/m^2</u>	
	<u>HW-39-4</u>	<u>HW-39-2</u>
Si	0.69	0.22
B	4.29	0.53
Li	2.93	0.58
Na	2.77	0.50
Ca	0.03	0.01
Sr	<0.01	<0.01
Al	<0.01	0.04
Fe	<0.01	<0.01
Mg	<0.01	<0.01
Cs	0.19	0.09
Final pH	10.41	10.55

7.2.2 Feed Redox Adjustment

Various quantities of formic acid^(a) and sugar were added to the waste feed to determine a suitable combination to be used for PSCM-23 feed redox adjustment. The feed redox adjustment testing was required by the higher-than-expected nitrate (oxidant)^(b) concentration in the simulated waste feed received from the vendor. The first batch of simulated HWVP feed tested was formatted by adding 20 mL formic acid per liter of waste (Table 7.9). This level of formatting was chosen to convert a maximum quantity of the hydroxides that would participate in formate reactions to formate salts. Testing demonstrated that 15 to 20 g of sugar were required to adjust the glass redox to within the required range. Sugar addition has been observed

TABLE 7.9. Summary of Laboratory Melter Feed Forming Tests

Sample #	Formic Acid, mL/L	Sugar, g/L	TOC, (a) g/L	Fe ⁺² /Fe ⁺³
GD11	10	15	8.6	0.000
GD1	20	0	5.2	0.000
GD7	20	15	11.5	0.039
GD6	20	20	13.6	0.210
GD2	30	0	7.8	0.000
GD3	30	5	9.9	0.000
GD4	30	10	12.0	0.000
GD8	30	15	14.1	0.063
GD5	30	20	16.2	0.305
GD9	40	0	10.4	0.000
GD10	40	10	14.4	0.009

(a) Total Organic Carbon

- (a) Quantities of formic acid described throughout this report refer to use of a 90 wt% formic acid solution. The phrase "formic acid" is used for brevity.
- (b) The nitrate concentration was subsequently listed within the nitrate range of the HWVP Feed Specification upon its revision in third quarter, FY 1988.

to reduce melting rates (Perez and Nakaoka 1986). Therefore, further testing was conducted to determine if the amount of sugar added could be reduced or eliminated by increasing the amount of formic acid added to the HWVP feed. Glasses were produced from slurry batches formatted using 10 to 40 mL/L formic acid and with sugar additions of 0 to 20 g/L. The results from these tests are presented in Table 7.9 and Figure 7.3. Figure 7.3 is a plot of total organic carbon (TOC) in the feed versus the $\text{Fe}^{+2}/\text{Fe}^{+3}$ of the glass.

The results show that up to 40 mL/L formic acid did not provide enough reductant to reduce the glass to a measurable $\text{Fe}^{+2}/\text{Fe}^{+3}$ ratio, and additional reductant (sugar) needed to be added. Sugar levels of ~15 g/L were required to reduce the glass in the laboratory. A slightly lower level (10 g/L) was expected to be required in the PSCM-23 test because of the "closed" nature of the melter.

Figure 7.4 shows the $\text{Fe}^{+2}/\text{Fe}^{+3}$ results from glasses in the PSCM-22 melter test (a "closed" system) with the $\text{Fe}^{+2}/\text{Fe}^{+3}$ ratio obtained from the same melter feeds melted in the laboratory. No sugar was required to achieve a reduced glass during the PSCM-22 run (Perez and Nakaoka 1986). However, approximately 3.5 g/L of sugar were added during a part of the PSCM-22 test to intentionally achieve a more reduced $\text{Fe}^{+2}/\text{Fe}^{+3}$ state ratio (see Figure 7.4). The major contributing factor for increased TOC requirement for the PSCM-23 feed is the large increase in the amount of nitrate (i.e., oxidant) in the NCAW 87 test composition (35 g/L compared to 10 g/L reference composition).

7.2.3 Characterization of PSCM-23 Glass Product Samples

Thin sections were cut and polished from the glass bars (taken from melter pours) and a cold cap sample. The optical analysis at 630X magnification found no detectable crystalline phases in the glass bar samples. The lack of any observable crystalline phases compared with PSCM-22 glass samples is due to the Cr_2O_3 concentration in the HW-39-4 glass composition (~0.13 wt%) being below the solubility limit of ~0.5 wt% typical of these glasses. Glass from the PSCM-22 melter test had a significant amount of Fe-Cr spinel due to the high Cr_2O_3 concentration in the glass (~1.3 wt%).

FIGURE 7.3. $\text{Fe}^{+2}/\text{Fe}^{+3}$ Versus the Total Organic Carbon in Pre-PSCM-23 Slurry Feeds. TOC is the total amount of carbon from forming the waste (each curve) plus the addition of sugar (the value in parentheses).

The cold cap sample received did not provide a total cross section of the cold cap and the molten glass underneath. The sample provided from the PSCM-23 test did have a small section with part of the cold cap/glass interface intact. The thin section of this part of the cold cap sample was observed optically up to 630X magnification. The crystalline material present appeared to be calcined-but-not-yet-melted feed with no observable segregation of the feed components.

FIGURE 7.4. Redox Response of PSCM-22 Feeds (laboratory) and Glasses (melter)

The viscosity and electrical conductivity of the PSCM-23 glass was measured using glass taken from the top of canister #8 (sample #441). This sample corresponds in time to glass sample #236 which was obtained at the overflow section of the melter during the pour. Elemental analysis by inductively coupled plasma atomic emission spectroscopy (ICP) was conducted on both #236 and #441. The compositions of these two samples were found to be essentially the same and very close to the target.

The viscosity curves for both the laboratory version and the PSCM-23 glass are presented in Figure 7.1. Both viscosities and T100Ps are within

experimental error of each other ($\pm 10^{\circ}\text{C}$). The electrical conductivity curves for both the laboratory version and the PSCM-23 glass are presented in Figure 7.2. Both electrical conductivities and E1150s are within experimental error of each other ($\pm 0.02 \text{ ohm}^{-1}\text{cm}^{-1}$).

8.0 FEED PREPARATION

Feed preparation studies for the PSCM-23 test were designed to qualitatively investigate the effects of formic acid addition rate and slurry agitation on the generation of the foam layer associated with the reaction of formic acid and selected slurry components. Characterization of the effects of these operational parameters on the generation and stability of the foam layer was based on visual observations made during the feed preparation process. The overall boiling heat transfer coefficient was calculated for the pilot-scale equipment using simulated HWVP feed. This value was compared with the HWVP design value and other available design/test values.

8.1 TEST APPROACH

8.1.1 Feed Preparation Performance

The approach for evaluating the feed preparation parameters (formic acid addition rate and level of agitation) was to increase the acid addition rate with each subsequent batch of feed until an excessive and stable foam layer occurred. The slurry agitation level was then increased and the conditions of the previous batch were repeated. In this manner, the maximum rate of acid addition would be established and the effects of slurry agitation evaluated.

The qualitative characterization of the effects of operational parameters on foam generation during PSCM-23 feed preparation was based on visual observations. These observations included the presence of foam, foam thickness and density, and the rate of foam accumulation. The operational parameters evaluated during the process were formic acid addition rate and slurry agitation. During the formic acid addition procedure, the required amount of acid was initially transferred from a storage drum to a container located on a platform scale. The acid was then pumped from the container to the process vessel and the addition rate was determined by observing the weight change over a given time period. Agitation in the process vessel was evaluated based on observations of slurry surface movement. The controller setpoint of the variable speed system was used to quantify agitation. Approximate

measurements of agitator rotational speed using a hand-held tachometer were also taken on a single batch of feed following formic acid addition and heat treatment.

8.1.2 Heat Transfer Evaluation

Using existing capabilities associated with the pilot-scale feed preparation system, an estimate of the overall heat transfer coefficient of boiling was made. The process vessel, Tk 311, was used to concentrate a batch of feed (prior to formic acid treatment). Measurements of tank volume were taken before and after the concentration step. These values were used to determine the quantity of water boiled off during the activity. Steam pressure and feed temperature were also monitored during the process. Based on fundamental heat transfer relationships, an overall boiling heat transfer coefficient was calculated. During the feed preparation process, the temperature of the feed was monitored using a Type K thermocouple and a chart recorder. Tank level was measured using a dipstick, and resulting feed volume was determined from a tank calibration. Boil off rate as a function of concentration time was not determined because of equipment limitations.

8.1.3 Slurry Property Analyses

The physical and chemical properties of PSCM-23 slurry samples were evaluated to determine the changes in slurry properties during the course of feed preparation. Samples of slurries were evaluated following initial batching, formic acid addition, and frit addition. Analyses included pH, density, liquid to solids ratios, wt% water in the sludge, and rheological measurements.

8.2 TEST ANALYSES

8.2.1 Feed Preparation Performance

A total of five batches of feed were prepared in support of the PSCM-23 test. A summary of the operational parameters and observations made during the formic acid treatment activity is presented in Table 8.1. The formic

TABLE 8.1. Summary of Formic Acid Treatment During Feed Preparation for PSCM-23

Conditions During the Addition of the Initial 60 wt% of Formic Acid					
Batch #	Target Rate, L/h	Actual Rate, L/h	Agitator Controller Setpoint, %	Rotational (a) Speed, rpm	Observations
1	60	63	70	85	No foam observed.
2	60	60	70	85	No foam observed.
3	60	61-35	70-80	85-100	Three-in. foam layer observed after 46 wt% of required formic acid added - increasing. Pump shut off, agitation increased, and foam allowed to dissipate. Addition rate decreased to 35 L/h and pump turned on. Three-in. foam layer observed - stable.
4	60	60-43	70-80	85-100	One-in. foam Layer observed after 32 wt% of required formic acid added - stable. Increased agitation to dissipate foam. Rate declined to 43 L/h during addition.
5	40	38	75-85	90-110	Initial rate reduced to avoid foaming. Four-in. foam layer observed after 55 wt% of required formic acid added - increasing. Pump shut off, agitation increased, and foam allowed to dissipate. Pump on at same rate, three-in. foam layer observed - stable.
Conditions During the Addition of Final 40 wt% of Formic Acid					
Batch #	Target Rate, L/h	Actual Rate, L/h	Agitator Controller Setpoint, %	Rotational (a) Speed, rpm	Observations
1	20	18	70	85	No foam observed.
2	25	8	70	85	Target rate of 25 L/h was unattainable due to pump - no foam observed.
3	25	20	80	100	Rate reduced due to foaming during addition of initial 60 wt%.
4	30	30	85	110	No foam observed.
5	35	23	85	110	Three-in. layer of foam observed throughout addition - stable.

- (a) Rotational speed values are approximate.
 Measurements taken on Batch #5 following formic acid addition and heat treatment.
 Tank volume = 2488 L.

acid addition rate for the initial 60 wt% of formic acid was set at approximately 60 L/h. This rate corresponded to the maximum rate for the peristaltic addition pump used initially. Refer to Sections 4.0 and 5.1 for details of the formic acid treatment and equipment details, respectively.

Inconsistencies created by equipment problems and varying preparation conditions between batches limit the number of conclusions **that can** be drawn from the formic acid treatment activities of this test. Varying amounts of dilution water used to rinse the precipitated slurry drums caused the **con-**centration of feed undergoing formic acid treatment to vary as much as 25% from batch to batch. In addition, control of the formic acid addition pump was less than optimum. The addition rate tended to decrease over time and had to be adjusted frequently. As a result, the addition rate was increased above the target during pump rate adjustment to achieve the desired average addition rate.

Foam was observed during the addition of the initial 60 wt% of acid for the last three batches of feed (foaming during treatment of Batch #3 was very light). No foam was observed during the addition of the final 40 wt% of acid, except for Batch #5. Prior to this test, foaming incidents had been observed only after the initial 60 wt% of the required formic acid had been added (Nakaoka et al. 1986). For this reason, the addition rate of the first 60% of the formic acid has been set quite high. The formic acid concentration at the beginning of the foaming incidents encountered during the treatment of Batch #3 and Batch #5 was calculated to be approximately 0.3 M. A review of the past data revealed that the concentration of formic acid at the initiation of the foaming incident observed during the preparation of HBCM-85-1 feed for FY 1986 testing was also approximately 0.3 M (Nakaoka et al. 1986). These data suggest that formic acid molar concentration should be used as the benchmark for controlling foam generation instead of the percent of total acid required.

Although the results of these tests are inconclusive, **it** appears that the degree of slurry agitation may have accounted for the fact that no foaming was observed during the formic acid treatment of the first two batches. The volume of feed for these batches was approximately 25% lower than that of

the final three batches. The initial controller **setpoint** for the agitator motor was approximately 70% for all five batches. The relative agitation and surface turbulence during the formic acid treatment of the first two batches was higher than for the final three batches. In general, increased agitation was unsuccessful in dissipating an established foam layer while acid addition was in progress.

The observations made during the acid treatment of Batch #5 cannot be explained at this time. This batch was prepared by shift operators while the PSCM-23 test was in progress and foam was observed during most of the formic acid treatment sequence. The initial formic acid addition rate of 40 L/h, a 33% reduction over Batch #3 and Batch #4, was selected in an attempt to prevent foaming. Relative agitation during the treatment of this batch was similar to that used in the treatment of the previous two batches. The acid addition rate for the final 40 wt% of formic was inconsistent due to the loss of pump prime on a number of occasions.

8.2.2 Heat Transfer Evaluation

A batch of feed was concentrated from approximately 190 g WO/L to 225 g WO/L. The feed concentration required 3.4 h and was conducted prior to formic acid addition. An evaluation of the effects of steam pressure on boiling action was also conducted by varying the pressure over the range of 35 to 62 psig during concentration. The overall heat transfer coefficient for boiling was determined by estimating an average steam pressure, establishing the boiling temperature of the feed, and measuring the volume change that occurred during the process. Combined with the properties associated with these parameters and the dimensions of the equipment, the overall heat transfer coefficient for the concentration of HWVP-87 feed in the pilot-scale process vessel was calculated to be 88 Btu/h·ft²·°F (see Table 8.2). Heat losses from the tank to the surroundings were calculated to account for 14% of the heat input. An estimate of error for this calculation suggests that it could vary as much as 50%. The majority of the error is associated with the inaccuracy of the feed volume measurement (± 0.5 in.).

TABLE 8.2. Estimation of the Average Overall Heat Transfer Coefficient During Concentration

$$q = U_o A_o \Delta T = U_o A_o (T_s - T_f)$$

where q = heat rate, **Btu/h**

U_o = overall heat transfer coefficient, **Btu/h·ft²·°F**

A_o = heat transfer area, **ft²**

T_s = steam temperature, **°F**

T_f = feed temperature, **°F**

$$q = q_1 + q_2$$

where $q_1 = \frac{m \lambda_{\text{vapor}}}{\Delta t} = \text{average heat rate during boiling}$

where m = mass of water boiled off, **lb**

λ_{vapor} = heat of vaporization for water at boiling point, **Btu/lb**

Δt = time required for boiling, **h**

$$m = 335 \text{ L} \times 1.0 \text{ kg/L} \times 2.2 \text{ lb/kg} = 737 \text{ lb}$$

$$\lambda_{\text{vapor}} = 969 \text{ Btu/lb at } 214^\circ\text{F}$$

$$\Delta t = 230 \text{ min} = 3.83 \text{ h}$$

$$q_1 = \frac{737 \text{ lb} \times 969 \text{ Btu/lb}}{3.83 \text{ h}} = 186,482 \text{ Btu/h}$$

$$q_2 = U_t A_t (T_f - T_R) = \text{heat losses from the tank to its surroundings}$$

where U_t = overall tank heat transfer coefficient, **Btu/h·ft²·°F**

A_t = surface area of tank, **ft²**

T_R = temperature of room, **°F**

$$U_t \approx 1.8 \text{ Btu/h·ft}^2\text{·°F}$$

$$A_t = \text{area of tank wall} + \text{area of top} + \text{area of bottom} = 127 \text{ ft}^2$$

$$T_f \approx 214^\circ\text{F}$$

$$T_R \approx 80^\circ\text{F}$$

$$q_2 = 1.8 (127) (214 - 80) = 30,680 \text{ Btu/h}$$

$$\text{Therefore, } q = 186,482 \text{ Btu/h} + 30,680 \text{ Btu/h} = 217,162 \text{ Btu/h}$$

$$q = U_o A_o (T_s - T_f)$$

$$U_o = \frac{q}{A_o (T_s - T_f)} = \frac{217,162}{28.9 (299 - 214)}$$

$$U_o = 87.9 \text{ Btu/h·ft}^2\text{·°F}$$

The boiling action during the concentration of the feed became more vigorous as steam pressure was increased. Based on observations, it did not appear that the boiling mechanism changed over the steam pressure range tested (35 to 62 psig). The shift from nucleate to transition boiling is generally marked by a decrease in the random generation of bubbles and the appearance of vapor jets. Further testing would be required to characterize the concentration process and establish the steam pressure at which this transition occurs in the pilot-scale system.

The value for the overall heat transfer coefficient currently being used to estimate cycle time for concentration of HWVP feed is the DWPF design value of $120 \text{ Btu/h}\cdot\text{ft}^2\cdot^\circ\text{F}$ (see Table 8.3). This value seems to be appropriate, based on DWPF full-scale, prototypic test results. However, further testing with HWVP feed under design conditions will be required to establish a suitable boiling heat transfer coefficient. The need for further testing is apparent from the significant differences between the PSCM-23 and the DWPF tests in the SRAT. The PSCM-23 and HWVP bench-scale test heat transfer values may not be representative of plant equipment because of design and scale differences. However, the importance of these values in achieving HWVP process capacities warrants additional consideration.

8.2.3 Slurry Property Analyses

Four PSCM-23 feed samples were selected for further characterization. The characterization effort included the collection and evaluation of the following data: pH, density, rheology, supernate/sludge volume ratio, wt% water in the sludge fraction, and analysis of feed fractions by IC, ICP and carbon analyses.

Table 8.4 summarizes the pH, density, and rheological data collected for the selected PSCM-23 feed samples. Also included in Table 8.4 are comparative data from two previous HWVP studies. Samples 13 and 28 are of the slurry prior to formic acid treatment, sample 39 was obtained after formic acid treatment and concentration, and sample 42 was obtained after frit addition and formic acid addition in the SHT.

TABLE 8.3. Comparison of Boiling Heat Transfer Coefficients

	Steam Pressure, <u>psig</u>	Heat-Transfer Coefficient, <u>Btu/h·ft²·°F</u>
PSCM-23	52	88
HWP Bench-Scale Tests	50	85
SRL SRAT Tests (a)	57-81	123-144
DMFF Process	100	120

TABLE 8.4. Physical Properties of PSCM-23 Feed Samples

<u>Sample/Study</u>	<u>Type Sample</u>	<u>Densitv. g/ml</u>	<u>pH</u>	<u>Yield Stress. Pa</u>	<u>Apparent Viscosity, cP</u>		
					<u>183 s⁻¹</u>	<u>383 s⁻¹</u>	<u>468 s⁻¹</u>
PSCM-23-13	NCAW 87	1.19	8.95	32	30.7	19.8	17.9
PSCM-23-28	NCAW 87	1.16	8.94	3.67	34.0	22.1	20.0
PSCM-23-39	Formatted NCAU 87	1.24	4.16	2.71	29.4	19.9	18.1
PSCM-23-42	Melter Feed	1.47	4.42	(a)	(a)	(a)	(a)
Thornton 1987	NCAW 86	1.13	11.7	7.7	10.8	8.1	7.3
	Formatted NCAU 86	1.14	4.20	3.9	7.3	5.6	5.1
Wiemers, Andersen, and Peterson 1987	NCAU 86	1.13	11.9	52.6	46.2	30.6	23.4
	Formatted NCAW 86	1.12	4.2	149.7	110.9	65.8	47.5

(a) Data not available.

The pH of the feed before forming is approximately 9 and after **forming** approximately 4. The initial pH of the PSCM-23 samples is lower than measured for previous feed simulants (pH >11). Previously, a significant quantity of the sodium was added as NaOH. Because of the high nitrate loading in the current NCAW feed, much less NaOH is present. The final pH of approximately 4 indicates that an acceptable amount of formic acid has been added based on past studies.

The density of the feed prior to concentration and **frit** addition (samples 13 and 28) is comparable to past studies, 1.1-1.2 g/ml. A significant increase in density is observed for sample 42 (after **frit** addition). The rheological properties of samples 13, 28, and 39 were measured. These samples have yield stresses of approximately 3 Pa and are somewhat pseudo-plastic (flow behavior index, $n = 0.8$; where $n=1$ is Newtonian). The apparent

viscosities as a function of shear rate are shown graphically in Figure 8.1. In a shear rate range of 200 to 468 s^{-1} the average apparent viscosities range from 30 to 18 cP . Insufficient sample volume was available for rheological measurements of sample 42.

The PSCM-23 feed simulant was prepared using a scale-up of the procedure developed in FY 1987. In accordance with this procedure, the soluble metal nitrates were precipitated as metal hydroxides using sodium hydroxide as opposed to beginning with the hydroxide salts. The intent of this feed preparation procedure is to more closely simulate the actual waste processing history.

The rheological properties of the PSCM feed differ from those measured in past studies. In general, the apparent viscosity range for the PSCM-23

FIGURE 8.1. Average Apparent Viscosities as a Function of Shear Rate for PSCM-23 Samples 13, 28, and 39

samples is 1/3 to 2 times greater than those from previous studies. The PSCM-23 feed simulant yield stresses are 20X less for initial feed and 50X less for formed feed.

The rheological properties of the feed are greatly dependent on feed preparation due in part to the formation and aging of pH-dependent hydrolyzed polymeric colloids by three of the major constituents: ferric ion, aluminum ion, and zirconium ion. Other minor constituents (e.g., nickel and cupric ions) may also contribute to the polymeric concentration. The physical state of the feed influences both the agitation and pumping requirements and potentially, the kinetics of the forming reactions.

A 20 mL aliquot of the slurry from each sample was centrifuged and the supernate and sludge recovered. Observations and the chemical composition of these phases are discussed below.

The sludge was dried at 105°C for 20 hours. This temperature was selected to evaporate water without decomposing the organics. Table 8.5 presents the ratio of supernate to sludge recovered, qualitative observations concerning the supernate and sludge, and wt% of water in the sludge.

