Summary Report

Defense Waste Vitrification Studies During FY-1981

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SUMMARY REPORT
DEFENSE WASTE VITRIFICATION
STUDIES DURING FY-1981

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Richland, Washington 99352

SUMMARY

Both simulated alkaline defense wastes and simulated acidic defense wastes (formed by treating alkaline waste with formic acid) were successfully vitrified in a number of direct liquid-fed melter experiments this fiscal year. The vitrification process was much improved while using the formate-treated waste, due to the ease of pumping the slurry and general improvements in melting behavior. The glass produced from the formate-treated waste was essentially identical to the glass produced from alkaline feed with respect to leach resistance.

Off-gas entrainment (averaging ~0.2 wt% of the total mass fed to the melter), as opposed to volatilization, was determined to be the primary mechanism for material exiting the melter. Entrainment appeared to be independent of the development or size of the melter cold cap. The material leaving the melter, however, was enriched in volatile and semivolatile components such as ruthenium, cesium, Cl^- , $\text{SO}_4^{=}$, boron, etc. When formate waste was vitrified, the flow behavior of the off gas from the melter changed dramatically from an erratic surging behavior to a more quiet, even flow. Hydrogen and CO were detectable while processing formate feed; however, levels exceeding the flammability limits in air were never approached.

Liquid feeding operations were successfully demonstrated on the former calcine-fed ceramic melter, illustrating the ability to use one set of top-entering plate electrodes when slurry feeding, as opposed to two sets of submerged electrodes.

Two types of melter operation were tested during the year. One method used the electrode power as the sole source of energy input, and the second used additional power from above the cold cap to "boost" the melting rates of the melter.

Several boosting methods located within the melter plenum were tested, including radiant heat from electric resistance heaters, propane combustion and plasma torches. The resistance heaters are the preferred option. Propane combustion was successful, but it was no more efficient than radiant heating. The plasma torches were tested, but the current "state-of-the-art" technology does not appear suitable for long-term use of these units in the melter plenum

environment. These units are not recommended for application in other than short-term heating needs such as melter startup. Microwave testing was also initiated during the year and was found to be an encouraging boosting mechanism.

When lid heating was being used, the off-gas exit temperatures were much higher than without lid heat (~600 versus 300°C), and water spray cooling in the off gas was required. Countercurrent spray cooling was found to be more effective than cocurrent spray cooling; however, a truly satisfactory system design has not been achieved. Without cooling, the particulates exiting the melter tend to melt and stick to the off-gas pipe, causing plugs. With cooling, this behavior was minimized. The wet-dry interfaces caused by incomplete spray atomization also caused some particulate buildup, but of a much less tenacious nature.

During melter idling, deposits are formed in the plenum and off-gas lines which are highly enriched in semivolatiles.

Materials of construction for the off-gas system were examined and preliminary results indicate Inconel®-690 is preferred in the plenum area. Inconel-600, -601, -617 and titanium or tantalum were found to be not acceptable. Plasma-sprayed oxide coatings were also briefly tested, but need more development to be considered a candidate for corrosion protection. Stainless steel is not acceptable for wet off-gas scrubbing components. Studies will continue to identify acceptable materials.

The pilot-scale ceramic melter was inspected after 239 days at temperatures of >1000°C. Corrosion of the K-3 refractory and Inconel-690 electrodes was minimal. The floor of the melter contained ~94 kg of sludge which did not drain. Approximately 2 kg of metal-like material (Ni_3S_2) were also found on the melter floor.

Control of the melter by resistance feedback was the preferred operating mode during all tests.

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An overheating incident occurred with the LFCM in which glass temperatures up to 1480°C were experienced. The most serious result was corrosion of the melter lid liner (Inconel-601). Some minor melting of the Inconel-690 electrodes was noted.

Lab-scale vitrification tests to study mercury behavior in a vitrification system were also completed this year. A lab-scale spray calciner/in-can melter system was used. All mercury feed to the system was volatilized. Ninety percent of the mercury reacts in the gas phase to form dense particulates of HgI, HgCl and HgO; ten percent of the mercury was recovered in the metallic form.

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1.0 INTRODUCTION

During FY-1981 the Pacific Northwest Laboratory (PNL) continued testing the vitrification of defense waste using a liquid-fed joule-heated ceramic melter. This work is in support of the Savannah River Laboratory effort to provide technology for a Defense Waste Processing Facility (DWPF) at the Savannah River Plant in South Carolina.

Liquid feeding a ceramic melter has become the reference process for the DWPF, and an accelerated testing program in support of this choice was undertaken at PNL. Three melters were operated throughout the year, testing various feed compositions and operating modes to provide data for process optimization and characterization. This work is a continuation of ongoing technology transfer (Bjorklund 1981) to Savannah River in the area of ceramic melter technology, which began in 1977.

This report describes the process equipment which was operated, the feed compositions which were tested and the detailed results of the individual experiments performed.

2.0 PROCESS AND EQUIPMENT DESCRIPTION

Defense waste testing during FY-1981 was carried out on three joule-heated ceramic melters (JHCM) and a lab-scale spray calciner/in-can melter (LSSC/ICM). The ceramic melters used included: 1) the liquid-fed ceramic melter (LFCM), 2) the pilot-scale ceramic melter (PSCM), and 3) the experimental ceramic melter (ECM). This equipment, as well as the associated feed and off-gas systems, are discussed briefly in this section.

2.1 LIQUID-FED CERAMIC MELTER (LFCM)

The LFCM features remain essentially the same as those from last year's testing (Bjorklund 1981). The LFCM (Figure 1) was specifically designed for liquid feeding. It is a joule-heated melter with two sets of Inconel-690 electrodes and a melting surface area of 1.05 m². Both sets of electrodes enter from the side of the melter and are completely submerged in the molten glass. The upper set of electrodes has twice the surface area of the lower set, which allows for a large amount of the power to be dissipated near the melting surface. The lower set of electrodes is used for power dissipation near the floor to raise the floor temperature, which results in better convective mixing and reduction in the precipitation of insoluble crystals near the floor. With this electrode design, only the lower set of electrodes need be used when the melter is in an idling state. The exposed glass surface temperature is thus lowered, which reduces heat losses and, more importantly, reduces volatility from the glass during idling. For a liquid feeding operation, the energy is required near the surface, so the upper set is utilized. A single 0.13-cm-thick platinum-10% rhodium alloy thermowell with eight Type S thermocouples is used to continuously monitor the glass temperatures. The thermowell is placed on the tank centerline.

During operation, the glass is continually pouring into a canister by way of an overflow system. A tilting mechanism is used to stop the pouring for canister changeout.

2.2 PILOT-SCALE CERAMIC MELTER (PSCM)

Prior to a rebuilding effort which allowed liquid feeding tests to be performed on this melter in FY-1981, the PSCM (Figure 2) was called the

FIGURE 1. Liquid-Fed Ceramic Melter (LFCM)

FIGURE 2. Pilot-Scale Ceramic Melter (PSCM)

calcine-fed ceramic melter (Dierks 1980). During the rebuilding process, the melter tank lid was redesigned, and the under-lid insulation was improved to minimize lid corrosion. The tank interior dimensions were changed slightly and now are 69 x 117 cm; and the electrode cross section has been changed slightly to 5 x 61 cm, resulting in a melter surface area of 0.73 m². The glass depth has been increased to 37 cm, and the electrodes were modified with wedge-shaped feet, resulting in a glass holdup volume of 255 L. The tapered electrodes are intended to minimize the accumulation of low-conductivity slag on the electrode face and to direct some of the electrical current flow away from the melter tank walls toward the center and floor of the tank.

Four thermocouple bundles in 0.64-cm-thick Inconel-690 thermowells, extending to within 2.54 cm of the melter tank floor, continuously monitor the glass temperature in the melter tank. Each bundle contains seven thermocouples spaced 7.6 cm apart. Three of the thermowells are placed symmetrically around the centrally-located feed inlet to stabilize the position of the melter cold cap. One of these three is positioned on the tank centerline 7.6 cm from the entrance to the discharge throat. The fourth thermowell is located tangent to the melter wall directly opposite the discharge throat. The underflow throat has been fabricated from a 45.7- x 30.5- x 56-cm monolithic block of K-3 to minimize refractory joints and horizontal refractory surfaces around the throat. The throat is a 7.6-cm-dia hole, drilled flush with the melter floor and angling upward at 30° to intersect a 5.1-cm-dia riser channel drilled vertically downward in the center of the throat block. The discharge trough butts against the back side of the throat block and slopes downward at a 5° angle. The discharge trough matches a horizontal trough drilled in the back side of the throat block to intersect the 5.1-cm riser channel. The melter is operated without tilting, with an airlift lance inserted in the throat block riser channel to decrease the glass inventory in the melter tank as required.

2.3 EXPERIMENTAL CERAMIC MELTER (ECM)

The ECM (Figure 3) is a laboratory-scale melter for developing new design concepts such as microwave boosting and particulate removal systems, and for evaluating new glass and feed formulations prior to large-scale testing. The ECM trough block design differs from the previous melter block designs in two

FIGURE 3. Experimental Ceramic Melter (ECM)

ways: 1) it incorporates a one-piece riser and throat to limit joints, thus reducing glass leakage; and 2) it has an enclosed, circular trough in place of the open semicircle to avoid inadvertent splashing of glass onto the trough heaters during airlifting operations, and to prevent debris like lid insulation or heater fragments from obstructing the glass flow in event of a failure.

The lid is an Inconel parabolic dome with four access ports to accommodate a feed nozzle, microwave waveguide, off-gas line and viewport. Castable Alfrax® provides the lid insulation with a protective Inconel sheetmetal liner sealed over the melter cavity to prevent microwave interaction with the lid insulation. Isolation of the waveguide from the environment inside the melter is achieved with the use of quartz windows across the waveguide.

2.4 LAB-SCALE SPRAY CALCINER/IN-CAN MELTER (LSSC/ICM)

The laboratory-scale spray calciner/in-can melter (LSSC/ICM) and gaseous effluent cleanup system is a bench-scale mockup of an industrial waste solidification system. A simplified schematic of this system is shown in Figure 4, and a photograph of the system is shown in Figure 5.

Simulated liquid waste is pumped through the spray calciner feed system and atomized by air in a commercially-available spray nozzle (Spraying Systems®) located at the top of the spray calciner. Liquid waste droplets (~0.1 mm dia) formed by the spray nozzle are dried and partially decomposed to metallic oxides and salts as they fall through the heated wall spray calciner chamber. The nominal operating temperature of the spray calciner is 650 to 750°C. The dried waste powder is called calcine. The calcine is mixed with glass-forming chemicals as it falls from the cone section of the spray calciner into a heated receiving canister. The solid calcine/glass-former mixture is heated to a temperature of 1000 to 1050°C and converted to a vitreous product.

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© Registered trademark of Spraying Systems Company.

FIGURE 4. Laboratory-Scale Spray Calciner/In-Can Melter and Off-Gas Cleanup System

FIGURE 5. Photograph of Laboratory-Scale Spray Calciner/
In-Can Melter and Off-Gas Cleanup System

Off gas from the solidification process consists primarily of atomizing gas, water vapor and NO_x from nitrate decomposition, volatile and semivolatile components. This off gas is filtered through the spray calciner filters before being decontaminated by successive stages of scrubbing, condensation, physical separation and filtration in the off-gas cleaning system.

The design features of the SC/ICM are summarized in Table 1. The SC/ICM was designed to solidify liquid wastes at a rate of 1 to 4 L/h, corresponding to a glass production rate of 0.3 to 1.3 kg/h.

The cyclone separator was designed for a gas flow rate of 190 L/min ($6.75 \text{ ft}^3/\text{min}$) at 350°C . The dimensions of the cyclone are those recommended by the Stairmand (Koch and Licht 1980) design for a high-efficiency cyclone. With recommended dimensions, the cyclone has an 88% efficiency for removing entrained water droplets and particulate from the gas stream. The cyclone was fabricated from 304-L stainless steel (SS) bar stock. A 2-L glass vacuum flask was used to collect condensates from the cyclone.

TABLE 1. Summary of Design Features of the Laboratory-Scale Spray Calciner/In-Can Melter System

<u>Feature</u>	<u>Values</u>
<u>Spray Calciner</u>	
Spray Chamber Diameter	5.05 in. (12.8 cm)
Spray Chamber Height	41.5 in. (105.4 cm)
Ten-Element Single-Phase Furnace Total Power	10.1 kW
Filters (three)	
Pall	Inconel-600
Diameter	1.88 in. (4.8 cm)
Length	18 in. (45.7 cm)
Surface Area	149.9 in. ² (966.9 cm ²)
Filter Heater	
Six-Element Single-Phase Total Power	7.02 kW
<u>In-Can Melter</u>	
Furnace Diameter	5.75 in. (37.1 cm)
Furnace Height	20.25 in. (130.6 cm)
Eight-Element Single-Phase Furnace Total Power	8.6 kW
Canisters	
5-in. dia x 21-in. height	
<u>System Capacity</u>	
Liquid Waste to Spray Calciner	1 to 4 L/h
Glass Production Rates	0.3 to 1.3 kg/h

The downdraft condenser is a commercially-available American Standard shell and tube heat exchanger. The condenser is fabricated from 10.6-cm-dia 316 SS pipe. The tubes are 0.64-cm dia, having a total surface area 0.4 m². Water at a temperature of 8 to 15°C (40 to 60°F) and a pressure of 30 psig is used as a coolant on the shell side. A 4-L glass vacuum flask was used to collect condensates from the condenser. During experimental operations, the condenser cooled the off-gas stream from ~50 to 12°C.

An off-gas heater was installed in the off-gas system to heat the gaseous effluent above its dew point before passage through a HEPA filter. The heater was constructed by mounting and thermally and electrically insulating Thermcraft® heaters around 5.08-cm-dia 304L SS pipe. The power rating on the 120-V heaters is 10.4 W.

The HEPA filters used were manufactured by American Air Filter Company. The size used had a depth of 20.32 x 20.32 x 14.92 cm. The filters are rated for a gas flow of 190 L/min (50 ft³/min).

2.5 JHCM SLURRY FEED SYSTEMS

Two feed-system concepts for the liquid-fed ceramic melters have been tested during the year: 1) an airlift system (Figure 6), which has the obvious advantage of having no mechanical parts to maintain, and 2) a positive-displacement pump system (Figure 7). Both systems were initially plagued by plugging of horizontal lines and flowmeter orifices due to foreign material (>0.4-cm dia) present in the feed chemicals and frit. Strainers were required to remove this material to allow sustained operation. Airlifts were effective in metering the slurry feed to the melter; however, drying of the slurry was encountered in the lift lines and return lines where air venting contacted the liquid. The buildup of solids in the lift lines resulted in a drifting of the flow, along with other occasional plugging problems. The need for quick installation of a reliable feed system on the melters precluded the further development needed to perfect the airlift system, and efforts were concentrated on using the pump system.

Two types of positive displacement pumps were tried. A variable-speed, flexible tubing pump performed satisfactorily; however, its eventual use in a hot cell is impractical. Currently being used is a positive-displacement, air-operated diaphragm pump to create a pressurized feed loop.

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FIGURE 6. Airlift Feed System

FIGURE 7. Slurry Feed System

In this system, the air-operated diaphragm pump^(a) sends the slurry through a recirculation loop using a flexible "pinch-type" valve^(b) to regulate the loop pressure. The feed line exits from this loop, and flow to the melter is monitored using an electromagnetic volumetric flowmeter^(c) and a mass flowmeter.^(d) Both flowmeters are connected to controllers, and both have been successful (used in the control loop) for maintaining the feed rate within $\pm 5\%$ over 100-h tests. The mass flowmeter has been used more frequently, as it shows less tendency to drift.

A feed composition change from alkaline waste to a formate waste improved the rheological characteristics of the waste slurry and generally improved the feed system's performance. See Section 2.7.

2.6 OFF-GAS SYSTEM

Effluents from the vitrification processes are treated in a generic off-gas system which has been designed to accommodate a wide range of flows and conditions encountered in programs of previous years. Although the system does not have specifically-sized components, it does provide a tool for off-gas characterization studies to be carried out.

The Primary Off-Gas System (POG) consists of an ejector venturi, condenser, packed tower, HEPA filter and blower (Figure 8). Specifications for the system are shown in Table 2. The scrubbing equipment components can be valved out so melter tests can be performed while testing various equipment pieces.

The primary off-gas system is capable of producing a 10-in. H₂O vacuum and a flow of 125 scfm at the head end of the system. Its all-stainless-steel construction allows it to handle corrosive off gas. It can condense over 500 acfm steam at 400°C and cool the gas to room temperature. It is a quantitative tool. Both liquid and off-gas temperature, flow and pressure can be monitored. Each piece of the system can be valved in separately to evaluate its performance. Both in-line liquid and gas samples can be taken for analysis. The gas can be continuously analyzed for H₂, O₂, N₂, CO and CO₂. In

(a) Warren Rupp Co. Model ST 1-1/2A Sandpiper.

(b) Flexible Valve Co. Model 6300.

(c) Fischer and Porter Model 10 D1418A, 1/4-in. bore, ceramic tube.

(d) Micromotion Model B-25, 1/4-in. bore, SS tube.

MATERIAL BALANCE (60 l/h FEED RATE)

	OFF GAS FROM MELTER	VENTURI RECIRCULATION LINE	OFF GAS FROM VENTURI	CONDENSED COOLING WATER FLOW	VENTURI TANK OVERFLOW	VENTURI CONDENSATE DRAIN	CONDENSATE DRAIN	OFF GAS FROM CONDENSER	PACKED TOWER AND CIRCULATING SOLUTION	OFF GAS FROM PACKED TOWER	TO BLOWER
STREAM NO:	1	2	3	4	5	6	7	8	9	10	11
PARAMETER:											
TEMP°C	200	20	25	15	25	30	18°C	20°C	20°C	25°C	
PRESSURE	-5" H ₂ O	60 psig	-1" H ₂ O	80 psig				-2" H ₂ O	5 psig	-3" H ₂ O	-75" H ₂ O
FLOW RATE:											
GASES ^(a) SLM	1,000		1,000					1,000		1,000	1,000
WATER(L) kg/hr		5,000	TRACE	0-2,000	48	5,000	TRACE		1,100	TRACE	TRACE
WATER(V) kg/hr	48		TRACE							TRACE	TRACE
SOLIDS kg/hr	0.06	8.1	0.01		0.068	8.1	TRACE	0.01		<0.01	<0.0001 ^(b)
									NO STEADY STATE		

^(a) INCLUDES INLEAKAGE
^(b) ESTIMATED

GAS COMPOSITION

N ₂	77%
O ₂	18%
CO ₂	3%
CO	0.5%
NO _x	TRACE
SO ₂	2 ppm
H ₂	0.5%

FIGURE 8. Off-Gas Treatment System, Liquid-Fed Ceramic Melters

addition, grab samples may be taken and analyzed for Ar, SO₂, H₂, He and CH₄. Liquid grab samples can be analyzed for elements and anions (F⁻, Cl⁻, NO₃⁻ and SO₃⁼).

TABLE 2. Off-Gas System Details

Ejector Venturi Scrubber

Type: Schutte & Koerting, 316 stainless steel (SS)

Size: 6" inlet

Capacity: 500 acfm steam (equivalent feed rate is ~300 L/h)
50 acfm NO₂ at 400°C and 25" H₂O vacuum

Scrub Solution: 20 gpm H₂O at 95°F and 60 psig and provides a 5" H₂O draft

Condenser

Type: Shell and tube heat exchanger, floating head, 304L SS single pass tube-side process

Size: 12-1/2" shell OD, 6'3" tube length, 152.7 ft² surface area

Cooling Water: 85°F and 60 psig.

Packed Tower

Type: 304L SS with 1" cooling coil (12 ft² surface area)

Size: 14" Sch.10 by 11'9"

Bed: 8.6' of 1" x 1" x 1/32" Raschig rings

HEPA Filter

Type: Adjustable heated inlet

Size: 12" x 12" x 5-7/8" filter

Capacity: 185 ft³/min at 1" H₂O pressure drop

Blower

Type: Spencer multistage centrifugal turbo compressor, 4-bearing outboard type, load bleed control valve to prevent surging

Capacity: 320 scfm at 80" H₂O vacuum.

The system was operated without the condenser for most of the year. The condenser was not necessary for liquid-fed melter runs. Flow rates were low, and the ejector venturi could effectively condense all of the steam in the off gas.

Vacuum in the melter is automatically controlled by adjusting a plug valve upstream of the blower.

