MASTER

Investigation of Corrosion Experienced in a Spray Calclner/Ceramic Melter Vitrification System

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August 1980

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Pacific Northwest Laboratory
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VITRIFICATION SYSTEM

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SUMMARY

Sponsored by the Department of Energy, the Pacific Northwest Laboratory has been operating a large-scale spray calciner/ceramic melter vitrification system to test simulated high-level radioactive defense waste compositions representing those now stored at the Savannah River Plant in South Carolina. One of the objectives of these studies is to test extreme conditions on a scale large enough where meaningful conclusions can be made. After periodic testing over a 2-yr period, sufficient corrosion was noted on various parts of the vitrification system to warrant its disassembly and inspection.

A majority of the 316 SS sintered metal filters on the spray calciner were damaged by chemical corrosion and/or high temperature oxidation. Inconel-601 portions of the melter lid were attacked by chlorides and sulfates which volatilized from the molten glass. The refractory blocks, making up the walls of the melter, were attacked by the waste glass. This attack was occurring when operating temperatures were greater than 1200°C. The melter floor was protected by a "sludge" layer and showed no corrosion. Corrosion to the Inconel-690 electrodes was minimal, and no corrosion was noted in the offgas treatment system downstream of the sintered metal filters.

It is believed that most of the melter corrosion occurred during one specific operating period when the melter was operated at high temperatures in an attempt to overcome glass foaming behavior. These high temperatures resulted in a significant release of volatile elements from the molten glass, and also created a situation where the glass was very fluid and convective, which increased the corrosion rate of the refractories. Specific corrosion to the calciner components cannot be proven to have occurred during a specific time period, but the mechanisms of attack were all accelerated under the high-temperature conditions that were experienced with the melter.

Operation of similar melters at high temperatures is not recommended using glass of the composition used in these tests. A review of the materials of construction has been made, and it is concluded that with controlled operating

conditions and better protection of some materials of construction corrosion of these systems will not cause problems. Other melter systems operating under similar strenuous conditions have shown a service life of 3 yr.

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INTRODUCTION

The immobilization of radioactive waste by forming it into a glass or vitreous form has been under study at Pacific Northwest Laboratory (PNL) at Richland, Washington, for a number of years. A recent concept has been to calcine the waste and feed the resultant dry powder into an electric-heated (Joule principle) ceramic-lined melter. A large-scale spray calciner/ceramic melter system under study at PNL tested simulated nuclear wastes representative of those stored at the Savannah River Plant located in South Carolina. After ~2 yr of testing, an unexpectedly large amount of corrosion was discovered on the refractory blocks of the melter, the melter lid, and the filters of the spray calciner. Although corrosion was a known consideration, the extent was more than predicted. A study was undertaken to document this corrosion, and to establish what the probable causes were so that the design and/or operating features for this process could be modified to minimize this problem.

This report describes the process and equipment involved in the waste immobilization tests, discusses the history of the testing and then gives a detailed description of the findings made during a tear-down of the system. A discussion of the corrosion mechanisms is included based on the inspection findings. Reference data is included in the appendices which describe some details of interest to a specialized audience.

CONCLUSIONS/RECOMMENDATIONS

Specific conclusions and recommendations related to components of the spray calciner/ceramic melter vitrification system--the refractories, walls and floor, throat liner, lid, filters, and vibrator impact pad--and the materials of construction follow:

- Refractories

The excessive attack on the K-3 refractory was due to high temperatures ($>1200^{\circ}\text{C}$) in the melter. The mechanism of attack consisted of a corrosion/erosion sequence. Corrosion of the refractory left a protective layer which was eroded away by convection in the glass. This erosion occurred more easily at high temperatures and loss of the protective layer allowed fresh brick to be attacked. It is recommended that the glass composition used not be run in the melter at a temperature $>1200^{\circ}\text{C}$. Steps are being taken to adjust the glass composition to reduce its corrosiveness. Operation at lower temperatures and other PNL melters ($<1200^{\circ}\text{C}$) has been demonstrated to provide life times of >3 yr.

Upward drilling was seen on the underside of the horizontal refractory surfaces. As a result, a recommendation is made to place refractory blocks vertically and minimize the number of horizontal joints.

Little corrosion was noted on Zirmul refractories used to back up glass-contact bricks.

More extensive corrosion testing under conditions more representative of actual operations is recommended, such as higher glass temperatures, variations in the glass composition, and dynamic corrosion tests. These tests can be done on a laboratory scale with only minor revisions to existing test practices.

- Walls and Floor

The temperature gradient across the K-3 refractory was not sufficient to prevent glass leakage, although glass which penetrated beyond the K-3 refractory on the north, south and west walls of the melter did not cause problems

since it was stopped by the backup refractory. Glass which penetrated the floor might have caused problems if more operating time had been accumulated. A monolithic, joint-free, refractory backup layer is recommended for the floor in the melter when it is rebuilt.

As expected, the east wall (or throat wall) of the melter was the most difficult to design. Multiblock construction was not adequate due to poor fitting of the refractory blocks. A large monolithic throat block is being used in a new design. Also, a minimum of joints and careful fitting of bricks is being incorporated in this new design.

- Throat Liner

The Inconel-690 throat liner was not of optimum design. Inconel-690 throat liners might be desirable if drilled K-3 is too "soft" or not corrosion-resistant enough. At present, PNL recommends a drilled throat from a large K-3 monolith. Also, the discharge throat should be sloped.

- Lid

Inconel-601 is strongly attacked by chlorine at high temperatures. Other chromium-containing alloys are also attacked by this material. It is recommended that the temperatures of metallic portions of the lid be kept below 300 to 400°C to reduce lid corrosion. Also, placement of a refractory roof between the lid and melt would further reduce corrosion, especially if used in conjunction with lid cooling. In this manner, lid temperatures could be kept low enough so that corrosion would be essentially eliminated.

LDS moldable refractory was used for the above application. However, this material was found to be attacked by glass foam which occasionally came into contact with it, dissolving the material. Thus, use of LDS moldable above a melter tank is not recommended. Although the material does provide excellent thermal features, a castable refractory which is more dense and glass corrosion-resistant is suggested.

- Filters

Sintered 316 SS is not recommended as a filter medium for spray calcination in the presence of chlorides, fluorides, sulfates or high temperature

conditions. Also, it is not apparent that Inconel would be a better filter material if sulfate attack on chrome is occurring. More evaluation of this problem is needed.

- Vibrator Impact Pad

Welding a vibrator impact pad for the spray calciner onto the outside of, or into a hole cut in, the chamber is not recommended. Differences in heat retentions of the pad and chamber wall can cause stresses that cause weld failure or deformation of the spray chamber. A spray-chamber wall thickness of sufficient strength ~ 1.27 cm ($\sim 1/2$ in.) to allow direct impaction of the vibrator on the chamber wall should be used.

- Materials of Construction (General)

Not enough is known about the corrosion properties of various volatiles, Cl^- , F^- , $\text{SO}_4^{=}$, etc., to presently predict the future behavior of materials of construction. It seems desirable to protect all metal surfaces which might have temperatures where volatiles could condense. Types of protection being considered are castable or moldable refractories, and glass or ceramics coatings.

Additional corrosion analysis must be completed before 310 SS could be recommended for long-term applications for a spray calciner using defense-type waste. Inconel-type alloys would likely be superior.

- Miscellaneous

The electrochemical influences on melter tank corrosion are not fully understood and deserve further investigation; however, it is believed that these did not play a major role in the corrosion.

It is not apparent what role the lack of mixing played in the corrosion of the melter, although it cannot be ruled out as high alkali glass would be more corrosive.

The application of resistance corrosion measuring devices to look at short-term corrosion rates while operating equipment is advised. This type of equipment will be tested at PNL in future operations.

PROCESS AND EQUIPMENT DESCRIPTION

The vitrification process used for immobilizing the Savannah River Plant simulated waste was that of the Spray Calciner/Electric-Heated Ceramic Melter system.^(a) The system is shown schematically in Figure 1. Effluents were discharged to the offgas system. Each component will be briefly described in this section. A typical process flowsheet is shown in Figure 2; Figure 3 is a photograph of the system.

SPRAY CALCINER

The spray calciner (Figures 4 and 5) consists of a spray chamber, cone section, furnace, vibrators and offgas filter assembly. Atomized waste feed is sprayed into the top center of the spray chamber, which is a vertical cylinder externally heated by a concentric, cylindrical furnace. The high velocity at which the atomizing air and waste feed droplets enter the spray chamber, in addition to the temperature difference between the chamber wall and the evaporating water droplets, creates a high degree of turbulence in the calciner. The combination of this violent convective heat transfer, along with radiant heat transfer, allows drying and calcination of the liquid waste at a high rate.

After passing through the chamber, water vapor and atomizing air entrain a large percentage of the calcine particles. More than 99.9% of the particulates are removed from the offgas by sintered metal filters. A periodic pulse of blowback air removes the layer of calcine that collects on the filters. This calcine then falls into the cone section and is discharged to the melter along with the calcine that falls directly from the calcination chamber. All surfaces are sloped at least 60° from horizontal to avoid calcine accumulation by allowing the calcine to slide off the surfaces.

Frit is added to the calciner cone section through an airlock valve. This airlock valve can be timed simultaneously with the filter blowbacks to obtain

(a) Also called the Calcine-fed Ceramic Melter (CFCM) system.