The supernate-to-sludge volume ratio was approximately 50/50 until addition of frit. Concentration and dilution steps were not apparent from these

TABLE 8.5. Supernate and Sludge Data

<u>Sample Label</u>	<u>Vol. Ratio: Supernate/ Sludge</u>	<u>Wt% Water in Sludge</u>	<u>Qualitative Observations</u>
PSCM-23-13	50/50	71	Supernate - yellow color; Sludge - 2 distinct layers
PSCM-23-28	50/50	71	Supernate - yellow color; Sludge - 2 distinct layers
PSCM-23-39	45/55	64	Supernate - blue color; Sludge - 2 distinct layers
PSCM-23-42	35/65	39	Supernate - blue color, less intense than -39; Sludge - 3 distinct layers

data. As one might predict, the ratio of supernate to sludge decreased to 35/65 after the addition of frit.

The supernates were observed to be two different colors, the alkaline supernates being yellow and the acidic supernates being blue. Table 8.6 lists ionic species which may potentially contribute to the observed coloring. The yellow color observed in the alkaline supernate may be due to a hydrolysis product of ferric ion. Hydrated ferrous and cupric ions are likely candidates for the blue color in the acidic supernate. The presence of copper in the acidic supernate was confirmed by ICP analysis as discussed later. Although somewhat unstable in an oxidizing environment, ferrous ion may be present as a product of reduction of ferric ion by formic acid.

Between two and three different fractions of particle densities were observed in the sludges recovered from centrifugation. The three layers may be due to 1) gelatinous polymers, 2) precipitated salts, and 3) frit. Samples 13, 28, and 39 had two distinct layers after centrifugation. The top layer composed approximately 95% of the total sludge volume and was a dark brick red color. The second, bottom layer was a light orange-sand color and contained visible black particulate, approximately 0.5 mm in diameter. The bottom layer appeared to be more compact, containing less water. An additional third layer beneath the orange-sandy colored layer was observed in

TABLE 8.6. Potential Ionic Species Contributing to Supernate Color

<u>Ionic Species</u>	<u>Characteristic Color</u>
$[\text{Cr}(\text{H}_2\text{O})_6]^{+2}$	Blue (presence of Cr^{+2} uncertain)
$[\text{Cr}(\text{H}_2\text{O})_6]^{+3}$	Violet
$[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$	Green
$[\text{Ni}(\text{H}_2\text{O})_6]^{+2}$	Green
$[\text{Cu}(\text{H}_2\text{O})_6]^{+2}$	Blue
$[\text{Fe}(\text{H}_2\text{O})_6]^{+2}$	Blue-green
$[\text{Fe}(\text{H}_2\text{O})_6]^{+3}$	Pale purple (exists only at $\text{pH} = 0$)
$[\text{Fe}(\text{H}_2\text{O})_5\text{OH}]^{+2}$	Yellow
$\text{MoO}_2(\text{OH})$	Blue
$\text{MoO}_{2.5}(\text{OH})_{0.5}$	Blue

sample 42. In sample 42 the top layer composed approximately 30% of the total sludge volume; the orange sandy layer composed approximately 4% and the additional third layer, an orange brick color, made up the remaining 66%. The additional third layer was relatively grainy compared to the other two layers, perhaps because **it** contained most of the **frit**. Each of these **centrifuged** samples was homogenized before drying.

The amount of water loss on drying the sludge fractions from samples 13 and 28 was 71 **wt%**. The **wt%** water in the sludge decreased after forming and concentrating to 64 **wt%**. Sludge containing the **frit** contained the least amount of water, 39 **wt%**. The chemical composition of the supernate fraction and total slurry as determined by ICP analysis is compiled in Table 8.7.

The solubility behavior of **lithium** (observed only after **frit** addition) and those ions associated primarily with one fraction (concentration ratios **<0.001**) throughout the forming and **frit** addition are **outlined below**:

Ion	Associated Fraction(a)
Barium	solids; 0.2% in supernate after forming
Cerium	solids; 0.3% in supernate after forming
Iron	solids; 0.002% in supernate prior to forming 0.01% in supernate after forming
Lithium	solids; 2.4% in supernate (observed only after frit addition)
Sodium	supernate
Silica	solids (prior to forming); 0.2% in supernate after forming 0.01% in supernate after frit addition
Titanium	solids
Zirconium	solids; 0.003% in supernate after forming

(a) % refers to the ratio: grams in fraction divided by total grams present.

Table 8.7. Chemical Composition of Selected HWVP Feed Samples

Element (as Oxide)	Sample Number and Oxide Concentration Distribution (g/L)							
	PSCM-23-13		PSCM-23-28		PSCM-23-39		PSCM-23-42	
	Total	Supernate	Total	Supernate	Total	Supernate	Total	Supernate
Al ₂ O ₃	15.5	<dl (a)	14.7	<dl	20.0	1.53	16.6	0.68
B ₂ O ₃	0.28	0.009	0.18	0.009	0.35	0.31	70.6	1.56
BaO	0.67	nd	0.63	nd	0.87	0.0002	0.66	0.0002
CaO	0.58	0.002	0.53	0.002	0.72	0.68	5.61	0.73
CeO ₂	0.94	<dl	0.89	<dl	1.00	0.003	0.97	0.002
Cr ₂ O ₃	0.93	0.15	0.88	0.15	1.25	0.12	0.92	0.056
CuO	1.05	<dl	1.01	0.002	1.37	0.27	0.97	0.21
Fe ₂ O ₃	46.1	0.001	43.5	0.001	59.1	0.006	42.8	0.003
La ₂ O ₃	8.66	0.001	8.20	0.001	11.1	0.29	8.07	0.22
Li ₂ O	<dl	<dl	<dl	<dl	<dl	0.003	24.8	0.006
MgO	0.69	0.026	0.65	0.28	0.89	0.90	5.22	0.91
MnO ₂	1.24	<dl	1.16	<dl	1.61	1.13	1.14	1.04
MoO ₃	2.02	0.63	1.90	0.63	2.64	<dl	1.94	<dl
Na ₂ O	26.3	28.2	25.8	28.2	41.9	35.9	40.0	61.2
Nd ₂ O ₃	3.92	<dl	3.18	<dl	4.71	0.15	3.50	0.099
NiO	3.92	<dl	3.75	<dl	5.07	0.046	3.71	0.051
SiO ₂	6.79	<dl	6.09	<dl	9.14	0.017	365	0.035
SrO	0.74	0.011	0.70	0.011	0.95	0.54	0.68	0.51
TiO ₂	0.11	<dl	0.10	<dl	0.15	<dl	0.57	<dl
Y ₂ O ₃	0.38	<dl	0.36	<dl	0.48	0.18	0.36	0.16
ZnO	3.28	<dl	3.10	<dl	4.24	0.008	3.10	0.007
ZrO ₂	23.8	<dl	23.1	<dl	31.8	0.001	23.8	0.001

(a) **dl** = below detection Limit.

Of the five major constituents, four remain primarily with one fraction throughout the forming process: iron, zirconium, and silica remain with the solids and sodium with the supernate. Before forming, the remaining major constituent, aluminum, is contained in the solids fraction. After forming, 8% of the aluminum is solubilized.

The significant solubilization changes of HWVP feed ions observed during forming, concentrating and frit addition are illustrated graphically in Figure 8.2. These data are derived from ICP analyses of supernate and slurry samples. The behavior of these ions is described below by contrasting solubilities before and after the addition of formic acid and frit.

Solubilization of Ions in HWVP Feed

Figure 8.2. Solubilization of Ions in HWVP Feed During Forming, Concentrating, and Frit Addition

Ions with increase in solubility after forming

- Significant change (ratio **supernate/total** after forming **>0.5**)

boron
calcium
magnesium
manganese
strontium

- Slight change (ratio **supernate/total** after forming **>0.1**)

copper
yttrium
zinc

- Relatively small change, however, detectable (ratio **supernate/total** **<0.1**, i.e., **<10 wt%** solubilized)

aluminum
lanthanum
neodymium
nickel

Ions with decrease in solubility after forming

chromium - from 16% to 9% of total (by wt) in supernate
molybdenum - from 33% to **<0.1%** of total (by wt) in supernate

Ions with increase in solubility after frit addition

boron
calcium
magnesium
aluminum
chromium

Ions with decrease in solubility after frit addition

manganese
strontium

The increase in solubility after forming may be due to the neutralization of slightly insoluble hydroxide species, forming soluble formates:

As a first approximation, the observed solubilization ratios given in Figure 8.2 may represent the extent to which individual neutralization reactions have occurred.

Molybdenum and chromium in the supernate decreased after forming. The explanation for this behavior is not apparent.

The large decrease in the **supernate/total** wt ratio for boron, calcium, and magnesium ions and the relatively smaller decrease for aluminum and chromium ions after **frit** addition (sample 42) is attributed to the addition of these ions to the solid fraction via the **frit** matrix. The observed increase solubility of manganese and strontium after **frit** addition is not presently understood.

The concentration of soluble fluoride, chloride, nitrate, sulfate, and **formate** as determined from IC analysis is reported in Table 8.8. Evaluation of the these data indicate the following:

After concentration (1.35 concentration factor) and forming steps (sample 28 compared with sample 39):

- The concentration of sulfate decreases by 42 wt% (approximately 1.44 g/L) sulfate). This may be due to the reduction of sulfate to gaseous sulfur oxides via formic acid.
- The concentration of nitrate decreases by 3 wt% (approximately 1.90 g/L). Reduction of nitrate to gaseous oxides of nitrogen (NO, NO₂, N₂O) by formic acid may account for this loss.

Table 8.8. HWP PSCM-23 Feed Anion Concentration During Formating, Concentrating, and Frit Addition

Sample Number	Fluoride, g/L	Chloride, g/L	Nitrate, g/L	Sulfate, g/L	Formate, g/L
13	19.2	0.58	49.4	2.58	<dl
28	18.7	0.58	48.6	2.53	<dl
39	49.1	0.82	63.7	1.98	20.9
42	36.7	0.77	61.3	1.91	20.0

- The fluoride concentration increases by 95 wt% (0.023 ppm). One source of excess fluoride may be as a contaminant in the formic acid.
- The concentration of soluble formate after formic acid addition and concentration (sample 39) was 20.9 g/L (5.6 gC/L).
- After frit addition the concentration of formate concentration is 27 g/L (6.9 g C/L feed) after forming and concentrating. Assuming a 1.35 concentration factor, the concentration of formate in the initial feed would be 20 g/L. This formate concentration is equivalent to the addition of 19 ml (90 wt%, 23 M) formic acid/L feed. The sludge fraction contains 33 g formate/L. The supernate concentration is 18 g formate/L frit addition phase.

Carbon analyses were performed on the supernate and dried sludge fractions. Table 8.9 summarizes the carbon data. Evaluation of these data indicates the following:

- Insoluble carbonate concentration was <2 gC/L throughout the forming, concentrating, and frit addition steps.
- The measured organic carbon values were high relative to predicted amounts. In the preformate samples (#13 and 28) the average measured TOC was 7 gC/L compared to the predicted, 2.5 gC/L derived from added oxalate ion. In the post formate sample (#39) the measured TOC was 16.9 (adjusted for a 1.35 concentration factor) compared to 8.9 gC/L (2.5 gC/L from oxalate and 6.4 gC/L from HCOOH).

Table 8.9. HWVP PSCM-23 Feed Carbon Content During Forming, Concentrating, and Frit Addition

Sample Number	Total Organic Carbon (a)				Total Inorganic Carbon		
	mg C /g solids	mg C /g sludge (b)	g C /L sludge (c)	g C /L supernate	gC/L slurry	mg C /g solid	g C /L supernate
13	17.3	5.0	6.9	0.38	7.2	0	0
28	17.0	4.9	6.5	0.37	6.9	0	0
39	34.0	12.2	17.6	5.2	16.96	0	0.25(e)
42	13.8	8.4	14.4	5.0	19.4	0	0.17

- (a) To convert g C/L to g oxalate/L multiply by 90/24. To convert g C/L to g formate/L multiply by 45/12.
- (b) Wt% water as presented in Table 8.5 used for conversion from dried solids to sludge.
- (c) Density of sludge estimated based on supernate/sludge ratio given in Table 8.5 and the density of the feed slurry given in Table 8.4.
- (d) The measured value, 22.8 gC/L, has been adjusted to 16.9 gC/L to account for a 1.35 concentration factor calculated from sample 28 and 39 ICP data.
- (e) The measured value, 0.34 gC/L has been adjusted to 0.25 gC/L per footnote (d).

- The carbon and IC values for soluble **formate**, **5.2 gC/L (19.9 g HCCOOH/L)** and **20.9 gHCCOOH/L**, respectively, are in good agreement: **rsd = 4.4%**. Applying a concentration factor of **1.35** as calculated from **ICP** data to the measured carbon value yields a **formate** concentration of **3.85 gC/L** prior to slurry concentration. This amount represents only **60%** of the formic acid added (**6.4 gC/L**). **Formate** may be present in the solids as insoluble **formate** salts and/or some decrease in **formate** ion may have occurred due to oxidation to **CO₂**.
- After forming and concentrating, the supernate contains carbonate (**0.34 gC/L**). This represents approximately 5% of the formic acid added (**6.4 gC/L**) to the slurry. The carbonate is potentially derived from hydration of **CO₂** released during the oxidation of formic acid or decomposition of formic acid and/or oxalate.

9.0 MELTER PROCESSING

During the off-gas system characterization, it was necessary to maintain steady-state operating conditions in the PSCM to ensure a consistent off-gas effluent stream. Once steady-state conditions were established, the nominal melter processing characteristics were evaluated. The PSCM-23 process data are compared with previous HWP melter tests to determine whether changes in the composition had any significant effects on melter processing. The PSCM-23 test was the second pilot-scale test using NAW feed. The first test was PSCM-22, conducted in FY 1985 (Perez and Nakaoka 1986). Thus, PSCM-23 test results provide a verification of the processing results achieved during the PSCM-22 test. Data collected throughout the PSCM-23 test were used to evaluate process performance, perform mass balances, and provide equipment design data.

9.1 TEST APPROACH

9.1.1 Establishment of Steady State

The PSCM-23 test established a feed rate that generated a cold cap that covered not more than 80% of the melt surface and was not excessively thick. Limiting the size of the cold cap provided steady melter operating conditions that generated a consistent off-gas stream and allowed sufficient flexibility in processing to avoid large deviations in processing parameters. At the same time, a realistic operating condition was maintained.

9.1.2 Characterization of Nominal Processing Conditions

In the evaluation of nominal processing conditions, the feed rate was adjusted until an average cold cap coverage of approximately 80% was established. Once the cold cap was stabilized, the average thickness was determined and the flexibility and venting behavior were evaluated. Based on experience, an acceptable melter feed is judged to be one that generates a cold cap having an average thickness of less than 5 cm (2 in.), remains relatively flexible, and allows consistent, stable venting of gases generated during processing. Average glass temperature, plenum temperature, electrode power, and melter pressure were monitored to establish the stability of the

process. Cold cap characteristics associated with 80% coverage are not always optimal (i.e. the cold cap may be too thick or violent off-gas surges are occurring). In this situation, engineering judgement was used to adjust the feed rate in an appropriate manner to maximize efficiency while maintaining operational stability.

9.1.3 Glass Discharge System Performance

The glass discharge system consists of a riser block, a trough and a discharge nozzle. The riser is a monolithic Monofrax^(a) K-3 block with a vertical riser for airlifting. The trough is an Inconel-690 block with a 2-in. hole drilled in it to transport the glass over to the discharge nozzle. At the end of the trough is a machined pouring tip in the shape of a "V." The trough also has a metal dam to prevent glass from migrating from the melting cavity or the joint between the riser block and the trough block to the discharge nozzle. The trough is sloped down 20°, 15° more than in the previous PSCM design, so the trough would drain residual glass quickly from the trough. The discharge nozzle is an 8-in. pipe nozzle extending through the melter floor shell. The nozzle was connected to a 55-gal drum about 8 ft below the glass pouring tip. Within the connection section, a 10.8-cm- (4.25-in.-) ID ring was placed to simulate the opening in the reference HWP canister. The overflow trough used during PSCM-23 is shown in Figure 9.1.

The reference glass pouring system for the HWP does not use an airlift but uses a vacuum pouring technique. The pouring glass stream would behave the same for both techniques with similar glass pouring rates, but the effects of the glass level would be different.

During PSCM-23, glass was periodically airlifted from the melter into the 55-gal drums. The quality of the glass stream associated with the new pour trough and pour tip was assessed by the ability of the glass stream to pour through the center of the ring placed above the opening of the receiving drum. The amount of deflection was determined visually and compared to the glass pouring rate. The glass pour rate was determined by a load cell underneath the receiving drum and the change in the resistance of the glass

(a) Monofrax is a tradename of Carborundum Co., Niagara Falls, New York.

FIGURE 9.1. PSCM Modified Overflow Trough

in the melt cavity. Three Type K thermocouples, one each located in the trough section, the face section, and imbedded in the trough block, were used to monitor the discharge section temperature. The nominal temperature of the trough block was established at about 1100°C during most of the experiment, as shown in Table 9.1. The overflow temperature was maintained constant so that it would not be a variable in the glass pouring tests. The air flow rate for the airlift was also monitored during the glass pour to establish a relationship between the air flow rate, the submergence, and the glass pouring rate.

9.1.4 Process and Mass Balance Flowsheet

Data was collected throughout the **PSCM-23** run and used to prepare process and mass balance summary sheets. Average steady-state stream flow

TABLE 9.1. PSCM-23 Glass Pouring Data

Day	Time	Avg. Glass Temp. °C	Glass ^(a) Tank Res. Ω	Air Flow, cfh	Cardinal Scale, kg	Stream Deflect, in.	Trough Block Temp., °C	Measured ^(b) Glass Pouring Rate, kg/h	Calculated ^(c) Glass Pouring Rate, kg/h
6/15	11:00	1,163	0.1166	4	96		1,083		
	11:05	1,158	0.118		103		1,086	84	105
	11:10	1,156	0.1222		145		1,095	504	309
	11:17	1,154	0.1253		172		1,098	231	159
	11:22	1,149	0.1274		187		1,097	180	147
	11:28	1,136	0.1292		203		1,098	160	104
	OVERALL					1		229	177
6/15	14:54	1,158	0.1185	4	196		1,067		
	15:00	1,163	0.1215		217		1,080	210	184
	15:11	1,162	0.1288		266		1,096	267	240
	15:24	1,172	0.1325		295		1,096	134	100
	15:26	1,171	0.1331		299		1,096	120	99
	OVERALL					0		193	166
6/15	19:55	1,163	0.118	4	298		1,083		
	20:00	1,159	0.123		330		1,094	384	368
	20:05	1,151	0.1262		357		1,098	324	227
	20:10	1,156	0.1288		372		1,099	180	180
	20:15	1,148	0.1308		386		1,099	168	136
	20:21	1,139	0.1316		398		1,095	120	46
	OVERALL							231	201
6/16	00:25	1,165	0.1205	1	417		1,093		
	00:30	1,167	0.1212	1	425		1,093	96	52
	00:35	1,163	0.1218	1	432		1,093	84	45
	00:40	1,161	0.1224	1	437		1,093	60	44
	00:50	1,161	0.1239	1.5	451	NA	1,094	84	56
	00:55	1,160	0.1241	1.5	457		1,094	72	16
	01:00	1,155	0.1245	2	463		1,094	72	30
	01:20	1,168	0.1255	2	487		1,094	72	24
	01:30	1,157	0.1263	2	500		1,095	78	31
	OVERALL							77	55
6/16	07:32		0.116	2.5	0		1,085		
	07:39		0.119	2.5	77		1,093	660	162
	07:44		0.1196	1.5	94		1,092	204	45
	07:50		0.121	0	102		1,092	80	86
	OVERALL					0.5		340	110

(a) Glass Tank Resistance measured in ohms.

(b) Based on receiving drum scale weight readings.

(c) Based on glass tank electrical resistance readings.

TABLE 9.1. (contd)

<u>Day</u>	<u>Time</u>	<u>Ave. Glass Temp. °C</u>	<u>Glass Tank Res. Ω</u>	<u>Air Flow, cfh</u>	<u>Cardinal Scale, kg</u>	<u>Stream Deflect, in.</u>	<u>Trough Block Temp., °C</u>	<u>Measured Glass Pouring Rate. kg/h</u>	<u>Calculated Glass Pouring Rate. kg/h</u>
6/16	09:34		0.1164		81		1,086		
	09:42		0.12	2.5	118		1,094	278	170
	09:45		0.1205	1.5	128		1,094	200	61
	09:50		0.1214	1.5	139		1,095	132	66
	09:55		0.1218	1.5	144		1,095	60	30
	10:00		0.1244	2.5	152		1,097	96	186
	10:15		0.1258	2.5	188		1,098	144	38
	10:25		0.1261	0	198		1,097	60	14
OVERALL						0.5		138	88
6/16	14:35	1,165	0.1156	25	198		1,089		
	14:43	1,162	0.1186	25	221		1,093	173	143
	14:50	1,156	0.1212	25	244		1,097	197	138
	14:55	1,163	0.1213	15	248		1,092	48	9
	15:10	1,160	0.1232	25	269		1,096	84	50
OVERALL						1		122	93
6/16	19:35	1,162	0.1134	25	303		1,086		
	19:40	1,168	0.1155	25	321		1,092	216	162
	19:46	1,167	0.1184	25	343		1,096	220	183
	19:50	1,173	0.1195	25	351		1,097	120	102
	19:55	1,173	0.1211	25	364		1,098	156	117
	20:00	1,158	0.1221	1.5	371		1,097	84	73
OVERALL						1		163	141
6/17	11:25		0.1139	NA	134		1,088		
	11:31		0.1153	NA	149		1,089	150	91
	11:37		0.1165	NA	156		1,091	70	77
	11:46		0.12	NA	183		1,096	180	147
	12:02		0.1227	NA	212		1,098	109	66
	12:05		0.123	NA	217		1,099	100	36
OVERALL						2		125	100
6/17	15:36	1,155	0.1176	25	232		1,092		
	15:59	1,154	0.1197	25	264		1,096	83	42
	16:05	1,153	0.1238	25	295		1,102	310	249
	16:10	1,147	0.1232	25	301		1,096	72	-40
OVERALL						-1		122	72

TABLE 9.1. (contd)

<u>Day</u>	<u>Time</u>	<u>Ave. Glass Temp. °C</u>	<u>Glass Tank Res. Ω</u>	<u>Air Flow, cfh</u>	<u>Cardinal Scale, kg</u>	<u>Stream Deflect, in</u>	<u>Trough Block Temp., °C</u>	<u>Measured Glass Pwring Rate, kg/h</u>	<u>Calculated Glass Pouring Rate, kg/h</u>
6/17	18:40	1,159	0.1146	25	300	-1	1,089		
	18:45	1,160	0.1171	1.5	332		1,095	384	190
	18:50	1,172	0.1188	15	348		1,099	192	127
	18:55	1,173	0.1203	15	360		1,099	144	111
	19:00	1,159	0.122	1.5	369		1,100	108	124
	19:05	1,156	0.1225	1.5	378		1,099	108	37
	19:13	1,167	0.124	1.5	389		1,098	83	69
	19:23	1,175	0.1244	15	<u>400</u>		<u>1,097</u>	<u>66</u>	<u>17</u>
					OVERALL	0		140	101
6/18	05:15	1,164	0.1199	15	56		1,100		
	05:20	1,163	0.1214	1.5	69		1,101	156	110
	05:25	1,172	0.1228	1.5	80		1,102	132	101
	05:30	1,164	0.1241	1.5	91		1,101	132	93
	05:35	1,166	0.1248	1.5	<u>98</u>		<u>1,100</u>	<u>84</u>	<u>50</u>
					OVERALL			126	95
6/18	09:40	1,169	0.118	2.5	142		1,098		
	09:46	1,176	0.123	2.5	173		1,103	310	307
	09:50	1,174	0.124	2.5	186		1,104	195	89
	09:56	1,165	0.126	1.5	<u>195</u>		<u>1,099</u>	<u>90</u>	<u>118</u>
					OVERALL			199	189
6/18	13:57			1.5	211				
	14:38			1.5	305				138

rates, temperatures, pressures, compositions, etc., were obtained directly from the DAS system as well as calculated using data transcribed on data and status sheets.