The off-gas system is adequate for developmental tests on liquid-fed melters; but the system is not specifically designed with respect to this process; hence, construction materials and particulate scrubbing efficiency can be improved. The system is constructed of 304L and 316 SS, which showed significant corrosion in the presence of Cl^- and acids. The condensate from the melter off gas has a pH of about 3 and Cl^- concentrations >1000 ppm. The corrosion rate has been slowed by neutralizing the off-gas condensate.

The overall scrubbing efficiency of the off-gas system has been compromised by the corrosion. A stainless steel demister pad in the packed tower corroded severely, allowing entrained water droplets to pass. The water droplets prevented continuous use of the HEPA filter, thus lowering the system particulate removal efficiency. No device for effectively removing submicron particulate was used after the HEPA filter was valved out of the system. The system particulate DF was estimated at $<10^3$ without the HEPA filter. For an actual radioactive facility, DFs would have to be much higher.

2.7 SIMULATED WASTE COMPOSITIONS

Significant changes in the waste compositions were made during this fiscal year's testing program. The waste composition tested in FY-1980 was designated TDS Frit-211.⁽⁴⁾ In FY-1981, a different frit composition (Frit-131) was first used during the test designated PSCM-1; also, the waste composition was modified. The resultant waste glass is referred to as TDSM Frit-131. The significant changes in the new waste flowsheet were the elimination of cornstarch and $\text{Na}_4\text{-EDTA}$, and reduced levels of anthracite coal and Na_2SO_4 . The composition is shown in Table 3.

The next major feed change was initiated for run PSCM-3. The defined waste was assumed to have undergone treatment with formic acid for mercury removal. In this step, many of the major components are converted to formates. The resultant pH is ~ 5.5 to 6.5 . Anthracite coal was also eliminated from this flowsheet. The composition of the formic-acid-treated waste with Frit-131 is shown in Table 4 and is designated TDSF Frit-131. The feed composition change from the alkaline waste to the formate waste improved the rheological characteristics of the waste slurry and generally improved the feed system performance.

TABLE 3. Simulated Waste Slurry and Glass Compositions
of TDSM Frit-131

Waste Slurry (2090 L)			Assumed Oxide Forms in Waste Glass					Final Glass Comp. (Wt%)
Feed Compounds	Wt. (kg)	Conc. (g/L)	Assumed Oxide	TDSM Waste	Frit- 131	Zeolite	Total	
Frit-131 ^(a)	706.8	338.0	See (a)	--	(a)			
Zeolite ^(b)	30.8	14.7	See (b)	--		(b)		
Anthracite Coal	6.9	3.30	CO ₂	--				
Fe(OH) ₃	189.9	90.9	Fe ₂ O ₃	141.9			141.9	14.2
Al(OH) ₃	43.8	21.0	Al ₂ O ₃	28.6		5.9	34.5	3.5
MnO ₂	40.7	19.5	MnO ₂	40.7			40.7	4.1
Ni(OH) ₂ (NiO·2H ₂ O)	21.7 (25.9)	10.4 (12.4)	NiO	17.5			17.5	1.7
CaCO ₃	18.6	8.90	CaO	10.4		3.3	13.7	1.4
SiO ₂	12.2	5.84	SiO ₂	12.2	409.2	14.7	436.1	43.9
NaOH	10.3	4.93	Na ₂ O	8.0	125.1	0.8	135.4	13.6
NaNO ₃	4.2	2.01		1.5				
Na ₂ SO ₄	1.5	0.73	Na ₂ SO ₄	1.5			1.5	0.2
			B ₂ O ₃	--	103.9		103.9	10.4
			Li ₂ O	--	40.3		40.3	4.0
(pH 10 - 11)			MgO	--	14.1		14.1	1.4
(Density ~1.35)			TiO ₂	--	7.1		7.1	0.7
			La ₂ O ₃	--	3.5		3.5	0.4
			ZrO ₂		3.5		3.5	0.4
TOTAL	1091.6	522.2 ^(c)		262.3	706.7	24.7	993.7	100.0

(a) Frit-131 Composition (-200 mesh)

Oxide	Wt%	(Frit-211) ^(d)
SiO ₂	57.9	(58.3)
B ₂ O ₃	14.7	(11.1)
Na ₂ O	17.7	(20.6)
Li ₂ O	5.7	(4.4)
MgO	2.0	--
TiO ₂	1.0	--
La ₂ O ₃	0.5	--
ZrO ₂	1.0	--
CaO	--	(5.6)

(b) Zeolite Composition
(Linde Ionsiv IE-95®)

Component	Wt%
CaAl ₂ Si ₄ O ₁₂ ·6H ₂ O	80
Na ₄ Ca _{1.5} Al ₃ Si ₈ O ₂₄ ·8H ₂ O	20
	100

(c) Equiv. glass oxide content = 475.5 g/L.

(d) For comparison.

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TABLE 4. Simulated Waste Slurry and Glass Compositions
of TDSF Frit-131

Waste Slurry (2090 L)			Assumed Oxide Forms in Waste Glass					Final Glass Comp. (Wt%)
Feed Compounds	Wt (kg)	Conc. (g/L)	Assumed Oxide	TDSF Waste	Frit- 131	Zeolite	Total	
Frit-131 ^(a)	713.4	341.3	See (a)		(a)			
Zeolite ^(b)	20.7	9.9	See (b)			(b)		
Fe(OH) ₃	169.8	81.2	Fe ₂ O ₃	126.9			126.9	12.7
Al(OH) ₃	71.4	34.2	Al ₂ O ₃	46.7		4.0	50.7	5.1
Mn(CHO ₂) ₂ (MnCO ₃)	58.9 (46.7)	28.2	MnO ₂	28.8			28.8	2.9
Ni(CHO ₂) ₂ (NiCO ₃)	17.3 (13.5)	8.3	NiO	8.5			8.5	0.8
Ca(CHO ₂) ₂ (CaCO ₃)	35.0 (26.9)	16.7	CaO	15.1		2.2	17.3	1.7
SiO ₂	32.6	15.6	SiO ₂	32.6	413.0	9.9	455.5	45.6
NaCHO ₂ (Na ₂ CO ₃)	17.6 (13.7)	8.42	Na ₂ O	8.0 1.5	126.3	0.5	136.3	13.6
NaNO ₃	4.2	2.01						
Na ₂ SO ₄	1.5	0.72	Na ₂ SO ₄	1.5			1.5	0.1
			B ₂ O ₃	--	104.9		104.9	10.5
			Li ₂ O	--	40.6		40.6	4.1
(pH 5-7 with HCHO ₂)			MgO	--	14.3		14.3	1.4
(ρ = 1.34)			TiO ₂	--	7.1		7.1	0.7
			La ₂ O ₃	--	3.6		3.6	0.4
			ZrO ₂	--	3.6		3.6	0.4
TOTAL	1142.4	546.6 ^(c)		269.6	713.4	16.6	999.6 ^(c)	100.0

(a) Frit-131 Composition (-200 mesh)

Oxide	Wt.%
SiO ₂	57.9
B ₂ O ₃	14.7
Na ₂ O	17.7
Li ₂ O	5.7
MgO	2.0
TiO ₂	1.0
La ₂ O ₃	0.5
ZrO ₂	0.5
	100.0

(b) Zeolite Composition
(Linde Ionsiv IE-95®)

Component	Wt.%
CaAl ₂ Si ₄ O ₁₂ ·6H ₂ O	80
Na ₄ Ca _{1.5} Al ₃ Si ₈ O ₂₄ ·8H ₂ O	20
	100
Assumed Oxide Forms	Wt.%
CaO	10.6
Al ₂ O ₃	19.2
SiO ₂	47.7
Na ₂ O	2.5
H ₂ O	20.0
	100.0

(c) Feed slurry glass content = 0.4783 kg/L

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The simulated waste slurry is routinely spiked with semivolatile or key radioactive analogs for effluent studies. Typical concentrations are shown in Table 5.

TABLE 5. Concentrations of Trace Elements in Simulated Feed Slurry

<u>Trace Additives</u>	<u>Concentration, g/L</u>	
	<u>Oxides</u>	<u>Elemental</u>
Cs ₂ O	0.25	0.24
SrO	0.098	0.083
Sb ₂ O ₃	0.16	0.060
SeO ₂	0.04	0.029
CdO	0.38	0.033
TeO ₂	0.05	0.036
RuO ₂	0.085	0.064

3.0 MELTER PERFORMANCE

A summary of all melter experiments conducted in FY-81 is shown in Table 6. Six major experiments were conducted as well as several short-term scoping tests. Capacities exceeding the design basis reference of $\sim 39 \text{ kg/h-m}^2$ were achieved when lid heating was used. Tests without lid heat were not able to consistently achieve the design base rate.

The melter capacity, expressed as the slurry rate in L/h-m^2 , as well as glass melting rate in kg/h-m^2 , was plotted as a function of the off-gas particulate DFs^(a) for total mass entering the system for each of the major experiments. This data is shown in Figure 9. It does not appear to be particularly important whether feed slurry or glass rate is plotted, as the solids loading of the feed is generally in the same range for all experiments. Higher-capacity runs on the LFCM, which were achieved by boosting, all resulted in lower DFs than lower-capacity unboosted runs performed on the PSCM. However, the operation of the propane torch on PSCM-2 produced unusual convective disturbances within the plenum, resulting in lower DFs. Further off-gas data for the major experiments are summarized in Tables 7 and 8.

(a) Mass in $\div$ mass out.

TABLE 6. Summary of FY-81 Melter Tests

Run/Month	Slurry, L	Glass, kg	Hours	Slurry Rate, L/h-m ²	Glass Melt Rate kg/h-m ²	Comments
LFCM-3 Nov.	1240	397	22	53.7	17.2	Dilute TDS-211 feed, (320 g oxide/L), no lid heat, dilute feed max rate 63.7 L/h-m ²
PSCM-1 Dec.	4657	2020	169	46.6	22	TDSM-131 feed, first test on modi- fied PSCM melter
LFCM-4 Jan.	8036	3778	113	66.6	41.1	TDSM-131 feed, lid heaters, max. rate 47 kg/h-m ²
LFCM-5 Feb.	1964	982	20	92.6	46.2	high-capacity run
PSCM-2(a) Mar.	6630	2988	96	110	46	combustion boosting, 55 kg/h-m ² with melter at 1180°C
LFCM-6"A" (Pretest) May	1909	674	16	113	40.1	prerun shakedown of equipment using dilute feed
LFCM-6 June	9194	4399	117	82.6	39.5	plasma torch and lid heat boosting, rates to 51.6 kg/h-m ²
PSCM-3 July	5400	2500	124	60	27.9 Avg.	first run on formate feed, very quiet, no boosting, max. liquid rate 72 L/h-m ²
LFCM-7 Aug.	9750	4480	111	121	55.6	high inleakage, lid heat boosting, rates from 44.5 + 61.3 kg/h-m ²
ECM	70	--	13	--	--	small-scale tests
LSSC/ICM (12 Tests)	220	56	63	--	--	small-scale tests
TOTALS	49070	22274	864			

(a) Data combined from two operating periods.

FIGURE 9. Melter Capacity Plotted as a Function of Decontamination Factors

TABLE 7. Off-Gas Data Relevant to Melter Runs

DATE: RUN NO: Parameter	11/06/80 LFCM-3	01/18/81 LFCM-4	02/03/81 LFCM-5	05/05/81 LFCM-6A	06/01/81 LFCM-6	08/20/81 LFCM-7	01/13/80 PSCM-1	03/24/81 PSCM-2	07/19/81 PSCM-3
Operation Plenum Temp, °C	350	600	N/A	630-685	600	500	400	400-800	250
Off-Gas Operating Temp, °C	300-350	375	375	360-380	300	302	375	375	210
Feed Rate, L/h-m ² (a)	54	87	50	113	100	130	44	110	62
Off-Gas Velocity, ft/min	N/A	1250	N/A	N/A	1500	1800	480 ^(b)	2400 ^(b)	920
Decontamination Factors	500	300	N/A	N/A	180	50-140	1200	400	980
Lid Boosting Power	0	30	33	~45	45	17	0	40 ^(c)	0
Days Idling Before Run	38	73	30	--	97	79	12	92	116
Days of Operation	1	5	1	2/3	5	5	7	5	5
Cold Cap, %	50-90	90	90+	--	90+	90+	50	90	90+
Plenum Temperature, Idling, °C	1000	1000	1000	--	1000	1000	1000	1000	1000
Off-Gas Cooling Nozzle	No	Yes	Yes	Yes	Yes	Yes	No	Yes	No
Average Flow, scfm	50	90	N/A	--	185	240	25 ^(b)	70 ^(b)	70
Surge, scfm ±	N/A	220 ±80	N/A	--	185	710	N/A	N/A	220
Max. Peak, scfm/ Duration, minutes	--	620/2.3	N/A	--	~465	710	N/A	N/A	~440
scfm Inleakage	24	N/A	N/A	--	--	50-100	N/A	N/A	<20
Melting Rate, kg/h-m ²	20.5	41	N/A	--	45	37 w/o LH(d) 53 w LH	22	46-55	33
Melter Surface Area	1.05	1.05	1.05	1.05	1.05	1.05	0.73	0.73	0.73

(a) Corresponds to rate taken during the sampling period, not necessarily the overall average.

(b) No inleakage considered.

(c) Propane boosting heat.

(d) LH: Lid Heating.

NA: Not Available

TABLE 8. Off-Gas Decontamination Factors

Run No.: Component	PSCM-1	PSCM-2	PSCM-3	LFCM-3	LFCM-4	LFCM-6	LFCM-7(a)	Average
Cs ₂ O	51	3	3.8	7	57	10	12	20.2 ±23.3
SrO	7400	640	640	1500	204	290	55	1531 ±2631
Sb ₂ O ₃	--	100	--	--	1800	>80	67	508 ±861
SeO ₂	--	--	--	--	--	--	<1	--
CdO	190	47	--	84	70	80	8.0	79.7 ±61
TeO ₂	170	68	32	270	62	210	5.6	115.3 ±100.9
RuO ₂	32	48	--	60	26	13	16	35.8 ±18.5
Cl ⁻	3.1	3	4	9	2.2	2.5	--	4.0 ±2.5
SO ₄ ⁼	--	19	8	5	--	11	--	10.8 ±6.0
Total Particulate	1140	430	980	480	290	170	71	512 ±400

(a) Feed for this run was treatment with formic acid pH = 6-7.

4.0 INDIVIDUAL RUN SUMMARIES (FY-1981)

Descriptions of the individual runs performed during the year are described in this section. Detailed operating data as well as run objectives are discussed. Summary tables of the runs were presented in Section 3.0.

4.1 RUN 1 - LFCM-3 (NOVEMBER 1980)

The first run of the year was a short, 22-h liquid-feeding test designed to compare operation of the LFCM without plenum heaters to a previous run performed in September 1980 (Bjorklund 1981) in which plenum heaters were used.

The feed slurry for this test was not as concentrated as in the previous test, because during the five weeks that the feed was left agitating in a chemical makeup tank, it became thick and gel-like. This, apparently, was caused by the slow dissolution of the glass-forming frit. The gel-like feed slurry made it necessary to dilute the slurry so it could be pumped by the feed system. The resulting equivalent oxide concentration of the feed was 320 g/L, as opposed to the normal ~500 g/L.

During the test, 1240 L were fed at an average rate of 53.7 L/h-m². Glass production at this rate was only 17.2 kg/h-m² because of the dilute feed. The feed rate for the first 17-1/2 h was 53.6 L/h (17.1 kg/h-m²) and was 66.9 L/h (24 kg/h-m²) for the last 4-1/2 h.

During this test, the cold cap appeared to form in an area ~0.7-m dia below the feed nozzle. The dried edge of the cap occasionally broke away and floated towards the walls, where it slowly melted. It appeared that the entire melt surface was covered with a cold cap containing numerous cracks; however, the actual liquid pool covered <50% of the melter surface. Heat transfer from the molten glass surface to the plenum was severely reduced with this type of cold cap. The off-gas temperature during the run remained between 300 and 350°C. Considerably more hair-like cobwebs were also formed in the plenum area than in the previous lid-heating run. No reboil or foaming was detected, and the overall melter test performance was very good.

4.1.1 Off-Gas Analysis

The off-gas analytical results obtained during the LFCM-3 test are summarized in Tables 9 and 10. Table 9 presents the melter DFs associated with LFCM-3 feed components. Also included in this table are DFs associated with the volatile elements chlorine and sulfur, which were collected as anions through gas scrubbing techniques.

TABLE 9. LFCM-3 Decontamination Factors

<u>Element</u>	<u>Average DF</u>
Al ₂ O ₃	2400
B ₂ O ₃	121
CaO	1850
CdO	84
Cs ₂ O	7
Fe ₂ O ₃	690
LiO	660
MgO	1800
MnO ₂	3100
Na ₂ O	280
NiO	430
RuO ₂	60
Sb ₂ O ₃	--
SiO ₂	2600
SrO	1500
TeO ₂	270
TiO ₂	--
SeO ₂	--
<u>TOTAL OXIDE</u>	<u>480</u>
Cl ⁻	9
SO ₄ ⁼	5

TABLE 10. LFCM-3 Noncondensable Off-Gas Compositions (Vol%)

<u>Gas</u>	<u>Sample 1</u>	<u>Sample 2</u>
Ar	1.20	1.14
CO ₂	0.14	0.16
CO	1.4	1.2
O ₂	0.01	5.02
N ₂	97.1	92.4
H ₂	0.09	0.05
NO _x	<0.01	<0.01
SO _x	<0.01	<0.01

The compositions of noncondensable gases within the melter plenum were analyzed using mass spectrometry. The results obtained from these analyses are summarized in Table 10. These very perplexing results suggest that inleakage oxygen is being almost entirely converted to nonvolatile oxides within the melter plenum. The mechanism responsible for this oxygen consumption is not understood. However, the very low O₂ concentrations in the analytical off-gas samples cannot be accounted for by assuming chemical conversion to CO, which was then mistakenly combined with the nitrogen response during mass analysis. The electron bombardment ion source of the mass spectrometer employed in these analyses will produce significant mass responses at both 12 and 16, in addition to 28, if CO concentrations are present at concentrations >1%. It is inconceivable to personnel operating the mass spectrometer laboratory that more than a fraction of a percent of CO could be mistakenly identified as N₂ in this type of analysis. The high, ~10:1, CO to CO₂ ratios exhibited by these samples further suggest low O₂ plenum partial pressures.

A comparison of the particle size of the off gas leaving the melter between this and the previous run showed that particles between 2- and 3- μ m dia comprised the highest percentage of mass when lid heaters were used, and particles between 0.32 μ m and 1 μ m comprised the highest mass percentage without lid heaters.

The average mass loading of the off gas (obtained by use of an aerosol spectrometer) without plenum heating was 7.5×10^{-5} g/scf, as compared to 2.5×10^{-3} g/scf with lid heaters.

4.2 RUN 2 - PSCM-1 (DECEMBER 1980)

This was the first test of the liquid-fed Pilot-Scale Ceramic Melter (PSCM) (formerly called the Calcine-Fed Ceramic Melter, or CFCM). The objectives of the experiment were to conservatively introduce liquid feed into the melter and observe its operating behavior while maintaining the exiting off-gas temperature at $375 \pm 25^\circ\text{C}$. The conservative feeding approach was felt necessary, as this was the first large-scale, liquid-fed test to a melter with one set of top-entering electrodes. The 375°C off-gas temperature limit was based on the possibility that wastes containing mercury would need this high temperature to prohibit condensation of mercury in the melter plenum and to assure volatilization. This was also the first experiment with the modified waste composition type TDSM-131 (See Section 4.7).

The run was very successful, with two canisters (2020 kg) of glass produced. Resistance control of the melter power was utilized as the controlling mechanism and worked very well throughout the run. The glass production rate was slowly brought up to $\sim 16 \text{ kg/h}$ (22 kg/h-m^2) and then held constant. A chronological depiction of key variables is shown in Figure 10. A summary of the run performance is shown in Table 11.

TABLE 11. PSCM-1 Run Summary

<u>Parameter</u>	<u>Characteristic</u>
Aqueous Slurry Feed	Type TDSM-131
Plenum Power Boosting	None
Glass Temperature	$1150 \pm 25^\circ\text{C}$
Off-Gas Temperature Control	$375 \pm 25^\circ\text{C}$
Off-Gas Temperature Control	By Feed Rate
Experiment Duration	169 h
Down Time	12.5%
Melter Surface Area	0.73 m^2
Maximum Feed Rate	34 L/h
Longest Sustained Period	40 h
Oxide Content	0.478 kg/L
Melting Flux	22 kg/h-m^2
Electrode Power	60 kW
Total Glass Produced	2020 kg

FIGURE 10. PSCM-1 Operating Parameters

The "Off-Gas Temperature" plot reflects the poor feed rate control experienced in this run. Its overall appearance matches the steady increase in the feed rate to mid-experiment and to its subsequent stable feed rate indication. The "Off-Gas Temperature" plot also shows the steady effort to bring the off-gas temperature within its run plan constraint of $350 \pm 25^{\circ}\text{C}$ by feed rate control.