FIGURE 1. Process Schematic of the Spray Calciner/Ceramic Melter System

NORMAL OPERATING PARAMETERS
@ FLOW CONDITIONS BELOW

FILTER PRESSURE DROP 8-10 IN H₂O

<p>CALCINER FURNACE POWER CONSUMPTION (kW)</p> <p>ZONE 1 90</p> <p>ZONE 2 92</p> <p>ZONE 3 55</p> <p>ZONE 4 53</p> <p>TOTAL 290</p> <p>CALCINER BARREL TEMPERATURE (°C)</p> <p>ZONE 1 750</p> <p>ZONE 2 755</p> <p>ZONE 3 755</p> <p>ZONE 4 800</p> <p>CALCINER FURNACE TEMPERATURE (°C)</p> <p>ZONE 1 875</p> <p>ZONE 2 875</p> <p>ZONE 3 840</p> <p>ZONE 4 840</p> <p>CALCINER FILTER HOUSING TEMPERATURE (°C)</p> <p>UPSTREAM OF FILTERS 250</p> <p>DOWNSTREAM OF FILTERS 240</p> <p>CALCINER CONE TEMPERATURE (°C)</p> <p>DIRECTLY UNDER BARREL 230</p>

		<div> ATOMIZING AIR (A) SLURRY FEED (B) FRIT (C) AIR IN LEAKAGE (A) AIR BLOWBACK (A) CALCINE (D) TOTAL OFF-GAS (E) GLASS (F) </div>							
PARAMETERS	STREAM #	1	2	3	4	5	6	7	8
MASS FLOW kg/hr		174.8	323.7	50.4	21.9	1.97	19.6	502.8	70
VOLUMETRIC FLOW	SCFM	80			10	0.90		310	
	STANDARD liters/hr	1.36x10 ⁵	300		1.70x10 ⁴	1.53x10 ³		5.28x10 ⁵	
TEMPERATURE °C		AMBIENT	<50	AMB	AMB	AMB	250	250	1150
PRESSURE	psig	30	12		0	40			
	inches H ₂ O VACUUM			5			5	5	5
SPECIFIC GRAVITY			1.08						2.8
VOLUMETRIC FLOW AT LISTED CONDITIONS	CFM	28.7			10.9	0.26		606	
	liters/hr	4.88x10 ⁴	300		1.86x10 ⁴	448		1.03x10 ⁶	25
POWER INPUT	kW								50
COOLING LOSSES	kW								40

<p>(A) AIR ASSUMED TO BE 79% N₂ AND 21% O₂ (BY MOLE OR VOLUME)</p> <p>(B) FEED CHEMICAL COMPOSITION (WT. %)</p> <p>Fe(OH)₃ 53.16</p> <p>Al₂O₃ - 3H₂O 13.33</p> <p>MnO₂ 10.61</p> <p>CaCO₃ 4.84</p> <p>NiO - 2H₂O 6.86</p> <p>NaNO₃ 2.23</p> <p>Na₂ - SO₄ 1.09</p> <p>ZEOLITE 7.89</p> <p>4286 LITERS OF SLURRY IS COMPOSED OF 367.6 kg OF THE ABOVE COMPOSITION AND 4261 LITERS OF WATER AND WILL YIELD 1000 kg OF GLASS WHEN COMBINED WITH 720 kg OF FRIT.</p>	<p>(C) FRIT 211 COMPOSITION (WT. %)</p> <p>SiO₂ 58.3</p> <p>Na₂O 20.6</p> <p>Li₂O 4.4</p> <p>B₂O₃ 11.1</p> <p>CaO 5.6</p> <p>(D) CALCINER COMPOSITION (ASSUMING FEED CHEMICALS ARE CONVERTED 100% OXIDE FORMS) (WT. %)</p> <p>Fe₂O₃ 52.14</p> <p>Al₂O₃ 11.43</p> <p>MnO₂ 13.93</p> <p>CaO 3.56</p> <p>NiO 6.07</p> <p>Na₂O 1.07</p> <p>Na₂SO₄ 1.43</p> <p>ZEOLITE 10.36</p>	<p>(E) OFF-GAS COMPOSITION (VOLUME OR MOLE %)</p> <p>H₂O 84.37</p> <p>O₂ 3.26</p> <p>N₂ 12.27</p> <p>CO₂ 0.06</p> <p>NO_x 0.04</p> <p>(F) GLASS COMPOSITION (WT. %)</p> <p>Fe₂O₃ 14.6</p> <p>Al₂O₃ 3.8</p> <p>MnO₂ 3.9</p> <p>CaO 5.3</p> <p>NiO 1.7</p> <p>Na₂O 15.4</p> <p>Na₂SO₄ 0.4</p> <p>B₂O₃ 8.0</p> <p>Li₂O 3.2</p> <p>SiO₂ 43.6</p>
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FIGURE 2. Spray Calciner/Ceramic Melter Flowsheet

FIGURE 3. Photograph of Spray Calciner/Ceramic Melter System

FIGURE 4. Photograph of Spray Calciner

FIGURE 5. Spray Calciner Schematic

as much frit and calcine mixing as possible as the frit and calcine fall through the calciner cone into the melter below.

Two vibrators are mounted 180° apart at mid-height of the chamber. These vibrators are supported independently of the furnace to minimize vibration to the furnace elements and insulating fire brick. To assure the calciner is kept free of calciner powder buildup, each vibratory is usually actuated for 2-s pulses several times/h.

Design features of the full-scale spray calciner are shown in Table 1.

ELECTRIC-HEATED GLASS MELTER

As is seen in Figure 1, the bottom of the spray calciner is connected to the lid of the glass melter with a short section of 15-cm (6-in.)-dia, flexible metal pipe. This pipe enables the spray-dried and partially calcined metal salts formed in the calciner, and the glass-forming frit that is added to the calciner cone, to drop directly onto the surface of the molten glass in the melter below. This connection also enables the gases that accompany the melting process to vent back up through the calciner to the offgas system.

Some of the salient features of the melter can be seen in Figure 6. The melter is totally contained within a rectangularly shaped Inconel-601 box about 206 cm x 155 cm x 114 cm (81 in. x 61 in. x 45 in.) in size. The melting tank directly under the calciner is about 117 cm x 71 cm x 89 cm (46 in. x 28 in. x 35 in.) in size and lies across one end of the containment vessel. Normally, the glass is about 30-cm (12-in.) deep in the tank; with 18-cm (7 in.) of insulation under the melting tank lid, the vapor space above the glass is limited to 41 cm (16 in.).

Two massive Inconel-690 electrodes are positioned one at either end of the melting tank, are pressed tightly against the end walls and rest on the melter tank floor. While glasses are effective insulators at room temperature, their electrical resistance decreases as the glass temperature increases, until in the range of 900 to 1200°C they become good electrical conductors. Thus, if the glass is initially brought up to this temperature range by some startup technique, then by applying an electrical voltage to the two immersed slab

TABLE 1. Design Features - Full-Scale Spray Calciner

Calcination Chamber

Inside Diameter (m)	0.91 (36 in.)
Height (m)	3.20 (10.5 ft)
Heat Transfer Area (m ²)	9.15 (99.0 ft ²)
Material	310 SS
Wall Thickness (cm)	0.64 (0.25 in.)

Furnace

Type	Electric Resistance
Number of Zones	4
Length of Zones (m)	0.76
Zone Power (kW)	150
Heating Elements	Kanthal 1-A
Maximum Temperature	1000 ⁰ C
Voltage	480
Phase	3

Filters^(a)

Mean Pore Size (μm)	10	65
Number	51	34
Surface Area (m ²)	7.44 (80 ft ²)	6.82 (73.4 ft ²)
Filter Size (cm x cm)	5.1 x 91.4 (2.0 x 36 in.)	7.0 x 91.4 (2.75 x 36 in.)
Material	316 SS	316 SS

Vibrators

Number	2
Type	Pneumatic, Dry Lubricant
Location	180 ⁰ Apart at Midplane of Chamber Side
Size	1300 ac
Motive Air Pressure	276 kPag (40 psig)
Manufacturer	Cleveland Vibrator Company

(a) Prior to December 1979

FIGURE 6. CFCM Schematic

electrodes, an electrical current will flow through the glass, and energy will be dissipated through the glass (as it is in any electrical conductor) by virtue of the Joule-heating effect. By controlling the voltage applied to the electrodes, the current flow through glass and the resultant glass temperature can be controlled.

Molten glass is very corrosive and tends to dissolve most materials of construction. Fuse-cast refractories (ceramic-type materials) have been shown to have excellent resistance to glass corrosion and generally are used to line melting tanks and molten glass conduits. However, these linings have relatively poor thermal insulating properties and must be backed with other refractories, perhaps not as corrosion-resistant as the lining refractories, but with more desirable insulating properties.

As the mixture of spray-dried metal salt and glass former materials falls on the surface of the molten glass in the melter, the temperature of the mixture rises and the metal salts calcine completely to oxides and fuse with the glass formers into a fluid glass material. As the glass level rises in the melter tank, molten glass from the floor of the melter flows through the underflow throat in the base of the wall and rises in the riser channel behind the melter wall. At the top of the riser, the glass flows down the discharge trough, spills over the end of the trough and free-falls from the discharge lip to the receiving canister below. The receiving canister is coupled securely to the melter containment vessel with a short section of flexible metal pipe to prevent air from leaking into the melter which is normally operated at 13 cm (5 in.) of water vacuum.

Subsequent discussions, drawings and photographs will provide additional detail for the aforementioned figures.

OFFGAS SYSTEM

The offgas system is shown in Figure 7. In addition to sintered filters, the system consists of an ejector venturi scrubber, a condenser, a packed tower and a high-efficiency particulate air (HEPA) filter followed by a vacuum-producing blower. The pressure on the system ranges from approximately 1.9 cm Hg

(10-in. H_2O) vacuum at the calciner to 1.5-cm Hg (80-in. H_2O) vacuum at the blower. Each liquid stream can be sampled, and gas samples can be taken at inlets and outlets and between each piece of equipment. Each piece of equipment can be valved-in separately to evaluate its performance. Typical flow through the system is 125 scfm at a 300 ℓ /h calciner feedrate (after any steam has been condensed).

The ejector venturi scrubber is a 316 SS venturi with a 152-m-(6-in.)-dia inlet. The scrubber is designed to handle 14,200 ℓ /min (500 acfm) steam and 1,420 ℓ /min (50 acfm) NO_x at 400°C and 4.7 cm Hg (25-in. H_2O) vacuum. The scrub solution is 185 ℓ /min (40 gpm) at 30°C and 310 cm Hg (60 psig). The gas is cooled to 50°C, and the scrubber is designed to remove 90% of the 1- μ m or larger particles.

The condenser, a 304 SS shell and tube heat exchanger with floating heads, is a single-pass tube-side process unit with 14.2-m² (153-ft²) heat transfer area. Cooling water is fed to the shell side at 13°C and 310 cm Hg (60 psig).