9.1.5 Evaluation of Trough Block Thermocouple

The PSCM was reconstructed with an Inconel 690 glass discharge trough. As a part of the rebuild, a thermowell was attached to the trough near the discharge opening (see Figure 9.1). During PSCM-23 temperature measurements from the trough block, face, and trough area thermocouples were recorded. The objective being to evaluate whether the trough block thermocouple could be used as 1) a means by which to control the overflow section

heaters, 2) an accurate measure of the glass temperature during pouring periods, and 3) a means to detect slight glass discharges that might otherwise go undetected. The results of this analysis are provided in Section 9.2.4.

9.1.6 Melter Process Control

Along with electrode power, resistance, and current signals the prime instrument signal by which the melter is controlled is the bulk glass temperature. Unfortunately, the glass thermowell and thermocouples have a limited life and may have to be replaced as often as every three months. To minimize the reliance placed on the bulk glass temperature, secondary temperature measurements are being evaluated to determine their usefulness. During PSCM-23, plenum, refractory, and electrode temperature data were recorded to determine how well the thermowell and thermocouples responded to varying conditions in the PSCM.

9.2 TEST ANALYSES

The major PSCM operating parameters are given in the process flowsheets for each period of the test (see Tables 9.2 through 9.4 and Figure 9.2). Appendix A Figures A.1 through A.14 show data plots for the entire feeding portion of PSCM-23. Feed to the melter was started on June 6, 1988, at 1100 and continued for 351 h until June 21, 1988, at 0200. The feed rate to the melter was consistent at 43 to 44 L/h [$-57 \text{ L/h}\cdot\text{m}^2$ ($1.4 \text{ gal/h}\cdot\text{ft}^2$)]. Including downtime periods when feed was not being fed to the melter, the average feed rate for the entire test was just over 41 L/h. Approximately 15,000 L of melter feed were processed, producing approximately 7450 kg (16,390 lb) of glass at a glass production rate of $28.4 \text{ kg/h}\cdot\text{m}^2$ ($5.8 \text{ lb/h}\cdot\text{ft}^2$).

9.2.1 Establishment of Steady State

As seen from Figures A.1 and A.3 average glass and plenum temperatures reached steady-state values after about 35 h of operation. Over that time the melter feed rate was established at between 40 and 45 L/h. With the exception of short periods of downtime, resulting chiefly from occasions of feed pump failure and feed nozzle plugging (see Section 6.0), the PSCM

TABLE 9.2 PSCM-23 Process Flowsheet--Period One

STREAM NUMBER	1	2*	3*	4	5*	6	7	8	9	10	11	12*	13*	14*	15	16*	17	18	19	20*	21	22	23	24*	25*
STREAM DESCRIPTION	FEED HOLD TANK (TS 48)	PSCM FEED TANK (TS 88)	FLM COOLER INJECTION AIR	FEED NOZZLE COOLING	ELECTRODES N S	SIDE WALL COOLING	FLOOR COOLING	IRC PANELS N S	HEAT EXCHANGER	FREEZE VALVE	FREEZE VALVE COLLAR	GLASS AIR LIFT	TROUGH HEATERS	FACE HEATERS	GLASS RECEIVING DRUM	MELLER OFF GAS	888 CONDENSATE (TS 23)	DEMISTER DRAIN	888 COOLING N S	888/ DEMISTER OFF GAS	HEME WATER SPRAY	HEME AIR SPRAY	HEME CONDENSATE	HEME OFF GAS	HEPA PREHEATER OFF GAS
FLOW (Mass)																									
Liquid kg/hr				204		323			188		318						26.8	0.04	2,930	1,087		OFF	OFF	0.38	
Solid/Chisel kg/hr																									
Gas kg/hr			86.8				74.8	33.2	50.4		94.1														
TOTAL kg/hr		58.1	86.8	204		323	74.8	33.2	50.4	188	94.1	318					26.8	0.04	2,930	1,087				0.38	
FLOW (Volume)																									
Liquid L/hr		43.0		204		323			188		318						26.8	0.04	2,930	1,087				0.38	
Gas M ³ /hr			73.3				47.8	17.7	21.8		40.0														186.4
Vol(Wil Batch L/8g)	1100(1485)											1107			1484										
Temperature C			-25		822 865	23	80	251 194					1122	1088		188	27			-24	-24	27		28	58
Pressure psia						-80	50	80 14.5	-80	150	-80					-0.24				-80	-80	-1.5		-1.7	-2.3
Specific Gravity	1.35	1.35	1.0	1.0		1.0	1.0	1.0 1.0	1.0	1.0	1.0	2.5			2.6		1.0	1.0	1.0	1.0			1.0		
Power kW					61 61								4.2	6.7											

* Values obtained from calibrated equipment

TABLE 9.3. PSCM-23 Process Flowsheet--Period Two

STREAM NUMBER	1	2*	3*	4	5*	5	7	8	9	10	11	12*	13*	14*	15	16*	17	18	19	20*	21	22	23	24*	25*
STREAM DESCRIPTION	FEED HOLD TANK (TS 60)	PSCM FEED TANK (TS 60)	FLM COOLER INJECTION AIR	FEED NOZZLE COOLING	ELECTRODES N S	SIDE WALL COOLING	FLOOR COOLING	IRC PANELS N S	HEAT EXCHANGER	FREEZE VALVE	FREEZE VALVE COLLAR	GLASS AIR LIFT	TROUGH HEATERS	FACE HEATERS	GLASS RECEIVING DRUM	MELTER OFF GAS	BBB CONDENSATE (TS 29)	DEMISTER DRAIN	BBB COOLING N S	BBB/ DEMISTER OFF GAS	HEME WATER SPRAY	HEME AIR SPRAY	HEME CONDENSATE	HEME OFF GAS	HEPA PREHEATER OFF GAS
FLOW (Mass)				200		320			202		318						25.1	0.17	2,907	1,099		OFF	OFF	0.76	OFF
Liquid kg/hr																									
Solid(Chisel) kg/hr																									
Gas kg/hr			109.4			75.6	32.9	49.7		92.7															
TOTAL kg/hr		57.2	109.4	200		320	75.6	32.9	49.7	202	92.7	318					25.1	0.17	2,907	1,099			0.76		
FLOW (Volume)																									
Liquid L/hr		43.4		200		320			202		318						25.1	0.17	2,907	1,099			0.76		
Gas m ³ /hr			142.0				47.7	17.5	21.5		39.4										292.7				
Vol(Wt) Batch L(tg)	1100(1452)											[103]			[494]										
Temperature °C			-25		914	841	25	81	270	209			1125	1097		114	27		-24	-24	27			27	
Pressure psig							-80	5.3	8.0	14.5	-80	15.0	-80			-0.20			-80	-80	-1.5				-1.9
Specific Gravity	1.32	1.32	1.0	1.0		1.0	1.0	1.0	1.0	1.0	1.0	2.5			2.8		1.0	1.0	1.0	1.0			1.0		
Power kW					61	61							32	6.6											

TABLE 9.4 PSCM. Process Flowsheet--Peri Three

[illegible]

FIGURE 9.2 PSCM Process Flowsheet

operation was very **stable**. As a result, on-stream efficiency was excellent--better than 98%. The feed rate plot, Figure A.2, shows the feed outages as downward spikes. The longer feed outages can also be seen as upward spikes in the plenum temperature plot (see Figure A.3).

9.2.2 Characterization of Nominal Processing Conditions

9.2.2.1 Cold Cap Conditions

Throughout the test, the cold cap characteristics remained consistent. Initially, during the first 8 h of startup some degassing of the glass inventory occurred. This was expected, given the initial oxidized condition of the glass batch. The degassing resulted in a light foam accumulation forming over the open glass surface. It dispersed as melting of the HWP glass gradually displaced the original glass tank contents.

The processing conditions produced by the current melter feed composition were very good. The slurry spread over the glass and cold cap easily without any signs of accumulation. The cold cap coverage of the glass surface ranged from between 60 and 80%. For short periods (e.g., <4 h) the cold cap coverage grew as large as 90%. The cold cap remained flexible throughout the run period. Venting was routinely observed, and the cap thickness appeared to remain consistent at about 2 to 5 mm (1 to 2 in.). The cold cap was judged to be equal in processability to the previous HWP tests in which NCAW-based melter feeds were processed. At the termination of the feeding portion of PSCM-23, the cold cap melted into the glass quickly (i.e., <30 min), and no refractory or molten salt accumulations were observed to be present.

9.2.2.2 Process Rate Evaluation

The average melter feed rates given in Tables 9.2 through 9.4 were for the feeding portion of the test. Normalizing these rates by the PSCM surface area, the PSCM processed at between 56 to 58 L/h·m² (–1.4 gal/h·ft²) for the duration of the test. These rates are quite comparable to the PSCM-22 rates (Perez and Nakaoka 1986). During PSCM-22, nominal rates of 51 L/h·m² (formated feed with 3.5 g/L sugar added) to 62 L/h·m² (formated feed without sugar added) were achieved. Although PSCM-23 rates were 7% lower than the

higher PSCM-22 value (case for no sugar added), they are in excess of the design basis value of $45 \text{ L/h}\cdot\text{m}^2$ used for the HWP melter and are very close to the design maximum value of $60 \text{ L/h}\cdot\text{m}^2$.

These process values also compare quite favorably with rates achieved in the PSCM under other vitrification programs and by other test systems. During the recent WDP melter test, SF-10, nominal rates of about $36 \text{ L/h}\cdot\text{m}^2$ were achieved; cold cap coverage of the glass surface was estimated to be 80 to 95%.

Comparisons to previous PNL and SRL tests results are also favorable (see Figure 9.3). Based on FY 1987 tests in the scale-glass melter (SGM-6 and -7) (Guidotti et al. 1987), normalized glass production rates have been estimated to range from 190 to 205 lb/h for slurry processing rates of 45 to 54 gal/h (reported values were extrapolated for the case of a 27 ft^2 glass surface area for use in Figure 9.3), equivalent to 1.7 to $2 \text{ gal/h}\cdot\text{ft}^2$. Given that the scale-glass melter (SGM) utilizes lid heating to boost production rate, comparable normalized production rates in the PSCM indicate that the current HWP melter feed has very good melter processing characteristics.

Based on the processing characteristics of the melter feed, and rates achieved in past PSCM tests and by other programs, the HW-39-4 glass composition can be judged to be acceptable.

9.2.3 Glass Discharge System Performance

The glass pour rate was determined by monitoring the initial and final weights of the receiving drum and the length of time of the pour. The glass pouring rate was also calculated from the change in PSCM glass level based on the change in electrical resistance between the melter electrodes. The glass pouring rates were adjusted for the glass produced during the pour. The overall glass pouring rates were lower than the glass pouring rates calculated using the drum scale. The differences are thought to be caused by errors in estimating the glass resistance and the glass volume of the melt tank. Overall, the glass pouring rates gave consistent values about 20% lower than the scale readings. The calculated glass pouring rates are shown in Table 9.1.

FIGURE 9.3. Comparison of Production Performance for PNL, SRL, and WNS Melters

The glass pour rate varied during each glass pour period because of the change in submergence of the airlift with time. An airlift glass flow rate is based on the air flow rate, the submergence, the fluid channel size, and fluid viscosity. The channel size was fixed and the fluid viscosity was held fairly constant, so the glass flow rate was a function of the air flow rate and the submergence. The actual submergence of the airlift was not measured because the glass level sensors corroded after the first few days of the experiment. Submergence was estimated based on maximum glass resistance measured during the test and the glass resistance at the time of a pour. The accuracy of the air flow rates was estimated to be about $\pm 20\%$. The results of the data shown in Figure 9.4 show the rapid decrease in glass flow rate

FIGURE 9.4 . Results of PSCM-23 Glass Pour Tests Using a Pseudosubmergence

with submergence. The data fit typical airlift fluid flow rates, which decrease exponentially with submergence. No correlation of air flow rate with glass flow rate could be obtained at low submergences because of the accuracy of the data. The data show that the reference glass pouring rate of 500 lbs/h is achievable with a submergence of 0.95 and an airflow rate of 2 cfh or a submergence of 0.92 and air flow rate of 4 cfh. The reference glass pouring system for the HWVP does not use an airlift but uses a vacuum pouring technique. The pouring glass stream would behave the same for both techniques with similar glass pouring rates, but the effects of the glass level would be different.

The ring used to assess the quality of the glass pouring stream was used during only part of the run to ensure that the melter operation would not be interrupted and interfere with off-gas test objectives. The ring was in place for 21 glass pours. The major characteristics of each pour are

shown in Table 9.1. The ring was placed approximately 5 ft below the pouring tip, which, at the time, **was** the approximate distance between the pour tip and canister opening in the HWVP reference design. The ring was centered underneath the glass discharge spout visually with each changeout of the receiving drum to minimize any misalignment between the pour tip and ring insert. The glass stream was observed to deflect back underneath the trough at high glass flow rates (**ie.**, **>500 lb/h**). The magnitude was sufficient to cause the glass stream to miss the opening in the ring and strike the ring surface. Based on model tests, the major stream deflection occurs near the pour tip. Glass flow rates of about 500 lb/h (225 kg/h), which is the maximum HWVP reference pour rate, caused the glass stream to deflect back underneath the trough a maximum of 1.0 in. (as observed at the pour ring), and glass pour rates of 300 lb/h (135 kg/h) caused a glass stream deflection of less than 0.5 in. Higher glass flow rates were achieved, but could not be maintained long enough to estimate a glass flow rate. Maintaining the high flow rates would have caused an interruption in the experiment because the glass stream would strike the ring, causing an obstruction in the glass discharge port. Glass flow rates in excess of 500 lb/h could occur in the HWVP melter due to high pour spout vacuums or off normal melter operations such as a severely overfed melter. Administrative and operation procedures should be required to prevent or minimize glass pour rates in excess of 500 lb/h within the HWVP.

Sampling of the glass stream just below the pour tip caused glass fibers to contact and stick to the side of the glass discharge nozzle. Sampling at the higher glass flow rates made **it** much more difficult to keep the glass from overflowing the sample boat and contacting the sides of the discharge nozzle. The deposits left on the side of the discharge nozzle caused pouring problems because the deposits protruded into the discharge nozzle. During routine glass pouring, the glass stream hit the protrusion and caused a large deflection of the glass stream. The glass deposits could be removed only manually during drum changes. Glass sampling was judged to be the major cause of glass build-up in the discharge pipe. Therefore, **it** is recommended

that glass sampling of a falling glass pour stream should be performed within the canister or canister throat. The canister opening should be maximized to allow for upsets caused by sampling or off-normal melter operation.

The tendency of the glass stream to deflect underneath the trough was very similar to that observed in physical model tests as shown in Figure 9.5. The results indicate that the physical modeling tests are applicable to actual glass pouring tests and that pouring rates above 500 lb/h (230 kg/h) will cause a stream to be deflected about 1 in. The glass pouring rates should be less than 500 lbs/h to minimized the glass stream deflection.

The PSCM-23 glass pouring tests also showed that a 20° down-sloped trough will continue to pour a stream of glass for 3 min after the airlift air is turned off. After 3 min, the glass stream breaks up into droplets. These results also match the results of physical modeling tests. The formation of droplets as opposed to stringing of the glass is a function of the

FIGURE 9.5. PSCM-23 and Physical Model Test Comparison Data

glass viscosity, and therefore the glass temperature, at the pouring tip. The drips appeared to stop less than 15 min after the airlift was turned off. This indicates that the glass canisters should not be moved within 15 min of turning off the **airlift**. The results of the physical modeling tests also indicated that an up-sloped pouring trough would minimize glass dripping by reducing the post-lift pouring to only a couple of minutes. Therefore, an up-sloped trough should be considered as an **alternative** design.

9.2.4 Material Balance Calculation

A material balance, based on PSCM-23 test results, was prepared to compare the agreement between feed and glass production measurements and the elemental off-gas mass flow rates. Input into the mass balance included average feed and glass compositional results, the total quantities of feed processed and glass produced, and the MOG DF values. Given in Table 9.5 are the results of the calculations. The difference between the measured feed rate and the combined glass and off-gas rates (last column) is 10 to 100 times larger than the MOG loss rates. As a result, significant improvement in feed and glass measurements must be achieved before an accurate mass balance can be performed. This will require multiple and repetitive samples and analyses to achieve the desired accuracy and precision.

9.2.5 Evaluation of Trough Block Thermocouple

The reader is directed to the process data plotted in Appendix A, specifically Figures A.1, A.10, A.11, and A.12. During the run the bulk glass temperature operated between 1140°C and 1160°C for the majority of the run (see Figure A.1). In contrast, the trough block temperature was in the region of 1080°C to 1100°C (see Figure A.10). From the sharp spikes in temperature recorded by the trough block thermocouple, **it** certainly sensed the glass airlift pour events. However, the maximum temperature indicated by the trough block thermocouple rarely reached 1110°C. The molten glass is known to be very near the bulk glass temperature when **it** reaches the end of the trough (Perez and Nakaoka 1986). Therefore, the trough block thermocouple does not accurately indicate the pouring glass temperature. In fact, comparing the trough block temperature with the face temperature (see Figure A.11), **it** can be seen that the trough block thermocouple follows the face

TABLE 9.5. PSCM-23 Component Material Balance

Element	Measured Melter Feed Rate, 1b/h	Measured Glass Prod. Rate, 1b/h	Measured Off-Gas Rate, 1b/h	Difference Feed - (Glass + Off Gas), 1b/h
Al	6.15E-01	6.38E-01	5.13E-04	-2.39E-02
Ba	4.38E-02	4.19E-02	3.65E-05	1.88E-03
B	1.48E+00	1.44E+00	4.72E-03	3.82E-02
Ca	2.96E-01	3.11E-01	5.38E-05	-1.51E-02
Ce	5.28E-02	6.09E-02	1.60E-05	-8.10E-03
Cl	5.26E-02	3.74E-02	1.32E-02	2.09E-03
Cr	4.50E-02	5.12E-02	1.13E-02	-1.74E-02
Cs	7.36E-02	7.50E-02	7.67E-04	-2.13E-03
Cu	5.78E-02	5.60E-02	7.23E-05	1.74E-03
F	1.04E-01	8.42E-02	1.74E-02	2.81E-03
Fe	2.23E+00	2.24E+00	2.23E-03	-1.55E-02
La	5.07E-01	4.98E-01	3.90E-04	8.77E-03
Li	7.88E-01	7.58E-01	4.38E-04	2.95E-02
Mg	2.36E-01	2.34E-01	4.73E-05	2.37E-03
Mn	5.29E-02	5.32E-02	4.81E-05	-3.50E-04
Mo	9.90E-02	9.35E-02	7.62E-04	4.77E-03
Na	3.83E+00	3.54E+00	9.83E-03	2.84E-01
Nd	2.38E-01	2.32E-01	1.59E-04	5.15E-03
Ni	2.14E-01	2.13E-01	1.79E-06	1.17E-03
P	2.17E-02	2.04E-02	8.80E-05	1.26E-03
S	3.11E-02	2.65E-02	3.88E-03	6.56E-04
Si	1.17E+01	1.14E+01	6.52E-04	3.20E-01
Sr	4.29E-02	3.95E-02	4.38E-05	3.35E-03
Y	2.07E-02	1.84E-02	1.48E-05	2.31E-03
Zn	1.53E-01	1.51E-01	1.39E-04	2.58E-03
Zr	1.31E+00	1.24E+00	1.31E-03	7.58E-02

area temperature quite closely. The stability of the trough area temperature indicates that the closed trough design minimizes temperature effects to that area that may be caused by the glass stream.

It would seem quite reasonable that overflow section heaters could be controlled based on a single thermocouple feedback signal. The trough block thermocouple could be used to provide such a function. To minimize heater cycling, however, the heaters should be placed on constant power and the thermocouple signal used to ensure proper operation.

During the PSCM-23 test there were no occasions when the glass was allowed to slowly move into the trough. As a result, the ability to detect glass in the trough with the trough block thermocouple could not be evaluated. However, due to the disparity between the bulk glass and trough block temperature during pouring events it is doubtful that such an indication could be obtained.

9.2.6 Melter Process Control

Figure 9.6 is a plot of electrode, refractory, and bulk glass temperatures during the first 24 h of PSCM-23 operation. The slurry to the melter was started approximately at the 1-h point. The approach to steady-state values is readily apparent. The three alternative temperature measurements are each located 15 cm (6 in.) above the melt tank floor. The glass temperature is the average bulk glass temperature. How closely each alternative thermocouple mirrors the bulk glass temperature is dependent on the insulation between the glass and the thermocouple. The electrode thermocouple that rests in the north Inconel electrode has the greatest sensitivity because of its proximity. Unfortunately, this placement is not very practical for the air-cooled HWVP electrodes.