Figure 11 shows the correlation of the bulk glass temperature with tank resistance, and Figure 12 shows various glass tank temperature profiles at various resistance values.

4.2.1 Off-Gas Analysis

In preparation for this experiment, all appropriate off-gas-line components were cleaned and preweighed so that the extent of off-gas deposition within the process line could be assessed after completion of the run. However, very little deposition was, in fact, found. The total deposition mass which was scraped from these components amounted to 68 g. The results are summarized in Table 12. Idling deposits were also collected from these same process line components 2 months after completion of PSCM-1. These deposits were found to be highly enriched with the semivolatile elements cesium, ruthenium and tellurium, and the anion $\text{SO}_4^{=}$. For comparative purposes, these results are included in Table 12.

FIGURE 11. PSCM Melter Tank Electrical Resistance Versus Average Glass Temperature (TDSM-131)

FIGURE 12. PSCM Glass Temperature Profiles at Various Resistance Values (TDSM-131)

TABLE 12. PSCM-1 Process Line Deposits (Wt%)

Element	PSCM-1	PSCM-1 Idling	Feed
Al ₂ O ₃	--	1.2	3.5
B ₂ O ₃	4.6	14.2	9.9
CaO	--	0.22	1.2
CdO	--	0.02	0.01
Cr ₂ O ₃	--	0.57	0.02
Cs ₂ O	0.80	3.7	0.06
Fe ₂ O ₃	10.0	0.10	16.0
LiO ₂	--	1.92	4.1
MgO	--	<0.05	1.4
MnO ₂	--	0.05	3.8
Na ₂ O	20.0	31.0	15.5
NiO	--	0.25	1.5
RuO ₂	--	0.82	0.02
Sb ₂ O ₃	--	<0.01	0.008
SiO ₂	--	<0.02	44.0
SrO	--	<0.005	0.02
TeO ₂	--	0.70	0.01
TiO	--	<0.01	0.70
ZnO	--	0.02	0.008
ZrO ₂	--	--	--
Cl ⁻	--	0.5	--
SO ₄ ⁼	--	62.0	--
F ⁻	--	0.02	--

The feed component DFs achieved with PSCM-1 are summarized in Table 13. Again, these values are compared to those obtained from the previous melter run, LFCM-3. Clearly, much less volatilization and entrainment occurred during PSCM-1 than in the two previous experiments discussed in this report.

TABLE 13. PSCM-1 Decontamination Factors (DFs)

<u>Element</u>	<u>PSCM-1 Average DF</u>	<u>DF Ratio of PSCM-1/LFCM-3</u>
Al ₂ O ₃	11000	4.58
B ₂ O ₃	210	1.74
CaO	1840	1.00
CdO	190	2.26
Cs ₂ O	51	7.28
Fe ₂ O ₃	3800	5.51
LiO	1900	2.88
MgO	9000	5.00
MnO ₂	5700	1.84
Na ₂ O	830	2.96
NiO	1500	3.49
RuO ₂	32	0.53
Sb ₂ O ₃	--	--
SiO ₂	15000	5.77
SrO	7400	4.93
TeO ₂	170	0.63
TiO ₂	--	--
SeO ₂	--	--
TOTAL	1140	2.38
Cl ⁻	3.1	0.34
SO ₄ ⁼	1.0	0.20

Grab samples taken from PSCM-1 plenum were analyzed using a gas mass spectrometer. These results are summarized in Table 14. Aeration of the feed slurry with CO₂ and the oxidation of the coal component of the feed are responsible for the unusually high concentrations of CO₂ in the melter plenum. Oxygen, on the average, appears to be slightly depleted with regard to room air, which is consistent with moderate inleakage rates and feed component oxidation. Although Sample C appears to be enriched in oxygen (relative to nitrogen), no observable frothing or reboil was observed to have occurred during that or any other sampling period. The mechanism responsible for total depletion of oxygen in Sample B is unknown.

TABLE 14. Noncondensable Off-Gas Results of PSCM-1 (Vol%)

<u>Sample</u>	<u>CO₂</u>	<u>Ar</u>	<u>O₂</u>	<u>N₂</u>	<u>CO</u>	<u>H₂</u>
A	2.86	1.06	7.11	88.9	<0.01	0.08
B	0.92	1.16	<0.01	96.9	<0.01	1.06
C	6.35	0.88	19.8	73.0	<0.01	<0.01
D	1.81	0.96	17.0	80.1	<0.01	0.03
E	4.54	0.95	14.9	79.6	<0.01	<0.01
F	1.50	1.03	11.8	85.6	<0.01	<0.01

4.3 RUN 3 - LFCM-4 (JANUARY 1981)

This melter experiment on the LFCM was an attempt to establish a high-capacity rate with the new TDSM-131 feed while using lid heaters for boosting. Another objective was to evaluate the effectiveness of cooling the exiting off gas with a water spray nozzle to minimize particulate deposition in the off-gas piping.

The off-gas system was equipped with a water spray nozzle inserted in the line leaving the melter, as shown in Figure 13. The water atomizing nozzle was designed to produce a fine mist by hydraulic pressure alone. The nozzle was operated to cool the off gases to $375 \pm 25^\circ\text{C}$, as measured by a thermocouple in the center of the stream ~1 m downstream of the cooling nozzle. At a slurry feed rate of 100 L/h, ~19 L/h of water was required to cool the off gases with this nozzle.

Glass production rates in excess of the design basis of 39.1 kg/h-m^2 were successfully demonstrated during the run. The average rate during one 35.7-h period of stable operation was 41.1 kg/h-m^2 .

The high melting rates for this test are attributed to the lid heater boosting. The primary drawback with the lid heaters has been the greater buildup of particulates in the off-gas line when lid heating is utilized. The use of the water spray to cool the off gas during this test drastically reduced the buildup of fused deposits; however, overall entrainment still remained unacceptably high. The first 3 m of off-gas piping were inspected for solids, and ~560 g were obtained.

FIGURE 13. LFCM-4 Off-Gas Piping

The total elapsed time for this run was 113.3 h, with 99.1 h of actual melter feeding. The downtime was caused by feed blockages in the flowmeter and pump. During the test, 3778 kg of glass were produced for an overall average of 31.8 kg/h-m², or an average feed rate of 70 L/h. Table 15 shows a summary of the run.

TABLE 15. LFCM-4 Run Summary

Parameter	Characteristic
Run Time (Elapsed)	113.3 h
Actual Melter Feeding Time	99.1 h
Total Glass Produced	3778 kg
Total Feed Slurry Used (based on mass flowmeter totals @ 1.3 sp gr)	8036 L
Average Glass Production Rate	31.8 kg/h-m ²
Maximum Sustained Glass Production Rates	49.3 kg/h (47.0 kg/h-m ²) for 7 h 43.2 kg/h (41.1 kg/h-m ²) for 35.7 h
<u>Typical Melter Operating Parameters @ 43 kg/h</u>	
Electrode Power	117 kW
Lid Heater Power	30 kW
Lid Liner Wall Temperature	810°C
Average Glass Temperature	1150°C
Off-Gas Cooling Water Spray Flow Rate	7.5 L/h
Off-Gas Temperature (After Water Cooling spray)	375°C

Operating parameters for this test are plotted in Figures 14 and 15. Each of these figures contains a plot of the average feed rate for reference. The average feed rate was obtained from flowmeter totalizer readings taken approximately every 2 h. Brief feed outages (caused by feed blockages in the flowmeter) do not show up on this plot; they appear as a reduction of the average feed rate during the 2-h period.

Figure 14 indicates power and resistance readings for both the primary and secondary electrodes. The primary electrode is controlled by a constant power setpoint, whereas the secondary electrode is controlled by constant electrical current.

FIGURE 14. LFCM-4 Operating Parameters

Figure 15 compares the average glass temperature with the average feed rate and total electrode power. The average glass temperature is the average of temperatures indicated by thermocouples 6.4, 12.7, 19.0, 25.4 and 31.8 cm above the melter floor. These temperatures were normally within $\pm 10^{\circ}\text{C}$ of the average temperature. The average glass temperature was maintained fairly well within the desired temperature limits of $1150 \pm 25^{\circ}\text{C}$.

The total lid heater power, average lid wall temperature, and melter off-gas temperature are also plotted in Figure 15. The average lid wall temperature is the average temperature of three different locations. The melter off-gas temperature shown is measured downstream of the cooling water spray used to cool the off gases to $375 \pm 25^{\circ}\text{C}$. Fluctuations in these temperatures indicate the relative size of the melt surface cold cap. Bridging of the cold cap was not a problem during this test, although at higher feed rates a conical-shaped feed pile (stabilized by a thermowell for measuring glass temperatures) would build up and then collapse. Occasionally, the collapse of this feed pile would release sufficient steam to cause the emergency off-gas

bypass vent to open. This occurs when the gas generation rate exceeds the off-gas system capacity, and the melter vacuum drops to 0 mm Hg. The magnitude of gas release required to pressurize the melter depends upon the degree of off-gas filter loading and the extent of off-gas line plugging from entrained solids deposits.

FIGURE 15. LFCM-4 Operating Parameters (Power, Temperature Feed Rate)

4.3.1 Off-Gas Analysis

The particulate off-gas-line deposition rate occurring during this run was found to be greater than in the previous PSCM-1 experiment. The total quantity of material deposited was only 560 g (~1 lb), which is a vast improvement over the 5.9-kg (13-lb) deposit formed during LFCM-2. The compositions of the material collected from these pipe components are summarized in Table 16, where they are also compared with previously-obtained process line deposition data. It is clear, from this table, that all melter-generated pipe deposits investigated to date possess more or less comparable compositions.

TABLE 16. LFCM-4 Pipe Deposition Composition (Wt%)

<u>Element</u>	<u>LFCM-4</u>	<u>PSCM-1</u>	<u>LFCM-2</u>	<u>Feed</u>
Al ₂ O ₃	2.0	--	1.7	3.5
B ₂ O ₃	5.6	4.6	4.6	9.9
CaO	6.5	--	4.4	1.2
CdO	0.08	--	--	0.01
Cs ₂ O	0.31	0.80	0.26	0.06
Cr ₂ O ₃	0.31	--	--	0.02
Fe ₂ O ₃	14.0	10.0	20.0	16.0
LiO	3.4	--	2.0	4.1
MgO	2.5	--	0.22	1.4
MnO ₂	3.4	--	1.2	3.8
Na ₂ O	15.0	20.0	17.0	16.0
NiO	--	--	2.5	1.5
RuO ₂	0.16	--	0.3	0.02
Sb ₂ O ₃	--	--	--	0.003
SiO	31.0	--	31.0	44.0
SrO	0.05	--	0.04	0.02
TeO ₂	0.11	--	0.07	0.01
TiO	0.11	--	0.07	0.70
ZrO ₂	0.29	--	--	--

Total feed component DFs obtained for the LFCM-4 test are summarized in Table 17. These values are also compared with DF results obtained from all previous experiments described in this report. Although overall volatilization and entrainment are higher for LFCM-4 relative to all previous runs, the emissions of several semivolatiles are lower in LFCM-4 than they were in the two previous LFCM tests.

TABLE 17. LFCM-4 Decontamination Factors (DFs)

Element	LFCM-4 Average DF	DF Ratio		
		$\frac{\text{LFCM-4}}{\text{LFCM-2}}$	$\frac{\text{LFCM-4}}{\text{LFCM-3}}$	$\frac{\text{LFCM-4}}{\text{PFCM-1}}$
Al ₂ O ₃	530	0.35	0.22	0.05
B ₂ O ₃	130	0.5	1.07	0.62
CaO	260	0.35	0.14	0.14
CdO	70	<0.20	0.83	0.37
Cs ₂ O	57	1.42	8.14	1.12
Fe ₂ O ₃	260	0.62	0.38	0.07
LiO	310	0.34	0.47	0.16
MgO	350	0.73	0.19	0.04
MnO ₂	420	0.26	0.14	0.07
Na ₂ O	340	1.00	1.21	0.41
NiO	260	0.60	0.60	0.17
RuO ₂	26	3.7	0.43	0.81
Sb ₂ O ₃	1800	<3.8	--	--
SiO ₂	420	0.45	0.16	0.03
SrO	204	0.54	0.14	0.03
TeO ₂	62	1.01	0.23	0.36
TiO	--	--	--	--
SeO ₂	--	--	--	--
TOTAL	290	0.52	0.60	0.25
Cl ⁻	2.2	0.13	0.24	0.71
SO ₄ ⁼	1.0	0.05	0.20	1.0

Particulate entrainment occurring during LFCM-4 was characterized by HEPA filtration. The particulate DFs listed in Table 18 were calculated using both HEPA and off-gas-line deposition data. The elemental (oxide) composition of HEPA-trapped particulates is also listed in this table along with the feed makeup composition. Clearly, the HEPA-trapped material cannot be explained compositionally on the basis of a simple feed entrainment model.

TABLE 18. LFCM-4 Particulate Data

Element	DF	HEPA (Wt%)	Feed (Wt%)
Al ₂ O ₃	1583	1.44	3.5
B ₂ O ₃	1250	5.34	10.0
CaO	620	1.34	1.2
CdO	225	0.04	0.01
Cr ₂ O ₃	--	0.23	0.02
Cs ₂ O	100	0.70	0.06
Fe ₂ O ₃	660	15.1	16.0
LiO	840	3.21	4.1
MgO	895	0.87	1.4
MnO ₂	1100	2.64	3.8
Na ₂ O	605	19.0	15.5
NiO	--	--	1.5
RuO ₂	25	0.64	0.02
Sb ₂ O ₃	--	--	0.008
SiO ₂	1100	26.4	44.0
SrO	595	0.20	0.02
TeO ₂	129	0.18	0.01
TiO ₂	--	0.49	0.70
SeO ₂	--	--	0.008
ZnO	--	0.06	0.008
ZrO ₂	--	0.22	--
TOTAL	600	78	100

A summary of the gas chromatographic analysis of the LFCM-4 plenum gas composition appears in Table 19. Due to the large melter inleakage rates, the oxygen-nitrogen ratios of the plenum gas samples were found to be completely indistinguishable from room air throughout the duration of the melter run. As in PSCM-1, aeration of the feed slurry with CO₂ and the oxidation of coal present in the feed are responsible for the high concentrations of CO₂ in the melter plenum.

TABLE 19. LFCM-4 Noncondensable Off-Gas Composition

Date	Percent			
	CO ₂	O ₂ ^(a)	N ₂	CO
01/20/81	1.1	21.2	77.7	<10 ppm
01/20/81	0.3	21.5	78.2	<10 ppm
01/21/81	0.5	21.8	77.7	<10 ppm
01/22/81	0.9	21.2	77.9	<10 ppm
01/22/81	0.7	21.6	77.7	320 ppm
01/22/81	0.3	21.4	78.3	250 ppm
01/23/81	0.4	21.6	78.0	>100 ppm
01/23/81	0.6	21.0	78.4	570 ppm
01/23/81	0.4	21.7	77.9	310 ppm

(a) Includes ~1% Ar.

Gas-scrubbing techniques were utilized for investigating the nature of idling emissions associated with LFCM-4. Sampling was initiated seven days after the completion of LFCM-4, and again after 14 days. This data appears in Table 20, along with the final makeup composition of the LFCM-4 glass. The data in this table support the intuitive notion that the semivolatile elements and compounds present in the molten glass matrix are escaping at rates which are proportional to their concentrations and their volatilities.

The off-gas flow rate behavior of liquid-fed melters was first examined during the LFCM-4 experiment. What was observed was a noisy, erratic flow rate, replete with surges mixed with periods of relative calm. Portions of the strip-chart record generated by the flow transducer during this experiment are illustrated in Figure 16. The conditions illustrated in this figure represent extremes within which the melter operations were maintained. A statistical analysis of the surging behavior (magnitude and duration) was conducted during an active ~8-h period of continuous melter operation. These results are summarized in Table 21. The uncertainties listed with the averages represent 1- standard deviation of the data examined and, consequently, are measures of the spread or dispersion of this data (i.e., 68% of all data examined statistically lie within 1- standard deviation of the average).

FIGURE 16. LFCM-4 Off-Gas Flow Characteristics

TABLE 20. LFCM-4 Idling Emissions (Wt%)

Element	1 Week	2 Weeks	Glass
Al	0.06	--	3.2
B	10.2	2.2	5.6
Ca	0.33	0.01	1.5
Cd	0.17	--	0.036
Cr	1.7	0.23	--
Cs	6.7	1.6	0.06
Fe	8.3	0.20	20.0
K	1.5	--	--
Li	2.8	0.78	3.2
Mg	--	--	1.5
Mn	0.12	0.002	5.2
Na	61.7	18.7	20.0
Ni	0.82	0.04	2.2
Ru	0.11	0.02	0.006
Sb	--	--	0.03
Si	2.9	1.0	37.0
Sr	--	--	0.04
Te	1.0	0.13	0.07
Ti	0.03	--	--
Zr	0.02	--	--
Se	--	--	--
Cl ⁻	1.07	71.0	0.19
SO ₄ ⁼	0.64	4.2	--

TABLE 21. LFCM-4 Flow Surging Characteristics^(a)

Steady-State Flow (ft ³ /min)	Average ^(b) Surge Flow (ft ³ /min)	Average Surge Duration (min)
90	220 + 80	2 ± 1

(a) Study conducted over an 8-h period on 01/22/81.

(b) Total average flow (steady-state plus spike) is listed.

During the LFCM-4 experiment, a significant number of off-gas surges exceeded the full-scale range of the flow transducer employed. These events were reexamined in order to extract information regarding their frequency, duration and extrapolated flows (triangular approximation). This data appears in Table 22, where all emergency venting occurrences are so designated. It should be noted that conductance-limiting restrictions involving loaded HEPA filters and/or valve throttling of the system exhaust were, in all cases, responsible for the brief melter pressurizations that led to the emergency venting situations. The flows recorded during these melter pressurizations are probably not totally ascribable to the events which triggered the venting occurrence but, rather, are due (in part) to atmosphere flowback into the melter through the venting butterfly valve. This situation results primarily from the slow response time of the venting valve, coupled with an automated melter exhaust system that attempts to maintain a negative plenum pressure even when the melter is opened to the atmosphere.

TABLE 22. Frequency, Duration and Extent of Maximum (overrange) LFCM-4 Surges

<u>Date</u>	<u>Time</u>	<u>Duration (min)</u>	<u>Flow (scfm)</u>	<u>Vent</u>
1/21/81	1328	1.8	450	Yes
	1600	2.4	450	
	1655	3.0	450	Yes
	1845	0.5	450	
1/22/81	1300	1.0	470	
	1345	1.5	520	
	1440	1.5	570	Yes
	1505	1.0	500	
	1515	3.2	450	
	1700	3.2	450	
	1815	3.2	450	
	1820	2.7	580	
	1948	3.2	590	Yes
	2040	2.3	620	Yes
1/23/81			None	

4.4 RUN 4 - LFCM-5 (FEBRUARY 1981)

The purpose of this short test was to run at high rates for ~24 h to demonstrate a higher capacity than achieved during LFCM-4, which had several

feed interruptions. Rates averaging 46.2 kg/h-m^2 were maintained for this test. Operating conditions are summarized in Table 23.

Figure 17 is a plot of the glass temperatures at various distances from the melter floor. Note that the glass temperatures at the 6.4-, 19.0-, 26.7-, 31.8- and 38.1-cm levels are very similar, while the 0 level (on the melter floor) is $\sim 100^\circ\text{C}$ cooler than the other temperatures. Due to the short term of the tests, no off-gas data were collected during LFCM-5.