The packed tower is made of 14-in. Sch. 10 304L SS pipe. The bed height is 2.62 m (8.6 ft) of 2.45-cm x 2.54-cm x 0.08-cm (1-in. x 1-in. x 1/32-in.) Raschig rings. The bed volume is ~ 0.25 m³. The tower has a 2.54-cm (1-in.) cooling coil with 1.1-m² (12-ft²) heat transfer area.

The HEPA filter is a 30-cm x 30-cm x 15-cm (12-in. x 12-in. x 5-7/8-in.) filter rated at 5.25 m³/min (185 ft³/min) at a pressure drop of 0.19 cm Hg. The gas is heated above its dewpoint before passing through the filter.

The blower is a multistage, centrifugal, turbo compressor rated at 9,062 ℓ /min (320 scfm) at 15 cm Hg (80-in. H_2O) vacuum.

OPERATING HISTORY

The first period of operation for the ceramic melter vitrification system began with initial startup in April 1978 and continued until shutdown for modification in September 1978. The second period of operation began with restart in April 1979 and continued until the system was shut down again for inspection in November 1979. Approximately 11,000 and 51,000 kg of glass made from calcined, simulated nuclear waste slurries were discharged from this melter during its first and second periods of operation, respectively.

Table 2 summarizes the use of the melter system during the two periods and lists the activity periods, the composition of the glass in the melter, and frit used, the average temperatures, the average current, the average power experienced during the various activities and the amount of glass formed during each activity period. In addition, pertinent observations made during these periods are noted. Figure 8 plots the average glass temperature and the average electrode current flow experience during these two periods, in addition to the cumulative amount of glass discharged from the melter and the chronological occurrence of significant events. Table 3 summarizes the compositions of frits and glasses used in the two periods of operation.

TABLE 2. Calcine-Fed Ceramic Melter Chronology of Events

PERIOD 1											Remarks
From	To	Activity	Hours	Feed ⁽²⁾	Frit ⁽³⁾	Glass Temp. (°C)	Glass Rate (kg/h)	Current (amps)	Power (kW)	Glass (kg)	
4-21-78	4-25-78	Startup	110	PW7a	76-199	975	--	0-200	0-34	364	Startup charge foamed (heated from the top only).
4-25	5-08	Idle		"	"	1000	--	230	30	--	Obtained temp. distribution for 15 cm (6 in.) glass depth.
5-08	5-08	CFCM-1 ⁽¹⁾	8	"	"	~950	--	200-300	30-40	--	Effect of electrode cooling.
5-08	5-24	Idle		"	"	~900	--	180	28	--	Obtained glass temp. dist.
5-24	5-26	CFCM-2	15	"	"	~850-900	--	250	31-36	623	Added 623 kg of batch feed.
5-26	6-01	Idle		"	"	~950	--	280	30	--	
6-01	6-01	CFCM-3	7	"	"	~980	10-40	350	35	155	Calciner feed - auto. resistivity control - stable but cyclic.
6-01	6-23	Idle		"	"	~900	--	220	28	--	
6-23	6-23	CFCM-4a	4	"	"		50	400	50	190	Foaming.
6-23	6-24	Idle		"	"		--	250	30	--	
6-24	6-26	CFCM-4b	4	"	"	975	60	300	40	230	8 to 15 cm (3 to 6 in.) cold - feed pile near inlet nozzle.
6-26	6-27	Idle		"	"	925	--	230	33	--	
6-27	6-27	CFCM-4c	3	"	"	975	80	330	50	215	Feed pile to inlet nozzle.
6-27	6-29	Idle		"	"	1015	--	320	43	--	
6-29	6-29	CFCM-4d	4	"	"	900	50	380	50	10	Filled discharge flex pipe & 1/4 of discharge tube with glass.
6-29	9-08	Idle		"	"	990	--	270	28	--	Sludge in tank bottom ~3 cm (1 in.) thick.
9-08	9-08	CFCM-5	3	SRP-COMP	411	~1045	30	270	28	0	Calciner feed line problems.
9-08	9-11	Idle		"	"	~1075	--	270	28	--	
9-11	9-11	CFCM-5	3	"	"	970-1190	30		40	60	Excessive foaming, solids feeder problems.
9-11	9-14	Idle		"	"	~1075	--	270	28	--	
9-14	9-14	CFCM-5	7	"	"	~1000	50		35	250	Foaming problems & tilt mechanism failure, frit feeder problems, ~463 kg of 411 frit added to melter without any calciner addition to "flush" the old glass from the tank.
9-14	9-19	Idle		"	"	~1100	--	330	35	--	
9-19	9-29	CFCM-5	245	"	"	~1150	20-45	700-800	40-50	9039	Feed nozzle plugs, leakage under trough observed.
9-29	10-12	Idle		"	"	1030	--	480	30	--	Took sludge core sample.
10-12	10-12	Reboil 1	3	"	"	1185	--	680	60	--	Slight reboil noted.
10-12	10-18	Idle		"	"	1030	--	380	25	--	
10-18	10-18	Reboil 2	5	"	"		--	720	65	--	Foam over entire surface.
10-18	10-23	Idle		"	"	900	--	380	31	--	
10-23-78	10-24-78	Drain & Shutdown	18	"	"	~1120	--	500-0	38-0	--	Drained melter, max. rate - 108 kg/h.
Total "ON" Time 6 months			4380 hours	439 h (10%)							11,136
END PERIOD 1 OPERATION											
10-24-78	4-13-79	Melter modifications: Added Inconel-690 "feet" to electrodes, chipped sludge from melter tank, installed Inconel-690 throat liner, increased feed inlet pipe and nozzle from 10 cm (4 in.) to 15 cm (6 in.), replaced the 10-cm (4-in.) feed inlet sleeve through the lid insulation with an Inconel-601 cone tapering at 45° from 58 cm (19 in.) OD, added cooling jacket to upper 8 cm (3 in.) of feed inlet cone.									

- (1) Denotes an experimental run number for the melter.
 (2)(3) See Table 3 for feed and frit compositions.

TABLE 2. (contd)

PERIOD 2		Activity	Hours	Feed(2)	Frit(3)	Glass Temp. (°C)	Glass Rate (kg/h)	Current (amps)	Power (kW)	Glass (kg)	Remarks
From	To										
4-13-79	4-17-79	Startup	100	SRP-TDS	411	0-900	--	0-700	0-40	418	Foamy startup.
4-17	4-22	CFCM-6	106	"	"	1025-1170	35-70	700-970	39-52	3550	3 feed interruptions due to foaming. Experiment current ltd.
4-22	4-27	CFCM-6	133	"	211	1075-1215	60-80	920-1000	63-76	7450	2 feed interruptions due to air-lock failure. Exp. current ltd.
4-27	6-04	Idle		"	"	~1150	--	675	43	--	Incr. electrode power cables to realize 1560 A. Moved electrode voltage sensing location.
6-04	6-10	CFCM-7	137	"	"	1150	60-70	950	50	5900	
6-10	6-14	CFCM-7	102	"	"	1250	60-75	950-1150	60-80	6100	
6-14	6-17	CFCM-7	75	"	"	1280-1260	75-85	1150-1200	75-90	5400	
6-17	6-23	CFCM-7	145	"	"	1250	70	1000	60-75	6700	6-18 - Dischg. tube floor covered with ~3 cm (1 in.)
6-23	6-30	CFCM-7	155	"	"	1275	70	1150	85	10600	6-22 - Air leakage into melter below liquid level noted to right of C. 6-24 - No electrode short to ground but perhaps a tank leak to ground. Arcing noted to viewports. 6-27 - No electrode short to ground (4 amp flow when shorted). 7-26 - Melter moved to "Idle" position (South electrode probably shorted to ground at this time).
6-30	7-27	Idle		"	"	~1150	--	700	42	--	7-26 - S. electrode appears to be shorted. Arcing noted to viewports
7-27	7-31	Reboil 3	96	SRP-TDS	211	1090	--	735	43	--	
7-31	8-03	Reboil 4	72	"	"	1065	--	567	37	--	Peak values; ~1100°C glass
8-03	8-07	Reboil 5	96	"	"	950	--	492	33	--	" " ~1100°C gl. 818 A, 61 kW
8-07	8-09	Reboil 6	48	"	"	1030	--	558	37	--	" " ~1175°C " 1077 A, 79 kW
8-09	8-13	Reboil 7	96	"	"	~1050	--	560	~37	--	" " ~1175°C " 1088 A, 79 kW
8-13	8-16	Reboil 8	72	"	"	~1050	--	560	37	--	" " ~1150°C " 1052 A, 80 kW
8-16	8-20	Reboil 9	96	"	"	~1050	--	557	36	--	" " ~1175°C " 1136 A, 87 kW
8-20	10-19	Idle		"	"	1075			38		8-16 - S. electrode is shorted to gr. probably thru a Conax insulator 8-22 - Elect. acc. 8-28 - Discharge lip cooler cut away. 8-28 - Plumbing removed to remove electrode short to case. 8-30 - Voltage to gr. measurements made at dischg. lip. 9-06 - No electrode short, but small tank short. 10-3 - Chipped glass from "T" bar & dischg. floor, meas. dischg. V to ground (see 6-18-79 note). 10-15 - OSI CT reads directly, GE CT reads directly 0-500.
10-19	10-19	Reboil 10	4	"	"	1075	--	590	38	--	Peak values; 1175°C glass, 1032A, 80kW. Samples Na ₂ SO ₄ layer (~2%) on glass surface.
10-19	10-22	Reboil 11	72	"	"	1085	--	590	38	--	Peak Val; 1180°C gl., 1070A, 79.5kW
10-22	10-31	Idle		"	"	1075	--	588	38	--	10-24 - Mod. Conax fit. to elim. pos. of shorting elect. to gr.
10-31	10-31	Reboil 12	4	"	"	1070	--	588	38	--	Peak Val; 1175°C gl., 1080A, 79kW.
10-31	11-02	Idle		"	"	1070	--	588	38	--	Argon purge tank.
11-02	11-02	Reboil 13	4	"	"	1065	--	580	38	--	Peak Val; 1150°C gl., 1060A, 79.5kW
11-02	11-05	Idle		"	"	1070	--	584	38	--	
11-05	11-09	CFCM-8	110	"	"	1150	60	700-800	40-65	4302	11-8 - (10:53-13:45) The gl. dischg went from "slow & cold" to "hot, foamy & fast" w/ "chunks of un-wetted calcine floating over." Apparently the bridgeblock was breached at this point.
11-09	11-29	Idle		"	"	1050	--	510	35	--	
11-29	11-29	Reboil 14	4	"	"	1100	--	620	42.5	--	Peak Val; 1175°C gl., 1020A, 82.5kW.
11-29	11-30	Idle		"	"	1050	--	510	35	--	
11-30-79	11-30-79	Drain & Shutdown	4	"	"	~1175	--	~1050	85		
Total "ON" Time, 7½ months 1731 h (32%) 5475 hours									TOTAL	61,500 kg	

END OF PERIOD 2 OPERATION

(1) Denotes an experimental run number for the melter.
 (2)(3) See Table 3 for feed and frit compositions.