The most promising thermocouple is the thermocouple placed at the interface of the Monofrax K-3 and Zirmul^(a) refractories. This thermocouple produced a time constant response to temperature changes and about a 200°C temperature off-set. The values are very steady and could be very useful to back up the bulk glass temperature readings or, if sufficient data are

(a) Zirmul is a tradename of the Charles Taylor's Sons Co., Cincinnati, Ohio.

FIGURE 9.6 Comparison of PSCM Process temperatures

gained, even be used in place of the bulk glass thermocouples should they fail. With powerful statistical tools available today, the refractory thermocouple readings could be used quite effectively. The third and final thermocouple, the Alfrax-66^(a)/Zirmul interface thermocouple, has a significant amount of scatter in the data. As such, this thermocouple placement has less value than the Monofrax K-3/Zirmul interface thermocouple.

The plenum temperature measurement has been used at PNL and PAMELA as a process control tool. Its response to cold cap coverage makes it a reliable indicator of cold cap coverage, and hence process stability. Prior to the rebuild of the PSCM the nominal plenum temperature corresponding to 75 to 85% cold cap coverage was 200°C to 300°C. Throughout PSCM-23, steady-state plenum temperature was in the region of 500°C (Figure A.3). It is apparent that the steady-state plenum temperature is a very good process feedback signal. However, the steady-state temperature range for HWVP operation must be established during cold testing of the melter.

(a) Alfrax is a tradename of the Carborundum Resistant Materials Co.,
Niagara Falls, New York.

10.0 MELTER OFF-GAS PROCESSING

PSCM-23 off-gas studies were conducted to 1) characterize the melter source under steady-state processing and non-processing (idling) conditions, 2) establish the impact of each off-gas component upon the melter effluent source under a reasonable range of off-gas system and melter operating conditions, and 3) compare observed equipment performance with similar and/or component test data to facilitate melter off-gas system design. The melter and equipment conditions under which PSCM-23 off-gas performance studies were conducted are chronologically summarized in Figure 6.1.

10.1 TEST APPROACH

The off-gas system studied during this test was the HWVP advanced conceptual design. This design is similar to that of the WVDP and includes, in sequential order, a film cooler, an SBS quench scrubber, a low-efficiency chevron demister, a high-efficiency mist eliminator (HEME) or deep bed washable filter, and a final HEPA filter (see equipment descriptions). To characterize individual components as well as integrated off-gas system behavior, effluents were sampled before and after each major off-gas treatment device (i.e., the SBS, HEME, and HEPA). All samples were obtained by extending sampling probes into off-gas lines interconnecting off-gas equipment. The pre-SBS sample, along with feed rate and compositional information, was also used to characterize the melter source term. Equipment operating conditions were continuously monitored, including temperature, pressure, and flow rates of process and service streams.

The sampling network developed in support of these melter and off-gas system characterization studies was designed to determine the composition of the melter exhaust with regard to condensible as well as non-condensable effluent. To characterize condensible or treatable effluent losses, the multi-component sampler shown in Figure 10.1 was utilized. The manner in which any given element is distributed across the various discrete sampling fraction of this device is indicative of the physical state or states assumed by this effluent.

FIGURE 10.1. Multi-Component Sampler

Melter-generated aerosols have been characterized with regard to concentration, size, and composition through use of appropriate aerosol collection devices and isokinetic sampling conditions. Total off-gas particulate loading was established by filtration of the unquenched melter exhaust. Particle size information was obtained using a cyclonic sampling system consisting of a series arrangement of three cyclones and a final absolute filter. The three cyclones separated particulates into four size groups (cut points) $16\ \mu\text{m}$, $6\ \mu\text{m}$, $1\ \mu\text{m}$ and $<1\ \mu\text{m}$ at a flow rate of 18 actual liters per minute (ALPM).

Aerosols in the quenched melter exhaust stream were similarly characterized. Total off-gas particulate loading was directly measured by filtering a portion of the process stream. Particle size information was obtained through use of a cascade impactor that consists of a series arrangement of 10 impaction stages and a final absolute filter. The cut points of the impactor stages ranged from $10\ \mu\text{m}$ to $0.05\ \mu\text{m}$ at a flow rate of

2.8 ALPM. The final impaction stage was not used during PSCM-23 because of an excessive pressure drop across this stage; however, the final backup filter collected **a**ll aerosols too small to be removed by previous impaction stages, thus ensuring quantitative removal of **a**ll airborne particulate matter in the sampling stream.

The composition of **m**elter-generated, noncondensable effluent emissions was established using a variety of gas analysis techniques. The process exhaust concentrations of **O**₂, CO, **C**O₂, and **N**O_x were continuously monitored and recorded using specific gas analyzers. In addition a mass spectrometer was periodically used to quantify process exhaust concentrations of important noncondensable effluent gases such as H₂ and **S**O₂.

Daily samples were collected at points in the effluent stream before and after each off-gas component with the exception of the **HEPA**. A limited exhaust blower capacity, coupled with an unacceptable pressure drop across the **HEPA** and its associated pre-heater, forced the latter two devices to be valved out of the off-gas system when higher film cooler air injection rates were used. However, a high-volume, long-duration sampler was set up to monitor **HEPA** aerosol influent rates. Effluent concentrations were so low down stream of the **HEPA** that daily samples were combined to reduce **lower**-detection-limit analytical uncertainties.

10.2 MELTER OFF-GAS SYSTEM RESULTS AND EVALUATION

Operational data and experimental results from **m**elter off-gas treatment studies conducted during PSCM-23 testing are subsequently discussed.

10.2.1 Melter Off-Gas Characterization

To evaluate the performance characteristics of the PSCM-23 off-gas system, the nature of the melter effluent source was characterized.

Effluent Gases

For the simulated HWVP melter feed used during the PSCM-23 test, **C**O₂, and **N**O_x are the major noncondensable (–25°C) gases produced by the vitrification process. For a quenched off-gas flow rate of –110 scfm and a **steady**-state feeding rate of 43 L/h, the MOG concentrations of these effluent gases

were nominally 0.64% and 0.18%, respectively. The combustible gases CO and H₂ were also detected, but at much lower concentrations: <0.10% and 0.01%, respectively. These concentrations are well below the lower flammability limits of these combustible gases, 4.65% for H₂ and 15.5% for CO. Even without the benefit of film cooler dilution, off-gas concentrations of these gases were found to be well below lower flammability limits at the 43 L/h feeding rate employed during this test. In the plenum and prior to the SBS, steam is the primary factor that eliminates the flammability hazards of H₂ and CO. The dilution caused by air inleakage and the film cooler preclude any possibility for auto-ignition downstream of the SBS.

Table 10.1 summarizes the results obtained from mass spectrometric analysis of the quenched melter exhaust with and without film cooler air injection. The lack of SO₂ results in this data does not mean that volatility losses for sulphur are small; rather, it is a reflection of the fact that SO₂ production is not thermodynamically favored when plenum temperatures are <600°C (Goles and Sevigny 1983). SO₃ is a reactive condensible gas that cannot be detected by the gas analyzers used during PSCM-23.

The time-dependent behavior of process emissions of NO_x, CO, and CO₂ were followed in real time with specific gas analyzers during PSCM-23. Because steady-state feeding conditions were maintained throughout most phases of testing, the process exhaust concentrations of these gases were quite invariant throughout the test. They were perturbed only by planned changes in film cooler injection rates, i.e., MOG flow rate. Figure 10.2 illustrates the temporal behavior of these off-gas effluent gases.

TABLE 10.1. Melter Off-Gas Composition

Sample Date/Time	MOG Flow, scfm	Mole %								
		H ₂	Ar	N ₂	O ₂	CO	CO ₂	NO _x	SO _x	CH ₄
6/10	110	0.01	0.92	77.0	21.2	<0.10	0.64	0.18	<0.01	<0.01
6/20	70	0.13	0.90	75.5	20.4	<0.10	2.51	0.47	<0.01	<0.01

FIGURE 10.2 Time-Dependent Beh

Melter-Generated Gases

Condensable gases are also generated during LFCM processing. Boron, chlorine, fluorine, phosphorous, and sulphur feed components are all volatilized to some extent during LFCM processing; however, the volatile species involved are efficiently removed (physically and/or chemically) by the aqueous off-gas system quencher--in this case the SBS. The percentage of effluent losses due to gas phase escape for each of these volatile elements is summarized in Table 10.2. These data demonstrate that a majority of the boron and fluorine and most of the chlorine, phosphorous, and sulphur exhausted to the SBS are in the gas phase. The present volatility data agree quite well with similar data collected during the previous two HWVP melter tests, as shown in Table 10.3.

Nitrogen and carbon, having no appreciable glass solubility, should be evolved quantitatively from the melter as volatile oxides. Although this is ostensibly true for carbon, nitrogen oxide releases during the present test can only account for -75% of the nitrogen fed to the melter. Since condensed phase nitrates represent less than 1% of off-gas system nitrogen, there are

TABLE 10.2. Volatile Melter Effluent Losses

<u>Date</u>	<u>% Losses Due to Gaseous Escape</u>				
	<u>B</u>	<u>Cl</u>	<u>F</u>	<u>P</u>	<u>S</u>
6/6	51	11	72	75	32
6/7	59	33	86	12	23
6/8	89	52	96	22	75
6/9	85	52	96	--	47
6/10	87	43	97	--	41
6/11	92	63	99	--	44
6/13	88	45	97	12	56
6/14	93	73	98	--	59
6/15	88	52	98	25	60
6/16	88	52	96	70	51
6/17	80	41	97	--	63
6/18	94	39	95	--	54
6/19	90	49	95	55	72
6/20	94	(15)	98	--	66
6/21	96	56	95	38	25
6/22	85	61	95	--	12
6/23	<u>82</u>	<u>19</u>	<u>83</u>	<u>--</u>	<u>78</u>
Avg.	84±15	44±37	94±7	45±53	53±28

TABLE 10.3. Percent Volatile Melter Effluent Losses

<u>Element</u>	<u>Average % Loss by Volatility</u>		
	<u>PSCM-23</u>	<u>PSCM-22</u>	<u>HBCM-85-1</u>
B	84	89	73
Cl	44	62	--
F	94	85	85
S	53	80	32

apparently undetected chemical pathways of melter nitrogen loss. The effort to identify alternate nitrogen bearing effluent led to the detection of NH_4^+ in off-gas condensate solutions at ten times the concentrations expected from feed compositional data. Although the quantities of NH_3 effluent detected are only -5% of the nitrogen evolved during processing, it illustrates that gas phase losses of nitrogen are not restricted to only two chemical forms: NO and NO_2 . This fact would explain the inability to achieve a nitrogen mass balance in the present test and could also explain similar results obtained by SRL during past LSFM melter tests (Crow 1987).

The off-gas evolution rates of all melter generated volatiles were quite uniform throughout most phases of feed processing. The initiation of melter idling, however, affected emission rates of these volatile effluents in differing ways. Nitrogen and carbon emission rates decrease immediately upon cessation of melter feeding and, essentially, cease once the melter cold cap has burned away (Goles and Sevigny 1983). The data collected during the present test support this fact, as is clearly shown in Figure 10.3.

Sulfur effluent behavior is somewhat like that of nitrogen and carbon when melter feeding is terminated, but unlike carbon and nitrogen, melter sulphur emission rates will begin to increase, and level off as the melter plenum temperature increases and stabilizes (Goles and Sevigny 1983) as shown in Figure 10.3.

Boron, chlorine, and fluorine behave quite similarly in that their volatile emission rates steadily decrease once idling has been initiated. However, boron gaseous emission rates decrease much more quickly than those

FIGURE 10.3. Emission Characteristics of Nitrogen and Sulphur

associated with chlorine and fluorine. This situation is quite reasonable as the primary boron volatile during processing is boric acid, which cannot be formed under melter idling conditions. Since other volatile oxides of boron have higher boiling points and condense before being carried out into the off-gas system, gaseous boron emissions should drop off quickly as the melter heats up and the plenum dries out. The volatile emission characteristics of these gaseous effluents throughout all phases of PSCM-23 testing are summarized in Figure 10.4.

Although there are significant differences in the idling emission rate characteristics of the previously described volatile effluents, the proportion of total losses due to gaseous escape remains constant for most of them for at least two days idling, as is shown in Table 10.2.

Apart from the classic volatiles discussed above, other gaseous effluents were also observed during PSCM-23. Silicon volatility was strongly indicated by melter samples collected during the initial stages of idling. The volatile species involved was most assuredly SiF_6 as the sample also contained large quantities of fluorine. However, SiF_6 may have not been the primary off-gas effluent in that HF effluent interactions with the sampler's aerosol glass filter may have volatilized the silicon that was subsequently

FIGURE 10.4. Emission Characteristics of Boron, Chlorine, and Fluorine

collected and detected in the sampler's condensate fraction. In either case, the chemical behavior of fluorine was apparently altered during some part of the first day of idling to have produced this unique and previously unobserved result.

Trace levels of other "normally" non-volatile feed components were also detected in the condensate fraction containing the high levels of silicon. Their proportions were, however, inconsistent with the composition of the aerosol sample fraction; this evidence precludes the possibility that the condensate could have been contaminated by aerosols penetrating the filter media. On the other hand, this result, like that of silicon, has not been previously observed.

Aerosol Emissions

Effluents that enter the MOG system, and which require long-term environmental isolation, are primarily condensed-phase matter (i.e., aerosols). Many feed components are volatilized to some extent within the melter; however, rapid condensation in the melter plenum transforms most of these effluent vapors to airborne aerosols before the effluent can be carried into the off-gas system. Feed and/or glass matter can also be physically hurled into the melter plenum by cold cap and/or glass surface turbulence.

Once in the plenum, it can become entrained in gas currents and exhausted from the melter as an aerosol. Both of these loss mechanisms produce off-gas system aerosols; however, the physical characteristics and chemical composition of these two types of aerosols are markedly different.

Entrained aerosols typically have mass median diameter $1\text{ }\mu\text{m}$ and are compositionally similar to the feed. Consequently, entrainment losses, to first approximation, will influence all feed components in the same way. Condensation aerosols are predominantly submicron and are chemically dissimilar to the bulk feed. The importance of the volatilization/condensation loss mechanism is totally dependent upon the physical and chemical properties of the feed components and the range of compounds they can form. Consequently, melter aerosol loss rates will be exacerbated by the presence of semi-volatile feed components, and effluent emission rates of elements capable of forming semi-volatile compounds will always be greater than those elements forming refractory compounds. Effluent loss rates are traditionally expressed in terms of equipment DFs. A device DF value for a particular feed component is derived by taking the ratio of the rate at which the component enters the device to the rate at which it exits. Aerosol DFs are partial decontamination factors that relate to only one off-gas effluent form: aerosols. Melter and off-gas system aerosol mass DFs derived throughout the duration of PSCM-23 are tabulated in Table 10.4.

Melter aerosol mass DFs were consistent throughout most of the PSCM-23 test. The low DFs recorded during the first and last two days of testing illustrate the impacts of non-steady-state processing conditions upon melter performance. The low performance for the first 2 days was due to startup instability, which is normal. During the last 2 days of processing, cold cap and melting conditions were perturbed by continual changes in feed composition, which decreased overall melter performance. These unstable periods of processing are dramatically illustrated by large increases in aerosol off-gas loadings, which are plotted in Appendix B. If the data obtained during unstable processing is excluded, the average overall mass DF obtained during PSCM-23 is 1500, with a relative standard error of $\pm 13\%$. The internal consistency of these data suggest that steady-state processing conditions were indeed achieved during most of the PSCM-23 test. The

TABLE 10.4. Melter and Off-Gas Component Aerosol Mass Decontamination Factors

Mo/ Day	Melter Condition	MOG Flow, scfm	HEME Spray, L/h	DF		
				Melter	SBS	HEME
6/6	Processing	110	0	410	79	1700
6/7	Processing	110	0	490	39	
6/8	Processing	110	0	1800	14	
6/9	Processing	110	0	1400	7.6	340
6/10	Processing	110	0	1500	8.0	
6/11	Processing	110	0	1600	14	2400
6/12	Processing	110	0			
6/13	Processing	170	0	1400	7.6	780
6/14	Processing	170	0	1500	4.7	
6/15	Processing	170	0	1200	--	--
6/16	Processing	170	0	1400	5.5	--
6/17	Processing	170	15	1400	5.6	1700
6/18	Processing	170	15	1800	5.1	
6/19	Processing	170	15	1400	--	1500
6/20	Processing	170	15	640	9.2	--
6/21	Idling	100	0	--	4.6	7500
6/22	Idling	100	0	--	--	
6/23	Idling	100	0	--	4.5	
6/24	Idling	100	0	--	2.0	
6/25	Idling	100	0	--		
6/26	Idling	100	0	--		
Average Steady State Processing				1500	7.4	1400

validity of this assessment is further confirmed by the stability of the time-dependent melter off-gas aerosol mass loadings graphically displayed in Appendix B.

The magnitude of the average PSCM-23 melter aerosol mass DF (1500) is high. It is four times greater than was achieved during the previous HWVP melter test (PSCM-22); however, the operating goals of these two tests were quite different. The PSCM-23 test was conducted at a single melter feeding

rate for the purpose of establishing and maintaining steady-state processing conditions for a single feed composition. Operating stability during the PSCM-22 test was not a prime experimental objective, and three separate feed formulations were processed during that test at several different feeding rates. Since the destabilizing influences of feed rate and compositional changes upon melter performance has been demonstrated by data obtained during PSCM-23 as previously described, the very high melter DFs recorded during PSCM-23 must certainly be due to the exceptional process operating stability achieved. The control required to establish this degree of processing stability may be difficult to achieve in a remote production facility environment; consequently, the aerosol mass DFs achieved during PSCM-23 should not be used for design purposes because they are unrealistically high. Rather, a range of values between 300 to 800 should be adopted for this purpose.

The physical and chemical characteristics of melter-generated effluent aerosols were studied to assess the relative importance of entrainment and volatilization on the melter source term. A cyclonic particle size analysis system was used to establish the size distribution of melter aerosols exhausted into the off-gas system. Table 10.5 details the manner in which melter particulate matter was distributed across the cyclonic size fractions. Melter aerosol size distributions always exhibit a bi-modal structure. The

TABLE 10.5. Size Distribution of Melter Aerosols

Date	Wt%			
	16 μm (a)	6 μm (a)	1 μm (a)	<1 μm
6/08/88	35.2	5.1	18.1	41.6
6/14/88	23.5	4.4	17.5	54.6
6/18/88	30.0	6.1	20.9	43.0
Average	29.6	5.2	18.8	46.4
6/22/88 (b)	18.6	--	--	81.4

- (a) Cyclone cut for which cyclone is 50% efficient.
(b) Idling sample.

bi-modal distribution is indicative of a composite source comprised of two independent components, each having its own characteristic size distribution. Gross compositional dissimilarities between the discrete cyclonic size fractions, illustrated in Table 10.6, further demonstrate this point. Since the 16- μm fraction is chemically similar to the feed, as shown in Table 10.6,

TABLE 10.6. Elemental Size Distribution of Melter Off-Gas Particulate

<u>El ement</u>	<u>Distribution, Elemental %</u>			
	<u>16 μm</u>	<u>6 μm</u>	<u>1 μm</u>	<u><1 μm</u>
Al	56	11	26	7
B	58	7.6	23	12
Ba	70	12	14	3.7
Ca	50	8.8	22	19
Cd(a)	4.5	0	4.2	91
Ce	64	13	13	9.8
Cl	16	2.9	14	67
Co(a)	5.2	20	3.9	71
Cr	35	7.5	21	37
Cs	6.8	2.2	15	76
Cu	16	2.5	6.1	75
F	20	7.5	16	56
Fe	54	11	27	7.9
K	3.4	1.9	6.7	88
La	64	11	21	4.1
Li	7.6	1.8	7.1	83
Mg	50	11	21	19
Mn	52	9.9	25	13
Mo	12	3.1	13	73
N	100	0	0	0
Na	11	2.6	9.2	77
Nd	62	10	23	4.6
Ni	38	2.4	4.2	55
P	8.7	4.3	10	76
Pb	9.5	0	10	80
S	13	3.5	15	68
Si	59	12	14	15
Sr	57	10	24	8.4
Ti	50	9.9	18	22
V	6.1	6.9	10	77
Y	59	10	24	6.3
Zn	54	8.4	18	20
Zr	54	10	26	10

(a) Elements not analyzed for in melter feed.

and the $<1\ \mu\text{m}$ fraction is composed of almost entirely of semi-volatile elements, the two components making up the bi-modal distribution must be associated with aerosols produced by entrainment and by volatilization. This result is consistent with past PNL melter tests when similar investigations were conducted.

The relative importance of entrainment and volatilization to overall melter aerosol losses can be assessed from Table 10.5. These data suggest that ~46% of the condensed-phase mass leaving the melter during the present test was transported by submicron aerosols, and that 65% of the mass was carried by aerosols having diameters $>1\ \mu\text{m}$. Gross entrainment obviously did not play a dominant role in establishing the overall melter aerosol emission source term. Melter-induced volatilization played an important role in enhancing loss rates for the following feed component elements: Cl, Cd, Co, Cs, Cu, F, K, Li, Mo, Na, Ni, P, Pb, S, and V, as the masses of these semi-volatiles are strongly concentrated in the $<1\text{-}\mu\text{m}$ cyclone size fraction.

Individual melter aerosol DFs have been calculated for all melter feed components using the compositional data derived from off-gas filter samples. These results are tabulated in Table 10.7. As with melter mass DFs previously discussed, the magnitudes of most individual feed component DFs are found to be greater than corresponding results obtained from most past melter tests. (This is necessarily true only for non-volatile feed components.) However, melter performance for strongly volatilized elements (Cs, Na, and Mo) did compare quite well with results obtained during the HBCM-85-1 test, which utilized PNL's high bay melter. These similarities were not apparent in the more recent PSCM-22 test, which also employed the pilot-scale ceramic melter. The reasons for the variability in semi-volatile effluent behavior cannot not be traced to any test dissimilarities.