TABLE 23. LFCM-5 Operating Summary

<u>Parameter</u>	<u>Characteristic</u>
Run Time (Elapsed)	20 h
Actual Melter Feeding Time	19.3 h
Total Glass Produced	982 kg
Average Glass Production Rate	48.5 kg/h (46.2 kg/h-m^2)
Total Feed Slurry Processed	1964 L
Average Feed Rate	97 L/h
Typical Melter Operating	
<u>Parameters During Test</u>	
Total Electrode Power	120 kW
Total Lid Heater Power	33-34 kW
Average Glass Temperature	$1150 \pm 25^\circ\text{C}$
Off-Gas Cooling Water Spray Flow Rate	4 to 7 L/h
Off-Gas Temperature (After Water Cooling Spray)	$375 \pm 25^\circ\text{C}$

4.5 RUN 5 - PSCM-2 (MARCH 1981)

The second experiment on the PSCM was unique in its use of plenum heating by a combustion source. Because the source was above the melt pool, it provided the heat to boost the capacity of the melter. Although the practicality of using a combustion-heating source in an actual radioactive hot cell may be questionable, the principle of providing a significant amount of heat from above the melter surface was tested. Boosting tests with previous electric plenum heaters were limited in the amount of kW available with existing

FIGURE 17. LFCM-5 Glass Temperatures

equipment and, at the most, represented about an additional 30% of the power being supplied by the electrodes.

For this experiment, propane was combusted in a burner[®] positioned in a viewport nozzle (Figures 18 & 19) and operated within the following constraints:

- The burner used premixed propane and air.
- A proportional mixer maintained a fixed fuel-air ratio over the range 150,000 to 250,000 Btu/h.
- The burner was capable of stable operation over the range of 40 to 70 kW at 9.3 mm Hg vacuum.
- The proportional mixer was adjusted to maintain the CO content of the off gas at 2% $\pm$ 1%.

PSCM-2 was operated for 88-3/4 h. Onstream factor for this test was >99%, and glass throughput was more than four melter tank turnovers. During this period, the slurry feed to the melter was interrupted briefly (average of ~4 min) 11 times for minor preventative maintenance activities.

During the experiment, 6630 L of feed were transferred through the feed tank into the melter, and 2872 kg of glass were discharged to the receiving canisters. With a glass temperature of ~1140°C, melting rates of 46 kg/h-m² were twice sustained (16 and 8 h), while melting rates of 50 kg/h-m² were twice abandoned because of a loss of visible venting activity (both times after 8 h). With a glass temperature of 1180°C, a glass melting rate of 55 kg/h-m² was sustained for 8 h, and it appeared that higher rates were possible. However, higher rates could not be attempted, as the maximum capacity of the melter off-gas system was reached because of particulates in the off-gas line which restricted flow.

The results of the test indicated that combustion boosting is an effective method for increasing the capacity of the melter, but that it was not any more effective than the electric resistance heater technique. The test also showed that operating an LFCM (with a high heat flux) from above the batch would not adversely affect the melter operation. The concern that heat from

[®] Eclipse Unitite Model 208-46-UT.

FIGURE 18. Pilot-Scale Ceramic Melter - Burner Orientation

FIGURE 19. PSCM with Propane Burner

above would melt the cold cap and restrict decomposition gases from escaping, which would cause foaming, was not supported by the test results.

The maximum glass production rate per square meter of melt surface was higher (55 kg/h-m² versus 46.2 kg/h-m²) than the rate demonstrated in the LFCM-5 test with lid heater boosting, due to the higher power input. This rate was still less than anticipated for the power input. The kilograms of glass produced per kilowatt hour of total heat input (electrode plus boosting) for the LFCM tests with lid heater boosting (LFCM-4 and -5) were roughly 15% greater than the PSCM-2 run. This difference could be explained by a less-than-ideal design of the burner system used on the PSCM.

A summary of the operating conditions is shown in Table 24.

TABLE 24. PSCM-2 Summary

Parameter	Characteristic	
Aqueous Slurry Feed	TDSM-131	
Plenum Power Boosting	Propane/Air Combustion	
Glass Temperature Goal	1150 ± 25°C	
Off-Gas Temperature Goal	375 ± 25°C	
Off-Gas Temperature Control	Water Spray	
Experiment Duration	89 h	
Down Time	0.7%	
Melter Surface	0.73 m ²	
Maximum Feed Rate	74 L/h	89 L/h
Sustained Period	16 & 8 h	8 h
Oxide Content	0.451 kg/L	0.451 kg/L
Melting Flux	46 kg/h-m ²	55 kg/h-m ²
Average Glass Temperature	1140°C	1180°C
Electrode Power	60 kW	80 kW
Plenum Boosting Power	40 kW	30 kW
Total Glass Produced	2872 kg	

Post-run inspection of the melter showed a fairly uniform 2- to 4-cm-thick layer of sludge covered the melter floor, with 2-cm-thick accumulation in the corners and immediately in front of the discharge throat.

Operational data from this run is plotted in Figure 20 with five operating periods of interest noted, labeled A, B, C, D and E. During periods A and C, the slurry feed rate averaged about 81 L/h and 79 L/h, respectively. After about 8 h of operation at this rate, in both cases, the visual condition of the melter was deteriorated.

Operating periods B and D were visually characterized by a dark, flexible cold cap with a continuously-shifting network of cracks and vent holes scattered across the cold cap. Operating period E was similarly characterized, but purposely had a higher average glass temperature than the previous periods.

The lower half of Figure 20 shows the power input to the melter. The lower curve depicts the "usable" power delivered to the melter plenum by the propane fuel combustion. The middle curve shows the power released in the glass by the electrode current flow, and the upper curve is the total of these two power sources. The "usable" power delivered by the propane combustion is considered the energy that is available to evaporate the water from the feed slurry, to raise the feed slurry to the molten glass temperature and to form the molten glass.

Figure 21 shows the temperature profile of the melter for the five periods of interest previously identified. The "•'s" on the feed rate plot (Figure 20) identify the times that the data were taken for the multiple temperature profile plots of Figure 21. It is of interest to note that during periods A and C, the temperature indications are unstable, while during periods B, D and E (periods of stable melter conditions), the temperature indications are quite stable, particularly at the bottom of the tank. The dotted lines on the temperature profile plots identify the desired glass temperature range ($1150 \pm 25^\circ\text{C}$), and the small arrows at the base of this temperature range zone indicate the average of the temperatures indicated at the 10.2-, 17.8- and 25.4-cm levels.

4.5.1 Melter Off-Gas Analysis

The nature and extent of PSCM-2 off-gas-line depositions were assessed upon completion of the experiment. Figure 22 identifies the components of the process exhaust line where depositions were observed to have occurred. The largest deposition found formed in the throat of the melter lid exhaust port. This deposit is thought to have resulted from the operation and positioning of the off-gas cooling nozzle, which was located just downstream from the plug

FIGURE 20. PSCM-2 Melter Slurry Feed Rate and Melter Power Input

FIGURE 21. PSCM-2 Temperature Profiles

FIGURE 22. PSCM-2 Off-Gas Piping

formation site. Total off-gas-line depositions, including as much of the lid plug as could be collected, amounted to ~2 kg, which represents 0.1% of the total oxides fed to the melter during this experiment.

The composition of the deposits collected from PSCM-2 off-gas-line components is summarized in Table 25. In addition, Table 26 compares the weighted, average composition of these PSCM-2 deposits with the off-gas-line deposits formed in previous melter experiments. All off-gas-line deposits are seen to possess a more or less similar composition, which is not strictly representative of the feed.

TABLE 25. PSCM-2 Pipe Deposits (Wt%)

<u>Element</u>	<u>"Y"</u>	<u>Flex Hose</u>	<u>Inside Lid</u>	<u>Pipe Corrosion Test</u>	<u>90° Elbow</u>
Al ₂ O ₃	1.8	1.5	1.5	1.6	1.2
B ₂ O ₃	4.0	3.7	1.6	5.0	3.1
CaO	4.8	3.6	3.5	3.7	3.6
CdO	0.04	0.10	0.02	0.08	0.10
Cs ₂ O	0.35	1.34	0.44	1.0	1.22
Cr ₂ O ₃	0.98	0.90	0.36	0.50	0.91
Fe ₂ O ₃	16.0	15.0	10.5	13.0	14.0
LiO	3.0	2.6	2.8	3.0	2.6
MgO	1.1	0.70	0.85	0.80	0.66
MnO ₂	3.9	3.4	3.3	3.6	4.2
Na ₂ O	13.0	16.6	23.0	17.0	21.0
NiO	2.5	2.4	1.8	1.9	2.6
RuO ₂	0.10	0.35	0.11	0.22	0.26
Sb ₂ O ₃	<0.04	--	<0.04	--	--
SiO ₂	25.0	21.0	21.0	27.0	13.0
SrO	0.038	0.03	0.03	0.03	0.03
TeO ₂	0.06	0.10	0.07	0.08	0.08
TiO ₂	0.46	0.38	0.38	0.50	0.25
ZnO	0.025	0.025	0.02	0.02	0.05
ZrO ₂	0.23	0.16	0.20	0.22	0.13
Se	0.097	0.11	0.006	0.13	0.28
Cl ⁻	6.63	10.7	19.8	9.56	22.9
F ⁻	0.096	0.05	0.13	0.097	0.15
SO ₄ ⁼	3.03	9.45	6.02	3.89	5.79

TABLE 26. PSCM-2 Pipe Deposition Composition (Wt%)

<u>Element</u>	<u>PSCM-2</u>	<u>LFCM-4</u>	<u>PSCM-1</u>
Al ₂ O ₃	1.6	2.0	--
B ₂ O ₃	3.4	5.6	4.6
CaO	4.1	6.5	--
CdO	0.05	0.08	--
Cs ₂ O	0.11	0.31	0.80
Cr ₂ O ₃	0.78	0.31	--
Fe ₂ O ₃	14.2	14.0	10.0
LiO	2.9	3.4	--
MgO	0.92	2.5	--
MnO ₂	3.6	3.4	--
Na ₂ O	16.8	15.0	20.0
NiO	2.3	--	--
RuO ₂	0.17	0.16	--
Sb ₂ O ₃	<0.04	--	--
SiO	22.7	31.0	--
SrO	0.03	0.05	--
TeO ₂	0.07	0.11	--
TiO	0.42	0.11	--
ZrO ₂	0.20	0.29	--

Experimental feed component DFs determined during PSCM-2 are listed in Table 27, where they are compared to all previous melter runs discussed in this report. It is clear from this table that combustion boosting, in conjunction with increased feeding rates, has dramatically increased effluent emission rates of this melter. Of the previous melter runs, only LFCM-4, which itself utilized electric lid boosting to maximize feeding rates, exhibited a lower overall DF.

TABLE 27. PSCM-2 Decontamination Factors

Element	PSCM-2 Average DF	DF Ratio		
		<u>PSCM-2</u> <u>LFCM-3</u>	<u>PSCM-2</u> <u>PSCM-1</u>	<u>PSCM-2</u> <u>LFCM-4</u>
Al ₂ O ₃	990	0.41	0.090	1.9
B ₂ O ₃	160	1.30	0.76	1.2
CaO	610	0.33	0.33	2.3
CdO	47	0.56	0.25	0.67
Cs ₂ O	3	0.43	0.059	0.053
Fe ₂ O ₃	680	0.99	0.18	2.6
Li ₂ O	340	0.52	0.18	1.1
MgO	930	0.52	0.10	2.6
MnO ₂	630	0.20	0.11	1.5
Na ₂ O	130	0.46	0.16	0.38
NiO	--	--	--	--
RuO ₂	48	0.80	1.5	1.8
Sb ₂ O ₃	100	--	--	0.056
SiO ₂	1600	0.61	0.11	3.8
SrO	640	0.43	0.086	3.1
TeO ₂	58	0.21	0.34	0.93
TiO ₂	1400	--	--	--
SeO ₂	--	--	--	--
TOTAL OXIDE	430	0.89	0.38	1.5
Cl ⁻	3	0.33	0.96	1.4
SO ₄ ⁼	19	3.8	19.0	19.0

Since one of the primary objectives of the PSCM-2 test was to investigate the effects of propane combustion boosting upon melter feeding rates, the gas composition of the melter plenum was of particular engineering interest during this test. Gas chromatographic analysis of the plenum gases was conducted throughout the entire duration of the PSCM-2 experiment. The results of these analyses are graphically illustrated in Figure 23. The relationship between the concentrations of N₂, O₂ and CO₂, depicted in this figure, are consistent with the stoichiometry of total combustion of C₃H₈. That is, the relative change in the percent composition of O₂, CO₂ and N₂, as a function of oxidation rate, will vary as -1:2/3:1/3, respectively, if complete combustion is

FIGURE 23. PSCM-2 Plenum Off-Gas Composition

assumed. These correlations are quite apparent in the data presented in Figure 23. Although the relative variations of the noncondensable gases are consistent with a variable combustion rate of propane, the mechanism responsible for these variations is not understood.

4.6 RUN 6 - LFCM-6 (JUNE 1981)

The objective of this test was to establish the melter capacity while using electric lid heating. In addition, plasma torch units were to be tested as an additional source of plenum heat. During this 117-h test^(a), ~4399 kg of glass were produced. Liquid feed was processed at an average rate of 86.7 L/h, and average melting rates were 39.5 kg/h-m². A data summary is shown in Table 28.

TABLE 28. LFCM-6 Run Summary

Parameter	Characteristic
Run Time (Elapsed)	117.5 h
Actual Melter Feeding Time	106.1 h
Total Glass Produced	4399 kg
Total Feed Slurry Used	9194 L (pH = 10.6 to 11.6, ρ = 1.33 to 1.39, 462 g oxide/L)
Avg. Glass Production Rate (Based on Actual Feeding Time)	41.5 kg/h (39.5 kg/h-m ²)
Maximum Sustained Glass Production Rates	51.6 kg/h-m ² for 8 h, 44.8 kg/h-m ² for 22.5 h and 44.8 kg/h-m ² for 17

Typical Melter Operating Parameters @ 43.9 kg glass/h (06-03-81 through 06-05-81)

Electrode Power	122 kW	Primary 80 kW	(95-105 V, 800-900 A), Temp. 900-1000°C
		Secondary 42 kW	(70 V, 60 A), Temp. 950°C
Plasma Torch Power		18-29 kW	
Lid Heater Power		33 kW	
Lid Liner Wall Temperature		800°C	
Average Glass Temperature		1150°C	
Off-Gas Cooling Water Spray Flow Rate			24 L/h
Off-Gas Temperature (After Water Cooling Spray)			405°C

(a) A 16-h pretest in which ~647 kg of glass were melted was performed to test the plasma torches. No significant melter data was obtained.

The only unusual operating behavior during this test was the periodic buildup of a conical feed mound on a thermowell. This feed mound would then collapse, leading to surges in the off-gas flow; however, no pressurizations occurred.

Initially, a standard plasma torch used for thermal spray coating was operated for 8.5 h. Later in the run, one plasma torch (with an extension for thermal spray coating the inside of the pipes that extend ~38 cm into the plenum space) was operated for 24 h before failing. A second plasma torch, also extending ~38 cm into the plenum, was installed and operated without incidence for the remaining 3.5 h of the experiment. Due to the large cooling water demand of the torches, a significant quantity of available heat was lost. The resulting thermal input efficiencies of the torches were 28% for the standard torch and 46% for the extended-head torch. The higher efficiency of the longer torch may have been due to its ability to dissipate heat better than the standard torch, since the field of view for the plasma flame was greater.

Maintenance on the torches limited their continuous operating time, and the general conclusion was that their advantages did not outweigh their disadvantages. The torches were typical "off-the shelf" units.

Feed rate control was less than desirable due to a control signal problem. A rate plot is shown in Figure 24.

The plenum space temperature (Figure 25) ranged from a low of ~350°C, which occurred during a lid heater power outage, to over 1200°C, which was reached during a feed interruption. During most of the experiment, plenum temperature stayed in the range of 600 to 700°C. The erratic behavior is, again, indicative of the feed rate fluctuations.

The average glass temperature throughout the run stayed, for the most part, within the set limit of $1150 \pm 25^\circ\text{C}$. The average bulk glass temperature is an average of the vertical glass temperatures. Figure 26 shows the glass temperatures throughout the run. Figure 27 shows four glass temperature profiles taken during the run. As can be seen, there is quite a bit of difference in the four profiles. This can be attributed to the erratic feed rate, which prevented the melter from reaching steady-state condition early in

FIGURE 24. LFCM-6 Feed Rate to Melter

FIGURE 25. LFCM-6 Plenum Space Temperatures

FIGURE 26. LFCM-6 Glass Temperatures

FIGURE 27. LFCM-6 Glass Melt Temperature Profiles

the run. The flattening of the profile is typical, as the melter approaches steady state, because of the increased convective mixing over an idling melter. When the melter is idling, the floor will often run as much as 100°C colder than the bulk temperature.

Table 29 shows a heat balance on the melter. The overall heat of reaction (Entry 6) was calculated (from published data) to be slightly exothermic. The largest sources of error in the calculations are attributed to the air inleakage, a variation in the feed solids loading, and heat losses through the melter lid.

TABLE 29. LFCM-6 Heat Balance (0130 to 0830 h on 06/05/81)

<u>Energy Inputs to Melter</u>	
<u>Source</u>	<u>kW</u>
North Lid Heaters	17.0
South Lid Heaters	16.7
Plasma Torch	29.1
Primary Electrodes	79.7
Secondary Electrodes	41.9
Exothermic Reaction	<u>0.6</u>
TOTAL	185.0
 <u>Energy Outputs To Melter</u>	
<u>Source</u>	<u>kW</u>
Plasma Torch Cooling	15.4
Steam In Off Gas	73.6
Heat of Fusion	5.6
Molten Glass Out	16.8
Melter Lid	2.4
Melter Walls	18.8
Melter Floor	5.3
Freeze Valve	7.3
Feed Nozzle Cooling	1.5
Air Inleakage	<u>8.2</u>
TOTAL	154.9

4.6.1 Off-Gas Analysis

In order to minimize the formation of fused off-gas-line deposits during the LFCM-6 test, a spray nozzle was used to introduce air-atomized water counter-current to the exhaust flow at the entrance of the melter off-gas

exhaust line. The deposits that did form in the melter off-gas-line components were collected and analyzed. It should be noted that the close-coupled vertical components had been cleaned 24 h prior to the end of the run in order to evaluate frit blasting as an off-gas cleaning technique. Nevertheless, the deposits that were removed by this technique were not massive; rather, they were light and hairlike in nature. The compositions of the deposits that formed in the various off-gas-line components (detailed in Figure 28) are listed in Table 30. A comparison of the weighted average composition of LFCM-6 line deposits with off-gas-line deposits formed in previous melter experiments is detailed in Table 31. Again, the similarities of these deposits are more striking than are their minor differences. The semivolatiles cesium, ruthenium, antimony and tellurium, which are minor feed components but major radiological hazards, are all seen to be enriched in these deposits relative to the feed.

Total feed component DFs obtained from three samples during the LFCM-6 test are summarized in Table 32. Efforts to establish a greater trace element homogeneity in the feed makeup tanks appear to have produced much more consistent results between sampling runs than has been achieved in previous experiments. Also presented in this table is a value of the total particulate DF as determined by absolute HEPA filtration. The agreement between these two sets of independent data is quite satisfying. Table 33 compares the average LFCM-6 feed component DFs with those obtained from previous melter runs. Clearly, LFCM-6 exhibited the highest effluent emission rates of all liquid-fed melter runs conducted to date. This result further supports the notion that boosting feeding rates will result in decreased effluent emission performance.