FIGURE 8. Melter Conditions During Major Operating Periods

TABLE 3. Frit and Glass Compositions (Oxide wt%)

Oxide Component	76-199(a) Frit	411 Frit	Composite- 411 Glass	TDS-411 Glass	211 Frit	TDS-211 Glass
SiO ₂	53.0	58.3	44.5	43.7	58.3	43.7
B ₂ O ₃	14.0	11.1	8.3	7.8	11.1	7.8
Na ₂ O	12.0	12.5	9.4	9.4	20.6	15.1
Li ₂ O	---	12.5	9.4	8.8	4.4	3.1
CaO	3.0	5.6	5.2	5.2	5.6	5.2
CuO	4.5	---	---	---	---	---
Fe ₂ O ₃	---	---	8.0	15.2	---	15.2
Al ₂ O ₃	1.5	---	12.0	3.6	---	3.6
MnO ₂	---	---	2.6	4.0	---	4.0
TiO ₂	9.0	---	---	---	---	---
NiO	---	---	0.6	1.9	---	1.9
K ₂ O	3.0	---	---	---	---	---
Na ₂ SO ₄	---	---	---	0.4	---	0.4
	100.0	100.0	100.0	100.0	100.0	100.0

(a) Used with PW-7a-type waste.

CORROSION INSPECTION

This section includes a discussion of what was found during investigation of the system after shutdown, November 1979. The primary concern of this study was to examine the corrosion to the ceramic melter; however, since corrosion of the filters and some minor components of the calciner was observed, a brief examination of this system was also made. Visual inspection of the offgas system downstream of the sintered metal filters showed no corrosion.

SPRAY CALCINER SYSTEM

Spray Chamber

The 310 SS of the heated-wall spray chamber was selected for its high-temperature properties. Wall thickness measurements have been made on calciners operated at PNL to determine the extent of corrosion. Measurements made on a pilot-scale, 53.3-cm (21-in.)-dia spray chamber after 522 h of acid waste calcining at 700°C, including six heatup and cooldown cycles, showed no detectable corrosion. The instrument used for the measurements had a precision of 5 μm (0.0002 in.). A calciner corrosion/erosion rate of <75 $\mu\text{m}/\text{yr}$ (<0.003 in./yr) was calculated based on this test (Bonner et al. 1976).

Wall thickness measurements were made in April 1977 and March 1980 on the full-scale 91.4-cm (36-in.)-dia spray chamber after 1650 h of actual operation ($\sim$ 200 h with acid-type feed and 1450 h with neutralized feed), 37 heatup and cooldown cycles and roughly 1000 h idle time at temperatures between 700 to 800°C. Hence, the spray calciner was operated at 700 to 800°C for $\sim$ 2650 h. The differences between wall thickness measurements made in April 1977 and March 1980 (see Table 4 and Figure 9) indicate a maximum average loss in thickness of 330 μm (0.013 in.). Based on the actual hours of equipment operation, a corrosion/erosion rate of 1780 $\mu\text{m}/\text{yr}$ (0.07 in./yr) is indicated. Based on the approximate hours at operating temperatures, a corrosion/erosion rate of 1020 $\mu\text{m}/\text{yr}$ (0.04 in./yr) is indicated. A corrosion allowance of 2540 μm (0.1 in.) would be exceeded in 1.4 to 2.5 yr at these corrosion rates.

TABLE 4. Wall Thickness Measurements for Spray Calciner Chamber (in.)
(see Figure 9 for locations)

April 1977				March 1980				Height from Bottom Flange (ft)
1	2	3	4	1	2	3	4	
0.254	0.249	0.251	0.249	(a)	(a)	(a)	(a)	1
0.255	0.249	0.254	0.253	(a)	(a)	(a)	(a)	2
0.256	0.257	0.256	0.256	0.248	0.246	(a)	0.251	3
0.256	0.257	0.258	0.258	0.247	0.247	0.252	0.247	4
0.260	0.259	0.259	0.259	0.250	0.246	0.248	0.249	5
0.260	0.257	0.259	0.258	0.247	0.248	0.248	0.247	6
0.256	0.257	0.258	0.257	0.244	0.242	0.243	0.244	7
0.256	0.254	0.256	0.256	0.243	0.247	0.241	0.243	8
0.254	0.256	0.258	0.055	0.244	0.249	0.239	0.238	9
<u>0.256</u>	<u>0.256</u>	<u>0.260</u>	<u>0.259</u>	<u>0.245</u>	<u>0.248</u>	<u>0.241</u>	<u>0.250</u>	10
0.256	0.255	0.257	0.256					Avg.: 1-10 ft
0.257	0.257		0.257	0.246	0.247		0.246	Avg.: 3-10 ft
		0.258				0.245		Avg.: 4-10 ft

(a) Lower furnace zone not removed at this time, making measurements at these locations is impossible.

• Average Loss in Wall Thickness (in.):

Location	April 1977	March 1980	
1 ^(b) (3-10 ft) ^(c)	0.257	0.246	0.11
2 (3-10 ft)	0.257	0.247	0.10
3 (4-10 ft)	0.258	0.245	0.13 ← greatest loss
4 (3-10 ft)	0.257	0.246	0.11

(b) See Figure 9.

(c) Height from Bottom flange of chamber

• Yearly corrosion rate based on hours of actual operation

$$= \frac{0.013 \text{ in.}}{1650/\text{h operation}} \times \frac{8760/\text{h}}{\text{yr}} = 0.07 \frac{\text{in.}}{\text{yr}}$$

• Yearly corrosion rate based on approximate hours at operating temperature

$$= \frac{0.13 \text{ in.}}{2650/\text{h}} \times \frac{8760/\text{h}}{\text{yr}} = 0.04 \frac{\text{in.}}{\text{yr}}$$

FIGURE 9. Location of Wall Thickness Measurements in Table 4

The two sets of measurements for the pilot-scale and full-scale calciners indicate widely differing results. Since different compositions were run in each calciner, no conclusive results can be drawn from these measurements. Stainless steel 310 is not recommended for long-term hot cell applications until further verification of corrosion rates are made. Inconel 601 would be superior to stainless 310 in oxidation resistance, scaling resistance, and mechanical strength. Inconel 625 would provide additional corrosion resistance, but would not be quite as resistant to high-temperature ($\sim 1200^{\circ}\text{C}$) oxidation as Inconel 601.

The cone section (304L SS) of the full-scale spray calciner did not show any visual corrosion after 1600 h of operation. The cone temperature varied between 200 and 350°C during calciner feeding and 400 to 700°C during equipment idling while at operating temperature. Comparative wall thickness measurements are not available to determine measurable corrosion rates.

Filters

Failure of the full-scale spray calciner sintered metal offgas filters occurred prior to the 5-day spray calciner/ceramic melter test in November 1979. The filter breaching was not detected until the run was underway. This breaching was indicated from the very beginning of the run by large amounts of

calcine in the off-condensate samples and venturi scrub solution samples. After the test, the filter assembly was removed from the filter housing for inspection and repair. A considerable amount of calcine was caked in regions of the 65- μm filters, whereas the 10- μm filters were fairly clean. Build-up of calcine between the 65- μm filters was possibly caused by a higher offgas flowrate through the filters due to their larger pore size and less flow resistance. The filters were washed with water, and several irregularly shaped pieces ~ 38 to 65 cm^2 (~ 6 to 10 in.^2) of sintered metal were gone from the 65- μm filters (see Figure 10). The filters were filled individually with water to indicate whether large pieces of metal or large openings were present. Fifteen of the thirty-four 65- μm filters and two of the fifty-one 10- μm filters could not be filled with water, or leaked water considerably faster than the other filters, indicating breaching of the sintered metal had occurred in these filters.

The sintered metal was very brittle, and analysis of the metal showed that corrosion products existed not only on the filter surface, but had penetrated the depth of the filter material. Metallurgical analysis of a section of the filter material by a scanning electron microscope did not indicate any residual chloride or fluoride within the filter pores, or any other residual compounds. Since the corrosion existed throughout the thickness of the metal and no residual compounds could be found within the filter pores, the corrosive species must have been volatile or soluble in the flush water. Chloride, fluoride and sulfate ions are likely the major cause of the corrosion (see "Filter Corrosion," p. 96 for further discussion).

Another contributing factor to the filter failure is that the filter temperatures exceeded 500°C during a SC/CM 25-day test in June 1979. The filters were at 475 to 525°C for 12 h, 525 to 575°C for 5 h and 575 to 590°C for 1 h during this period. While these temperatures do not usually cause any problems for 316 SS, the extremely fine metal-to-metal bonds in the sintered metal are very susceptible to the slightest oxidation. A small amount of corrosion that is hardly detectable in vessels or piping can severely damage filters.

FIGURE 10. Failed Filters

Material Fractures

Vibrator Impact Pad Failure

While not related to corrosion, a failure of a vibratory impact pad occurred in April 1979. The originally designed impact pads were 1.91-cm (3/4-in.)-thick plates that were rolled to match the curvature of the spray chamber and then fillet welded to the 0.64-cm (1/4-in.)-thick chamber wall. One of the plates fell off during a test. Dye penetrant inspection revealed cracks in the chamber in the fillet-weld region. Also, visible deformation (buckling) of the chamber existed within the area of the impact pad fillet weld.