The reproducibility of melter feed component DFs are, overall, quite good. If processing instabilities at the beginning and at the end of the test are not considered, relative standard deviations for most elemental DFs are found to be $<\pm 20\%$. The magnitudes of nonvolatile DFs, however, are atypical, as previously discussed, and should not be interpreted as

TABLE 10.7. Individual Element Decontamination Factors for Melter Aerosol

	DFs														
	6/6/88	6/7/88	6/8/88	6/9/88	6/10/88	6/11/88	6/13/88	6/14/88	6/15/88	6/16/88	6/17/88	6/18/88	6/19/88	6/20/88	
Element	Average	2110 h	1051 h	1243 h	1236 h	0954 h	1140 h	1441 h	1356 h	1312 h	1141 h	1108 h	1053 h	1133 h	1121 h
Al	1,000	180	220	960	850	1,000	1,000	960	1,000	880	940	1,200	1,600	780	540
B	3,700	450	640	3,800	2,900	3,600	4,300	3,500	4,100	2,600	3,500	1,800	6,900	3,700	1,500
Ba	980	150	180	920	850	1,100	1,100	950	1,000	820	830	990	1,500	790	500
Ca	4,700	840	1,200	4,300	4,200	4,700	5,200	4,800	4,700	3,700	4,400	4,700	7,400	4,200	1,600
Ce	2,700	850	250	5,700	4,000	3,900	3,900	2,600	1,100	1,100	1,300	2,400	2,100	1,300	500
Cl (a)	14	12	7.8	16	19	18	19	12	15	9.9	15	9.3	9.7	9.6	9.1
Cr	440	75	120	440	380	360	450	400	470	330	400	470	650	440	260
Cs	83	240	100	150	92	73	76	68	81	62	73	63	88	77	54
Cu	680	170	210	880	680	720	750	650	780	540	730	680	520	540	400
F (a)	290	71	70	220	220	310	470	300	330	360	270	290	210	200	180
Fe	870	150	190	820	720	880	890	820	900	710	820	1,000	1,300	650	470
La	1,100	160	210	1,000	900	1,200	1,200	1,100	1,200	910	1,000	1,400	1,900	910	560
Li	1,500	1,600	1,400	2,800	1,800	1,500	1,600	1,200	1,300	1,100	1,400	1,100	1,600	1,600	730
Mg	4,300	830	1,100	4,200	3,400	4,000	4,400	4,100	4,200	3,300	3,900	4,900	7,500	3,300	1,500
Mn	900	160	190	890	800	900	930	860	940	660	880	1,000	1,300	670	490
Mo	110	45	54	190	130	120	140	92	110	91	81	65	120	110	83
N (a)	41,000	16,000	14,000	--	--	--	--	--	--	--	--	--	65,000	16,000	7,700
Na	340	150	160	480	350	330	360	290	340	270	310	270	430	320	190
Nd	1,200	190	250	1,100	960	1,200	1,200	1,100	1,200	940	1,100	1,700	2,300	1,100	560
Ni	99,000	--	--	300,000	590	130,000	98,000	120,000	64,000	10,000	230,000	99,000	20,000	24,000	13,000
P	3,300	840	1,400	5,600	3,900	3,500	4,300	3,000	3,100	740	2,600	2,300	3,300	3,700	2,800
S (a)	16	20	12	38	13	9.4	10	11	12	11	11	12	25	23	19
Si	15,000	2,000	3,000	11,000	12,000	14,000	17,000	15,000	16,000	12,000	15,000	19,000	25,000	13,000	4,900
Sr	840	150	190	850	680	900	850	800	870	690	710	830	1,400	680	460
Y	1,200	180	220	990	920	1,200	1,200	1,100	1,300	970	1,100	1,600	2,200	1,000	660
Zn	960	160	190	930	790	1,000	1,000	940	1,000	770	920	1,100	1,300	730	540
Zr	890	160	190	860	750	900	900	850	940	700	880	1,000	1,300	660	450
TTL	1,500	410	490	1,800	1,400	1,500	1,600	1,400	1,500	1,200	1,400	1,400	1,800	1,400	640

(a) Assumed to form soluble anions (Cl: Cl^- , F: F^- , N: NO_3^- , and NO_3^- ; S: SO_4^{2-}).

representing average melter performance behavior. Melter tests characterized by very low aerosol emission rates, such as PSCM-23, have been observed in the past; however, the high performance values achieved have not, in general, been reproducible (Goles and Sevigny 1983). Test data from the recent HBCM-85-1 and PSCM-22 experiments are much more typical of the average melter source term than the PSCM-23 data.

Total Melter DFs

Since only a very few feed components are lost to the off-gas processing system in the gaseous state, essentially all the aerosol performance values listed in Table 10.7 also represent total melter DFs for these elements. Notable exceptions to this statement are B, Cl, F, N, P, and S. Since gaseous escape dominates melter off-gas system losses of these elements, total individual melter DFs will be completely determined by gas phase loss rates of these elements. Table 10.8 summarizes the total melter DFs established for these volatile elements during PSCM-23. Comparison of these total values with corresponding aerosol DF data illustrates how gas phase losses limit melter performance for these elements. Estimates of total melter DFs can also be extracted from quench scrubber solution concentration data, provided the volatiles are efficiently scrubbed and the scrub solution can be representatively sampled. These estimates are summarized and compared with average off-gas totals in Table 10.9. With the exception of phosphorous, the agreement between these two approaches is quite good, given the difficulties associated with sampling an inhomogeneous tank (see SBS discussion). Indeed the large differences in the phosphorous data are thought to be due to the limited solubility of phosphorous bearing effluent.

Although PSCM-23 melter loss mechanisms for B, Cl, F, and S have been shown to be quite similar to previous HWVP testing results, the magnitudes of these losses compare less favorably, as shown in Table 10.10. The present DF data are, with a single exception, greater than corresponding data collected during recent HWVP melter tests. This suggests that significantly higher concentrations of volatile elements are contained in PSCM-23 glass than are present in PSCM-22 and HBCM-85-1 glasses.

TABLE 10.8. Total Melter Decontamination Factors

ID	Avg.	6/6/88 2110 h	6/7/88 1051 h	6/8/88 1243 h	6/9/88 1236 h	6/10/88 0954 h	6/11/88 1140 h	6/13/88 1441 h	6/14/88 1356 h	6/15/88 1312 h	6/16/88 1141 h	6/17/88 1108 h	6/18/88 1053 h	6/19/88 1133 h	6/20/88 1121 h
B	390	220	260	420	430	470	360	430	300	310	430	360	410	370	92
Cl ^(a)	6.6	11	5.3	7.6	8.8	10	7.0	6.7	4.0	4.7	7.3	5.5	5.9	4.9	7.8
F ^(a)	9.2	20	9.7	9.9	9.2	10	6.9	10	7.5	8.6	10	9.5	10	9.3	3.6
P	2600	210	1300	4400	3900	3500	4300	1100	3100	550	780	2300	3300	1700	2800
S ^(a)	6.4	13	9.4	9.4	7.2	5.5	5.5	5	5.1	4.4	5.3	4.6	12	6.2	6.6

(a) Assumed to form soluble anions (Cl: Cl^- , F: F^- , N: NO_3^- , and WO_3^- , S: SO_4^{2-}).

TABLE 10.9. Total Melter Decontamination Factors of Volatiles

<u>Sample Basis</u>	<u>Average Total Melter DF</u>				
	<u>B</u>	<u>Cl</u>	<u>F</u>	<u>P</u>	<u>S</u>
Off-Gas Samples	390	6.6	9.2	2600	6.4
SBS Composition	314	4	6	247	8

TABLE 10.10. Comparison of Total Melter Decontamination Factors for Volatile Effluents

<u>Melter Test</u>	<u>Average Total Melter DFs</u>				
	<u>B</u>	<u>Cl</u>	<u>F</u>	<u>P</u>	<u>S</u>
HWVP-15/PSCM-23	390	6.6	9.2	2600	6.4
HWVP-12/PSCM-22	63	1.3	3.2	--	1.8
HWVP-11/HBCM-85-1	130	--	5	--	67

Melter Idling

When an LFCM is maintained at temperature by joule heating but is not processing slurry feed it is said to be idling. PNL has extensively studied the melter idling state to establish its importance upon the overall melter source term (Goles and Andersen 1986). What has been found is that once feeding has been terminated, overall emission rates decrease rapidly as the existing cold cap is consumed. Once the cold cap is dissolved, the melter plenum temperature begins to increase to a steady-state value of 1000°C. During this period, feed deposits on plenum surfaces burn away, causing melter emission rates to increase again. The temporal emission behavior of an effluent falls into one of two categories depending upon volatility. Non-volatile emission rates peak quickly and their peak magnitudes are small fractions of processing loss rates. Long-term (>2 day) non-volatile emission rates are small. Semi-volatile idling emissions also rise quickly but peak emission persists for several days and the magnitudes of these peak emissions are generally comparable to processing loss rates. After 4 to 5 days, the semi-volatile emission rates decrease significantly and level off as the glass pool begins to dominate the melter source term. Long-term idling emission characteristics are flat, unstructured, and only significant for the semi-volatiles (i.e., boron, cesium, sodium, ruthenium, etc.). However these

long-term semi-volatile loss rates are generally found to be significantly less than those occurring during feed processing. Details concerning melter idling behavior of off-gas effluents can be found in the literature (Goles and Andersen 1986).

Melter emission behavior was tracked for 5 days after PSCM-23 melter feeding was terminated. The sampling frequency used during idling (1 sample/24 h) was not high enough to resolve the temporal emission properties discussed above; however, it was more than sufficient to verify it. The idling data collected is graphically compared with melter off-gas conditions that existed throughout the test in Appendix B. All graphical concentration data has been normalized to an off-gas flow of 110 cfm, and as such the graphical data also directly represent relative melter emission loss rates. Examination of this emission rate data clearly verifies the idling model previously described.

A particle size analysis of melter idling emission was also conducted 2 days after feed processing was terminated. Since plenum feed deposits had been melted away by that time, very little entrained matter ($1\text{ }\mu\text{m}$) was expected in the melter exhaust. This was indeed found to be the case; >80% of the collected aerosol matter was collected on the final cyclonic collection stage ($<1\text{ }\mu\text{m}$) as shown in Table 10.5.

10.2.2 Off-Gas Film Cooler

The melter off-gas film cooler is not designed to stop or abate process effluent emissions. Its purpose is to facilitate transmission of aerosol effluent from the melter to the SBS with high efficiency. This is accomplished by an air injection system that establishes and maintains off-gas system velocities above 45 ft/s in an insulated, gradual radius 3 in. schedule 40 off-gas line (jumper) joining the film cooler to the SBS. Three off-gas system flow rates were used during PSCM-23 to study the impact of superficial face velocity on off-gas system component performance. These flow rates were established by controlling film cooler air injection rates.

The air injection rate to the film cooler during the first 7 days of the experiment averaged 40 scfm. The melter plenum temperature was 500°C and the air inleakage rate was about 80 scfm. These conditions resulted in a total

noncondensable off-gas flow rate of about 110 scfm entering the quench scrubber at a temperature of about 190°C. Based on an average feed rate during this experiment of 43 L/h, the actual gas velocity (i .e., combined condensable and noncondensable flows) in the off-gas line was about 75 ft/s during the first 7 days. The jumper (at mid-point) skin temperature was 230°C, and the melter off-gas inlet temperature to the SBS was 190°C.

During the next 9 days (days 7 to 16) the average film cooler air flow rate was adjusted to 85 scfm, and the SBS inlet temperature dropped to near 100°C. The increased air injection rate resulted in a total off-gas flow rate of 155 to 170 scfm which corresponded to a nominal gas velocity of 90 ft/s in the melter-SBS off-gas jumper.

Feed processing was terminated on day 15 of the test to conduct melter idling tests. During the idling portion of the test, the melter vacuum was reduced and film cooler air injection was decreased to 40 scfm. This resulted in a total off-gas flow of 100 scfm and an off-gas jumper, velocity of 46 ft/s. The film cooler air flow and the low melter vacuum kept the off-gas jumper skin temperature below 100°C; the melter plenum temperature was about 1000°C.

As previously mentioned, effluent transmission efficiency through the film cooler and adjoining off-gas line is the only criterion for evaluating film cooler performance. An ideal film cooler would prevent deposition of effluent solids between the melter plenum and the quench scrubber. No off-gas line blockages developed during the 15 days of PSCM-23 processing. However, some particulate deposition did occur within the off-gas jumper as revealed by post-test inspections. Two thin layers of light deposits, one white and one brown, with a combined thickness of 0.125 in. were observed. The deposit found adhering to the jumper wall was white, which is usually indicative of condensed salts collected during idling conditions. The outer deposit that overlaid the white wall accumulations had a definite brownish (iron) color, which is typical of calcined feed matter. The 0.125-in.-thick deposits occurred from the top of the film cooler flange to a point a few feet downstream. The deposit thickness decreased to about a 0.03 in. after the last bend in the off-gas line about 15 ft from the melter. Only a slight

dusting of calcine material was found in the vertical inlet section above the SBS, except for one deposit near the top of the SBS. This deposit was similar to damp sand and could be scrapped off easily, but would not be removed by the normal gas flow. The sandy deposit was **believed** to result from the low temperatures that occurred in that region of the off-gas line (near 100°C) during part of the PSCM-23 experiment. Based on this result, **it** is recommended that the off-gas temperature be maintained above **130°C** to ensure moisture condensation does not occur in the off-gas line jumper between the **melter** and the SBS.

The composition of the brown-colored accumulation was indeed found to be chemically similar to the feed, as is shown in Table 10.11; this deposit, however, was **also** found to be compositionally enriched in the semi-volatile elements (Cs, Mo and the halogens) and depleted in **frit** components (Si, B, Li, Ca, and Mg). As such, a fraction of the material would be expected to be water soluble. Should water spray **cleanout** techniques be considered, the spray action should strip away all the deposits, soluble and insoluble. In addition, this type of deposit is not expected to result in extensive accumulations because both types of deposits were friable and loosely bound to the jumper. Since this type of material should be easily stripped away by the turbulent shearing action of the gas stream, **it** is unlikely that these deposits could rapidly grow into an off-gas line blockage.

Because of the low entrainment and the high melter **DFs** achieved during this test, **it** is difficult to say how much the film cooler had to do with the off-gas line conditions found. Similar off-gas conditions have been observed at the conclusion of comparable **melter** tests where no off-gas film cooler was used. There is no doubt that film cooler technology helps maintain an unobstructed off-gas line and that such devices form a necessary part of melter off-gas systems; however, PSCM-23 results do not necessarily demonstrate these facts.

TABLE 10.11. Composition of Off-Gas Jumper Deposits (brown colored)

<u>Oxide</u>	<u>Pipe Deposit wt%</u>	<u>Glass wt%</u>
Al ₂ O ₃	4.50	2.7
B ₂ O ₃	9.40	10.0
BaO	0.24	0.09
CaO	0.29	1.1
CeO ₂	0.28	0.15
Cr ₂ O ₃	0.40	0.15
Cs ₂ O	1.10	0.16
CuO	0.24	0.13
Fe ₂ O ₃	13.8	7.0
La ₂ O ₃	2.30	1.1
Li ₂ O	0.74	3.5
MgO	0.31	0.86
MnO ₂	0.36	0.17
MoO ₃	1.30	0.28
Na ₂ O	12.2	9.9
Nd ₂ O ₃	0.93	0.53
NiO	1.15	0.52
SiO ₂	5.80	52.8
SrO	0.23	0.09
TiO ₂	0.05	0.08
Y ₂ O ₃	0.09	0.05
ZnO	0.93	0.43
ZrO ₂	7.78	3.1
Cl & F	12.0	0.60
SO ₄	5.1	1.0

10.2.3 Submerged Bed Scrubber

The SBS is the primary quench scrubber in the HWP Advanced Conceptual Design (ACD) off-gas system for the HWVP. Its main purposes are to quench the hot melter exhaust, condense process generated steam, and remove airborne effluents.

Physical Properties and Operating Conditions

The SBS was operated under three different off-gas flow conditions. The timing and duration of the various off-gas flows used during PSCM-23 are graphically summarized in Figure 10.5. At 110 scfm, the pressure drop through the bed was 34 in. WC with a 31 in. WC submergence. This average pressure drop increased to 37 in. WC when the non-condensable off-gas flow rate was increased to 170 scfm. Figures 10.6 and 10.7 show the inlet and outlet pressure conditions of the SBS throughout the duration of PSCM-23. It has been demonstrated by Owen and Postma (1981) that gas surging through the

FIGURE 10.5. SBS Outlet Gas Flow Rate

FIGURE 10.6. SBS Inlet Vacuum in H₂O

FIGURE 10.7. SBS Outlet Vacuum in H₂O

the SBS bed occurs. Such a phenomenon could hamper stabilizing the operation of the entire melter to blower vacuum system if sensitive automatic vacuum control is used. This might necessitate starting the vacuum system on manual setpoint control until the system has stabilized. At the start of operations no significant pressure fluctuations were observed.

The effluent modified composition of the SBS scrubbing liquor at steady state is summarized in Table 10.12 along with the average melter feed composition. The pH of the SBS scrub solution achieved a steady value of 4. The acidity of the solution was due to acid gas effluents, primarily NO_x , generated by the melter. The NO_3^- anion is found to be the major soluble component in SBS supernatant solutions. Other major ionic components in SBS solutions are associated with boron, sodium and cesium. Frit and calcine are found to be responsible for most of the insoluble elements found in SBS solutions (iron, silicon, and sodium). The buildup of selected elements in the SBS supernate are plotted versus time in Figures 10.8 and 10.9.

Examination of Figures 10.8 and 10.9 shows significant differences between the concentration build-up curves of soluble, insoluble, and total elements in the SBS supernate. The SBS concentrations of essentially all insoluble elements are found to increase rapidly in an almost stepwise fashion during the first days of feed processing. The SBS concentrations recorded for the soluble components, however, follow an exponential rise, which is in accord with a theoretical stirred tank model shown in Figure 10.10. The theoretical prediction was based on an average steady-state concentration in the supernate, the overflow rate, the overflow concentration, and the volume of solution in the SBS as given by the following equation.

$$\text{SBS Concentration} = C_1 \cdot (1 - e^{-f(C_f/V \cdot t)})$$

TABLE 10.12. Composition of SBS Solution

Element	Wt% Total	Wt% PPT	Wt% Supernate	Total, mg/L	Feed Average, g/L	Melter DF
Al	2.03	3.44	1.79	32	6.79	338
Ba	0.11	0.74	0.00	2	0.48	446
B	4.83	1.10	5.45	77	16.5	314
Ca	0.33	1.77	0.10	5	3.26	979
Ce	0.42	2.91	0.00	7	0.57	138
C	0.21	0.95	0.08	3	0.49	227
Cs(a)	0.00	0.00	0.00	12	0.8	77
Cu	0.18	0.58	0.11	3	0.63	346
F	20.69	0.00	24.14	330	1.2	6
Fe	5.77	33.77	1.10	92	24.6	431
K	0.19	0.00	0.22	3	NA	NA
La	0.95	6.63	0.00	15	5.57	595
Li	0.25	0.46	0.22	4	8.81	3054
Mg	0.50	2.90	0.10	8	2.6	519
Mn	0.15	0.52	0.08	2	0.58	400
Mo	0.43	2.27	0.12	7	1.09	234
Na	7.68	18.00	5.95	122	41.7	500
Nd	0.68	4.79	0.00	11	2.65	392
Ni	0.61	3.19	0.18	10	2.34	374
Nox	24.0	--	~30	-390	-36	NA
P	0.14	0.00	0.17	2	0.4	247
SO4	10.66	0.00	12.44	170	0.99	8
Si	2.67	9.44	1.54	43	129	4868
Sr	0.10	0.62	0.02	2	0.47	453
Ti	0.13	0.80	0.02	2	0.01	8
Zn	0.47	0.84	0.41	8	2.02	428
Zr	3.64	4.26	3.53	58	14.4	400
Cl	11.48	0.00	13.39	<u>183</u>	<u>0.54</u>	<u>4</u>
				1606	305.5	275

(a) Analyses did not include this compound.

FIGURE 10.8. Anion Concentration Buildup in SBS

FIGURE 10.9. Cation Concentration Buildup in SBS

FIGURE 10.10. Total Elemental Concentration Buildup in SBS Versus Theoretical Prediction

where C_1 = steady state concentration
 t = time
 f = overflow rate
 C_f = overflow concentration
 V = volume of SBS.

Consequently, it appears that the sampling of the SBS for insoluble matter was not representative of bulk average conditions within the tank. However, the suspended SBS solids concentrations in the samples collected were much higher (2X) than off-gas effluent sampling results would predict. Since SBS samples were extracted toward the bottom of the tank, the above results indicate that the SBS is not a uniformly mixed tank for suspended solids. It does not necessarily follow from this observation that significant settling of insolubles is occurring; however, it does not preclude it.

Quenching And Steam Collection

During PSCM-23, the SBS operated under maximum cooling conditions, which maintained the bulk temperature of the scrubbing liquid below 30°C under all off-gas flow rate conditions as shown in Figures 10.11 and 10.12. The SBS collected water at a rate of 26 L/h while the melter was being fed 42 L/h of feed. The total water collected in the SBS during PSCM-23 is plotted as a function of time in Figure 10.13. Since 1 liter of feed contains about

FIGURE 10.11. SBS Bed Temperature 2 Feet Below Surface

FIGURE 10.12. SBS Bed Temperature 4 Feet Below Surface

FIGURE 10.13. Water Collected from **SBS** Overflow

0.77 L of water (i.e., the water feed rate to the melter was 32 L/h), the data in Figure 10.13 indicate the **SBS** collected 84% of the steam generated during steady-state processing conditions. The chevron demister collected a negligible amount of water under normal operation and the HEME collected only about 1 L/h. Calculations indicate the off-gas stream could carry out a maximum of 6 L/h at the higher noncondensable air flow rates tested, and off-gas sampling equipment confirmed that the noncondensable gas leaving the **SBS** was indeed saturated. The saturated air accounts for the remainder of the process steam generated during steady-state feeding conditions; therefore, a water balance across the **SBS** has been achieved using the **operational** data collected during **PSCM-23** test.

The quenching capability of the **SBS** was evaluated under steady-state operations during the first 7 days of the test. The cooling water used in the **SBS** cooling coils was measured to have an inlet temperature of 15°C, an outlet temperature of 24°C, and water flow rate of about 25 gpm. The inlet

and outlet gas temperatures were 190°C and 28°C, respectively, during this same period. An overall heat transfer coefficient for the cooling coils was calculated to be 300 Btu/h·ft²·°F.