FIGURE 28. LFCM-6 Off-Gas Piping

TABLE 30. LFCM-6 Off-Gas Line Deposits

Point # Element	Weight Percent as Oxides					Feed
	#0	#2	#1	#3	Avg.	
Al ₂ O ₃	1.6	1.9	1.8	2.1	1.9	3.5
B ₂ O ₃	7.0	8.0	7.1	6.8	7.2	9.9
CaO	0.73	0.91	0.83	0.73	0.80	1.2
CdO	0.23	0.23	0.21	0.21	0.22	0.01
Cr ₂ O ₃	0.16	0.13	0.08	0.09	0.10	0.02
Cs ₂ O	0.21	0.16	0.20	0.20	0.19	0.06
Fe ₂ O ₃	13.7	12.3	12.0	11.0	12.0	16.0
La ₂ O ₃	0.20	0.23	0.22	0.22	0.22	--
LiO	3.0	3.2	3.0	3.2	3.1	4.1
MgO	0.81	0.95	0.93	0.93	0.90	1.4
MnO ₂	1.6	2.4	2.4	2.4	2.2	3.8
Na ₂ O	15.0	13.0	13.0	13.0	13.0	15.5
NiO	--	--	--	--	--	1.5
RuO ₂	0.49	0.36	0.57	0.44	0.47	0.02
Sb ₂ O ₃	--	0.03	0.03	0.04	0.03	0.008
SiO ₂	30.0	34.0	32.0	32.0	32.0	44.0
SrO	0.02	0.03	0.02	0.02	0.02	0.02
TeO ₂	0.06	0.05	0.05	0.06	0.06	0.01
TiO	0.78	0.88	0.62	0.61	0.72	0.70
ZrO ₂	0.22	0.29	0.29	0.28	0.27	--

TABLE 31. LFCM-6 Melter Pipe Deposition Composition

Element	Weight Percent				
	LFCM-6	PSCM-2	LFCM-4	PSCM-1	LFCM-2
Al ₂ O ₃	1.9	1.6	2.0	--	1.7
B ₂ O ₃	7.2	3.4	5.6	4.6	4.6
CaO	0.80	4.1	6.5	--	4.4
CdO	0.22	0.05	0.08	--	--
Cs ₂ O	0.19	0.11	0.31	0.80	0.26
Cr ₂ O ₃	0.10	0.78	0.31	--	--
Fe ₂ O ₃	12.0	14.2	14.0	10.0	20.0
LiO	3.1	2.9	3.4	--	2.0
MgO	0.90	0.92	2.5	--	0.22
MnO ₂	2.2	3.6	3.4	--	1.2
Na ₂ O	13.0	16.8	15.0	20.0	17.0
NiO	--	2.3	--	--	2.5
RuO ₂	0.47	0.17	0.16	--	0.3
Sb ₂ O ₃	0.03	<0.04	--	--	--
SiO	32.0	22.7	31.0	--	31.0
SrO	0.02	0.03	0.05	--	0.04
TeO ₂	0.06	0.07	0.11	--	0.07
TiO	0.72	0.42	0.11	--	0.07
ZrO ₂	0.27	0.20	0.29	--	--

TABLE 32. LFCM-6 Decontamination Factors

Sample #: Element	Experimental DFs			Avg. DF
	#1	#2	#3	
Al ₂ O ₃	272	342	390	330
B ₂ O ₃	89	95	90	90
CaO	230	180	140	180
CdO	85	84	82	80
Cs ₂ O	4	11	13	10
Fe ₂ O ₃	210	230	230	230
La ₂ O ₃	250	280	300	280
LiO	150	160	170	160
MgO	237	273	276	260
MnO ₂	210	330	400	330
Na ₂ O	89	83	95	90
NiO	710	990	1100	930
RuO ₂	10	22	9	13
Sb ₂ O ₃	>60	>100	>70	--
SiO ₂	284	260	290	280
SrO	290	300	270	290
TeO ₂	190	230	214	210
TiO	96	120	300	170
ZrO ₂	260	245	270	260
TOTAL	160	170	180	170

TOTAL PARTICULATE DF DETERMINED FROM HEPA 190

TABLE 33. LFCM-6 Comparative DFs

Element	LFCM-6 Average DF	DF Ratio				
		LFCM-6 LFCM-2	LFCM-6 LFCM-3	LFCM-6 PSCM-1	LFCM-6 LFCM-4	LFCM-6 PSCM-2
Al ₂ O ₃	330	0.067	0.14	0.030	0.62	0.33
B ₂ O ₃	90	0.35	0.74	0.43	0.69	0.56
CaO	180	0.24	0.097	0.099	0.69	0.30
CdO	80	>0.23	0.95	0.42	1.1	1.7
Cs ₂ O	10	0.25	1.4	0.20	0.17	3.3
Fe ₂ O ₃	230	0.55	0.33	0.060	0.88	0.34
Li ₂ O	160	0.17	0.24	0.084	0.52	0.47
MgO	260	0.53	0.14	0.028	0.74	0.28
MnO ₂	330	0.21	0.11	0.58	0.79	0.52
Na ₂ O	90	0.27	0.32	0.11	0.26	0.69
NiO	930	2.2	2.2	0.62	3.6	--
RuO ₂	13	1.8	0.22	0.41	0.50	0.27
Sb ₂ O ₃	--	--	--	--	--	--
SiO ₂	280	0.30	0.11	0.019	0.67	0.18
SrO	290	0.77	0.19	0.039	1.4	0.45
TeO ₂	210	3.4	0.78	1.2	3.4	3.6
TiO ₂	170	0.15	--	--	--	0.12
TOTAL OXIDE	170	0.30	0.35	0.15	0.59	0.40

The use of plasma torches within an operating melter presents a potential flammability hazard due to hydrogen generation resulting from plasma-initiated decomposition of H_2O . Pre-LFCM-6 tests of the plasma torches using building steam revealed that significant quantities of hydrogen (~4.5% dry basis) could be generated by this torch when low inleakage rates existed. Consequently, monitoring the noncondensable composition of the melter exhaust was of particular interest during this experiment. The results of these analyses are presented in Table 34. Because of the large melter inleakage rates, hydrogen was not detectable ($H_2\% < 0.1\%$) during the LFCM-6 test. Indeed, the inleakages were high enough that the plasma torch support gas (argon) had only a minimal effect upon the noncondensable off-gas composition. Argon and oxygen concentrations are combined in this table since they are not resolvable under the running conditions of the GC used in these analyses.

TABLE 34. LFCM-6 Noncondensable Off-Gas Composition

Date	Time	CO ₂	[O ₂ +Ar]	N ₂	CO	Comments
5/31	22:06	0.192	20.61	79.2	--	
5/31	23:15	0.361	20.53	79.1	--	
6/01	17:01	0.821	20.16	80.0	0.027	
6/01	18:19	0.680	19.84	79.4	0.038	
6/01	19:41	0.647	20.03	79.3	0.015	
6/01	21:28	0.624	20.06	79.3	0.015	
6/01	22:39	0.732	20.18	79.1	0.035	
6/02	00:10	0.510	20.30	79.1	0.050	
6/02	18:09	0.752	19.75	79.5	--	No Feed
6/02	21:56	0.869	20.69	78.4	0.014	
6/02	22:35	0.133	20.93	78.9	--	No Feed
6/03	15:52	0.527	20.06	79.4	0.067	
6/03	17:31	0.492	19.67	79.8	0.025	
6/03	18:30	0.436	19.67	79.9	0.021	
6/03	19:19	0.485	20.17	79.3	0.050	
6/03	20:16	0.669	20.03	79.3	>0.01	
6/03	20:55	0.482	20.12	79.4	>0.01	
6/03	21:43	0.551	20.13	79.3	0.015	
6/03	22:28	0.514	20.17	79.29	0.032	
6/03	23:15	0.421	20.04	79.5	0.035	
6/04	18:19	0.275	21.25	78.46	0.018	Plasma Torch On
6/04	19:44	0.391	22.27	77.32	0.020	Plasma Torch On
6/04	20:47	0.583	22.11	77.30	0.017	Plasma Torch On
6/04	22:19	0.437	22.88	76.66	0.024	Plasma Torch On
6/04	23:18	0.481	23.01	76.5	0.017	Plasma Torch On

One of the main objectives of the flow rate studies involving LFCM-6 was to characterize the maximum flow surges generated by normal melter operation. Because the dynamic range of the flow transducer employed during LFCM-4 was overranged by off-gas surges, a flow transducer was employed during the June LFCM run that responded to surge impulses but was relatively insensitive to the average flow rate. The maxima of the flow surges that did occur during this experiment were cataloged and treated statistically. These results are summarized in Table 35. It should be noted that no emergency venting occurred during this run. On the other hand, care was exercised to minimize conductance-limiting situations within the melter off-gas system.

TABLE 35. LFCM-6 Surging Flow Rate Behavior

<u>Mean Surge Flow</u> <u>(scfm)</u>	<u>Data Dispersion (1-σ)</u> <u>(scfm)</u>	<u>Maximum Flow</u> <u>(scfm)</u>
185	63	465

After the run, severe corrosion was observed on the melter lid liner and the off-gas line. The off-gas line corroded in the area where the pipe penetrates the melter lid, as previously shown in Figure 28. The corrosion mechanisms have been studied in detail and are reported elsewhere (Barnes and Larson 1981).

4.6.2 High-Temperature Excursion

Just prior to the LFCM-6 run, the melter unintentionally experienced a temperature excursion while in an idling mode. Over a 22-h period, the glass temperature steadily rose to a maximum of $\sim 1480^{\circ}\text{C}$. The glass temperature was above 1400°C for ~ 23 h. This high temperature caused the plenum heaters to burn out. Upon removal of the heaters, it was observed that the inner heater retaining walls had bowed out into the plenum space. The deformed retention walls did not interfere with the installation of the replacement heaters or with future melter operations.

After the overheating incident, the Inconel liner on the plenum ceiling was inspected using stainless steel mirrors. Most of the liner was missing except for a few scattered places around the walls. The outer containment lid

of the melter was observable in some places, indicating that some of the Duraboard® lid insulation had also been lost. When the melter was shut down and drained, four months and two five-day runs after the overheating incident, the Inconel-690 electrode surface showed definite signs of having reached its melting point (1343 to 1371°C) during the excursion.

4.7 RUN 7 - PSCM-3 (JULY 1981)

This experiment was the first test of the new formate feed composition (see Section 2.7, Table 3), the result of a proposed process change for the Savannah River Plant's (SRP) waste program.

The new SRP flowsheet calls for Hg removal in a slurry receipt adjustment tank with formic acid. The formic acid slurry is then sent to a slurry mix evaporator prior to being fed to the ceramic melter. Frit from canister decontamination, which has been treated with formic acid for transport purposes, will also be added to the evaporator. It is expected that the manganese, calcium, nickel and some of the sodium will emerge from this evaporator as formates. There will also be some sodium nitrate and sodium sulfate present. The iron and aluminum will emerge from the evaporator as hydroxides and the silica as silicon dioxide. Zeolite and coal will be unaffected. The product, referred to as TDSF waste, was simulated at PNL and used as feed for this and all subsequent melter experiments.

The melter performance characteristics peculiar to this flowsheet change included:

- slurry transport characteristics
- melting characteristics, i.e., venting, cold cap formation, spattering and foaming
- noncondensable off-gas composition
- solids deposition in the off-gas lines
- melter response to glass resistance characteristics
- sludge formation
- glass discharge characteristics.

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To keep from changing too many variables at one time, no boosting was employed during this run.

The experiment lasted 124.5 h. The melter at 0505 h and was terminated 124.5 h later at 0930 h on 07/25/81. The on-stream factor (i.e., feed on) was 98.6%, and 2400 kg of glass were produced for ~4 melter tank turnovers. Approximately 5400 L of waste slurry was fed to the melter during the period and, while the feed was interrupted five times for minor feed system adjustments (a total of 1.73 h), in no case was the feed interrupted long enough to significantly affect the condition of the cold cap. A summary of operating characteristics is shown in Table 36.

TABLE 36. PSCM-3 Production Summary

<u>Parameter</u>	<u>Characteristic</u>
Run Time	124.5 h
Actual Melter Feed Time	122.8 h
Total Feed Used	5400 L (pH 6-7, 463 g/L $\pm$ 22, ρ = 1.36)
Total Glass Produced	2500 kg
Average Glass Production Rate	20.4 kg/h (27.9 kg/h-m ²)
Average Feed Rate	44 L/h (60 L/h-m ²)
Maximum Feed Rate Over 26 h	53 L/h (72 L/h-m ²)

Typical Melter Operating Parameters

Electrode Power	60 kW
Glass Temperature	1150°C
Off-Gas Temperature	270°C
Electrode Temperature	800°C

The melter operation was very successful with indications that higher feed rates could be achieved. Also, the melting behavior of the formate feed could be characterized as resulting in much smoother operation of the melter. In particular, the feed system performance, a troublesome item in past runs, was much improved.

The pressurized loop feed control system performed quite well, maintaining a continuous flow of feed to the melter. No pump failure or line plugging was encountered during the experiment. Both the mass and magnetic flowmeters

performed well during the experiment, and the flow control systems utilizing each of the flow sensors performed as expected. Operating parameters, including the average feed rate, are shown in Figure 29. The graph shows a feed rate increase near the end of the experiment, which was performed to determine the melter's maximum feed rate capacity. The average feed rate for the last 26 h was 53 L/h (72 L/h-m²), and there were no bridging problems. The off-gas temperature dropped to the lower operating limit of 200°C, so the feed rate was not increased further. The plenum temperature is also shown.

A graph of four glass temperatures recorded from thermocouples located at various distances from the melter is shown in Figure 30. Other thermocouples closer to the floor reflect temperatures similar to the thermocouple 17.8 cm from the floor, but are not plotted.

The thermocouple located 40.6 cm from the floor is above the normal glass level; thus, it reflects the cold cap and plenum temperatures. The wide variation in temperature is due to the cold cap size, the liquid pool position, and the conductance of heat from the thermowell in contact with molten glass. Overall, the bulk glass temperature represented by the thermocouples ~15 and 25 cm from the floor remain within the operating parameter of 1150 ±25°C.

The average glass temperature increased slightly throughout the run, but a larger increase was noted in the melter tank's wall and floor temperature. The temperatures at the 2.5-cm glass level, 10.2-cm wall level, corner floor level and center floor of the melter are shown in Figure 31. These values show that the melter was not operating with steady-state conditions.

The glass discharge characteristics appeared similar to previous runs, as the glass stream flowed over the discharge trough smoothly and evenly. The TDSF glass flowed smoothly with the discharge heaters at ~1070°C and did not appear any different than TDSM glass.

The glass temperature was controlled by resistance feedback because the resistance is related to the glass temperature and is a more dependable measurement than thermocouple indication of the glass temperature. The resistance set point was manually decreased throughout the run because the composition of the glass in the melter was being changed from TDSM-131 to TDSF-131. An increase in the glass tank resistance at a constant temperature was

FIGURE 29. PSCM-3 Operating Parameters

FIGURE 30. PSCM-3 Glass Temperatures

FIGURE 31. PSCM-3 Floor and Wall Temperatures

anticipated as the glass composition was changed, but Figure 32 shows a decrease in the resistance. The rapid resistance decrease at the beginning of the run was caused by the changing glass temperature.

The power input shown on Figure 32 shows a steady increase, which reflects the increasing feed rate. A heat balance on the melter shows that only a small portion of the melter's electrical power is used to melt the sludge, while three times that value is used to evaporate water from the feed (see Table 37).

TABLE 37. PSCM-3 Heat Balance at 53 L/h Slurry Feed Rate

<u>In</u>	<u>Out</u>	
Electrodes, 70 kW	Off-Gas Steam	33 kW
	Off-Gas Air ^(a)	2 kW
	Molten Glass	10 kW
	Heat of Fusion	3 kW
	Heat Losses From Melter	
	Lid, Walls, Floor and Freeze Valve ^(b)	22 kW
	TOTAL	70 kW

(a) Based on 20 scfm inleakage.

(b) Based on energy left unaccounted for.

4.7.1 Off-Gas Analysis

The extent of feed component deposition occurring within the PSCM-3 off-gas exhaust lines was assessed at the completion of the 120-h test. Deposits were collected from various off-gas line components (Figure 33) in order to establish their elemental composition. This compositional data appears in Table 38. The average composition of these deposits is (not surprisingly) very much like those exhibited by deposits formed in previous melter tests using a neutralized feed formulation. This composition comparison is tabulated in Table 39.

FIGURE 32. Electrode Power and Tank Resistance

FIGURE 33. PSCM-3 Off-Gas Line Configuration

TABLE 38. PSCM-3 Pipe Deposition Composition

Element (Oxide)	Weight Percent					
	Lid Port #1	Lid Port #15	Elbow	"Y"	Flex Hose	Horizontal Pipe
Al ₂ O ₃	1.4	1.8	1.7	1.3	1.7	1.7
B ₂ O ₃	5.0	5.5	5.5	5.4	6.0	5.0
CaO	1.6	1.9	1.6	1.6	1.8	1.6
CdO	0.09	0.08	0.11	0.15	0.10	0.09
Cs ₂ O	0.93	0.53	0.55	0.68	0.72	0.55
Cr ₂ O ₃	0.14	0.15	0.21	--	0.12	0.17
Fe ₂ O ₃	10.2	12.1	11.3	10.6	11.7	10.7
La ₂ O ₃	0.19	0.21	0.20	0.19	--	--
LiO	2.5	2.3	2.5	2.5	2.5	2.4
MgO	0.61	0.71	0.68	0.60	0.69	0.64
MnO ₂	4.3	5.3	4.6	4.3	4.9	4.8
Na ₂ O	18.5	14.2	14.5	18.0	15.0	14.4
NiO	0.89	1.2	1.0	0.92	1.1	1.2
RuO ₂	0.11	0.04	0.11	0.03	0.29	0.08
Sb ₂ O ₃	0.02	0.02	0.02	0.04	0.02	0.02
SiO ₂	25.0	28.18	27.1	25.6	27.9	25.7
SrO	0.02	0.03	0.02	0.03	0.03	0.02
TeO ₂	0.13	0.11	0.14	0.18	0.16	0.12
TiO	0.48	0.57	0.55	0.50	0.55	0.51
ZnO	0.06	0.08	0.07	0.05	0.07	--
ZrO ₂	0.22	0.26	0.24	0.22	0.27	0.24
SeO ₂	0.14	0.24	0.30	0.31	0.32	0.30

TABLE 39. PSCM-3 Melter Pipe Deposition Composition Comparison

Element	Weight Percent					
	PSCM-3	LFCM-6	PSCM-2	LFCM-4	PSCM-1	LFCM-2
Al ₂ O ₃	1.6	1.9	1.6	2.0	--	1.7
B ₂ O ₃	5.4	7.2	3.4	5.6	4.6	4.6
CaO	1.7	0.80	4.1	6.5	--	4.4
CdO	0.10	0.22	0.05	0.08	--	--
Cs ₂ O	0.66	0.19	0.11	0.31	0.80	0.26
Cr ₂ O ₃	0.13	0.10	0.78	0.31	--	--
Fe ₂ O ₃	11.1	12.0	14.2	14.0	10.0	20.0
LiO	2.5	3.1	2.9	3.4	--	2.0
MgO	0.66	0.90	0.92	2.5	--	0.22
MnO ₂	4.7	2.2	3.6	3.4	--	1.2
Na ₂ O	15.8	13.0	16.8	15.0	20.0	17.0
NiO	1.1	--	2.3	--	--	2.5
RuO ₂	0.11	0.47	0.17	0.16	--	0.3
Sb ₂ O ₃	0.02	0.03	<0.04	--	--	--
SiO	26.6	32.0	22.7	31.0	--	31.0
SrO	0.03	0.02	0.03	0.05	--	0.04
TeO ₂	0.14	0.06	0.07	0.11	--	0.07
TiO	0.53	0.72	0.42	0.11	--	0.07
ZrO ₂	0.24	0.27	0.20	0.29	--	--

Total melter feed component DFs associated with PSCM-3 have been established for most elemental constituents. This data appears in Table 40. Overall, these results are strikingly similar to the data generated by the original pilot-scale melter experiment, PSCM-1. A comparison of PSCM-3 DFs with the results obtained from all previous melter experiments covered in this report is presented in Table 41. The effluent emission rates associated with PSCM-3 are, on the average, lower than those exhibited by all other melter tests, except PSCM-1. The low cesium DF associated with present data may not be an accurate measure of melter performance with regard to this element. The cesium composition of PSCM-3 feed was exceedingly low. On the other hand, the bulk glass within the melter possessed significant quantities of cesium from previous melter runs. Consequently, steady-state running conditions were never established with regard to this element during this test. DF values associated with ruthenium and antimony are not available from this experiment.