The postulated failure mode is that after welding, the vibrator pad, thicker than the wall, 1.91 cm versus 0.64 cm (3/4 in. versus 1/4 in.), retained its heat longer, and in the final stages of cooling, the fillet weld was drawn radially inward as the impact pad cooled. This phenomenon caused compression of this region of the spray chamber, and due to the difference in thickness of the pad and wall, the shrinkage of the thick plate controlled the compression process and the thinner barrel buckled. This buckling was restricted to the region within the fillet weld and, therefore, was not likely caused by the vibrator impact. The impact pad showed no corresponding buckling. The buckling of the barrel put the weld in tension. The tension field and the stress concentrations during vibrator impact combined to propagate fatigue cracks which led to the weld failure.

The impact pads were replaced by cutting a 38.1-cm (15-in.)-dia piece out of the spray chamber wall and replacing it with a circular plate (1.91-cm) 3/4-in.-thick rolled to match the diameter of the chamber (see Figure 11). This new impact design was tested but, because of poor weld penetration, the weld was found insufficient. The plate was ground out and rewelded. After the pads were rewelded, which required several weld passes to refill the groove that had been ground out, the spray chamber surfaces around the circular impact pad became deformed. The 1.91-cm (3/4-in.) impact pad retained heat longer than the 0.64-cm (1/4-in.) chamber wall, which again caused the chamber to buckle slightly while cooling. Other than being slightly out-of-round, no structural damage to the spray chamber was evident.

FIGURE 11. New Vibrator Impact Pad

As a result of the problems encountered with welding a vibrator impact pad onto or into the spray chamber, the above methods are not recommended. Instead, a spray chamber wall of sufficient thickness 1.27 cm ($\sim 1/2$ in.) that would allow direct impaction of the vibrator on the chamber wall could be used. This would eliminate the stresses between the chamber wall and impact pad caused by welding and differences in thermal expansion and contraction.

Calciners/Melter Connecting Bellows

A photograph of the 321 SS bellows that attaches the melter inlet nozzle to the calciner cone is shown in Figure 12. The chloride-stress corrosion cracking illustrated in the photograph is very localized, occurring only in the 15.2-cm (6-in.) section of pipe shown. The remaining 35.6 cm (14 in.) of bellows were unaffected, probably because of differing temperature conditions.

CERAMIC MELTER

Background

Table 2 and Figure 8 show that the first 6-mo operating period (Period 1) was relatively innocuous, with the glass temperature^(a) averaging $<1000^{\circ}\text{C}$ for

(a) Glass temperatures referred to in this report are generally those taken at a central position in the melter using a thermowell which is periodically inserted into the melter tank. Temperature profiles throughout the tank volume are not known from actual measurements.

FIGURE 12. Flexible Pipe Corrosion

the first 4 mo and about 1075°C for the last 2 mo. Likewise, the electrode current flow held at about 250 amps for the first 4 mo and then averaged about 600 amps for the last 2 mo. The majority of the 11,000 kg of glass produced during this initial operating period was produced during the last 2 mo of the period.

Figures 13, 14, 15, 16 and 17, taken after the first operating period, reflect the mild operating conditions experienced during the initial 6-month period. Only a very faint evidence of metal-line corrosion can be seen in Figures 13 and 14, although some unusual widening of some of the block-to-block refractory joints is evidenced. Some rounding of the originally square refractory edges around the throat inlet is shown in Figure 14, and Figure 15 shows almost no corrosion of the Inconel-690 electrodes. Figure 16 shows some minor melting and shrinkage of the LDS moldable refractory on the underside of the melter tank lid. The distribution pattern of the massive sludge deposit in the tank, due in part to the low average glass temperatures experienced during the first 6 mo of operation, is shown in Figure 17. The sludge pattern indicates weak convection activity in the tank. The greatest sludge accumulations are in the corners of the melter tank. In general, the accumulation sloped gently toward the discharge throat, reflecting the increasing velocity of the exiting glass as it neared the throat.

The operating conditions for the second 7-1/2-mo operating period (Period 2) were considerably more severe than for the first period. For the second period, the glass temperatures averaged about 1120°C; and for one 20-day period, the glass temperatures averaged about 1260°C. The electrode current averaged about 650 amps during the second period, and during the same 20-day period mentioned above, averaged about 1100 amps. The bulk of the 51,000 kg of glass produced during this second period was produced in the 20-day period.

During the first shutdown period, the electrodes were modified by the addition of a 15-cm (6-in.) "foot" as shown in Figure 18. Also during this period, the discharge throat was modified by the addition of an Inconel-690

FIGURE 13. East Wall After First Shutdown

FIGURE 14. Throat After First Shutdown

FIGURE 15. Inconel-690 Electrode

FIGURE 16. Underlid Insulation After First Shutdown

FIGURE 17. Sludge Deposit After First Shutdown

liner as shown in Figures 19 and 20. This liner was intended to reduce the throat size from 10 cm x 15 cm to 5 cm x 8 cm (4 in. x 6 in. to 2 in. x 3 in.) to test the capability of the product glass flow to keep the throat clear of sludge buildup.

Melter Tank Lid

Among the modifications to the melter tank lid during the first shutdown period (October 1978 to April 1979) was the enlarging of the feed inlet nozzle diameter from 10 cm to 15 cm (4 in. to 6 in.), and the changing of the inlet nozzle through the underlid refractory from a 10-cm (4-in.) straight pipe to a 15-cm (6-in.) conically shaped pipe, tapering at 45° from a 15-cm (6-in.) dia at the top to a 4.6-cm (1.8-in.) dia at the bottom of the insulation. The feed inlet nozzle in the melter tank lid was modified to eliminate the tendency for the incoming frit to accumulate on the red-hot feed nozzle surface, which eventually caused total blockage of the feed nozzle. Figure 21 shows the modified underside of the tank lid with the inlet nozzle cone backed with new LDS moldable refractory. In addition, the conical nozzle projected 3 cm (2 in.) above the top of the lid, and a water-cooled collar was welded to this section.

Several times while the melter was idling, the cooling water to the inlet nozzle was turned off so that the melter could be moved. This allowed the temperature of the inlet nozzle to rise to as much as 700 to 800°C. When the cooling water flow was resumed, it generally was turned on quickly, chilling the cooling collar and eventually cracking a weld on the cooling collar, which allowed cooling water to flood the melter lid. Adjustment of the cooling water flow to maintain a cool inlet nozzle temperature, while not permitting excess water to leak over the top of the melter, became very difficult to achieve, and control of the inlet nozzle temperature became marginal.

Prior to the start of experiment CFCM-8 on November 6, 1979 and during the routine probing of the bottom of the melter tank to estimate sludge depth, a 4.1 cm x 9 cm x 0.6 cm (1.6 in. x 3-1/2 in. x 1/4 in.) section of the inlet nozzle cone was retrieved from the melter floor through one of the viewport nozzles. The section removed is identified by the dotted lines in Figure 21.

ORIGINAL ELECTRODE (BACK SIDE)

MODIFIED ELECTRODE (FRONT SIDE)

FIGURE 18. Electrode Modification

FIGURE 19. Inconel-690 Throat Liner Installed

After the melter was shut down in November 1979 and the melter lid was removed, considerable damage to the lid refractory lining, to the 6-mm (1/4-in.)-thick Inconel-601 inlet nozzle cone and to the 1-cm (1/2-in.)-thick Inconel-601 lid itself, was revealed. A comparison of Figures 16 and 22 shows the extent of the damage to the LDS moldable refractory on the underside of the lid. Figure 23 is a drawing of the lid, illustrating the extent of the refractory and metal losses. Figure 24 is a drawing of the underside of the lid and illustrates the areas of total corrosion of the Inconel lid, the areas of total corrosion of the 304L stainless viewport nozzles, and the location of samples of the inlet nozzle and lid that were cut from the lid structure.

FIGURE 20. Inconel-690 Throat Liner Installed

FIGURE 21. Modified Feed Inlet Nozzle

FIGURE 22. Underlid Insulation After November 1979 Shutdown

FIGURE 23. Lid Drawing Showing Refractory Metal Losses

While the feed inlet nozzle cooling collar was effective in eliminating premature melting of the frit in the feed nozzle, it also provided a temperature zone just below the cone-to-lid weldment that was apparently ideal to promote the condensation of volatile chlorides, fluorides and sulfates, and their subsequent corrosion of this conical penetration. Below this condensation-corrosion zone, the Inconel-601 temperature apparently was too hot to permit condensation, and above this zone the temperature was apparently too cold to allow much corrosion to occur. This would account for the 41-cm (16-in.)-long piece of the Inconel cone that was retrieved from the melter tank, which showed little or no corrosion at the bottom of the cone and a feathered edge closer toward the cooler portion of the cone.

FIGURE 24. Underside of Lid Indicating Areas of Total Corrosion

With the cone missing up to the cone-to-lid weldment, the LDS moldable refractory behind the cone was unsupported. This lack of support, combined with the fluctuating lid temperature due to the loss of cooling control on the nozzle cooling collar, cause the refractory around the inlet nozzle to work loose and fall into the melt. After the 13 silicon carbide startup heating elements were withdrawn from the melter tank, a 2.5-cm (1-in.) layer of Duraboard refractory material was positioned in the bottom of the heating element cover box to isolate this box from the vapors inside the melting tank (see Figure 35). This Duraboard layer was an effective barrier for the melter tank atmosphere, but it also restricted the heat flow from the melter lid in this area, causing a local increase in the lid temperature. This situation, coupled with the large LDS surface area exposed to the melter vapor space because of the silicon carbide penetration holes, was conducive to additional refractory degradation.

On several occasions during the second operating period, foaming of the glass in the melting tank caused the glass level to rise in the melter until the glass contacted the bottom portion of the LDS moldable refractory. Since foaming in the melter had not been anticipated, the lightweight, low-thermal conductivity material of the moldable refractory, as specified in the original design was not particularly resistant to the corrosive attack of the molten glass. Thus, the corrosion of the low-density LDS by the glass was not entirely unexpected.