Typical heat transfer coefficients for heat transfer from warm water to cold with slight agitation are given as 100 to 400 Btu/h·ft²·°F by engineering handbooks. This compares very well with the calculated value. A heat transfer coefficient of 150 Btu/h·ft²·°F is recommended for design as a conservative value that would allow for some particulate build-up on the coils.

Gas Scrubbing Performance

The NO_x concentration in the melter off-gas projected to be about 0.3 vol% for the HWP, is difficult to remove by aqueous scrubbing at this low concentration. Aqueous scrubbing techniques that specifically target NO_x at relatively high concentrations can at best achieve only a 67% removal efficiency (Counce 1984). Since the composition and chemistry of the SBS is determined solely by feed composition, melter performance, and SBS operating temperature, optimum NO_x scrubbing efficiencies at any concentration would not be anticipated.

This expectation has been born out by results obtained from PSCM-23. Using the nitrate content of the feed, the measured steady-state composition and condensation rate of the SBS, and assuming 100% NO₃ to NO_x conversion, the average steady-state NO_x scrubbing efficiency of the SBS has been estimated to be 1%. This result is in agreement with packed column data collected during the PSCM-22 test and confirms the strong dependence of aqueous scrubbing techniques upon inlet NO_x concentrations.

Since aqueous scrubbing kinetics is much greater for NO₂ than for NO, a high NO/NO₂ ratio at the SBS inlet may have also contributed to the poor scrubbing performance of the SBS. An NO/NO₂ ratio of 2 was measured downstream of the HVE with an on-line chemi-luminescent NO_x analyzer. Since NO is rapidly converted to NO₂ at room temperatures and the SBS apparently did very little NO₂ scrubbing, the SBS inlet NO/NO₂ ratio must have been significantly greater than 2. Using a combined off-gas transit and sample stream hold-up time of >30 s and the kinetic equations developed by Thomas (Thomas and Munger 1978), the NO/NO₂ ratio at the SBS inlet is estimated to be >4,

assuming little or no NO_2 removal by the SBS and HEME. This result further illustrates why aqueous NO_x scrubbing techniques are ineffective when applied to LFCM processes utilizing reduced feed streams.

SBS scrubbing performance for condensible volatile gas phase effluent is summarized in Table 10.13. Although the data scatter is quite large, SBS scrubbing efficiency for boron, chlorine, and fluorine appears to be functionally dependent on off-gas flow rate and, possibly, moisture loading. The DFs for all three effluent elements decreased markedly, on the average, when the off-gas flow rate was increased from 110 scfm to 170 scfm (6/13/88). These elemental DFs increased again when the solids loading of the feed dropped during the last two days of processing. A further increase in these DFs subsequently occurred when off-gas flow rate was reduced to 100 scfm (6/21/88) when the melter idling campaign was initiated. Since gas contacting would be facilitated by both increased steam loading and reduced flow, the observed trends are at least consistent with a fairly simple, intuitive model.

The effect of off-gas flow rate upon gas scrubbing efficiency of the SBS was also evaluated from scrubbing solution concentration data. Figures 10.8 and 10.9 illustrate the time-dependent buildup of SBS effluent. Since most of these soluble anions have, to some extent, gaseous precursors, the time-dependent behavior of these ions can be used to track collection efficiency. As mentioned previously, the concentration increases recorded for all soluble anions follow theoretical homogeneous stirred tank predictions; consequently, no changes in gas scrubbing efficiency resulting from increased off-gas flow rate (bed residence time) is indicated by the concentration trend data. However, because of the limited and variable nature of the concentration data that are available, changes in scrubbing efficiencies would have to be quite large to be noticeable. As previously shown in Table 10.2, essentially all the boron and fluorine and most of the chlorine, phosphorous, and sulphur exhausted to the SBS are in the gas phase. Table 10.13 further illustrates that the SBS can interact and remove a significant fraction of this effluent. The nature of the residual effluent exhausted by the SBS has also been determined, as summarized in Table 10.14. The data in this table indicate that although the SBS partially removes volatile effluent elements, it does

TABLE 10.13. SBS Gaseous Decontamination Factors

Element	6/6/88 <u>2110 h</u>	6/7/88 <u>1054 h</u>	6/8/88 <u>1246 h</u>	6/9/88 <u>1239 h</u>	6/10/88 <u>0956 h</u>	6/11/88 <u>1146 h</u>	6/14/88 <u>1357 h</u>	6/15/88 <u>1317 h</u>	6/16/88 <u>1143 h</u>	6/17/88 <u>1109 h</u>	6/18/88 <u>1055 h</u>	6/19/88 <u>1135 h</u>	6/20/88 <u>1132 h</u>	6/21/88 <u>0216 h</u>	6/22/88 <u>1144 h</u>
B	54	51	18	17	14	16	1.8	12	2.6	2.9	4	22	13	89	11
C1	7.1	18	7.9	62	3.8	5.1	2.8	6.3	13	1.9	27	12	--	19	44
F	320	74	44	44	36	42	3	16	4.9	5.1	5.7	31	25	29	57
P	4.4	1.9	--	--	--	--	--	--	--	--	--	--	--	--	--
S	6.6	44	7.5	420	27	33	37	830	--	65	25	--	53	230	74

TABLE 10.14. Volatile SBS Effluent Losses

Day	% Losses Due to Gaseous Escape				
	B	Cl	F	P	S
6	93	18	60	--	42
7	69	30	91	74	5.7
8	75	28	83	--	51
9	74	39	89	--	1.3
10	77	35	89	43	17
11	80	44	81	--	21
14	95	72	98	95	13
15	78	85	93	--	3.4
16	84	85	99	--	--
17	84	64	92	86	10
18	84	47	89	91	17
19	76	63	92	--	--
20	85	52	95	87	14
21	89	17	83	--	--
22	71	14	88	--	1.3
23	78	21	93	--	81
24	74	16	91	--	2
	81±9	51±42	88±11	79±24	18±87

not change the physical characteristics of these effluents. Consequently, boron, chlorine, fluorine, and phosphorus are primarily carried over to the HEME as gas phase effluents.

Aerosol Scrubbing Efficiency

The SBS is designed to remove airborne particulate matter from the process exhaust. Since the efficiency of this device is strongly dependent on the size distribution of aerosols with which it is interacting, the physical characteristics of melter effluent aerosols need to be established in order to properly understand, rationalize, and inter-compare experimental performance measurements. As described in Section 10.2.1, a cyclonic aerosol size classifier was used to examine the size distribution of melter off-gas effluent aerosols. Table 10.5 details the manner in which melter particulate matter was distributed across the cyclonic size fractions. These data demonstrate that during processing only 35% of the particulate mass leaving the melter was in a size range ($>1 \mu\text{m}$) for which SBS efficiency is high, and only 20% of the airborne mass was in this range during idling. The average steady-state off-gas concentration of particulate matter ($\sim 100 \mu\text{g/L}$) was very

low throughout most of the test due to the extremely high melter mass DF achieved. Because of these off-gas conditions, only low to moderate SBS DFs would be predicted during steady-state processing and idling conditions.

Mass DFs are used as measure of overall SBS performance. A summary of SBS mass DFs is given in Table 10.15. If the first 2 days are excluded from consideration because of melter instabilities previously described, SBS mass DFs are fairly consistent and are found to be low, as expected. Previous comparable melter tests (PSCM-19 and PSCM-21) have achieved SBS mass DFs 5 times greater than was observed in the present test. However, the previous experiments did not achieve the stable steady-state melter operating conditions that distinguish PSCM-23. Indeed, melter stability was so low for the previous tests that entrainment losses substantially influenced the melter source and the value of the melter aerosol mass DF. When compared with PSCM-23 data, DFs for the previous tests were as much lower as their SBS DFs were higher--a factor of 5. Thus, variable off-gas conditions, rather than changing performance characteristics, are responsible for the differences in SBS efficiencies noted above. The SBS DFs are consistent with parametric tests performed in 1987 (Ruecker and Scott 1987) as shown in Figure 10.14.

The effect of off-gas conditions on SBS performance is clearly illustrated by the behavior of the SBS during first two days of testing. As noted in Section 10.2.1, the melter was relatively unstable until steady-state conditions were established on or about the third day of the test. The first two days of test were characterized by relatively high melter aerosol emission (entrainment) rates (Appendix B) and corresponding low melter DFs (Table 10.7). During this same period, the SBS exhibited mass DFs that were as much as a factor of 10 higher than was achieved during steady-state operations. The factor responsible for the enhanced initial performance behavior of the SBS was high melter entrainment during startup. These data illustrate that the SBS can act as an off-gas shock absorber by efficiently responding to increases in off-gas aerosol loadings caused by process upsets. A similar but more dramatic example of this behavior was observed during the PSCM-21 test. Wide swings in melter DFs occurring before, during, and after a process upset were found to be compensated for by opposing changes in SBS

TABLE 10.15. Individual Element Decontamination Factors for SBS Aerosol

Element	Avg. (a)	DF													
		6/6/88 2110 h	6/7/88 1054 h	6/8/88 1246 h	6/10/88 0956 h	6/11/88 1146 h	6/13/88 1446 h	6/14/88 1357 h	6/16/88 1143 h	6/17/88 1109 h	6/18/88 1055 h	6/20/88 1132 h	6/21/88 0216 h	6/23/88 1153 h	6/24/88 1123 h
Al	370	2,100	1,200	540	450	270	690	270	190	220	180	410	99	3.9	13
B	4.3	740	78	6.8	6.7	6	6.2	2.7	1.9	3.9	1.3	4.8	27	4.7	4.2
Ba	2,100	6,700	14,000	4,400	3,500	150	3,400	1,500	400	410	520	2,700	170	7.5	30
Ca	150	260	560	120	200	420	370	99	100	64	50	200	7.8	5.2	13
Cd	2.7	--	--	11	1	1.9	1.1	1.1	1	1.4	4	1.4	4.6	2.8	2.8
Ce	290	--	--	--	250	--	--	360	170	170	360	440	61	--	--
Cl ^(b)	5	13	16	2.9	2.8	2.4	12	2.6	6.7	4.9	3.7	4.4	3.1	2	1.3
Co	11	53	120	1.5	4.3	1	14	53	2.5	1	4.5	4.5	21	3.9	1
Cr	16	78	43	18	18	22	26	13	12	9.2	13	19	9.9	4	4.3
Cs	3.3	2	4.2	1.9	3.5	6.6	6.5	2.4	2.2	3.3	3.1	3.2	2.5	2	1.5
Cu	6.5	72	32	5.3	5.8	12	9.5	3.7	3.4	3.6	5.1	16	4.1	3.9	3.5
F ^(b)	7.6	190	120	10	9.4	2.7	5.6	3	19	1.9	2.4	9.4	7.6	6.7	6.8
Fe	810	5,900	1,500	1,300	1,400	1,300	900	590	380	350	870	670	160	6.3	26
K	7.1	--	17	4.7	8	14	12	4.9	6.7	8	6.5	5.8	8.2	4.2	3.8
La	1,400	8,500	4,700	4,100	1,800	2,500	2,400	1,200	340	320	420	730	330	3.8	8
Li	7.2	35	15	4	7.3	15	14	5.4	6	7.6	5.7	7.1	14	4.8	3.9
Mg	150	270	700	200	210	1.1	270	89	99	94	67	190	23	9.1	14
Mn	280	2,300	1,000	410	350	350	330	260	180	190	170	350	120	15	27
Nb	9.7	100	34	7.6	9.1	14	17	6.3	8.7	11	7.3	11	25	8.8	6.5
Na	9.9	57	34	7.7	10	18	18	7.1	8.3	9	6.7	11	9.9	4.5	3.7
Nd	1,600	--	4,500	6,300	1,400	2,100	2,100	880	310	310	410	790	160	25	29
Ni	3	--	--	1	1.8	1	2	2.9	1	1.1	6.3	8.9	46	3.1	6.4
P	11	--	41	22	11	13	15	12	6.6	8.1	6.8	7.6	16	5.8	6.4
Pb	6.1	--	--	2.6	5.2	33	13	--	4.9	6.6	4.5	5.6	1	1	1
S ^(b)	4.9	10	8.8	2.6	7.8	11	8.7	4.1	3.2	4.3	4.2	4.7	21	2	2
Si	140	3,500	900	180	47	23	350	89	95	53	54	260	6.7	2.9	1.3
Sn	370	1,600	1,100	490	430	53	700	330	230	270	210	290	310	5.2	16
Ti	410	--	410	910	680	730	610	230	140	120	170	370	41	9.6	38
V	21	--	25	--	7.8	13	14	5.5	7.2	9.4	7.8	94	22	8.6	6.2
Y	340	--	--	--	--	--	--	510	--	210	290	--	--	--	--
Zn	63	1,400	530	66	69	8.5	110	42	52	36	34	91	7	3.8	7.2
Zr	430	21,000	1,500	690	600	1,200	710	360	190	190	210	450	680	8.9	17
TTL	7.4	79	39	14	8	14	7.6	4.7	5.5	5.6	5.1	9.2	4.6	4.5	2

(a) Taken during melter processing.

(b) Assumed to form soluble anions (Cl: Cl^- , F: F^- , N: NO_3^- , and NO_2^- ; S: SO_4^{2-}).

FIGURE 10.14. SBS Decontamination Factors Versus Gas Velocity

performance such that the overall DF remained essentially constant. This type of behavior is hardly a unique property of the SBS, but it is a useful and an essential one.

The aerosol scrubbing performance of the SBS for individual feed component effluents are tabulated in Table 10.15. This data overall is comparable to results obtained from previous quench scrubber performance tests - SBS and Ejector Venturi Scrubber (EVS) alike. A common characteristic of all low-efficiency scrubbers is that aerosol effluent can be broken down into two groups: non-volatile and semi-volatile. Quench scrubber DFs for non-volatile effluents are typically >300, while semi-volatile effluents

have DFs <50. The spread of DFs within a given group is a manifestation of the differences in chemical properties of the effluents, which determines their relative proportioning between groups.

Cesium is an effluent whose off-gas system losses are totally dominated by its semi-volatile nature. Consequently, process upsets that increase mass DFs rarely affect cesium melter DFs or off-gas concentration of this effluent, as is clearly shown in Table 10.7 for the first two days of the PSCM-23 test. Since the melter cesium source is not sensitive to process operating conditions, SBS performance for this effluent is also quite invariant, as shown in Table 10.15. This would not be true for classic non-volatiles since processing conditions would directly affect melter DF, which would in turn affect off-gas loadings and SBS performance. However, most process effluents possess intermediate properties that are responsible for the broad range in observed DFs and the variable responses to operational changes. Since PSCM-23 melter effluent is not dominated by either entrainment or volatilization, the members of the non-volatile and semi-volatile groupings are easy to identify. With few exceptions, these same groups can also be identified in the results obtained from past EVS and SBS characterizations efforts. Just as with mass DFs, differences in magnitude reflect deviations only in operational conditions, not variable performance characteristics.

Influence Of Off-Gas Flow Rate. The effect of off-gas flow rate upon SBS performance is insignificant for the flow range tested. The SBS effluent emission rate data in Appendix B appear to definitely relate increases in effluent concentrations to increased flow rate; however, melter off-gas loadings, which are also shown in the appendix, also went up during this period. The graphical SBS DF data, although showing definite trends throughout the test for similar effluents, fails to show any consistent pattern that can be linked to off-gas flow conditions. Thus, even though a case could be made for specific effluents, a generalized correlation does not appear to exist between SBS performance and off-gas system flow rate, at least in the range of 110 to 170 scfm, which corresponds to face velocity range of 60 to 90 ft/min at the center of the bed. The HWP SBS could be designed for a

face velocity of about 90 ft/min based on a 3X noncondensable gas surge condition to minimize equipment size and still provide adequate particulate removal.

Influence Of Idling. The SBS performance responses to idling fall into essentially two groups: semi-volatiles and non-volatiles. For the non-volatile feed components, SBS DFs drop significantly, as shown in Table 10.15. On the other hand, semi-volatile DFs remain essentially the same or decrease slowly with time. The performance behavior of the SBS is understandable on the basis of the changing off-gas conditions resulting from the idling mode. When feeding is terminated and gross plenum deposits have melted, non-volatile off-gas loadings decrease to very low levels. The hot idling melter, however, continues to evolve semi-volatiles from both plenum and glass surfaces. These characteristics are graphically displayed in Appendix B, which presents the time-dependent off-gas concentrations of melter effluents throughout all phases of PSCM-23. Thus, the observed changes in SBS performance accompanying idling can be totally ascribed to concentration effects. It should be noted that even though non-volatile SBS effluent DFs become quite small during idling, the SBS effluent concentrations of all non-volatiles are a factor 5 to 10 less during idling than under processing conditions. SBS effluent concentrations of semi-volatiles during idling are, at worst, no greater than conditions existing during processing and are significantly less for most cases.

Influence of SBS Fluid Entrainment. Because the operation of the SBS produces significant entrainment of the SBS scrubbing liquor that is, to some extent, carried over (see Section 10.2.4) into the off-gas system, SBS performance could very well be influenced by the reentrainment of previously removed effluent matter. Examination of the time-dependent SBS effluent off-gas concentrations plotted in Appendix B reveals that when the melter source is turned down, as occurs for non-volatiles during idling, the SBS effluent off-gas concentrations of these feed components also dramatically decrease. For semi-volatiles also, decreases in SBS exhaust concentrations correspond to decreases in emissions during idling. This is true for both soluble and insoluble matter. Consequently, the effluent matter exhausted from the SBS

is airborne material that simply and directly penetrates the device, and the contributions from reentrainment are small.

Influence of Aerosol Size. A comparison of average off-gas condition entering and exiting the SBS is an effective way to demonstrate the functional dependence of SBS efficiency on off-gas aerosol characteristics. Previous melter data has shown that ~50% of the aerosol mass leaving the melter was $>1\ \mu\text{m}$ in size. A multi-stage cascade impactor was used to classify SBS aerosols sizes from $5\ \mu\text{m}$ to $<0.25\ \mu\text{m}$ in nine discrete steps. The aerosols exiting the SBS were always found to be exclusively submicron, independent of PSCM-23 process or off-gas operating conditions. Figure 10.15 is a picture of the aerosol deposits collected on consecutive impactor stages ($5\ \mu\text{m}$ to $0.25\ \mu\text{m}$: left to right and top to bottom). The aerosol deposits, which form white jet patterns (lines) on the stainless steel collector stages, are present only on the last four stages. The absence of deposits on the large-diameter collection stages illustrates how very efficient the SBS is for removing large-diameter (entrained) airborne particulate matter.

Total Performance

Since only a very few feed components are lost to the off-gas processing system in the gaseous state, essentially all the aerosol performance values listed in Table 10.4 also represent total SBS DFs for these elements. Notable exceptions to this statement are: B, Cl, F, N, P and S. Total performance values for these gaseous effluents have been directly derived from off-gas sampling data. The results are summarized in Table 10.16.

Because these effluents are largely gaseous, SBS total DFs will be strongly influenced by gas phase removal efficiency. This is especially true for boron and fluorine effluents, which are $>80\%$ gaseous. For these elements the same performance trend linking SBS efficiency with off-gas flow rate and steam loading is apparent in the total DF data. The total DFs for chlorine do not demonstrate this trend to any appreciable extent because of the influence of condensed phase chlorine, which apparently is not similarly affected. Overall, the magnitudes of these total DFs are very reasonable

FIGURE 10.15. Size Distribution of Off-Gas Aerosols as Collected on Cascade Impactor Stages. The cut points of the collection stages (left to right and from top to bottom) are: 23, 14, 5.6, 3.4, 2.2, 1.2, 0.69, 0.41, and 0.26 μm .

TABLE 10.16. SBS Total Decontamination Factors

<u>Element</u>	<u>Avg.</u>	<u>6/6/88</u> <u>2110 h</u>	<u>6/7/88</u> <u>1054 h</u>	<u>6/8/88</u> <u>1246 h</u>	<u>6/10/88</u> <u>0956 h</u>	<u>6/11/88</u> <u>1146 h</u>	<u>6/14/88</u> <u>1357 h</u>	<u>6/16/88</u> <u>1143 h</u>	<u>6/17/88</u> <u>1109 h</u>	<u>6/18/88</u> <u>1055 h</u>	<u>6/20/88</u> <u>1132 h</u>	<u>6/21/88</u> <u>0216 h</u>	<u>6/23/88</u> <u>1153 h</u>
B	7.1	99	59	15	12	14	1.9	2.5	3.0	3.6	11	82	1.1
Cl ^(a)	3.0	12	16	4.3	3.1	3.6	2.7	2.2	3.0	3.2	2.5	5.9	2.0
F ^(a)	16	270	78	38	33	34	3	5	4.8	5.4	24	26	2.9
P	8.6	5.9	12	28	6.5	13	1	22	1.1	1	1	26	5.8
S ^(a)	8.7	8.7	11	5.1	11	16	8.6	6.5	10	7.7	12	27	1.7

(a) Assumed to form soluble anions (Cl: Cl^- , F: F^- , N: NO_3^- , and NO_3^- , S: SO_4^{2-}).

given the physical nature of these effluents, and they are quite comparable to previous quench scrubber performance measurements made during PSCM-22, as is illustrated in Table 10.17.

10.2.4 Chevron Demister

The chevron demister, which is located down stream of the SBS, is primarily designed to control SBS water mist carry over into the HEME. The performance of this device was monitored throughout the test by recording water collection rates. Since chevron plates remove water mainly by impingement, this demister is capable of efficiently removing only large entrained droplets. During the first days of PSCM-23, the chevron demister collected water at a very high rate--5 to 10 L/h. Visual observation confirmed that the SBS was very turbulent, with large gas bubbles splashing water up the top of the SBS vessel where the exhaust port is located. It is believed that this vigorous splashing was created by an inadequate initial water level in the SBS, which caused erratic two-phase flow leaving the bed. The turbulent operating condition subsided early in the test as condensed steam produced and maintained overflow conditions in the SBS tank. Calm, stable SBS operations persisted throughout the remainder of the test with commensurately lower water collection rates by the chevron demister.