TABLE 40. PSCM-3 Feed Component DFs

Element	DF Values		Average
	<u>7/20/81</u>	<u>7/21/81</u>	
Al ₂ O ₃	4800	7500	6000
B ₂ O ₃	210	180	200
CaO	1200	1000	1100
CdO	--	--	--
Cr ₂ O ₃	--	--	--
Cs ₂ O	5.7	1.9	3.8
Fe ₂ O ₃	760	2500	1600
La ₂ O ₃	3400	6000	4700
Li ₂ O	3000	2200	2600
MgO	11000	5300	8200
MnO ₂	1500	5100	3300
Na ₂ O	1200	600	900
NiO	3700	15000	9400
RuO ₂	--	--	--
Sb ₂ O ₃	>117	>670	--
SiO ₂	2500	3600	3000
SrO	560	720	640
TeO ₂	45	20	32
TiO	2700	5600	4100
ZrO ₂	2500	1600	2000
TOTAL OXIDES	<u>970</u>	<u>990</u>	<u>980</u>

TABLE 41. PSCM-3 Comparative DFs

Elements (Oxides)	PSCM-3 Avg. DF	DF Ratio					
		<u>PSCM-3</u> <u>LFCM-2</u>	<u>PSCM-3</u> <u>LFCM-3</u>	<u>PSCM-3</u> <u>PSCM-1</u>	<u>PSCM-3</u> <u>LFCM-4</u>	<u>PSCM-3</u> <u>PSCM-2</u>	<u>PSCM-3</u> <u>LFCM-6</u>
Al ₂ O ₃	6000	1.2	2.5	0.55	11.0	6.1	18.0
B ₂ O ₃	200	0.77	1.6	0.95	1.5	1.2	2.2
CaO	1100	1.4	0.59	0.60	4.2	1.8	6.1
Cs ₂ O	3.8	0.10	0.54	0.07	0.07	1.3	0.3
Fe ₂ O ₃	1600	3.8	2.3	0.42	6.2	2.4	7.0
Li ₂ O	2600	2.8	3.9	1.4	8.4	7.6	16.0
MgO	8200	17.0	4.6	0.91	23.0	8.9	32.0
MnO ₂	3300	2.1	1.1	0.58	7.9	5.02	10.0
Na ₂ O	900	2.7	3.2	1.1	2.6	6.9	10.0
NiO	9400	22.0	22.0	6.3	36.0	--	10.0
RuO ₂	--	--	--	--	--	--	--
Sb ₂ O ₃	--	--	--	--	--	--	--
SiO ₂	3000	3.2	1.1	0.20	7.1	1.9	11.0
SrO	640	1.7	0.43	0.09	3.1	1.0	2.2
TeO ₂	32	0.52	0.12	0.19	0.52	0.55	0.15
TiO ₂	4100	3.7	--	--	--	2.79	24.0
TOTAL OXIDE	980	1.7	2.0	0.86	3.4	2.3	5.8

The composition of the noncondensable melter exhaust gases was of particular importance during this experiment due to the high organic loading of the feed. The possibility of generating H₂ and CO (water-gas) in sufficient quantities to present a flammable hazard downstream of the venturi ejector, was of genuine concern. Consequently, a GC was utilized to identify all pertinent gas components present in the melter exhaust. Quantitative compositional data was generated by the GC for all gaseous components except H₂. This data appears in Figure 34. A bipolar response of the GC detector for H₂ precluded area determination of the H₂ peak. However, GC responses for hazardous H₂ concentrations had been previously established. These served as comparative standards for the chromatograms generated during PSCM-3 and allowed operating safety, with regard to H₂, to be assessed throughout this experiment. In order to obtain quantitative H₂ data, grab samples were taken and analyzed by mass spectrometry. These results are included in Table 42,

which also contains a condensation of the data appearing in Figure 34. From the data and flammability limits listed in this table, it is clear that dilution air was never required to eliminate potentially-flammable conditions within the melter exhaust; however, these results also suggest that careful monitoring will have to be continued in all future experiments which utilize a formate-based feed.

FIGURE 34. PSCM-3 Noncondensable Off-Gas Composition

TABLE 42. PSCM-3 Off-Gas Composition

Day	Data Type	Molar Composition, % Dry Basis					
		CO ₂	O ₂ (a)	N ₂	CO(b)	H ₂ (b)	H ₂ O
7/20	Avg.	0.60	21.8	77.4	0.14	--	--
7/21	Avg.	0.79	21.9	74.8	0.19	--	--
7/22	Avg.	1.65	21.5	77.0	0.32	--	48
7/23	Avg.	1.42	21.3	76.1	0.58	0.64	74
7/24	Avg.	1.83	21.6	76.0	0.83	--	--
7/20 - 7/24	Hi	2.94	22.7	77.8	1.31	1.11	N/A
7/20 - 7/24	Lo	0.20	20.9	75.1	0.04	0.17	N/A

(a) Includes ~1% argon.

(b) Lower flammability limit (Air): H₂ - 4%; CO - 12.5%.

Attempts have been made to quantify the GC hydrogen data, without a great deal of success. The GC hydrogen response appears to be nonlinear in nature and insufficient data exists to construct a calibration curve. Because the amount of information with regard to H₂ generation within liquid-fed melters is so limited, a trend curve has been constructed from chromatographic peak parameters which are, functionally, monotonically related to concentration. It should be kept in mind that this data is not linearly related to concentration. This "trend" curve appears in Figure 35.

Finally, an IR analyzer was utilized to examine the melter exhaust for the corrosive gas SO₂. At the high sensitivity settings required of this instrument, water-vapor interferences proved to be an analytically-limiting variable. Consequently, no conclusive data was generated with regard to melter-generated SO₂ emissions during PSCM-3. Further SO₂ monitoring studies will be discussed in the LFCM-7 effluents section.

The modest off-gas flow characteristics of the unboosted pilot-scale melter allowed both the average and surging flows to be characterized by a single off-gas flow transducer. The data generated during PSCM-3 is summarized in Table 43.

TABLE 43. PSCM-3 Flow Rate Behavior

Flow, scfm		Number of Surges and flow (acfm)		
Avg.	Max.			
70	220	11(200)	2(300)	0(400)

FIGURE 35. H_2 Variation During PSCM-3

The characteristics of melter flow rate behavior appear to have been drastically altered by the nature of the new formate feed. No longer is flow rate characterized by an erratic surging behavior; rather, a quiet, even flow rate appears to be the dominant feature associated with steady-state melter operations.

4.7.2 Melter Shutdown

Following this experiment, the PSCM was shut down and drained so that planned modifications to its lid could be made. About 560 kg of glass were drained from the freeze valve in 5 min. Following the draining, an inspection was performed to note any effects on the melter tank after operating at high temperatures for 239 days (idling at 1000°C and operating at 1150°C for 389 h or ~16.2 days).

When the melter lid was removed, very little corrosion of the K-3 refractory in the tank was noted. No corrosion was seen behind the plate electrodes, above the glass level, or on the floor. No corrosion of the vertical joints in the four tank corners was seen, but at the centerline of the tank some widening of the vertical joints was noted. The maximum rounding of the vertical joint corner was about a 0.1-cm radius. Similar rounding, but with about a 0.3-cm radius, was noted on the underflow throat inlet edges. No significant cracking of the K-3 refractories was observed.

No corrosion of the submerged portion of the electrodes was apparent, but some pitting in the vapor-phase areas was seen. The north and south electrodes each lost ~10 kg of metal. Very little sludge accumulated on the filleted electrode feet.

The sludge layer was thicker than had been indicated by the sludge probes, although the probing technique is semiquantitative at best. The sludge varied in thickness from about 5 cm around the edges of the tank to about 2.5 cm in the center. Sludge completely filled the corners where the electrodes did not reach the walls. The total amount of sludge removed from the tank after draining was 94 kg. Little, if any, glass remained in the tank after draining.

Approximately 1 to 2 kg of globular accumulations of metal-like crystalline material were observed on the floor. Approximately 0.5 kg of these nodules were estimated to be still encapsulated within the sludge pieces. The approximate distribution of this material is shown in Figure 36. The globules

FIGURE 36. Metal-Like Globule Distribution After Draining PSCM

ranged in size from ~0.3-cm dia and smaller up to about a 7- x 4- x 1-cm slab. While the larger pieces rested on the floor of the melter, some of the smaller spheres were found on the top surfaces of the sludge. No globules were found in the center of the tank or discharge throat. This same material has been found in in-can melter canisters and ceramic melters when a reducing situation is present. The material has been previously reported as nickel subsulfide, Ni_3S_2 .

4.7.3 Spinel Formation in the PSCM

Analyses of the feed and glass produced during previous Runs (PSCM-1 and PSCM-2) were made to determine if spinel buildup was occurring. Table 44 shows the feed and glass analyses from the runs and the initial and final spinel-forming concentrations in the glass during the idling period between the runs.

TABLE 44. Spinel Production as Determined by Feed and Glass Analyses

<u>PSCM-1 - December Run</u>				
Composition				
<u>Oxide</u>	<u>Feed (wt%)</u>	<u>Glass (wt%)</u>	<u>Glass Produced (kg)</u>	<u>Spinel Produced (kg)</u>
Fe_2O_3	15.5 $\pm$ 0.4	14.8 $\pm$ 0.7	--	--
MnO_2	3.8 $\pm$ 0.1	3.9 $\pm$ 0.2	~2000	~16
NiO	1.4 $\pm$ 0.1	1.2 $\pm$ 0.1	--	--
<u>PSCM-2 - March Run</u>				
Fe_2O_3	13.0 $\pm$ 1.3	12.8 $\pm$ 0.6	--	--
MnO_2	3.8 $\pm$ 0.5	3.6 $\pm$ 0.2	~3000	~21
NiO	1.4 $\pm$ 0.2	1.1 $\pm$ 0.1	--	--
Total for 2 Runs				~37
<u>Idling</u>				
<u>Oxide</u>	<u>Glass Composition at End of PSCM-1 (wt%)</u>	<u>Glass Composition at Start of PSCM-2 (wt%)</u>	<u>~ Spinel Produced (700 kg glass in test) (kg)</u>	
Fe_2O_3	15.0	12.2	--	
MnO_2	4.0	3.8	25	
NiO	1.3	0.8	--	

Table 44 indicates that spinel may have formed during the two runs. The ~37 kg of total spinel produced would be equivalent to ~1 cm of spinel on the melter floor (melter surface area 0.73 m²; spinel density 5 g/cm³). As the "spinel" on the floor is probably ~50% crystals, a layer of ~3 cm might have been deposited (the glass has half the density of the spinel; this results in 3 rather than 2 cm).

During the idling period, significant spinel did form. If it is assumed that similar deposits occurred during the idling between later runs, then another 4 cm of deposits may have formed.

As the spinel is not deposited uniformly, a much thicker layer than 7 cm might be expected to be found in some places. During PSCM-3, additional spinel may have formed. This data correlates fairly well with the actual spinel quantities found after draining the melter.

4.8 RUN 8 - LFCM-7 (AUGUST 1981)

Run LFCM-7 was the counterpart to the previous PSCM-3 test. The new formate feed composition was tested to try to achieve high melting rates while using plenum heaters for boosting. In addition, further effluent characterization was emphasized.

Approximately 9750 L of feed were fed to the melter over a period of 110.9 h. Downtime accounted for 13.5% (15 h) of the total run time. About 43% of the downtime (6.4 h) was caused when the melter unexpectedly pressurized. No explanation for the pressurization is available, and no apparent damage was found.

Almost 4500 kg of glass were produced at an average glass production rate of 44.5 kg/h-m². This figure was based on an actual melter feeding time of 95.9 h.

The melter was operated without lid heating for the first two days so that the maximum rates could be established and off-gas characterizations could be made. A maximum feeding rate of 91.3 L/h was maintained over one 13-h period.

Due to equipment failure, only four of the eight lid heaters were available during the second half of the run. The electrical leads to the heaters had become badly oxidized, and they failed when power was increased. As a

result, the plenum temperature averaged between 500 and 600°C. Regardless, a maximum feed rate of 140 L/h was maintained over one 12-h period. A run summary is given in Table 45.

TABLE 45. LFCM-7 Run Summary

Parameter	Characteristic
Run Time (Elapsed)	110.9 h
Actual Melter Feeding Time	95.9 h
Total Glass Produced	4480 kg
Total Feed Slurry Used	9752 L
Avg. Glass Production Rate (Based on Actual Feeding Time)	46.7 kg/h (44.5 kg/h-m ²)
Maximum Sustained Glass Pro- duction Rates	
Without Lid Heating	39.8 kg/h-m ² (13-h period)
With Lid Heating	61.3 kg/h-m ² (12-h period)
Typical Melter Operating Parameters (entire period with lid heating)	
Feed Rate	127 L/h
Glass Production Rate	55.6 kg/h-m ²
Electrode Power	150 kW
Lid Heater Power ^(a)	17 kW
Lid Liner Wall Temperature	463°C
Avg. Glass Temperature	1146°C
Off-Gas Cooling Water Spray Flow Rate	10.6 L/h
Off-Gas Temperatures (after water cooling)	302°C

(a) Only half of the lid heater panels were used.

Figure 37 shows the feed rate versus time plotted throughout the experiment. The data points are values averaged over 2-h periods and are based on feed tank dropout data. Without lid heat, the feeding rates held fairly

FIGURE 37. LFCM-7 Feed Rate

constant. Two sharp turndowns on August 25, one at the beginning of the day and the other towards the end, were due to feed outages caused by the pump plugging.

The discontinuity in the feed rate on August 27 from 0930 to 1730 h was initiated by the melter's suddenly and unexpectedly pressurizing. The melter was maintained in an idling mode until possible causes of pressurization were investigated. It was determined that no system component had failed, so feeding to the melter was resumed.

The plenum space temperature during operation without lid heat was $\sim 290^{\circ}\text{C}$. As can be seen in Figure 38, the plenum temperature slowly dropped as the cold cap was built up. Spikes in the plenum temperature were due to feed outages allowing the cold cap to melt down, thus permitting the more exposed glass surface to radiate its heat to the plenum space. With lid heating, the plenum temperature was in the range of 450 to 550°C , depending again on the condition of the cold cap. Also shown in Figure 38 is the off-gas temperature measured out-of-sight of the melter. An air-atomized water-cooling spray nozzle (Figure 39), which sprayed just inside the plenum space, maintained the off-gas temperature at $300 \pm 100^{\circ}\text{C}$.

The voltage, current, and resultant power to the primary electrodes are given in Figure 40. Without lid heating and lower feed rates, the power to the electrodes averaged 69 kW, with 67 to 96 V and 730 to 1050 amps. With lid heat boosting, the power to the primary electrode averaged 116 kW with 65 to 110 V and 950 to 1630 amps. The operation of the primary electrodes was through resistance feedback control. The temperature of the electrodes ranged from 950 to 1050°C .

The secondary electrodes (lower set) operated on constant current feedback control. The power to the secondary electrodes averaged 40 kW without lid heat boosting and 35 kW with boosting. These electrodes ran at $\sim 850^{\circ}\text{C}$. An energy balance for the melter is shown in Table 46.

FIGURE 38. LFCM-7 Plenum and Off-Gas Temperatures

FIGURE 39. LFCM-7 Off-Gas Cooling Nozzle

FIGURE 40. LFCM-7 Primary Electrode Data

TABLE 46. LFCM-7 Energy Balance

Energy Inputs	
Primary Electrodes	+151.7 kW
Secondary Electrodes	+27.1 kW
Lid Heaters	+17.0 kW
TOTAL	+195.8 kW
Energy Outputs	
Water Jacket Cooling	-24.1 kW
Steam in Off Gas	-111.4 kW
Inleakage of Air	-11.2 kW
Molten Glass Out	-28.4 kW
Freeze Valve	-7.3 kW
Melter Lid	-2.2 kW
Feed Nozzle Cooling	-1.5 kW
TOTAL	-186.1 kW

The average glass temperature stayed, for the most part, within the set limit of $1150 \pm 25^{\circ}\text{C}$. The average bulk glass temperature is an average of vertical glass temperatures measured 6.4, 12.7, 19.0, 25.4 and 31.8 cm from the melter floor. Figure 41 shows the glass temperatures throughout the run.

Glass temperature profiles were taken six times during the experiment and are shown in Figures 42 and 43. Table 47 contains data pertaining to each plot. The August 24 profile on 0100 h (Figure 42) was made just prior to starting feeding slurry into the melter, so this profile is somewhat consistent with an idling condition. However, the power to both electrodes was steadily increased until the feed was started. The glass temperature was fairly constant down to the floor, where the temperature dropped off sharply to $\sim 1090^{\circ}\text{C}$.

The next profile was made on August 24 at 2300 h. At this time, a feed rate of ~ 1.1 kg/min was maintained and a cold cap was established, which resulted in an 80 to 90% coverage of the surface. From the very hot glass surface temperature of 1171°C , it is apparent that glass mixing was good, and that electrical current paths through the glass were maintained close to the surface.

FIGURE 41. LFCM-7 Glass Temperatures

FIGURE 42. LFCM-7 Glass Melt Temperature Profiles Without Plenum Heat Boosting

FIGURE 43. LFCM-7 Glass Melt Temperature Profiles With Plenum Heat Boosting

TABLE 47. Melter Data For Glass Temperature Profiles in Figures 42-43

Date/Time	Electrode Power (kW)		Plenum Temperature (°C)	Feed Rate (kg/min)	Melter Condition
	Primary	Secondary			
08/24 - 0100	82	47	519	0	No cold cap
08/24 - 2300	62	39	289	1.1	80-90% surface coverage
08/26 - 0100	133	40	520	1.9	lid heaters just started 90-100% surface coverage
08/26 - 0300	105	38	535	1.8	90% surface coverage
08/27 - 0300	65	39	547	1.8	40-60% surface coverage
08/28 - 0300	131	21	502	2.3	90% surface coverage decreasing secondary power

The temperature profile taken August 26 at 0100 h shows the glass temperatures shortly after the plenum heat boosting was started. The feed rate was ~1.9 kg/min at this time. The glass surface temperature had dropped much below that of the previous day. Also, the floor temperature had become much hotter. The cooler upper glass temperatures were probably due to the higher feed rate. The rate of heat withdrawal by the cold cap from the glass was higher than the rate of heat transport to the glass surface by both conduction and convective mixing. The cooling trend may have caused the electrical current profile to shift deeper into the glass, causing the floor to become hotter.

The profiles shown in Figure 43 were taken while plenum heat boosting was used. Throughout the last three days, the glass profiles were fairly consistent and steadily flattened out. The floor temperature, however, continued to rise despite lowering the power to the secondary electrodes. It was also noted that increasing the power to the primary electrodes caused the floor temperature to rise. The hot floor was not noticed in LFCM-6 or any other previous tests. It may have resulted from a buildup of metal or conductive sludge on the floor. After the test, the floor temperatures returned to normal levels typical of an idling melter. During LFCM-6, the ratio of primary electrode power to secondary electrode power was about two. During the last three days of LFCM-7, this ratio sometimes reached six, but was usually around three. The manual power skewing capabilities with this design are limited due to the

depth of the tank, which limits the separation between the primary and secondary electrodes to 10 cm.

Following this run, the LFCM was shut down and drained because no further testing was planned with this melter. Draining of the melter using its slit-freeze drain valve was accomplished in 3.25 h. At a rate of ~398 kg/h, 1290 kg of glass were drained.

4.8.1 Off-Gas Analysis

LFCM-7 represented the second liquid-fed melter experiment utilizing a formate-based slurry feed. Unlike the first test run (PSCM-3), LFCM-7 employed electric lid-heat boosting in order to maximize feeding rates. However, the run was structured so as to allow sampling to be conducted at various feeding rates with and without the use of lid heat. One of the major objectives of this melter run was to evaluate real time off-gas-line cleaning techniques. Consequently, the post-run examination of the off-gas line was of questionable value and, as such, was not carried out. However, qualitatively, off-gas depositions were quite light and easily removed. No formations were observed which could have grown into local off-gas-line restrictions.

Effluent sampling of LFCM-7 placed a great deal of emphasis on characterizing melter-generated aerosols. Sampling was conducted in order to establish the size distributions and concentrations of entrained particulate matter as a function of melter feeding rates. Size distribution information was obtained from a cyclone sampler consisting of a series arrangement of three cyclones and a final absolute filter. The cut points of the cyclones employed are 16 μm , 6 μm and 1 μm . The absolute final filter is designed to collect submicron fines which are able to pass through all three preceding cyclones. The data generated with this differential filtering system is summarized in Table 48. The distribution of particulates generated by LFCM-7 is clearly bimodal in nature. Compositional analysis of these size fractions, including the condensate, appear in Table 49. Clearly, the composition of the various size fractions differ markedly with the semivolatile constituents strongly concentrated in the submicron fraction. This fact suggests that the two distributions making up the overall bimodal distribution probably result from independent processes. The compositional evidence supporting this argument is necessary but, unfortunately, is not sufficient. That is, other mechanisms, however unlikely, could also be used to explain the observed compositional differences existing between the components of this bimodal distribution.

TABLE 48. LFCM-7 Differential Particulate Data

Date	Sampling Period	Wt% Versus Cut Point				Loading ^(a) (mg/L)	DF	Average Rates	
		16 μ m	6 μ m	1 μ m	<1 μ m			Glass (kg/min)	Feed (L/min)
8/24	0727 - 0925	79.5	2.0	10.2	8.3	1.1		100	--0.85
8/24	1635 - 1805	65.3	6.6	14.6	13.5	6.7		170	0.460.95
8/25	0553 - 0640	86.2	2.4	6.1	5.2	1.7		80	0.461.3
8/25	1415 - 1515	74.2	2.7	9.4	13.7	6.8		250	0.821.6
8/27	0811 - 0831	78.4	0.3	2.4	18.9	1.8		120	0.732.4
8/24-27	Average	76.7	2.8	8.5	11.9	3.5		140	----

(a) STP.