The corrosion of the 1-cm (1/2-in.)-thick Inconel-601 plate portion of the melter lid has been identified as sulfate and chloride corrosion (see "Melter Lid Corrosion," p. 106) and, in all probability, would not have occurred if the underlid insulation had not fallen away, allowing the Inconel temperature to rise and expose the hot metal directly to the corrosive melter tank atmosphere.

The areas where 304L stainless steel viewport nozzles corroded--again through a chloride corrosion mechanism--is diagrammed in Figure 24. Each of the nozzles corroded in the same general location--at their tips. These viewport nozzles were cut on a 45° angle to the axis of the pipe, and the pipes were then welded onto the lid after being fitted over appropriately shaped oval holes in the lid. A conical hole, in-line with the axis of the viewport, was shaped in the LDS refractory to allow as wide a field of view as possible without compromising the performance of the refractory.

Each of the viewport nozzles corroded at the outermost tip of the nozzles, that is, at the point where the angle between the outside surface of the lid and the outside surface of the nozzle measures 135° . Here at the outermost tip of the nozzle the lid insulation is the thinnest and the lid metal is the hottest, and it is here that the nozzle receives the most radiant energy from the molten glass surface. In effect, the tip of the nozzle is its hottest point. Above the lid the viewport nozzles are relatively cool and constantly condense volatiles coming from the molten glass (chlorides, fluorides, sulfates, etc.), forming a white film (see Table 5). Most of the nozzle apparently is too cool to promote significant corrosion; however, the temperature at the tip appears to be just right for rapid corrosion.

TABLE 5. Analyses of White Film Found on Metal Surfaces

<u>Elements</u>	<u>wt%</u>
Al	1.71
B	0.16
Ba	0.03
Ca	1.15
Cr	0.42
Fe	14.6
Li	0.44
Mn	0.35
Mo	0.10
Na	25.2
Ni	0.32
Si	0.74
Sr	0.05
Cl ⁻	39

NOTE: The results are expressed as percent of the total sample weight. the total percentages do not add up to 100% since elements, such as O₂, are not indicated in this analysis. For example, Fe actually exists as Fe₂O₃.

A number of other stainless nozzles welded to the lid and penetrating through the underlid insulation showed no indications of corrosion. However, these nozzles were much smaller than the others and were perpendicular to the glass surface, which minimized the nozzle temperatures.

The discharge section lid was insulated in the same manner as was the melter section lid, except there were fewer penetrations through the insulation. In addition, the temperatures were low (averaging 900 to 1000°C), the atmosphere was less hostile due to air in-leakage, and there were no foaming problems in the discharge section. As a result, the performance of the LDS moldable insulation was totally adequate on the discharge section lid, and no evidence of refractory damage or metal corrosion was noted on that lid.

Melter Tank

After the melter was drained and shut down for the second time, the melter tank lid and the discharge section lid were removed. A systematic disassembly of the refractories was begun to determine the extent of the corrosion of the refractories and the penetration of the glass into the refractories from the melting tank and from the discharge trough. The sludge was carefully removed from the tank bottom and the tops of the electrodes according to the excavation grid shown in Figure 25. The bulk of the material removed from the tank was packaged, labeled as to its grid location and stored. The refractories on the east (discharge throat) side of the melter were numbered according to the diagram shown in Figure 26. The scales shown in Figures 25 and 26 will be useful in judging the features shown in the photographs to be discussed.

K-3 Liner

Figure 27 is a photograph of the east wall of the melter tank after the melter was drained and shut down following the second operating period. Comparison of this figure with Figure 13 demonstrates the refractory corrosion that occurred during the second operating period. While the block-to-block joint enlargement and the gross corrosion of the bridge block over the throat liner is obvious, the uniform, horizontal corrosion of the hot face of the refractories is lost in the photograph. This corrosion is shown more clearly in Figure 28. Although the difference in the horizontal and vertical scaling of Figure 28 greatly exaggerates the penetration, the illustration clearly indicates the shape and location of the corrosion.

The disassembly of the K-3 liner from the east wall proceeded smoothly, and each of the blocks was weighed as it was removed from the melter. The initial weight, disassembly weight and the weight loss of each K-3 block is listed in Table 6. The initial weight of each block was calculated from its installed dimensions and an assumed specific gravity of 3.9 for each block.

Although the west wall K-3 blocks were not weighed as they were removed, their total weight loss is estimated to have been about 25.5 kg, giving a total K-3 weight loss of about 57 kg.

FIGURE 25. Excavation Grid

Figure 27 also shows the blistering of the Zirmul refractory that was in contact with the glass foam. The Zirmul course is the fourth course up from the floor and is the top course shown in the photograph. In the upper left corner of the photograph a blister on the Zirmul surface can be seen that has split open. Slightly to the right of this split is the cavity left from a blister, the outer layers of which have almost totally sloughed away. Two large pieces of blister skin can be seen having slid down the K-3 surface just under the blister cavity. Just to the right of center of the Zirmul course, another blister can be seen in its early stages of development.

Figure 29 shows the east wall K-3 refractories reassembled on the floor and gives another view of the corrosion pattern on the melter wall. Some evidence of upward drilling can be seen in Block 6 in the area of the greatest

FIGURE 26. Refractories on East Side of Melter

corrosion. Outlines of the electrode "feet" and of the sludge accumulation at the base of the refractory wall can also be seen in this photograph. What also appears to be upward drilling features can be seen on Blocks 5 and 7. It has been speculated that foam in the glass may contribute to this type of corrosion.

Figure 30 shows primarily the K-3 floor of the melter at the south end, but also shows the shallow 6-mm (1/4-in.) corrosion of the K-3 behind the south electrode. The imprint of the electrode foot can be seen on the floor of the melter; to the right is the imprint of the backside of the south electrode in the glass that was trapped behind the electrode as the tank was drained. The bright line running parallel to the bottom corner of the tank is the surface of the trapped glass; above this surface is the shallow corrosion pattern in the K-3 wall. A similar pattern was noted behind the north electrode.

Floor Inspection

While there was gross corrosion of the K-3 tank lining on the east and west walls and very minor corrosion on the north and south walls, no measurable corrosion was detected on the K-3 blocks that formed the melter floor. In

FIGURE 27. East Wall After Second Shutdown

FIGURE 28. K-3 Liner Refractory Corrosion Profiles

TABLE 6. Initial Weight, Disassembly Weight and Weight Loss of Each K-3 Block

<u>Block No.</u>	<u>Initial Wt. (kg)</u>	<u>Final Wt. (kg)</u>	<u>Wt. Loss (kg)</u>	<u>% Loss</u>
K-1	15.5	15.5	0.0	0
K-2	27.8	25.8	2.0	7.2
K-3	27.8	27.1	0.7	2.5
K-4	4.6	4.6	0.0	0
K-5	27.8	21.7	6.1	21.9
K-6	18.5	10.1	8.4	45.5
K-7	27.8	22.2	5.6	20.1
K-8	4.6	4.6	0.0	0
K-9	4.6	4.6	0.0	0
K-10	27.8	25.1	2.7	9.7
K-11	27.8	21.8	6.0	21.5
K-12	4.6	4.6	<u>0.0</u>	0
TOTAL			31.5	

Figure 30, the outline of K-3 floor tile can be seen at left center; no rounding of the edges or corners of this tile can be detected. Measurement made after the tile were removed from the floor showed no decrease in the original tile thickness.

Even the presence of the Inconel freeze valve in the floor (which was thought to influence the electrical path) did not appear to accelerate the corrosion of the floor tile. Here, perhaps the 2-cm (1-in.) recessing of the freeze valve into the floor negated the possible effect of the metallic freeze valve on the current path along the floor, since the freeze valve was covered with an electrically insulating sludge layer.

In any event, no corrosion of the floor tile was noted, even in the areas where the sludge depth was at a minimum.

Figure 31 is a photograph of the floor of the melter and can be compared with Figure 17 to note the differences in the sludge deposition patterns that occurred during the first and second periods of operation of the melter.

FIGURE 29. East Wall K-3 Refractory

FIGURE 30. Melter Floor, South End

FIGURE 31. Sludge Deposit After Second Shutdown

The modified electrodes (Figure 18) are still in place in Figures 27 and 31. The "feet" on the electrodes are 5-cm (2-in.) thick and 15-cm (6-in.) deep, and the lower course of the K-3 refractory is 15-cm (6-in.) tall. It can then be seen that the electrode "feet" are covered with sludge that has an angle of repose of $\sim 45^{\circ}$, and that the top edge of the "feet" project about 6 mm (1/4 in.) above the sludge level in front of the electrodes. The sludge level next to the east wall (throat side) is about 6 cm (2-1/2-in.) thick. The round hole in the center of this ridge is the top of the drain valve. On either side of this central ridge, in Figures 27 and 31, are seen the flat surfaces of frozen glass pools. As these glass pools were removed from the K-3 floor tile, the pattern of the sludge deposits here became clear. On both sides of the center ridge the sludge thickness is about 4-cm (1-1/2-in.) thick in front of the electrodes and tapers uniformly down to ~ 6 mm ($\sim 1/4$ in.), ~ 10 cm (10 in.) on either side of the tank centerline. The total sludge on the floor is estimated to be ~ 90 kg or ~ 30 λ . The electrical conductivity of the sludge was slightly less than that of the glass (see Appendix A), which probably accounts for the lesser degree of corrosion of the electrode "feet" and areas of the K-3 that were covered with sludge.

Convection Pattern

Several times during the operation of the melter during experiments CFCM-6, -7 and -8, and during each of the reboil tests 6 through 14, a glass flow had been noted rising in the center of the melting tank and spreading in a pattern across the surface of the glass toward each of the electrodes. From this observed surface flow pattern and from the observed sludge deposition, two major, counter-rotating, convection cells are indicated in the molten glass (Figure 31). The hot glass apparently rises along the east-west centerline of the tank, flows across the glass surface towards the electrodes, cools slightly and sinks, sliding off the electrode "feet" and back to the center of the tank, by which time it is heated and rises again to the glass surface. Some cooling is probably experienced along the west wall and a little less along the east wall, creating minor convection paths from the glass surface down the cooled walls and into the tank which join the major glass flow off the electrode feet.