Under steady-state processing conditions and with the SBS operating in a stable overflowing condition at 27°C, which is the same as the SBS outlet temperature, the average water collection rate of the chevron was 0.1 L/h. The composition of the fluid collected was predictably found to be very similar to the SBS scrubbing liquor as shown in Table 10.18. The fluid collected from the chevron was higher in sulfates, nitrates, and other gaseous compounds. The enrichment is caused by the additional contact time of the

TABLE 10.17. Comparative Quench Scrubber Decontamination Factors for Volatile Off-Gas Effluent

<u>Melter</u> <u>Test</u>	<u>Total Quench Scrubber DF</u>				
	<u>B</u>	<u>Cl</u>	<u>F</u>	<u>P</u>	<u>S</u>
PSCM-23	7.1	3.0	16	8.6	8.7
PSCM-22	11	6.2	14	--	4.3

TABLE 10.18. Comparison of Compositions of Chevron Demister and SBS Overflow Solutions

	<u>Demister, mg/L</u>	<u>SBS, mg/L</u>
Al	249	143
Ba	22	20.7
B	0.12	0.039
Ca	64.3	84.7
Ce	9.7	0.767
Cr	1.44	1.22
Cs	6	10.5
Cu	1.14	1.57
F	210	400
Fe	7.55	19.5
K	4.3	3.5
La	0.01	0
Li	2.4	3.29
Mg	3.13	1.2
Mn	1.22	1.14
Mo	1.42	2.22
Na	65	80
Nd	0.06	0.06
Ni	2.45	3.3
NOx	91	349
P	0.37	3.3
S04	91	250
Si	21.5	23.9
Sr	0.62	0.207
Ti	0.15	0.347
Zn	6.7	4.75
Zr	39.9	43.5
Cl	100	220

small quantity of water draining from the chevron. The actual quantity of gas removed from the off gas is very small. The quantity of mist penetrating the chevron demister was estimated from the water run-off from the downstream HEME. At an 110 scfm off-gas flow rate the demister water penetration rate was estimated to be 1 L/h. The functional dependence of fluid collection upon off-gas flow rate is shown in Table 10.19. These data show that SBS fluid entrainment losses did increase with off-gas flow rate, but even at high flow conditions the chevron removed only a small fraction of the total water content of the process exhaust. From the above, it is clear that under stable steady-state processing conditions the chevron demister does very

TABLE 10.19. Chevron Demister Water Collection Rates

<u>Airflow Rate. cfm</u>	<u>Water Collection Rate. L/h</u>
110	0.04
170	0.1

little ($\leq 10\%$) to reduce water carryover into the downstream HEME; however, the demister has also been clearly shown to be quite beneficial should SBS operations become turbulent.

10.2.5 High-Efficiency Mist Eliminator

The HEME is a high-efficiency filtration device designed to remove airborne condensed phase effluents penetrating previous low-efficiency off-gas treatment devices (SBS chevron demister) preceding it. This high-efficiency filter is usually operated wet; consequently, it is suitable for removing both water mists and particulate matter. Its off-gas function is to remove both with high efficiencies so as to preserve and maintain the design service life of the subsequent remote HEPA filters.

Physical Properties and Operating Conditions

The HEME was operated at two off-gas flow rates (110 and 170 scfm) without an auxiliary water spray. The water inlet rates to the HEME under these conditions were established by SBS mist carryover, which averaged 1 L/h. The pressure-drop data and corresponding gas face velocity data collected during this non-spray period are graphically displayed in Figure 10.16. The temperature is plotted in Figure 10.17. These data plots clearly show the significant impact that off-gas water loading can have upon HEME pressure drop. The 15 L/h spray rate increased the average pressure drop across the HEME by more than 50%. However, off-gas flow and water loadings were the only factors that affected HEME pressure drop throughout PSCM-23. This is hardly surprising in view of the low aerosol effluent concentrations characterizing this test. To put PSCM-23 HEME operating conditions in perspective, the total HEME water inlet rate with the spray was 30 times that recommended by DMFF (50 mg/scfm); without the spray, it was only a factor of 2 greater than recommended.

FIGURE 10.16. HEME Differential Pressure and Face Velocity

FIGURE 10.17. Inlet Temperature to the HEME

The water collection characteristics of the HEME are graphically displayed in Figures 10.18 and 10.19. The data in Figure 10.18 show that condensate did not drain from the HEME for about a day after the test was initiated, which indicates that the glass fiber bed has about a 20-L hold-up capacity. The composition of the fluid that finally drained from the HEME during the experiment is shown in Table 10.20. The sample at run hour 239 is typical of fluid drained from the HEME when the water spray was not used, and the sample at run hour 335 is typical of fluid drained when the water spray was on. The last sample of HEME solution was taken after all the idling was completed. When the water spray was not on, the pH of the solution was about 1, which is much lower than the fluid collected from the SBS. The lower pH value is attributed to the longer contact time of the mist with the gas, which contains an average of 2000 ppm of NO_x and the other acid gases. When the water spray was used, the pH of the HEME drain solution increased to above 2 (Figure 10.20). This result indicates that the HEME was collecting about the same amount of gas but that the concentration was being diluted by

FIGURE 10.18. Water Collected from HEME When No Spray Was Used

FIGURE 10.19. Water Collected from HEME When Spray Was Used (15 L/h spray)

a factor of about 15. The particulate concentrations were also dilute by a factor of around 15 when the water spray was turned on. This indicates that little if any buildup of particulate occurred in the HEME during PSCM-23.

Gas Scrubbing Performance

The HEME is a high-efficiency aerosol removal device; however, when operated wet, the fiber bed provides a huge surface area over which the adsorbed water and reactive process gases are in contact. Consequently, the bed can also act as a gas scrubber for the acid gases of nitrogen, fluorine, chlorine, phosphorous, and sulphur. Using the nitrate content of the feed, the measured steady-state composition and drain rate of the HEME and assuming 100% NO_3 to NO_x melter conversion, the average, steady-state NO_x scrubbing efficiency of the HEME was found to be ~1%--the same as that of the SBS. Moreover, this removal efficiency was not affected by the large (15X) increase in HEME irrigation rate produced by the auxiliary water spray.

TABLE 10.20. Elemental Concentration of HEME Liquid Drain Stream

<u>Element</u>	<u>Concentration, ppm</u>			
	<u>at 191 h</u>	<u>at 293 h</u>	<u>at 405 h</u>	<u>at 431 h</u>
Al	201	384	8.47	14.5
B	86.1	597	36.0	46.9
Ca	3,111	639	29.8	39.6
Cr	4.35	13.7	0.23	0.46
Cu	2.42	14.3	0.60	1.05
Fe	17.7	36.0	0.59	0.86
K	47	144	5.6	8.6
Li	8.61	65.0	2.75	4.01
Mg	108	236	10.4	15.6
Mn	1.56	2.84	0.04	0.07
Mb	7.63	80.2	3.89	5.72
Na	580	2,510	93	163
Ni	1.25	3.99	0.11	19
Si	27.6	106	67.9	79
Sr	1.42	2.49	0.13	--
Ti	0.33	1.07	0.02	0.04
Zn	0.02	14.3	0.18	0.30
Zr	0.46	5.05	0.23	0.67
Cs	37.5	251	12.3	22.4
F	26	605	88	98
Cl	210	1,920	120	190
NO₃	10,000	36,900	1,110	1,440
so4	180	10,300	60	90

Apparently, the kinetics of **NO_x** removal are being limited by a high **NO/NO₂** ratio (**NO/NO₂≈2**) and a low partial pressure of **NO₂**.

HEME removal efficiencies for condensible gaseous effluents are summarized in Table 10.21. The scatter in these data is a reflection of analytical uncertainties associated with limited sample size. However, the data clearly show that the irrigated **HEMES** are capable of interacting and removing gas phase effluent to a significant extent. The lack of available

FIGURE 10.20. pH of HEME Fluid

TABLE 10.21. Gaseous HEME Decontamination Factors

Element	HEME Gaseous DFs			
	6/6/88 2110 h	6/9/88 1240 h	6/17/88 1110 h	6/21/88 0217 h
B	6.5	57	260	29
Cl	19	19	96	66
F	4.2	75	40	18
P	1	--	--	--
S	2.5	4.4	--	--

data precludes any assessment of the influence of flow rate upon HEME gas phase scrubbing efficiency. However, HEME aerosol removal efficiency is so high, as discussed in the next section, that all traces of condensed phase material containing born, chlorine, fluroine, and sulfur are removed from the HEME process exhaust leaving only gas phase losses of these specimens, as shown in Table 10.22.

TABLE 10.22. Percent of HEME Effluent Losses of Condensable Gas Phase Effluents as Gaseous Phase Losses

<u>Day</u>	<u>% Losses Due to Gaseous Escape</u>				
	<u>B</u>	<u>Cl</u>	<u>F</u>	<u>P</u>	<u>S</u>
6	--	99	100	--	100
9	91	72	85	--	99
13	--	88	100	--	--
17	--	99	100	--	--
21	100	98	100	--	--

Aerosol Scrubbing Efficiency

As was discussed previously, the primary purpose of the HEME off-gas component is to efficiently remove airborne condensed-phase effluent so as to extend the service life of downstream remote HEPA filters. The performance of the HEME, unlike the SBS and chevron demister, is not severely limited by aerosol effluent size characteristics nor the physical state of the effluent. The size distribution of particulate matter at the HEME inlet was determined through use of a cascade impactor, which was described in the previous section. Figure 10.15 is a photograph of the aerosol deposits on successive impactor collection stages, which unequivocally demonstrates the submicron nature of the particulate effluent matter with which the HEME has to interact. This same result was obtained under all PSCM-23 operating conditions. Since chevron demisters exhibit relatively high removal efficiencies for mist droplets $>3 \mu\text{m}$, the water mist aerosols transmitted to the HEME are presumed to possess diameters $\leq 3 \mu\text{m}$. Consequently, the average effluent characteristics of off-gas aerosols incident upon the HEME during PSCM-23 are found to be composed almost entirely of submicron particulate matter and tiny ($<3 \mu\text{m}$) water aerosols.

Equipment performance is conveniently expressed in terms of mass DFs. The number of HEME aerosol mass DFs derived from PSCM-23 data are significantly less than for the other off-gas devices characterized during this test. The reason for this is minimum acceptable sample size. Daily aerosol samples were collected over ~20-h periods before and after all major off-gas components. Even though HEME samples were collected at maximum possible flow

rates for these sampling periods, the collected aerosol samples were massless, i.e., no detectable filter weight change. Consequently, daily samples were combined for chemical analysis. In addition to this, samples collected with the cascade impactor could not be used for performance measurements because of unacceptable impaction stage sample losses. A summary of HEME mass DFs were presented earlier in Table 10.4 along with similar data obtained from the melter and SBS.

The data in this table reveal that very high HEME DFs were recorded throughout all phases of PSCM-23 testing. The dearth and variability of these data makes it difficult to identify trends. Thus, it is not justifiable to conclude that HEME mass DFs increased during water spraying, although individual test results may suggest this. It is also tempting to infer that HEME performance increases during idling, but this conclusion would be based on a single measurement. What can be said is that overall HEME DFs during PSCM-23 were 1400. This value is in agreement with radioactive measurements made at the Belgium PAMELA facility.^(a) The PSCM-23 data is significantly higher (10X) than has been achieved at SRL during similar melter tests (Colven 1983), but the off-gas systems are quite different. Unlike the PAMELA and the HWP AOD design, the SRL off-gas system uses a high-efficiency scrubbing stage before HEME filtration occurs. The additional scrubbing stage reduces HEME inlet aerosol concentration by a factor of more than 30. Since HEME influent conditions are so dramatically different for the SRL design, further intercomparisons of PSCM-23 and SRL HEME performance data are not justifiable and will not be made.

HEME parametric tests were also performed at PNL in FY 1987 and FY 1988 before the PSCM-23 test to examine the decontamination abilities of the HEME under various operating conditions. The effect of water loading and off-gas flow rate were of primary interest and can be compared with PSCM-23 results. The variable ranges in the parametric tests were as follows:

(a) Stehle, M. Karlsruhe Nuclear Research Center, Federal Republic of Germany, private communications.

<u>Variable</u>	<u>Range</u>
Air Flow	50-250 scfm
Water Spray	0-500 mL/min
Inlet Temperature	20-70°C

Based on a statistical examination of the data, it was determined that the variability in the DF data were dependent on the magnitude of the DFs. In the discussion that follows, statistical significance is defined at the 95% confidence level. The results of the tests performed at room temperature are shown in Figures 10.21 and 10.22. Aerosols of NaCl and TiO₂ were used for tests. The tests results shown in Figure 10.21 indicate that the water spray rate did have a significant effect on the DF. The results showed that a water spray rate of about 50 mL/min provided a better DF than the high water spray rate or no water spray. The water spray rates used during the PSCM experiment would be most comparable to the 50 mL/min water flow rate. The parametric and melter test results indicate the water loading in the off-gas

FIGURE 10.21. Effect of Inlet Water Spray on HVE Performance

FIGURE 10.22. Effect of Air Flow on H₂O₂ Performance

stream entering the HWP H₂O₂ should be within the range used during PSCM-23. Significantly higher or lower rates would provide a decrease in performance.

The parametric test results also show that for the ranges tested; the gas flow rate did not have a significant effect on the DF (Figure 10.22). This is in agreement with PSCM-23 test results (see Table 10.4). The test data are also supported by literature data (Figure 10.23). Figure 10.23 shows the relationship between the superficial gas velocity, pressure drop, and collection efficiency. For the pressure drop range observed during PSCM-23 of 2 to 4 in. WC the collection efficiency varies less than 1%. This low variability is well within the parametric and PSCM-23 test data variability. The commercial data compared the changes in pressure drop versus efficiency (see Figure 10.23).

The aerosol scrubbing performance of the H₂O₂ for individual effluent elements is presented in Table 10.23. Like the mass DFs discussed above, H₂O₂ elemental DFs are consistently high, but also quite variable. With few exceptions, the highest H₂O₂ DFs occurred at the beginning of the test when

FIGURE 10.23 . Collection Efficiency and Pressure Drop of a Fiber Mist Eliminator as a Function of Gas Velocity Through Fiber Packing (Perry and Chilton 1973)

the filter was free of effluents. Most **DFs** decreased and leveled out at quite acceptable values by the middle of the test. Since most of the semi-volatiles behaved in this manner and since these elements are major components of the submicron particulate matter being transmitted to the **HME** as shown previously, this trend is probably real. Assuming that all **HME** surfaces were passivated midway through the test, essentially all important effluent elements exhibited **DFs** >200. This conclusion is in agreement with experimental data collected both at the Japanese **INC** facility and at the Belgium **PAMELA** plant. The low **HME** performance values for aluminum, iron, and silicon are believed to result from the filter's fiber glass material, which contributes to **HME** exhaust concentrations of these elements.

The **HME** performance values measured during **PSCM-23** do not compare very well with data obtained from the previous **PSCM-22** test. Present performance values are at least an order of magnitude greater than was achieved during **PSCM-22**. Superficial face velocity was the only significant operating

TABLE 10.23 Individual Element Decontamination Factors for HEME Aerosol

Element	DFs							
	Average	6/6/88 2110 h	6/8/88 2134 h	6/11/88 1148 h	6/13/88 2052 h	6/17/88 1110 h	6/17/88 2320 h	6/21/88 0924 h
Al	120	81	--	160	88	130	150	1,800
Ba	100	14	--	190	--	--	--	--
Ca	25	23	1	--	10	37	53	190
Cd	19	--	--	5.8	--	--	32	--
Cl(a)	6,700	3,500	2,200	13,000	310	6,200	15,000	56,000
Co	29	2 ²	82	--	2.8	30	--	--
Cr	200	260	190	--	220	--	120	4,10 ⁰
Cs	18,000	2,400	100,000	1,600	520	810	660	2,00 ⁰
Cu	1,500	1,600	2,800	2,500	480	680	710	4,90 ⁰
F(a)	3,000	1,200	510	7,000	1,600	4,000	3,600	9,10 ⁰
Fe	55	39	--	46	54	120	17	12 ⁰
Li	3,900	2,500	17,000	1,300	550	970	880	4,70 ⁰
Mn	37	26	41	--	--	--	45	--
Mo	1,500	3,200	2,200	1,700	570	760	800	4,000
N(a)	98	120	4.5	170	--	--	--	--
Na	1,500	4,500	200	1,400	630	1,100	930	5,600
Ni	170	57	78	490	95	240	48	--
P	23	--	23	--	--	--	--	--
S(a)	1,600	2,400	2,300	2,000	600	1,400	1,200	5,300
Si	130	14	--	--	5	33	470	8,400
Sr	430	--	--	430	--	--	--	--
Zn	1,400	86	--	6,100	140	220	310	1,900
Zr	180	--	--	180	--	--	--	--
TTL	1,400	1,700	340	2,400	780	1,700	1,500	7,500

(a) Assumed to form soluble anions (Cl: Cl^- , F: F^- , N: NO^- , and NO_3^- ; S: SO_4^{2-}).

condition that differed in the two tests. The face velocity used during PSCM-23 was 6 to 10 **ft/min**, a factor of 4 to 8 smaller than previous conditions. It is postulated that the low PSCM-22 **DFs** resulted from **reentrainment** of previously captured effluents that penetrated the filter element by solution transport. Apparently, this supposition was correct; there was no indication that such an effect was occurring during PSCM-23 as evidenced by the comparatively high **DFs** achieved. The contrasting results obtained during these sequential tests emphasize the need to over-design the size of process **HEMEs** so as to compensate for any subsequent increases in off-gas system (inleakage) flow.

Definitive assessments concerning the effects of off-gas flow, off-gas moisture loading, and idling upon **HEME** performance cannot be made because of the variable nature of the limited data available. However, all of the data taken together illustrate that extremely high **HEME DFs** are achievable under all the conditions tested during PSCM-23. The **HEME** should be sized for a superficial gas velocity of 10 **ft/min** to provide good performance and to allow for possible increases in system inleakage. The recommended overall **DF** for the **HEME** should be 400. A higher **DF** cannot be justified without additional test data.

Total DFs

Total performance calculations need to be performed for boron, chlorine, fluorine, phosphorus, and sulfur since these elements are present in both gaseous and condensed phase process effluents. Table 10.24 summarizes the results of these calculations. Because most of the mass of these effluents is carried by gaseous compounds, gaseous interactions will limit and determine **HEME DFs** for these elements. The data in this Table 10.24 confirm earlier observations that **HEMEs** exhibit significant gas phase effluent removal efficiency. Moreover, the magnitude of these **DFs** are at least as great as corresponding **SBS DFs** previously discussed.

TABLE 10.24. HEME Total Decontamination Factors

Element	6/6/88 2110 h	6/9/88 1240 h	6/11/88 1148 h	6/17/88 1110 h	6/21/88 0217 h
B	8.7	68	71	310	35
Cl(a)	65	38	17	170	400
F(a)	4.9	72	69	45	22
P	1	7.9	--	--	--
S(a)	6.6	38	2500	1600	

(a) Assumed to form soluble anions (Cl: Cl^- , F: F^- , N: NO_2^- and NO_3^- ; S: SO_4^{2-}).

10.2.6 High-Efficiency Particulate Air Filter

A dual HEPA filter assembly is the last in-cell element of the HWP ACD off-gas system. Each filter in this assembly will be mounted and tested out-of-cell to achieve a removal efficiency of **99.97%** for the most penetrating ($0.3\ \mu\text{m}$) aerosols.

Physical Properties and Operating Conditions

As previously explained, the PSCM-23 HEPA filter was used for only the first **7** days of the test because of the pressure drop associated with the HEPA's pre-heater. As a result, the HEPA accumulated very **little** aerosol, and no change in pressure drop occurred during this period. HEPA operating parameters during the test, such as the air flow rate, pressure drop, and inlet temperature, are graphically displayed in Figures 10.24 through 10.26, respectively. These data are invariably normal and are of **little** use in predicting the service life the HEPA under long-term projected exposure.

Influent Conditions And Service Life

The need for pre-filters and the loading capacity of HEPA filters are determined by the nature and composition of aerosol effluents to be treated by HEPA filtration. A multi-stage cascade impactor was used to classify the sizes of HEME effluent (HEPA influent) aerosols from $5\ \mu\text{m}$ to $<0.25\ \mu\text{m}$ in nine discreet steps. The aerosols exiting the HEME were always found to be exclusively submicron, independent of PSCM-23 process or off-gas operating

FIGURE 10.24. Air Flow Rates Through HEPA Filter

FIGURE 10.25. Pressure Drop Across HEPA Filter Housing

FIGURE 10.26. Inlet Temperature to HEPA Filter

conditions. Figure 10.15 is a picture of the aerosol deposits collected on consecutive impactor stages ($5\text{ }\mu\text{m}$ to $0.25\text{ }\mu\text{m}$: left to right and top to bottom). The aerosol deposits, which form white jet patterns (lines) on the stainless steel collector stages, are only visible on the last two stages. Clearly, the nature of HEPA influent aerosols during PSCM-23 obviate the need for HEPA pre-filters if the PSCM-23 data is truly representative of plant operations.

Although the size distribution of particulate matter incident upon the HEPA during PSCM-23 is compatible with a long service life, loading rates and/or exposure criteria will establish the operational life of the HEPA. The mass loading of the HEPA influent (HEME effluent) stream was determined under all process and off-gas operating conditions; it was never found to be greater than $0.02\text{ }\mu\text{g/L}$. Manufacturer's data show that industrial-size HEPA filters can be loaded with up to 5 lb of aerosol matter before an unacceptable pressure drop (3 in. WC) develops across the filter.^(a) At a 500 scfm

(a) Mine Safety Analysis Corporation, HEPA Technical Data Manual.

off-gas flow rate, plant HEPA assemblies would have a projected service life greater than 15 years if PSCM-23 data is representative.

Because of maintenance personnel exposure during filter replacement and disposal, HEPA filter dose rate accumulation may limit the filter operational life. Assuming that ^{137}Cs is the major activity in effluent samples, that the cesium represents 8 wt% of effluent aerosol matter, and that the isotopic abundance of ^{137}Cs in HWP waste is 1/3, 2 lb of effluent aerosol containing 2,000 Ci of ^{137}Cs could accumulate on the HEPA filter in about 10 yrs. The unshielded dose-equivalent rate from a 2000 Ci Cs-137 point source would be about 13,000, 500, and 60-rem/h at distances of 1, 5, and 10 ft, respectively. Depending on filter, equipment, and facility design and maintenance approach, this radionuclide accumulation may require filter change out.