TABLE 49. LFCM-7 Elemental Distribution Across Cyclonic Sampling System

Element	Elemental Distribution (%)									
	Sample Fraction 8/25/81					Sample Fraction 8/27/81				
	16 μ m	6 μ m	1 μ m	<1 μ m	Cond.	16 μ m	6 μ m	1 μ m	<1 μ m	Cond.
Al	95.93	0.90	2.48	0.41	0.21	97.68	0	0.65	1.49	0.18
B	35.28	0.72	3.15	1.06	59.8	55.75	0	0.80	0.87	42.58
Ba	83.72	5.75	10.53	0	0	97.0	0	3.0	0	0
Ca	77.42	2.70	15.11	4.45	0.32	88.87	0	3.84	5.30	1.99
Cd	10.66	0.86	7.32	81.17	0	11.29	0	3.94	84.76	0
Ce	92.08	0	7.92	0	0					
Cr	46.40	21.70	23.31	8.59	0	98.58	0	1.42	0	0
Cs	7.49	0	5.41	87.10	0	13.79	0	2.20	84.01	0
Cu	82.64	4.85	4.23	8.27	0	60.83	0	4.99	34.19	0
Fe	72.12	2.56	16.97	3.14	0.20	92.19	0	3.98	3.48	0.36
La	91.95	1.48	6.09	0.48	0	98.84	0	1.16	0	0
Li	83.16	1.54	5.32	9.98	0	87.46	0	0.99	11.55	0
Mg	91.52	1.60	5.79	1.08	0	95.31	0	1.29	3.40	0
Mn	89.38	6.41	3.61	0.61	0	93.99	0	3.27	2.61	0.13
Mo	77.46	5.62	9.80	7.12	0	68.65	0	31.35	0	0
Na	68.80	1.70	5.62	23.86	0.03	66.52	0	1.25	32.15	0.08
Nd	93.45	0	6.55	0	0	100.0	0	0	0	0
Ni	0	0	0	0	100.0	0	0	0	0	100.0
Pb	0	0	0	0	0	0	0	5.62	94.38	0
Sb	100.0	0	0	0	0	0	0	0	0	0
Se	56.89	1.92	11.36	29.83	0	87.25	0	2.85	9.90	0
Si	91.86	1.79	5.61	0.60	0.14	96.71	0	1.15	1.24	0.89
Sr	77.57	2.80	19.62	0	0	95.56	0	4.44	0	0
Te	5.48	0.39	3.22	90.91	0	0	0	4.97	95.03	0
Ti	91.19	1.80	6.04	0.96	0	97.88	0	0.98	1.14	0
Zr	90.58	1.58	5.52	1.24	1.09	81.07	0	0.98	2.28	15.68

Also presented in Table 48 are total particulate off-gas loadings and total melter entrainment DFs. Neither of these quantities nor the size distribution data seem to be correlated with feeding or glass-production rates that occurred during the various sampling periods. However, sampling times were relatively short and feeding rates were fairly erratic.

Total aerosol loading of the off-gas stream was also assessed at various times during the run by diverting all off-gas flow through a preweighed HEPA filter. The net (dry) weight gains of these filters were then compared with the quantity of glass produced during the filtration periods to obtain total melter DFs. Concentration information was obtained through use of total off-gas flow rates, which were recorded continuously throughout the run. This data is presented in Table 50 along with glass production rates. Again, no clear correlation appears to exist relating aerosol emission rates with feeding or glass production rates. Moreover, the average DF value established with these filters (130) is lower than the values achieved by the two previous LFCM experiments, which were 600 (LFCM-4) and 170 (LFCM-6). However, it compares quite well with the cyclonically-derived value of 140.

TABLE 50. LFCM-7 HEPA Filtration Data

Date	Sampling Period	Sample Weight (g)	Glass Rate (kg/min)	Glass Weight (kg)	Loading ^(a) (mg/L)	DF
8/24	0805 - 1013	390	0.25	32	0.45	82
8/25	0648 - 0815	370	0.59	51	0.63	137
8/25	2233 - 2336	360	0.97	61	0.84	170
8/27	0900 - 0938	420	0.98	37	1.6	89
8/28	0442 - 0534	360	1.1	57	1.0	158
8/24-28	Average	---	--	--	0.9	130

(a) Average flow (STP).

Additional off-gas particulate loading data was also generated by the prefilter associated with the off-gas sampling train apparatus. This data is summarized in Table 51. These particulate samples, unlike those previously discussed, were collected over relatively long periods of time and should be less sensitive to the erratic nature of the LFCM-7 feeding rates. As with the previous data, off-gas loading and DFs are compared to feeding and glass production rates averaged over the sampling intervals. This data does exhibit

a weak correlation between feeding or glass production rates and total particulate off-gas loading conditions. However, the quantity of entrained material per unit weight of feed processed (DF) appears to be more or less independent of the feeding rates. In other words, this suggests that DFs are independent of the extent of development of the melter cold cap.

TABLE 51. LFCM-7 Particulate Data From Off-Gas Sampling Train

Date	Sampling ^(a) Period	Net Sample Weight (g)	Particulate		Average Rates	
			Loading ^(b) (mg/L)	DF	Glass (kg/m)	Feed (L/m)
8/24	0913 - 1615	2.7	1.9	50	0.34	0.98
8/25	0840 - 1530	3.2	2.2	65	0.59	1.2
8/26	0833 - 1804	3.8	3.8	45	0.79	1.8
8/27	0857 - 1806	2.8	3.8	65	0.70	2.0
8/28	0830 - 1246	1.6	2.0	130	1.6	2.7
8/24-27	Average	--	2.7	71	--	--

(a) Not continuous sampling.

(b) STP.

Particulate and total melter feed component DFs associated with the LFCM-7 test have been established for most elemental constituents. This data appears in Table 52. A comparison of average LFCM-7 DFs with results obtained from previous melter experiments is presented in Table 53. Clearly, melter effluent emission rates associated with the LFCM-7 experiment were, with few exceptions, the highest ever recorded since effluent studies began in August of 1980. However, LFCM-7 melter performance with regard to Cs is better than has been achieved in the past three melter tests.

TABLE 52. LFCM-7 Particulate and Total Feed Component DFs

Element	Melter DFs											
	8/24		8/25		8/26		8/27		8/28		Ave.	
	Part	Total	Part	Total	Part	Total	Part	Total	Part	Total	Part	Total
Al	136	132	92	91	71	71	139	139	540	530	200	190
B	56	44	72	53	59	46	103	80	260	150	110	75
Ca	41	40	52	52	36	36	63	63	120	120	62	62
Cd	11	10	8.1	8.1	5.3	5.3	6.6	6.6	10	10	8.2	8.0
Cs	16	16	24	24	9	9	4.5	4.5	5.9	5.9	12	12
Fe	48	48	65	65	49	48	64	63	130	120	71	69
La	--	--	92	92	69	69	109	109	290	290	140	140
Li	52	57	66	66	55	55	77	77	200	190	90	89
Mg	79	78	89	89	66	66	106	106	270	270	120	120
Mn	46	46	64	64	44	44	64	64	162	160	76	76
Na	50	50	65	64	43	43	50	50	93	91	60	60
Ru	--	--	--	--	16	16	--	--	--	--	16	16
Sb	54	54	86	86	62	62	--	--	--	--	67	67
Se	--	--	1	1	--	--	--	--	--	--	1	1
Si	70	70	82	82	65	65	102	101	270	260	120	120
Sr	35	35	44	44	32	32	45	45	140	140	55	55
Te	6.4	6.3	3.3	3.3	4	4	6.1	6.1	8.5	8.5	5.7	5.6
Ti	73	73	91	91	66	66	106	106	280	280	120	120
Zr	78	78	94	94	63	63	95	95	270	270	120	120

TABLE 53. LFCM-7 Comparative DFs

Element	LFCM-7 Avg DF	DF Ratio						
		LFCM-7	LFCM-7	LFCM-7	LFCM-7	LFCM-7	LFCM-7	LFCM-7
		PSCM-3	LFCM-6	PSCM-2	LFCM-4	PSCM-1	LFCM-3	LFCM-2
Al	190	0.03	0.58	0.13	0.35	0.02	0.08	0.04
B	75	0.38	0.83	0.47	0.58	0.36	0.62	0.29
Ca	62	0.06	0.34	0.10	0.24	0.03	0.03	0.08
Cd	8	--	0.10	0.17	0.11	0.04	0.10	--
Cs	12	3.2	1.2	4.0	0.21	0.24	1.7	0.30
Fe	69	0.04	0.30	0.10	0.27	0.02	0.10	0.16
Li	89	0.03	0.56	0.10	0.25	0.01	0.05	0.18
Mg	120	0.01	0.46	0.13	0.34	0.01	0.07	0.25
Mn	76	0.02	0.23	0.12	0.18	0.01	0.02	0.05
Na	60	0.07	0.67	0.46	0.18	0.07	0.21	0.18
Ru	16	--	1.23	0.33	0.62	0.50	0.27	2.3
Sb	67	--	--	0.67	0.04	--	--	0.14
Se	1	--	--	--	--	--	--	0.004
Si	120	0.04	0.43	0.08	0.29	0.01	0.05	0.13
Sr	55	0.09	0.19	0.09	0.27	0.01	0.04	0.15
Te	5.6	0.18	0.03	0.10	0.09	0.03	0.02	0.09
Ti	120	0.03	0.71	0.09	--	--	--	0.11

Gross melter entrainment has been measured by several different approaches and at many different feed rates during LFCM-7. Table 54 is a collection of all the gross DF values established during this experiment.

TABLE 54. LFCM-7 Gross DF Values

Date	Sampling		Particulate		Average Rates	
	Period	Type	Loading (mg/L)	DF	Glass (kg/m)	Feed (L/m)
8/24	0727 - 0925	C	1.08	120	--	0.85
8/24	0805 - 1013	HEPA	0.45	82	0.25	--
8/24	0913 - 1615	S	1.90	50	0.34	0.98
8/24	1635 - 1805	C	0.67	170	0.46	0.95
8/25	0553 - 0640	C	1.70	80	0.46	1.3
8/25	0648 - 0815	HEPA	0.63	137	0.59	--
8/25	0840 - 1530	S	2.2	65	0.59	1.2
8/25	1415 - 1515	C	0.67	245	0.82	1.6
8/25	2233 - 2336	HEPA	0.84	170	0.97	--
8/26	0833 - 1804	S	3.8	45	0.79	1.8
8/27	0811 - 0831	C	1.8	120	0.73	2.4
8/27	0900 - 0938	HEPA	1.6	89	0.98	--
8/27	0857 - 1806	S	3.8	65	0.70	2.0
8/28	0442 - 0534	HEPA	1.0	158	1.1	--
8/28	0830 - 1246	S	2.0	130	--	2.7
8/24-28	Average	ALL	1.61	115		

C = Cyclone.

S = Scrub Train.

HEPA = Absolute Filtration.

Due to the potential hazards associated with melter-generated H_2 and CO , noncondensable gas monitoring was conducted throughout the duration of LFCM-7. As in PSCM-3, the gas samples were extracted and analyzed by a GC at the exhaust of the venturi ejector. The compositional data generated with this sampling system is graphically illustrated in Figure 44. The inleakage rates for LFCM-7 were much greater than those occurring during the previous PSCM-3 test. Consequently, CO and H_2 concentrations were never much of a safety concern throughout the run. In fact, H_2 was hardly detectable until one of the larger off-gas leaks was eliminated toward the end of the run. As in PSCM-3, H_2 concentrations were established using a gas mass spectrometer. These data, along with a condensation of the results appearing in Figure 45, are presented in Table 55. Again, a H_2 concentration versus time trend curve has been constructed from the GC data (see Section 2.2). The curve, displayed

FIGURE 44. LFCM-7 Noncondensable Off-Gas Concentrations

FIGURE 45. H₂ Concentration Variance Throughout LFCM-7

in Figure 45, is designed to give the reader a semiquantitative notion of the way in which H_2 concentrations varied throughout the LFCM-7 experiment. The reader is cautioned that the correlation presented in this figure is nonlinear.

TABLE 55. LFCM-7 Off-Gas Composition

Day	Date Type	Molar Composition, %					
		Dry Basis					
		CO ₂	O ₂ (a)	N ₂	CO	H ₂	H ₂ O
8/23	Avg.	0.49	21.6	77.9	<20 ppm	--	--
8/24	Avg.	0.43	21.6	77.8	0.12	--	22
8/25	Avg.	0.47	21.6	77.9	0.12	--	27
8/26	Avg.	0.91	21.4	77.5	0.18	--	35
8/27	Avg.	0.87	21.4	77.6	0.13	0.44	41
8/28	Avg.	1.19	21.3	77.4	0.21	0.63	46
8/23-28	High	2.2	21.8	78.8	0.44	0.63	46
8/23-28	Low	0.03	20.9	76.3	<10 ppm	0.40	22

(a) Includes ~1% Ar.

The sampling difficulties encountered with the SO₂ monitor during PSCM-3 were eliminated, allowing SO₂ monitoring to be conducted during LFCM-7. However, no significant responses were recorded during the sampling periods employed. This null result places an upper concentration limit of SO₂ in the melter exhaust at 50 ppm.

Due to the quiescent nature of PSCM-3 flow rate behavior, a flow transducer capable of measuring the average flow rate was utilized in LFCM-7, unlike LFCM-6. It was hoped that the dynamic range of this transducer would be adequate for any surges which might be generated by this formate-fed lid-boosted melter. This, indeed, did turn out to be the case, where only a single significant event occurred in ~120 h of melter operation. The event did, however, cause melter pressurization, which initiated emergency venting. The maximum flow recorded during this event was a factor of 3 greater than the average flow. It should be noted that a partially-loaded HEPA filter (ΔP ~10 in.) was present in the off-gas line when this event occurred. In addition, the water present in a seal pot, which was blown into the hot off-gas line by the pressurization, accounted for some of the flow recorded during this event. A summary of all pertinent off-gas flow rate data generated during LFCM-7 appears in Table 56.

TABLE 56. LFCM-7 Flow Rate Behavior

Flow Rate (scfm)			
Steady State			Surges
Minimum	Maximum	Average	Maximum
190	270	240	710

4.8.2 Corrosion Analysis

Rapid corrosion of the metal parts exposed to the LFCM plenum has occurred. To study this problem, corrosion sample coupons of the following materials were suspended into the LFCM plenum (see Figure 46):

- 304L SS
- Inconel-600
- Inconel-617
- Inconel-625
- Inconel-690
- Titanium
- Tantalum
- 304L SS coated with various oxides.

CORROSION SAMPLES

FIGURE 46. Samples Suspended from LFCM Lid

The coated sample coupons were grit-blasted before coating, and the samples were coated with a Ni-Cr base coat before the oxide coat. The coatings were applied by a plasma-torch spray system. Twelve coupons 3.8 and 3.2 x 0.32 x 7.62 cm of 304L SS were coated with various basebond coatings. Six of the coupons received second coatings of various oxides. Two uncoated reference samples were also installed. Coatings and coating compositions are shown in Tables 57 and 58.

After the LFCM-7 run, the corrosion samples installed in the melter plenum were removed and examined visually. The samples were exposed to the melter gases during two days of idling, five days of feeding and three more days of idling. The visual results of the solid samples are described in Table 59.

TABLE 57. LFCM-7 Protective Coating on Off-Gas Samples

Sample No.	Bond Coating		Outer Coating		Surface Preparation	
	METCO ID	Thickness (μm)	METCO ID	Thickness (μm)	Cleaned	Blasted
1	--	--	--	--	X	
2	--	--	--	--		X
3	43F-NS	380	--	--	X	
4	43F-NS	380	--	--		X
5	43C	250	--	--	X	
6	43C	250	--	--		X
7	443	250	--	--	X	
8	443	250	--	--		X
9	443	250	105SF	250		X
10	443	250	105	250		X
11	443	250	106	250		X
12	443	250	202NS	250		X
13	443	250	201	250		X
14	443	250	201B-NS-1	250		X

TABLE 58. Spray Powder Characteristics for Corrosion Coupons

Spray Powder	Powder ID	Constituent	Percent	Range, μm	Comments
Nickel-Chromium Alloy	43F-NS	Ni	80	-53 +10	Best single coating for oxidation resistance to 980°C.
		Cr	20		
Nickel-Chromium Alloy	43C	Ni	80	-105 +10	Good bond coat + O_2 barrier to 980°C.
		Cr	20		
Nickel-Chromium/ Aluminum Composite	443	Al	60	-120 +45	Best bond coat + O_2 barrier to 980 °C.
		Ni-Cr	Balance		
Ceramic	105SF	Al_2O_3	98.5	-25 +05	Wear resistant.
		SiO_2	0.5		
		Other Oxides	1.5		
White Alumina	105	Al_2O_3	98.5	-53 +15	Resists erosion from 840 to 1650°C. Wear resistant.
		SiO_2	1.0		
		Other Oxides	Balance		
Chromium Oxide	106	Cr_2O_3	98	-90 +15	Resists abrasion, cavitation & erosion to 540°C. Insoluble in acids, alkalis and alcohol.
Zirconium Oxide Composite	202NS	ZrO_2	80	-90 +10	Resists thermal shock and particle erosion to 1650°C.
		Y_2O_3	20		
Zirconium Oxide	201	ZrO_2	80	-90 +10	Resists thermal shock and particle erosion above 845°C.
		CaO	5		
		Al_2O_3	0.5		
		Other Oxides	Balance		
Zirconium Oxide Composite	201B-NS-1	ZrO_2	92		Resists thermal shock and particle erosion above 845°C.
		CaCO_3	8		

TABLE 59. LFCM-7 Metallic Corrosion Sample Results

<u>Material</u>	<u>Visual Observation</u>
Tantalum	No longer on sample rack; disappeared
Titanium ^(a)	Large flakes, deep pits; badly corroded
Inconel-690	Discolored spots
Inconel-625	Discolored spots
Inconel-617	Discolored, green spots; obvious metal loss
Inconel-600	Many discolored spots
304 SS	Lots of flaking metal; oxidizing rapidly

(a) Only one sample. Other materials had two samples each.

The results from the coated samples indicate the importance of surface preparation, coating selection and a precisely controlled application technique on the ability of the coatings to survive the plenum atmosphere.

All the oxide-coated samples spalled severely with the exception of the Cr_2O_3 , where only a little coating was lost. Applied alone, the Ni-Cr base coat did not spall, but there was some attack at the coating surface and some physical change at the coating substrate interface. A possible explanation for the spalling is that the small coupons were heated too high during the deposition step, causing the ceramic layer to be in severe compression upon cooling. The coating, already weakened, then spalled off when cycled back up to the plenum temperature.

An SEM analysis had been performed on the corroded LFCM Inconel-601 off-gas port. The results showed a large amount of chlorine and sulfur in the crystal boundary in the middle of the pipe. The analysis also showed titanium inclusions and possibly nickel-iron-chromium spinels. The pipe was severely attacked, primarily by chlorine and sulfur. The position of the elemental analysis is shown in Figure 47-A & -B. Point 1 showed chromium, iron and nickel in decreasing order even though a general scan of a slightly corroded area showed nickel to be the major constituent, confirming that the sample was Inconel.[®] The major elements identified at Point 2 were nickel, chlorine, iron and chromium, while at Point 3 a significant amount of sulfur and little chlorine were found. This analysis indicates that chlorine and sulfur are corroding the Inconel parts, but it does not rule out the possibility of metal degradation at the high temperatures this sample experienced.

FIGURE 47. SEM Analysis of LFCM Off-Gas Pipe

Corrosion is a problem in the off-gas quencher. In a somewhat similar application, flue-gas scrubbers for coal-fired power plants, which have fluorides, chloride and SO_2 in the gas, have had many corrosion failures in their primary quencher or scrubber. The off gas and the initial quench equipment are similar to the glass melters. The melter's quencher has a recirculating solution of ~1000 ppm chlorides, 100 ppm fluorides, 500 ppm SO_4 and a pH of 3. In similar situations, this type of solution has caused excessive pitting and crevice corrosion in 316 SS, 317L SS and 304L SS. Alloys which have performed satisfactorily most of the time are Inconel-625 and Hastelloy C-276. Inconel-625 and Hastelloy C-276 should work satisfactorily except at pH <1, or where fluoride concentrations exceed the 200 ppm range. If the condensate from the melters is recycled for further processing and concentrated by evaporation, these levels could easily be exceeded. Control of pH with limestone is universally used to decrease corrosion in coal-fired plants.

During run LFCM-7, an effort was made to use steam, injected into the off-gas line, as a means of cooling the off gas as it left the melter. However, due to mechanical difficulties with the steam delivery system and the generally poor quality of the building steam, the test was not long enough to be properly evaluated. Instead, the air-atomizing water spray was used.