While the corrosion pattern of the K-3 hot face is seen to some extent in Figure 27, the peculiarity of this corrosion is a bit clearer in Figures 32 and 33. Figure 32 shows a 5-cm (2-in.) straight edge held against the top edge of the second course of K-3 and shows the tapering of the corrosion pattern from nothing at the edge of the electrode (right center in the photograph) to about 3 cm (1 in.) at the tank centerline (left center). Figure 33 is similar to Figure 32 except that this figure shows the extent of corrosion at the top of the first K-3 course. Here the corrosion tapers from nothing at the edge of the electrode (upper right) to 4 cm (1-1/2 in.) near the tank centerline (upper center). The gap between the straight edge is resting on the outside of the Inconel throat liner, which puts the straight edge 6 mm (1/4 in.) away from the original K-3 surface at the tank centerline.

A comparison of Figures 15 and 34 shows the condition of the electrodes before and after the second melter operating period. Of interest is the greatly increased rounding of the front edge of the electrodes in a region 20 to 30 cm (8 to 12 in.) above the melter floor that occurred during the second melter operating period. This electrode rounding matches the beginning of the tapered corrosion of the K-3 hot face previously described and suggests the possibility of an electrical acceleration of the corrosion of the K-3 refractory. Only negligible material was lost from the electrodes. The south electrode lost 1.70 kg (3.75 lb) of its original 218.3 kg (481.25 lb), or 0.78 wt%. The north electrode lost 1.59 kg (3.50 lb) of its original 221.1 kg (487.5 lb), or 0.72 wt%.

Electrically accelerated corrosion of the K-3 refractory could conceivably be caused by a distortion of the electrical current flux distribution between the two electrodes, resulting in an increased flux density near the K-3 walls and significantly higher glass temperatures along the walls than in the center of the tanks where the glass temperatures are routinely measured. A reason for one mechanism that would distort a uniform current flux toward the side walls would be if the incoming feed material would accumulate in a stable, deep pile in the center of the melter tank. Since this unmelted feed material would be nonconductive, the current flow would be forced to go around and under that portion of the feed pile below the surface of the glass, increasing the flux density against the two K-3 walls and the floor.

FIGURE 32. K-3 Corrosion - Top of Second Course

FIGURE 33. K-3 Corrosion - Top of First Course

FIGURE 34. Electrode After Second Shutdown

Another mechanism that might distort the flux density to the sides of the melter might be the tendency of the current flow from the electrodes to discharge from the sharp forward edges of the electrodes rather than from their flat front surfaces, thus increasing the flux density along the melter walls. This effect may explain the rounding of the forward edges of the electrodes as seen in Figure 34. The rounding occurred only in the region 20 to 30 cm (8 to 12 in.) above the melter floor, probably because of the nonconductive sludge accumulations at the base of the electrodes.

A third possible corrosion mechanism might be the result of the "skin-effect" of the flow of alternating current through the glass. It has been observed that for alternating current the current density through a conductor is not uniform throughout the cross section of the conductor, i.e., the current density is the lowest in the center of the conductor and is the highest at the outer edge of the conductor. It has also been observed that the higher the alternating frequency of the current flow, the higher is the percentage of the total current flow that exists near the surface of the conductor. In addition, a significant fraction of the current output from a phase-angle-controlled SCR (Silicon-Controlled Rectifier) is of a high alternating frequency, particularly when the SCR is operated at low power levels (see Appendix B for a more detailed description of the "skin-effect" phenomenon). Thus, during idling or lower input operations, the outer edges of the glass "conductor" between the two electrodes may be carrying significantly more current than the central segment of the glass tank, resulting in higher glass temperatures along the outer side walls and the floor and subsequent increased refractory corrosion.

Glass Penetration Through Refractory Joints

Under normal operating conditions with the melter tank full of glass, there should be no measurable voltage between the melter containment vessel and either of the melter tank electrodes, if the measurements are made to only one electrode at a time. The electrical power that is supplied to the melter electrodes is referred to as "floating" above ground. This means that neither of the electrodes is connected directly to ground, nor is there a center tap on the power transformer connected to ground. The power transformer is an

"isolation" transformer that electrically isolates the secondary windings totally from the primary windings and from any direct connections to ground. However, some very small capacitive and eddy current coupling to ground is inevitable.

During the initial startup, a low reading from either electrode voltage to the containment vessel was present and was attributed to residual moisture in the refractories. This voltage decreased as the startup progressed and eventually became difficult to measure. As the use of the melter continued, periodic measurements confirmed the designed electrical isolation of the melting cavity from the containment vessel. Occasional observations of the existence of voltage readings between the electrodes and the containment vessel were traced to thermocouple shorts, Conax fitting failures, glass probe shorts, etc. that were quickly corrected. Later, a short-to-ground monitor was designed and installed (see Appendix D) that indicated the continued presence of a relatively high impedance electrical path between the glass in the tank and the containment vessel. The term "relatively high impedance" is used because, although the impedance measured only 10 to 20 ohms, the impedance between the electrodes through the molten glass averaged only 0.1 ohm. In addition, even though this electrical path existed, no electrical current could flow along this path unless one of the electrodes was shorted directly to the containment vessel. The electrical path(s) was never identified, and the monitor indicated that the path(s) shifted from one side of the geometric center of the melter tank to the other, and varied in value as the melter operation continued. Therefore, one of the objectives of the disassembly and inspection of the melter was to determine if molten glass ever reached the containment vessel, creating an electrical path from the melter tank to the containment vessel (see "Discharge Section").

Figures 35, 36 and 37 show the general refractory design of the melter tank and of the discharge section.

Although no photographs of the west K-3 liner were taken, the appearance of the corrosion was very similar to that of the east wall as shown in Figure 27, except the block-to-block joint corrosion was not as severe as that exhibited around Block 6 of the east wall.

FIGURE 35. Melter Tank East-West Cross Section

FIGURE 36. Melter Tank North-South Cross Section (Looking at East Wall)

FIGURE 37. General Refractory Design of Melter Tank and Discharge Section

The penetration of the glass through the block-to-block joints of the K-3 tank lining on the east and west walls was copious with a continuous sheet of glass existing between the K-3 and the backup Zirmul blocks. In the corners, where only 8 cm (3 in.) of Alfrax-66 separated the end of the Zirmul blocks from the cooling water jacket, the glass migration stopped about 8 cm (3 in.) short of the ends of the Zirmul backup blocks. Figure 38 shows these details fairly clearly. Some penetration of glass through the block-to-block joints of the Zirmul occurred, but only in a few places did the glass reach the Alfrax-66 layer behind the Zirmul on the west wall. One expansion crack was noted in the west wall Alfrax casting, and a very thin film of glass penetrated about 4 cm (1-1/2 in.) along this crack. Figure 39 shows a small amount of

FIGURE 38. Glass Leakage to Zirmul Backup Refractory

FIGURE 39. West Wall - Glass Leakage to Alfrax Backup

glass on the Alfrax surface and the penetration of the glass into the crack. Neither the Zirmul nor the Alfrax showed any evidence of corrosion by the glass that penetrated to these surfaces.

The construction of the east wall differed slightly from that of the west wall in that the K-3 was backed up with three layers of Zirmul and an air cooler (Inner Refractory Cooler) on either side of the tank centerline, and the throat, riser and discharge trough in the middle (see Figure 37). As on the west wall, the melter glass penetrated the east wall K-3 liner very easily, but penetrated only one layer of the Zirmul backup at the cooler ends of the east wall and only two Zirmul layers near the discharge throat area. No evidence of corrosion of the Zirmul backup was noted.

At the electrode ends of the melting tank, the Zirmul backup refractory was omitted specifically to provide some cooling of the electrodes which completely covered the ends of the melting tank. This cooling of the K-3 effectively reduced its corrosion to zero, and also reduced the penetration of the glass through the K-3 at the ends of the tank to very nearly zero. Figure 40 shows a small amount of glass on the Alfrax-66 behind the north electrode. No attack of the Alfrax was noted.

The increased fluid pressure and generally higher temperatures on the floor of the melter resulted in greater penetration of glass through the block-to-block joints than on the walls. The viscosity of this type of glass is very low, approximately an order of magnitude below the values of high-level waste glasses such as 76-68 or 72-68.

Figure 38 shows the K-3 melter floor up to the Zirmul backup on the west wall and to the Alfrax backup on the north wall. (The large rectangular object in the center of the tank is a sheet metal plate covering the freeze valve opening in the melter floor.) The outline of the K-3 walls of the melter tank are shown on the photograph. As can be seen, the glass penetrated under the side walls all around the tank, except in the extreme corners which were slightly cooler than the rest of the walls.

FIGURE 40. Glass Penetration Through K-3 Refractory

While the K-3 refractory on the floor of the melter did not show any signs of corrosion, glass penetrated the block-to-block joints with ease, forming a continuous sheet of glass between the K-3 and the top layer of Zirmul backup. Figure 40 shows this glass layer and, as in Figure 38, the outline of the K-3 walls of the melter tank are shown on the photograph. The outlines of the discharge throat and the riser channel are also shown on Figure 40.

While the K-3 floor tile separated very easily from the backup Zirmul blocks, the Zirmul blocks were firmly cemented to one another by the glass that penetrated the top Zirmul layer and spread between the two Zirmul courses. Figure 41 shows the extent of the glass sheet that spread between the two backup Zirmul layers and, again, the outline of the K-3 tank walls above are shown on the photograph for reference purposes.

A small amount of glass leaked through the bottom Zirmul layer and accumulated as small welts that outlined the block-to-block joints on the underside. Figure 42 shows the underside of the bottom Zirmul layer and shows the extent of the leakage through the bottom layer. Figure 43 shows the 1 cm (1/2-in.)-thick Duraboard layer that was positioned under the Zirmul refractory, and the slight depressions in the Duraboard where the glass had come through the lower Zirmul course. In no place did the glass penetrate the Duraboard layer. The outline of the K-3 tank walls above are shown for reference in both Figures 42 and 43.