As mentioned above, the service life projections of HEPA filters require accurate and representative information regarding the nature of influent aerosols. The size classification of the effluent is reliably correct; however, PSCM-23 mass loading data may not be prototypic of plant operations because of the very high melter DFs achieved during the test. As a result, the 5.8 year HEPA service life projected from the present test data may not be a very conservative estimate.

10.2.7 Melter Off-Gas Treatment System Performance Evaluation for HWP Application

To assess the MOG treatment system evaluated in PSCM-23 testing for HWP design application, the MOG treatment results for PSCM-23 were evaluated in context with other MOG treatment system studies performed at PNL (HBCM-85-1 and PSCM Tests No. 1, 3, 4, 7, 9, 15, 16, 19, and 22). To recommend the MOG treatment system decontamination for HWP design, the test run feed compositions, run conditions, particle size determinations/compositions, and element DFs were evaluated. Decontamination factors for elements were grouped based on test performance and chemical behavior. Modestly conservative DFs were selected for design application (Table 10.25). The selected DFs were weighted toward system performances observed in HWP tests PSCM-22 and HBCM-85-1. Runs for West Valley process development, which are expected to be more typical of a remotely operated plant process (HEME size increased

TABLE 10.25. Hanford Waste Vitrification Plant Design Recommendations

<u>Material</u>	<u>Melter</u>	<u>Melter Off-Gas Treatment System Decontamination Factors</u>	
		<u>Submerged Bed Scrubber</u>	<u>High Efficiency Mist Eliminator</u>
Nonvolatiles	500	40	400
B	100	5	50
C	1	1	1
Cd	7	3	400
Cl	2	5	40
Co	300	5	50
Cs	14	3	400
Cu	500	5	50
F	4	5	40
H ₃	1	5	1
I	1	1	1
K	300	5	400
Li (in frit)	500	5	400
Mo	100	5	400
Na	300	5	400
Ni	500	5	50
NO ₃ ^(a)	1	1	1
P	500	5	50
Pb	(10) ^(b)	(5) ^(b)	(50) ^(b)
Ru	40	5	400
S	5	5	5
Se	10	5	50
Sr	500	40	400
Tc	14	5	50
Te	10	5	50
V	500	5	50

(a) Conversion of nitrate to NO_x is ~75%. Traces of ammonia in MOG (<2% of nitrogen in NO₃).

(b) Projected based on chemical properties.

between PSCM-23 and West Valley test runs), were also considered heavily for off-gas treatment. In PSCM-23 testing, the process operating conditions were so conservative and well controlled that the results were much better than expected in the HWVP. For elements not shown in Table 10.25, DFs should be used for chemically similar analogs. The recommended DFs are based on limited data and will be updated as more test data become available and the associated chemistry is better defined.

The data were not adequate to determine HEPA filter performance for aerosol removal during PSCM-23. Thus, it is recommended that the rated efficiency of HEPA filters be used, 10^3 for 0.3 μm or larger particles for each filter, with up to two filters in series.

HEPA DFs for the following material existing the HEME should be considered to be -1 because the material at this point in the off-gas system is mainly gaseous (Table 10.22 PSCM-23) B, Cl, F, S, N, CO_2 , I, and H^3 . The demister DFs for all materials should be taken to be 1.

11.0 MATERIALS EVALUATION

Materials testing was performed to evaluate the performance of selected materials exposed to simulated HWP process conditions in the melter and off-gas systems.

11.1 TEST APPROACH

Metal coupons were installed on racks into the PSCM melter plenum and the SBS. The materials selected for the preliminary tests are shown in Table 11.1. The melter plenum coupons were used to evaluate corrosion resistance in conditions similar to those experienced near the inlet of the off-gas line and by other equipment installed in the melter plenum (IR-TV, thermowells, dip tubes, etc.). With the exception of the C-276, the materials for the melter plenum test were selected for high-temperature corrosion resistance. The C-276 was included as a comparison to other corrosion tests under the HWP materials evaluation activity. Selected melter plenum coupons were exposed to feeding-only conditions, to combined feeding and idling periods, or to idling-only exposure.

The SBS testing assessed corrosion resistance to the atmosphere above the SBS solution and to recirculating solution in the SBS. The coupons used in the SBS test represent the range of materials that have been evaluated for resistance to aqueous corrosion conditions in the HWP. SBS coupons were installed in the SBS before the start of the run and removed following completion of the run.

TABLE 11.1. Materials Selected for the PSCM-23 Materials Evaluation Tests

<u>Coupon Location</u>	
<u>Melter Plenum</u>	<u>Submerged Bed Scrubber</u>
Inconel 690	Hastelloy C-276
Incoloy 825	Carpenter Alloy 20 Cb-3
Haynes 214	304L Stainless Steel
Haynes 556	
Hastelloy C-276	

The coupons used for these tests were comparable to coupons used for other HWVP corrosion studies. The coupons were rectangular (1 in. x 2 in. x ~1/16 in.) with a hole drilled near one end for hanging. The installation and retrieval schedule for the coupons installed in the PSCM plenum and the SBS is shown in Table 11.2. The coupon numbers correspond to the same numbered coupons in Tables 11.3 and 11.4.

The specimens were observed in the "as-removed" condition for general evaluation. The surface deposits and corrosion products were then removed to evaluate the samples' conditions. The specimens were then repetitively cleaned in 50 wt% solution of HCl and evaluated for corrosion. Localized corrosion was evaluated by visual observation of the coupons using a 10X magnifying eyepiece.

The corrosion rates of coupons exposed to the various melter plenum conditions, along with the initial dimensions of the coupons, weight losses, alloy densities, and exposure times that were used in the calculation of corrosion rate, are tabulated in Table 11.3. Similar information for the SBS coupons is presented in Table 11.4.

11.2 TEST ANALYSES

11.2.1 Melter Plenum Corrosion Tests

The coupons exposed to melter feeding-only conditions resulted in measurable but slight corrosion, in general showing only tenths of a mil per year. Corrosion rates during idling-only periods were significantly higher, ranging from a few mils per year to tens of mils per year. The combined feeding and idling samples, expected to show the most severe corrosion (as seen on the Haynes 214 samples), actually ranged in between the feeding and idling rates for the other materials. It is postulated that a protective surface was established on those samples, except for the Haynes 214 alloy, during the lower-temperature feeding periods that helped protect the samples from the higher temperatures at melter idling conditions. Pitting was not evident on any of the samples. However, the surfaces of most of the samples were quite rough, apparently due to uneven corrosion rates over different areas of the samples. A nonuniform oxide layer, or possibly some splattering

TABLE 11.2. Coupon Exposure Schedule for PSCM-23 Materials Evaluation Tests

<u>Material</u>	<u>Location</u>	<u>Coupon</u>	<u>Date Installed</u>	<u>Date Removed</u>	<u>Exposure Time, h</u>	<u>Approx. Temp., °C</u>
Inconel 690	PSCM	1	6-06-88	6-21-88	360	500
	PSCM	2	6-06-88	6-21-88	360	500
		2(a)	6-29-88	7-18-88	450	1000
	PSCM	3	6-29-88	7-18-88	450	1000
Incoloy 825	PSCM	4	6-06-88	6-21-88	360	500
	PSCM	5	6-06-88	6-21-88	360	500
		5(a)	6-29-88	7-18-88	450	1000
	PSCM	6	6-29-88	7-18-88	450	1000
Haynes 214	PSCM	7	6-06-88	6-21-88	360	500
	PSCM	8	6-06-88	6-21-88	360	500
		8	6-29-88	7-18-88	450	1000
	PSCM	9	6-29-88	7-18-88	450	1000
Haynes 556	PSCM	10	6-06-88	6-21-88	360	500
		10(a)	6-29-88	7-18-88	450	1000
	PSCM	11	6-29-88	7-18-88	450	1000
Hast. C-276	PSCM	12	6-06-88	6-21-88	360	500
	SBS-vapor	13	6-03-88	6-29-88	550	30
	SBS-sol'n	14	6-03-88	6-29-88	550	25
Alloy 20 Cb-3	SBS-vapor	15	6-03-88	6-29-88	550	30
	SBS-sol'n	16	6-03-88	6-29-88	550	25
304L SS	SBS-vapor	17	6-03-88	6-29-88	550	30
	SBS-sol'n	18	6-03-88	6-29-88	550	25

(a) Coupons were exposed to feeding conditions then reinstalled in the plenum during idling period without cleaning to measure weight loss.

TABLE 11.3. Materials, Conditions, and Corrosion Data for Coupons from Plenum Materials Evaluation Test

<u>Material</u>	<u>Density</u>	<u>Condition</u>	<u>Coupon</u>	<u>Surface Area, cm²</u>	<u>Weight Loss, g</u>	<u>Corrosion Rate, mpy</u>
Inconel 690	8.19	Feed Only	1	26.966	0.003	0.1
		Feed/Idle	2	26.937	0.246	4.7
		Idle Only	3	26.917	0.500	17.4
Incoloy 825	8.14	Feed Only	4	26.542	0.004	0.2
		Feed/Idle	5	26.622	0.265	5.2
		Idle Only	6	26.358	0.222	7.9
Haynes 214	8.05	Feed Only	7	26.689	0.013	0.6
		Feed/Idle	8	26.665	0.130	2.6
		Idle Only	9	26.654	0.031	1.1
Haynes 556	8.23	Feed/Idle	10	25.966	0.584	11.6
		Idle Only	11	25.707	1.01	36.6
Hast. C-276	8.89	Feed Only	12	27.589	0.012	0.5

TABLE 11.4. Corrosion Data for Coupons from the SBS Material Evaluation Test

<u>Material</u>	<u>Density</u>	<u>Condition</u>	<u>Coupon</u>	<u>Surface Area, cm²</u>	<u>Weight Loss, g</u>	<u>Corrosion Rate, mpy</u>
Hast. C-276	8.89	Vapor	13	27.809	0.0008	0.02
		Submerged	14	27.524	0.0003	0.008
Alloy 20 Cb-3	8.08	Vapor	15	28.076	0.0014	0.04
		Submerged	16	28.114	0.0006	0.017
304L SS	7.90	Vapor	17	27.039	0.0010	0.03
		Submerged	18	27.119	0.0003	0.009

of the samples may account for the rough surface after the samples were cleaned to remove the corrosion products. The corrosion of the samples can generally be classified as uniform.

The INCO materials (Inconel 690 and Incoloy 825) and the Haynes 214 appear resistant to both feeding and idling conditions. They would

apparently be suitable preliminary candidates for plenum and off-gas line service. Resistance to molten glass, however, was not part of the scope of this initial evaluation.

11.2.2 Submerged Bed Scrubber Corrosion Tests

As would be expected, the SBS coupons showed very little corrosion during the melter run. Differences in the vapor space and submerged corrosion rates were measurable, tenths of a mil per year in the vapor space compared with hundredths of a mil per year in the solution. The low temperatures of the scrub solution and the vapor space above that solution facilitate minimizing the corrosion. Additionally, the pH of the scrubbing solution remained above -4 throughout the run, indicating that the solution never became very concentrated in the corrosive components of the off gas (halides and sulfur oxides).

Any of the three materials would appear adequate for the SBS service. This conclusion is supported by the fact that the SBS is made of stainless steel and has shown little if any corrosion. It is probable that more corrosive conditions could exist elsewhere in the SBS other than where the coupons were located for this test. The inlet pipe, for example, is exposed to humid gases at high temperatures relative to the rest of the SBS. A region probably exists in the lower portion of that pipe where the vapor could condense and possibly trap corrosive components. This environment could be significantly more corrosive than either the scrubber solution or the vapor space above the solution.

12.0 QUALITY ASSURANCE

12.1 GENERAL QUALITY ASSURANCE PROGRAM DESCRIPTION

The PSCM-23 melter run was performed under the PNL quality assurance program described within PNL-MA-70, Quality Assurance Manual and its sub-parts, Part 1, 2 and 3. The quality assurance program has been designed to meet the basic and supplementary requirements of **ANSI/ASME NQA-1 1983 Edition, Quality Assurance Program Requirements for Nuclear Facilities**.

12.2 QUALITY ASSURANCE IMPLEMENTATION

As prescribed by PNL-MA-70, a **Quality Assurance (QA)** plan was developed and approved by PNL (WTC-006). Subsequently, as required through contractual documents, the QA plan (WTC-006) was submitted to and approved by the Client, Westinghouse Hanford Company (WHC).

Following the QA plan, a test plan was developed to support testing activities as required by PNL-MA-70. A test plan, HWVP-88-V110204, **Pilot-Scale Ceramic Melter Run, PSCM-23/HWVP-15 Test Plan, Revision 0**, was internally approved by PNL, and also the client, WHC.

In accordance with PNL-MA-70, QA impact levels were assigned to the **subtask** activities as identified in Table 12.1. Overall, the PSCM-23 run was designated as an Impact Level **■** activity, as documented in QA Plan WTC-006. The basis for assigning this level is the importance of the off-gas treatment system.

The administrative procedural controls are contained in PNL-MA-70, Quality Assurance Manual, Parts 1, 2 and 3. Technical procedures were used to provide detailed planning, performance and control of activities during the PSCM-23 melter run. The procedures were prepared, reviewed, and approved in accordance with PNL-MA-70 procedure PAP-70-501. Distribution of technical procedures was in accordance with PAP-70-601. A listing of the technical procedures utilized on the PSCM-23 run are identified and listed in Table 12.2.

TABLE 12.1. PSCM-23 Run Objectives and Impact Levels

<u>Test Objectives</u>	<u>OA Impact Level</u>
5.1 Evaluate off-gas system performance	I
5.2 Evaluate melter feed preparation procedure	II
5.3 Evaluate pre-run laboratory crucible melt	III
5.4 Evaluate melter operation during integrated off-gas treatment system sampling	II
5.5 Evaluate nominal processing characteristics	II
5.6 Evaluate materials corrosion coupons	II
6.1 Determine maximum process rate	II
6.2 Evaluate effect of TOC increase on melter process characteristics	II
6.3 Analyze PSCM-23 post-run reference glass product	II
6.4 Characterize PSCM-23 feed properties	II
6.5 Perform vitrification process and mass balance	II
6.6 Evaluate glass discharge section and pour stream	II
6.7 Correlate secondary temperature measurements to bulk glass temp.	II
6.8 Evaluate ceramic melter tank mixing	II
6.9 Obtain process and parameter data important to waste form qualification	I

12.3 SURVEILLANCE ACTIVITIES AND RESULTS

There were a total of five surveillances performed on the PSCM-23 melter run. Two of the surveillances were performed by organizations external to PNL. Table 12.3 depicts the report numbers and the organizations responsible for conducting the surveillance.

TABLE 12.2. Technical Procedures for PSCM-23

<u>Procedure Title</u>	<u>Procedure Number</u>
Off-Gas Sample Collection	WTC-006-10
Laboratory Formic Acid Treatment of Melter Feed Slurries	WTC-006-8
Material Corrosion	WTC-006-1
Glass Viscosity	PSL-417-VSC, PSL-417-VIS
Glass Electrical Conductivity	PSL-417-ECC, PSL-417-ELE
Glass From Slurry Feed	Unnumbered (QA IL#3)
Laboratory Procedure for the Physical & Rheological Characterization of Newtonian and Non-Newtonian Fluids	WTC-006-4
PSCM-23 Feed Preparation Procedure	WTC-006-9
PSCM-23 Sampling Procedures for Liquid and Glass Samples	WTC-006-11
Feed Slurry Transfer and Line and Tank Flush Practices During PSCM-23 Test Activities	PSCM-23-1

TABLE 12.3. Surveillances Conducted on PSCM-23

<u>Surveillance Number</u>	<u>Organization</u>
JWS-88-205-A	PNL
JWS-88-206-A	PNL
BDS-88-011-A	PNL
88-P-834	WHC
PEL-88-1	DOE

In summary, the results of the surveillances indicate that the PSCM-23 melter run was conducted in accordance with the quality assurance program described in PNL-MA-70.

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APPENDIX A

PILOT-SCALE CERAMIC MELTER PROCESS RUN DATA

APPENDIX A

PILOT-SCALE CERAMIC MELTER PROCESS RUN DATA

FIGURE A.1. PSCM Average Bulk Glass Temperature

FIGURE A.2. PSCM Average Melter Feed Rate

FIGURE A.3. PSCM Plenum Temperature

FIGURE A.4. PSCM Plenum Pressure

FIGURE A.5. PSCM Electrode Power

FIGURE A.6. PSCM Electrode Resistance

FIGURE A.7. PSCM Electrode Current

FIGURE A.8. PSCM North Electrode Temperature

FIGURE A.9. PSCM South Electrode Temperature

FIGURE A.10. PSCM Glass Discharge Trough Block Temperature

FIGURE A.11. PSCM Glass Discharge Face Area Temperature

FIGURE A.12. PSCM Glass Discharge Trough Area Temperature

FIGURE A.13. PSCM Glass Discharge Face Heater Power

FIGURE A.14. FSCM Glass Discharge Trough Heater Power

APPENDIX B

OFF-GAS EFFLUENT CONCENTRATIONS DURING PSCM-23

APPENDIX B

OFF-GAS EFFLUENT CONCENTRATIONS DURING PSCM-23

PSCM-23 off-gas effluent concentrations measured in the melter, SBS, and H₂O exhausts are presented here. Axis identification and scale definitions are given in the title of each graph. T_0 is the origin of the time axis whereas ΔT represents the time interval between axis markers. All experimental concentration data have been adjusted to a single off-gas flow rate-- 110 scfm. Moreover, all plotted concentrations have been normalized to the maximum value of the set. As a result, the ordinate scale represents 0-100% of this maximum concentration value which is listed in the title of each graph. The dashed vertical lines appearing in each graph, from left to right, mark the beginning of high off-gas flow conditions (170 scfm), the beginning of the 15 L/h H₂O water spray, and the start of idling conditions (100 scfm flow and no H₂O spray), respectively.

TOT MELTER EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=358.86 UGMS/L)

AL MELTER EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=9.40 UGMS/L)

B MELTER EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=9.15 UGMS/L)

BA MELTER EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=.82 UGMS/L)

CA MELTER EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=.96 UGMS/L)

CD MELTER EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=1.30E-03 UGMS/L)

CE MELTER EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONCT(FS=.56 UGMS/L)

CL MELTER EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONCT(FS=21.57 UGMS/L)

CO MELTER EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONCT(FS=.03 UGMS/L)

CR MELTER EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=1.65 UGMS/L)

CS MELTER EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=7.49 UGMS/L)

CU MELTER EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=.93 UGMS/L)

F MELTER EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=4.55 UGMS/L)

FE MELTER EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=40.55 UGMS/L)

K MELTER EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=.39 UGMS/L)

LA MELTER EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=8.75 UGMS/L)

LI MELTER EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=2.09 UGMS/L)

MG MELTER EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=.75 UGMS/L)

MN MELTER EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=.89 UGMS/L)

MO MELTER EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=6.06 UGMS/L)

N MELTER EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=.36 UGMS/L)

NA MELTER EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=69.26 UGMS/L)

ND MELTER EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=3.44 UGMS/L)

NI MELTER EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=1.03 UGMS/L)

P MELTER EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=.07 UGMS/L)

FB MELTER EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=.01 UGMS/L)

S MELTER EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=9.88 UGMS/L)

SI MELTER EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=16.32 UGMS/L)

SR MELTER EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=.78 UGMS/L)

TI MELTER EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=.12 UGMS/L)

V MELTER EMISSION TIME DISTRIBUTION

T-→(T₀=6/6/88 0000; dT=24H): CONC↑ (FS=0.05 UGMS/L)

Y MELTER EMISSION TIME DISTRIBUTION

T-→(T₀=6/6/88 0000; dT=24H): CONC↑ (FS=.31 UGMS/L)

ZN MELTER EMISSION TIME DISTRIBUTION

T-→(T₀=6/6/88 0000; dT=24H): CONC↑ (FS=3.12 UGMS/L)

ZR MELTER EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC1(FS=22.93 UGMS/L)

TOT ~~SBS~~ EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=21.53 UGMS/L)

AL ~~SBS~~ EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=9.85E-03 UGMS/L)

B ~~SBS~~ EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=.62 UGMS/L)

BA SBS EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=7.73E-04 UGMS/L)

CA SBS EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=3.77E-03 UGMS/L)

CD SBS EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=2.49E-04 UGMS/L)

CE SBS EMISSION TIME DISTRIBUTION

T→(T₀=6/6/88 0000; dT=24H): CONC↑(FS=7.02E-04 UGMS/L)

CL SBS EMISSION TIME DISTRIBUTION

T→(T₀=6/6/88 0000; dT=24H): CONC↑(FS=5.59 UGMS/L)

CO SBS EMISSION TIME DISTRIBUTION

T→(T₀=6/6/88 0000; dT=24H): CONC↑(FS=6.30E-03 UGMS/L)

CR SBS EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONCI(FS=.11 UGMS/L)

CS SBS EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONCI(FS=3.08 UGMS/L)

CU SBS EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONCI(FS=.08 UGMS/L)

F SBS EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=.64 UGMS/L)

FE SBS EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=.02 UGMS/L)

K SBS EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=.06 UGMS/L)

LA SBS EMISSION TIME DISTRIBUTION
T->(T₀=6/6/88 0000; dT=24H): CONC↑!FS=4.18E-03 UGMS/L)

LI SBS EMISSION TIME DISTRIBUTION
T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=.30 UGMS/L)

MG SBS EMISSION TIME DISTRIBUTION
T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=.14 UGMS/L)

MN SBS EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=1.10E-03 UGMS/L)

MO SBS EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=.40 UGMS/L)

N SBS EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=.06 UGMS/L)

NA SBS EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=4.61 UGMS/L)

ND SBS EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=2.07E-03 UGMS/L)

NI SBS EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=7.02E-03 UGMS/L)

F SBS EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=3.59E-03 UGMS/L) ·

PB SBS EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): ~~DONC~~↑(FS=7.31E-03 UGMS/L)

S SBS EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=2.57 UGMS/L)

SI SBS EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=.08 UGMS/L)

SR SBS EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=2.84E-03 UGMS/L)

TI SBS EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=2.80E-04 UGMS/L)

V SBS EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=6.18E-04 UGMS/L)

Y SBS EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=1.80E-04 UGMS/L)

ZN SBS EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=.06 UGMS/L)

ZR SBS EMISSION TIME DISTRIBUTION

T->(T₀=6/6/88 0000; dT=24H): CONC↑(FS=.02 UGMS/L)

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