Various off-gas cleaning concepts were to be tried during the test; however, the deposition of material onto the off-gas line was light throughout the experiment. A mechanical vibrator and frit blaster were both tried, but the results were inconclusive. There is little doubt that a frit blaster will clean the line, but the degree of cleaning as a function of frit quantity or size is not established.

4.8.3 Glass Analysis

The composition of the glass samples taken during LFCM-7 is listed in Tables 60 and 61. Most of the oxides in the glass remained fairly constant throughout the run. The CaO concentration increased and the Fe_2O_3 concentration decreased during the last two days of the run in both the feed and glass samples. This may have been caused by a calcium impurity in the iron hydroxide. Based on a comparison of chloride and sulfur levels in the feed and glass, 70 to 90% of the chloride and sulfur remained in the glass.

Table 62 shows the results of the leach testing of the glass samples. The results of both the Soxhlet and pH 4 leach tests were similar to glass samples from previous runs.

The Soxhlet leach test is a standard leach test in which the sample is placed in deionized water and maintained at a constant temperature of 98°C . After 24 h, the sample is removed and a weight-loss determination is made. Leach rates typically decrease one to two orders of magnitude with time, so the weight loss results must be interpreted relative to other similar test data. In the pH 4 leach test, the glass is ground to a mesh size range of +60 -40. It is then put into a -200-mesh screen envelope and placed in a sodium-acetate-buffered solution of pH 4 and maintained at room temperature. The envelope is then stirred for 19 h, after which a weight loss determination is made of the remaining glass.

TABLE 60. LFCM-7 Glass Sampled for Major Oxides (Wt%)

Date	Time	SiO ₂	Al ₂ O ₃	B ₂ O ₃	CaO	Fe ₂ O ₃	Li ₂ O	Na ₂ O	MnO ₂	NiO	MgO	TiO ₂	La ₂ O ₃	ZrO ₂
8/24	1000	44.36	4.23	10.21	0.99	13.82	4.02	14.03	3.30	1.96	1.34	0.83	0.32	0.36
	1400	44.05	4.30	10.28	1.05	14.26	3.99	13.74	3.36	1.89	1.36	0.83	0.33	0.36
	2200	44.30	4.43	10.10	1.13	14.32	3.91	13.70	3.30	1.75	1.34	0.82	0.32	0.36
8/25	0600	43.98	4.60	10.02	1.13	14.32	3.99	14.01	3.27	1.64	1.33	0.82	0.32	0.36
	1400	43.68	4.58	10.09	1.25	14.97	3.85	13.52	3.43	1.56	1.35	0.85	0.32	0.35
	2204	43.98	4.61	10.16	1.36	15.18	3.67	12.99	3.46	1.47	1.36	0.87	0.34	0.37
8/26	0610	44.17	4.52	10.07	1.34	14.79	3.90	13.56	3.39	1.23	1.34	0.84	0.32	0.35
	1412	43.70	4.67	10.06	1.52	14.43	4.07	14.02	3.35	1.22	1.32	0.83	0.32	0.36
	2200	43.86	4.70	10.13	2.72	13.89	3.76	13.05	3.55	1.25	1.36	0.88	0.32	0.37
8/27	0600	43.88	4.81	10.13	3.55	12.75	3.87	13.16	3.55	1.25	1.36	0.88	0.32	0.37
	1850	44.16	4.63	10.23	4.31	13.03	3.45	11.85	3.77	1.40	1.40	0.93	0.34	0.38
	2200	44.92	4.71	10.04	4.39	12.34	3.66	12.86	3.56	1.25	1.36	0.88	0.32	0.37
8/28	0205	43.89	4.81	10.03	4.60	12.33	3.66	12.64	3.55	1.25	1.36	0.89	0.32	0.37
	0600	43.90	4.81	10.03	4.91	12.02	3.76	12.96	3.45	1.15	1.36	0.86	0.32	0.38
	0950	43.94	4.81	09.94	4.92	12.16	3.66	12.66	3.45	1.26	1.36	0.87	0.32	0.37
As Defined		45.6	5.1	10.5	1.7	12.7	4.1	13.6	3.0	0.8	1.4	0.7	0.4	0.4

TABLE 61. LFCM-7 Glass Sampled for Trace Oxides (Wt%)

Date	Time	CdO	RuO ₂	Sb ₂ O ₃	SrO	TeO ₂	Cs ₂ O	SeO ₂	Cl	S
08/24	1000	0.009	<0.001	0.042	0.026	0.012	0.029	<0.005	0.055	0.016
	1400	0.007	<0.001	0.039	0.027	0.012	0.028	<0.005	0.055	0.107
	2200	0.008	<0.001	0.043	0.027	0.012	0.037	<0.005	0.048	0.095
08/25	0600	0.008	<0.001	0.039	0.027	0.011	0.042	<0.005	0.040	0.130
	1400	0.009	<0.001	0.040	0.027	0.008	0.047	<0.005	0.031	0.121
	2204	0.009	<0.001	0.039	0.027	0.007	0.052	<0.005	0.058	0.156
08/26	0610	0.007	<0.001	0.035	0.026	0.005	0.059	<0.005	0.068	0.129
	1412	0.007	<0.001	0.033	0.026	0.005	0.055	<0.005	0.108	0.148
	2200	0.006	<0.001	0.026	0.028	0.005	0.057	<0.005	0.315	0.113
08/27	0600	0.007	<0.001	0.020	0.029	0.005	0.062	<0.005	0.535	0.106
	1850	0.009	<0.001	0.015	0.032	0.004	0.054	<0.005	0.589	0.108
	2200	0.011	<0.001	0.017	0.031	0.005	0.063	<0.005	0.693	0.104
08/28	0205	0.007	<0.001	0.017	0.031	0.005	0.053	<0.005	0.712	0.095
	0600	0.007	<0.001	0.013	0.031	0.004	0.054	<0.005	0.714	0.068
	0950	0.007	<0.001	0.013	0.031	0.005	0.054	<0.005	0.758	0.054
As Defined		0.008	0.018	0.034	0.021	0.011	0.050	0.008	0.12 ^(a)	0.03 ^(b)

(a) Based on flowsheet value, chloride only introduced as an impurity.

(b) Balance of sulfur introduced as an impurity.

TABLE 62. LFCM-7 Leach Test Results

Date	Time	Weight Percent Lost			
		Soxhlet-a ^(a)	Soxhlet-b	pH 4-a	pH 4-b
08/24	1400	1.55	1.37	61.42	60.13
08/25	1400	2.38	2.32	54.99	67.59
08/26	1412	2.64	2.66	63.90	64.72
08/27	1850	1.37	1.41	84.58	78.86
08/28	0600	1.36	1.46	90.35	77.95
Average wt% Lost		1.85		70.45	
Standard deviation		0.57		11.71	

(a) a and b are duplicate samples.

4.9 ECM MICROWAVE TESTS

Several short experiments were conducted in FY-81 to test the application of microwave energy for assisting the vitrification process. All experiments utilized the Experimental Ceramic Melter (ECM).

Initial startup of the ECM was achieved using the microwave energy from the 25-kW generator to melt a TDSM-131 black frit. Twelve kW of microwave power were used to obtain an average glass temperature of 900°C, at which point joule heating was started.

During startup, the reflected power^(a) was <10% of the total up to the point where glass temperatures were ~800°C. However, when the glass temperatures were increased to 900°C, the reflected power increased to 17%. This may have been due to a buildup of condensed volatile material on the waveguide window that isolates the melting cavity from the generator.

Two oval-shaped hot spots (~900°C) in the refractory were noted during startup when using the microwave heating. The hot spots were caused by a concentration of microwaves and were located opposite each other ~11 cm above the melt line in the K-3 and Uni-Chrome refractory vapor space walls. The occurrence of these hot spots did not adversely affect startup, nor did it appear to damage the brick.

(a) Power reflected back through the waveguide toward the microwave generator.

Preliminary results with the microwave heating are quite positive. Temperature profiles taken during the startup prior to the changeover to joule heating show slightly higher temperatures near the surface of the glass. This behavior would have a positive effect during liquid feeding by increasing the temperature below the cold cap without overheating the rest of the glass. Also, since the reflected power increased when the glass became molten, it would indicate that waves passing through the cold cap during operation would tend to be reflected from the glass and pass back through the cold cap to create a high concentration of microwaves in the cold cap, as desired.

Two short equipment tests were conducted. The first test lasted 3.5 h, during which 15.7 L of TDSM-131 slurry were fed to the melter. A 90% cold cap was allowed to develop before the microwave boosting was started. Once the microwave heating was introduced, the feed slurry no longer spread out over the surface of the melter. Instead, within 30 min, a cone was formed below the feed nozzle that built up until it reached and plugged the nozzle. This terminated the test.

During the second test, the electrode power was left at the setting required for idling the melter (~7 kW), and the microwave power was varied up to 10 kW to maintain the cold cap at 80% coverage. If any significant change in the glass temperatures (as indicated by the tank resistance) had occurred, the electrode power would have been appropriately adjusted. No adjustment was necessary during the test. The test lasted 3 h, during which 14.2 L of slurry was fed. This method of operation was stable. The tests used the TDSM-131 composition at a concentration of 522.2 g solids/L (475.5 g oxides/L).

4.10 LAB-SCALE SC/ICM TESTS

During FY-1981, 12 experiments (Holton 1981) were conducted within the LSSC/ICM to study the behavior of mercury and iodine during vitrification of simulated Savannah River Plant waste. The behavior of mercury and iodine during the vitrification process is of concern. Because of the high concentrations of mercury present in the waste (0.1 to 2.8 wt%), mercury will react with iodine and other halogens present in the waste during vitrification, forming volatile compounds that will place a particulate load in the vitrification system off gas.

The experimental study characterized the chemical and physical behavior of mercury during vitrification. The behavior of mercury, as influenced by the following three process variables, was studied:

- iodide-to-mercury molar ratio in the simulated SRP waste feed
- vitrification system outlet off-gas temperature
- oxygen concentration (O_2) in the vitrification system atmosphere.

4.10.1 Experimental Design

The experimental approach was based on a Yates 2^3 experimental design, shown in Figure 48. The three study variables (iodide to mercury molar ratio, temperature to vitrification system off gas and oxygen concentration of vitrification off gas) form 8 nodes in the 2^3 experimental design. The iodide-to-mercury ratio in the simulated waste was controlled at 0.10 and 0.90 along each of two experimental planes; the off-gas outlet temperature of the vitrification system was controlled at 300 and 600°C along each of two experimental planes; and the vitrification system atmosphere was controlled at a condition where virtually no free oxygen was present and at a condition where the oxygen concentration was approximately atmosphere. Four experiments, indicated by the shaded nodes in Figure 48, were repeated to improve experimental certainty.

FIGURE 48. Yates 2^3 Experimental Design for Mercury Study

4.10.2 General System Behavior

Some generalizations can be concluded about the behavior of mercury during vitrification of alkaline Purex waste. Essentially all of the mercury is volatilized from the vitrification system. Approximately 90% of this mercury reacts in the gas phase with other chemical components in the system (predominately iodine, chlorine and oxygen) to form a dense particulate. The remaining 10% of the mercury is recovered as metallic mercury. Mercury was detected in the glass product; however, its concentration was $<5 \times 10^{-4}$ wt%. The majority of this mercury volatilized from the vitrification process was recovered by the venturi scrubber (20 to 50%), and lesser quantities were recovered in the cyclone (0.5 to 3%) and condenser (1 to 5%). A large fraction (37 to 90% of Hg in original waste) of mercury was not recovered in the scrub or condensate solutions. The unrecovered mercury was deposited within the off-gas piping as mercury and mercury compounds formed from reaction with chlorine, iodine and oxygen. The off gas leaving the condenser was cooled to a temperature of 7 to 13°C. The condenser, acting as a cold trap (mercury vapor pressure <0.001 mm Hg), is believed to have contained all the mercury within the off-gas system.

Mercury recovered from the vitrification system off gas formed either a dense solid or mercury globules. Particulate solid recovered by the venturi and cyclone scrubbers were comprised primarily of mercury halide and oxide compounds. Mercury recovered by the condenser was primarily metallic mercury formed by condensation of mercury vapor. These two different forms of mercury indicate that effective mercury removal from the vitrification off gas will require both particulate scrubbing and condensation.

The fate of iodide in the vitrification and off-gas system was strongly influenced by the oxygen content of the system. As shown in Figure 49, iodide retention in the glass formed varied from 27 to 55% when the vitrification system atmosphere contained a small oxygen concentration (<1 vol%). Iodide retention in the glass was reduced to 3 to 15% when the oxygen concentration of the vitrification system was $\sim 20\%$. Uncertainties in the experimental data did not allow any conclusions to be drawn from the variation in iodide content in the glass as a function of vitrification system outlet gas temperature or iodide-to-mercury ratio in the alkaline waste feed. Differences in the amount of iodide retained in the glass between the two atmospheric conditions

suggest that iodide volatilization from the vitrification process is a function of oxygen content in the vitrification off gas. Iodide and chloride, which exhibit similar behavior, react with oxygen to form volatile iodine and chlorine.

FIGURE 49. Percent Iodide Retention in Glass for Experiments Performed in Mercury Study

Iodide can react in basic solutions to form iodine, which has a low solubility ($\sim 10^{-3}M$) in the solution. Iodine evolution from the slightly basic waste solution is, therefore, possible; however, this does not explain the significant difference in iodide retention in the vitrous product with change in vitrification system atmosphere.

Once volatile iodine and chlorine are formed, they will be removed from the process and potentially react with mercury metal, which is also believed to be formed in the gas phase. Iodide and chloride not converted to volatile iodine or chlorine will remain in the glass as a salt, such as NaI and NaCl.

Recovery of iodine from the vitrification system off gas was low. Iodine losses ranged from 30 to 75%, dependent upon the atmospheric conditions as

discussed before. It is believed that the majority of the unrecovered iodide is combined with mercury as solid deposits in the off-gas piping. The only significant iodine trapping mechanism is reaction with mercury in the gas phase to form a semivolatile compound (probably HgI_2), which can be removed from the off gas by scrubbing. Iodine recovery efficiencies by reaction with mercury ranged from 20 to 50%, based on the collected solids only. Recovery efficiencies were not significantly dependent upon the vitrification system outlet gas temperature. However, the iodine recovery efficiency was found to be dependent upon the iodide-to-mercury ratio in the simulated waste. Table 63 illustrates these results.

TABLE 63. Recovery of Iodide by Venturi Scrubber

<u>Oxygen Concentration in Vitrification System Atmosphere (vol.%)</u>	<u>Molar Ratio I/Hg in Simulated Waste</u>	<u>Percent Recovery in Venturi</u>
~20	0.1	39 to 51
	0.9	21 to 28
~ 0	0.1	32 to 38
	0.9	5 to 6

Iodide retention in solids recovered from the venturi scrubber tank is significantly reduced at high iodide-to-mercury ratios (0.90) in the simulated waste. The iodide retention in the glass did not vary significantly with the iodide-to-mercury ratio in the waste (refer to Figure 49). This suggests that there is competition between iodine and other compounds for reaction with mercury. These other chemical species are probably oxygen and chlorine. The lack of dependence of iodide recovery on the vitrification system temperature is important because this confirms that the reaction kinetics between mercury and iodine are fast.

4.10.3 Characteristics of Mercury Solids

The majority of the mercury recovered from the vitrification off gas condensed to form a dense, finely-divided solid. Mercury solids were formed in all experiments conducted; however, the chemical composition of the solids varied between each experiment. Fluoride was not detected in the mercury solids. The physical characteristics of the mercury solids were identified

from x-ray diffraction, scanning electron microscopy and x-ray microprobe analysis. The mercury concentration in the solids was determined by x-ray fluorescence, the iodide concentration by neutron activation analysis and the chloride concentration by ion chromatography. Unidentified material in the mercury solids is thought to be comprised of oxygen and water.

Mercury solids were also recovered from the cyclone condensate. The quantity of these solids was small (<1 g), such that chemical analysis of these solids was not practical. The cyclone solids appeared to be very similar in physical appearance to the venturi solids. It was assumed the cyclone solids had the same chemical composition as the venturi solids for material balance purposes. Metallic mercury was the primary mercury species recovered from the condenser condensate.

The chemical composition of the mercury solids for eight different experiments conducted is shown graphically in Figure 50 for mercury, in Figure 51 for iodide and in Figure 52 for chloride. The axis for iodide-to-mercury molar ratio in the simulated waste and off-gas outlet temperature is approximate, based on average values.

FIGURE 50. Mercury Composition of Off-Gas Solids Collected During Experiments

- VITRIFICATION SYSTEM ATMOSPHERE AIR
- VITRIFICATION SYSTEM ATMOSPHERE, 95% ARGON 5% HYDROGEN

FIGURE 51. Iodide Composition of Off-Gas Solids Collected During Mercury Study Experiments

- VITRIFICATION SYSTEM ATMOSPHERE AIR
- VITRIFICATION SYSTEM ATMOSPHERE, 95% ARGON, 5% HYDROGEN

FIGURE 52. Chloride Composition of Off-Gas Solids Collected During Mercury Study Experiments

There are significant differences in the chemical composition of the mercury solids in the waste, which are related to the process operating variables, the vitrification system atmosphere, the outlet gas temperature and the iodide-to-mercury molar ratio. As shown in Figure 50, the mercury concentration of the mercury solids was 75 to 85 wt% when there was essentially no oxygen present in the vitrification off gas. The mercury concentration was reduced to 65 to 75 wt% when atmospheric concentrations (~20 vol%) of oxygen were present in the vitrification off gas. The difference was due to the low oxygen concentration present in the vitrification off gas, which retained a greater fraction of iodide and chloride in the glass, being unavailable to react with mercury in the gas phase. It cannot be deduced from the chemical composition of solids whether or not there was less mercury as oxide in the solids formed (in experiments performed with very little oxygen present), as compared to the experiments performed with ~20 vol% oxygen present. The key to drawing this conclusion is in characterization of the unidentified solid components of the mercury solids. It is believed that the unidentified chemical species are principally oxygen and water.

The iodide and chloride concentrations in the mercury solids were greater in the experiments conducted with atmospheric concentrations of oxygen present in the vitrification system. This was the result of two phenomena: First, the iodide and chloride are converted to volatile iodine and chlorine to a greater extent when large quantities of oxygen are present; and secondly, the higher relative concentrations of iodine and chlorine in the gas phase react with mercury to produce higher concentrations of mercury-halide compounds.

The mercury solids recovered from the scrub solution were identified as HgI (or Hg₂I₂) and HgCl (or Hg₂Cl₂) by x-ray diffraction analyses. These two compounds are relatively insoluble and are in equilibrium with Hg, HgI₂ and Hg, HgCl₂, respectively. The equilibrium constants for these reactions are summarized below.

$$\frac{[\text{Hg}] [\text{HgI}_2]}{[\text{Hg}_2\text{Cl}_2]} = 2.2 \times 10^{-3}$$

$$\frac{[\text{Hg}] [\text{HgCl}_2]}{[\text{Hg}_2\text{Cl}_2]} = 8.3 \times 10^{-6}$$

The reaction equilibria between Hg , Hg_2I_2 and HgI_2 ; or Hg , Hg_2Cl_2 and HgCl_2 are disproportionate. The mercuric form (Hg^{+2}) is readily soluble by complexation with excess chloride or iodide. However, because mercury metal is essentially insoluble in water (10^{-7}M @ 25°C), the disproportion can occur only to a very limited extent, explaining the small equilibrium constants. It is thought that HgI_2 and HgCl_2 are the chemical species formed in the gas phase. Upon quenching the off gas by the scrub solution or condenser, HgI_2 disproportionates to Hg_2I_2 . A similar mechanism is postulated for HgCl_2 and Hg_2Cl_2 . The HgI_2 compound is more stable than Hg_2I_2 in the gas phase; the opposite is true in the liquid or condensed phase.

Figure 53, from Experiment No. 1, displays the difference in physical structure between the HgCl and HgI particles. The HgCl compound is comprised of particles which are crystalline in character (Point 1). The HgI compound is comprised of particles which are largely amorphous in character (Point 2). No metallic mercury was found in the sample. The reason for this is that mercury has completely reacted with the halogens (chloride and iodide) and oxygen present in the system. Mercury is the limiting reactant in this system. HgI comprises ~65% of the sample and HgCl comprises ~22% of the solid sample. The remaining weight fraction is thought to be HgO or water.

FIGURE 53. Photograph of Mercury Solids Collected From Venturi Solution, Experiment No. 1, Showing HgCl and HgI Particulate (10,000X)

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