Glass samples that penetrated the melter floor were analyzed on the induction-coupled plasma spectrometer (ICP) unit to determine the glass type. The results are shown in Table 7. The first glass in the melter was PW-7a (power reactor) followed by the SRL TDS-411 glass and SRL TDS-211. The inner Zirmul sample was taken from between the two Zirmul layers on the floor; the TC well glass sample was taken from the trough between the Zirmul layers; and the glass between the joint board and the Zirmul was taken from underneath the second Zirmul layer (see Figures 35 and 36). It appears that the glass samples are similar to TDS-211. It does not appear that the PW-7a (the first charge to the melter) penetrated the floor because the B, Ca, Fe, Li, Mn and Ni concentrations more closely resemble the SRL-type glass than the PW-7a type.

FIGURE 41. Glass Sheet and Outline of K-3 Tank Walls

FIGURE 42. Underside of Bottom Zirmul Layer (Extent of Leakage)

FIGURE 43. Duraboard Layer Under Zirmul Refractory

TABLE 7. Analysis of Glass that Penetrated the Melter Floor

Oxide Component	Inner Zirmul Glass (wt%)	TC Well Glass (wt%)	Glass Between Joint Board and Zirmul (wt%)	TDS-411 Glass (wt%)	211 Glass (wt%)	PW-7a Glass (wt%)	Zirmul (wt%)
Al ₂ O ₃	9.39	5.84	11.6	3.1	3.39	1.0	70
B ₂ O ₃	6.23	6.08	7.83	7.8	8.47	9.5	
BaO	0.02	0.02	0.02				
CaO	4.69	4.69	3.84	5.2	4.62	2.0	
Ce ₂ O ₃	0.23	0.12	0.10				
Co ₂ O ₃	0.02	0.02	0.01				
Cr ₂ O ₃	0.33	0.35	0.07				
CuO	0.33	0.19	0.527			3.0	
Dy ₂ O ₃	0.03	0.01	0.02				
Eu ₂ O ₃	<0.01						
Fe ₂ O ₃	16.3	19.4	5.54	15.1	10.7	0.013	
K ₂ O	0.45	0.23	0.56				
La ₂ O ₃	0.06	0.03	0.07				
Li ₂ O	5.39	3.89	5.61	8.8	3.29		
MgO	0.34	0.24	0.16				
MnO ₂	3.78	4.60	2.51	4.0	4.56		
MoO ₂	0.04	0.02	0.05				
Na ₂ O	7.65	10.1	7.95	9.0	15.2	8.0	
Na ₂ SO ₄				0.4			
Nd ₂ O ₃	0.04	0.01	0.04				
NiO	1.9	3.43	0.41	1.9	1.42		
SiO ₂	37.2	36.5	43.9	42.2	47.4	35.5	10.2
TiO ₂	0.80	0.37	0.81				
ZnO	0.03	0.05	0.04				
ZrO ₂	1.3	0.45	0.75				19.5
Zeolite				2.5			

DISCHARGE SECTION

The original underflow discharge throat, as seen in Figure 13, was a 10 cm (4-in.)-wide gap in the 15-cm (6-in.)-tall lower course of the K-3 tank liner. This 10-cm x 15-cm (4-in. x 6-in.) throat was filled with an Inconel-690 throat

liner (Figures 20 and 21) to reduce the throat opening to 5 cm x 8 cm (2 in. x 3 in.) to see if the glass velocity through the reduced throat size would prevent sludge accumulation from blocking the throat. The 10-cm x 15-cm (4-in. x 6-in.) liner fit snugly in the refractory gap except for the slightly rounded throat edges that can be seen in Figure 13. To minimize glass leakage around the liner, the front of the liner was fitted with an Inconel-690 flange that was flush against the refractory wall when the liner was in position.

The corrosion of the liner flange and the slight rounding of the upper corners of the liner are seen in Figures 27 and 29. These figures also show the lack of any corrosion of the K-3 refractories on either side of the liner and the gross corrosion of the bridge block. Closer examination of Block 6 in Figure 29 and the same block in Figure 44 suggests that upward drilling (see Appendix C) may have been the corrosion mechanism responsible for the major portion of the damage to this particular block. As mentioned earlier, the liner fit the throat well along the sides but was less tight at the top. The liner was apparently loose enough to allow gas accumulation to start the upward drilling process and yet tight enough to keep the glass stagnant, which kept the glass bubbles in place. The liner lost 1.09 kg (2.4 lb) of its original 10.0 kg (22 lb), or 10.9 wt%.

Corrosion of the riser block was negligible; however, the backside of the bridge block, which formed the flat side of the semicircular riser channel, was corroded slightly until the riser channel became more oval shaped than semicircular. A vertical split in the riser block, probably resulting from the first shutdown/restart operation, leaked a small amount of glass which did not migrate more than 15 cm to 23 cm (6 to 9 in.) into the discharge section refractories.

Corrosion of the discharge trough was negligible, although there were several transverse cracks which leaked a small amount of glass into the surrounding refractories causing no significant problems.

The refractory arrangement in the discharge section is illustrated in Figure 35, showing clearly the relationship between the throat, the riser and the discharge trough. The extent of the leakage from under the foot of the riser channel and its backup K-3 refractories can be seen in Figure 40.

FIGURE 44. Bridgeblock Refractory (From Below)

The discharge trough, which butted against the riser channel, was supported by the backup K-3 refractories at the riser channel end and by a Zirmul paving block at the discharge end (see Figure 35). Furthermore, an Inconel-690 discharge lip, which was welded to a 6-mm (1/4-in.)-thick, slotted Inconel-690 plate, was positioned under the discharge trough. The purpose of the lip was to provide a pouring spout, or low point, from which the glass that drained down the discharge trough end face could cleanly fall free of the discharge trough and drop into the receiving canister. The Inconel discharge lip was held in place by positioning its support plate between the discharge trough and the Zirmul support block. The Zirmul support block was held in position with an Inconel "T" bar which spanned the discharge tube and was anchored to refractories on either side of the discharge tube. The "T" bar, the Zirmul support block and the discharge trough were all bedded in the castable refractory Alfrax-66. The Alfrax bedding continued up the sides of the discharge trough to the level of the top of the trough, as shown in Figure 37. The Alfrax bedding was contained by vertically positioned Zirmul blocks which formed the discharge trough cavity. Figure 45 shows the discharge trough inside of the trough cavity. A few of the transverse cracks in the trough can be seen, as well as the "high glass" mark on the Zirmul side wall. The circumstances surrounding the flooding of the discharge trough are not known, since the normal glass level is perhaps 2 cm (3/4 in.) below the top of the 4-cm (1/2-in.)-radius semicircular groove that forms the discharge trough.

Leakage of glass into the Alfrax bedding refractory on either side of the discharge trough caused the Alfrax to expand (Figure 45), pushing the original surface of the Alfrax up about 5 mm (3/16 in.) in the far back corner. A very small amount of glass leaked through the joints of the Zirmul side walls of the cavity and flowed perhaps another 5 cm (2 in.) to 8 cm (3 in.) radially away from the trough. A very small amount of glass leaked through the discharge trough-to-riser channel joint and flowed about 15 cm (6 in.) toward the discharge end under the trough block before it stopped.

As discussed earlier, glass from the melter tank flowed easily through the east K-3 wall but penetrated only two of the three Zirmul backup refractory

FIGURE 45. Discharge Trough

layers. The inner refractory air coolers, shown in Figures 37 and 40, were very effective in stopping the migration of glass from both the tank and the riser and discharge trough glass passages. These 8-cm x 38-cm x 50-cm (3-in. x 15-in. x 20-in.), internally baffled, Inconel slab coolers remove about 1.8 kW of heat each with an airflow of about 20 scfm.

There were no glass penetrations that reached the containment vessel proper. The closest penetration was through the joint-to-joint cracks between the lower Zirmul subfloor refractory layer. Here about 1 cm (1/2 in.) of Duraboard insulation and a 2-mm (1/16-in.) layer of sheet mica separated the glass from the containment vessel. The Inconel thermowell, positioned in the groove between the two Zirmul subfloor layers, was completely encased in the glass, but the thermowell was insulated from the containment vessel by an electrical bulkhead connector. In a similar manner, molten glass contacted the tip of the thermowell buried in the refractories alongside the discharge trough, but it was also insulated from the containment vessel by a similar electrical bulkhead connector. The electrical insulating properties these two bulkhead fittings were unimpaired when tested during the disassembly operation.

However, the area under the discharge trough, i.e., the discharge lip, the "T" bar, Zirmul support block and the outer discharge tube flange (Figure 35), all appear as though they conceivably could have formed an electrical path of the containment vessel, although no positive measurements of the impedance of such a path was ever measured. The observations and the circumstances of the performance of this section of the equipment bear some review, as follows.

During experiment CFCM-5 (September 19, 1978), glass was observed flowing down the sloped front face of the Zirmul support block under the discharge trough (Figure 35). From this sloping rear wall the glass was observed to drip from the "T"-bar support under the front edge of the Zirmul support block, onto the floor of the discharge cavity, and eventually down the inner discharge tube to the receiving canister. At this time the discharge trough and the discharge face heater systems were maintaining temperatures in the order of 1000°C to assure a clean separation of the glass from the Inconel-690 discharge lip. By reducing the discharge face temperature to 800°C, the

glass flow from under the discharge trough ceased and a relatively clean separation of the glass from the lip was still achieved.

Just prior to CFCM-6 (April 22, 1979), a water-cooling pad fashioned from 6-mm (1/4-in.) Inconel tubing was positioned snugly against the negative-sloped face of the Zirmul support block under the discharge trough. The intent of this cooler was to chill the Zirmul support block and to stop the movement of any glass under the discharge trough. This modification appeared to be effective since during experiment CFCM-6 no glass flow was observed down the rear wall of the discharge cavity.

During experiment CFCM-7 (June 17, 1979) an obstruction at the top of the inner discharge tube caused glass to flood the discharge cavity floor to a depth of about 2 cm (~ 1 in.). The level of the flooding is clearly seen in the right background of Figure 46, a floor-level photo of the partially disassembled discharge section. A glass bridge may have been established at this point between the "T"-bar support and the upper flange of the outer discharge tube.

Apparently, during the period when the obstruction of the inner discharge tube was being cleared, a considerable quantity of glass flowed onto the Zirmul support block cooler where it chilled and possibly made contact with the discharge lip of the discharge lip support plate. Then, after the completion of experiment CFCM-7, probably during the period when the melter was being moved into the idle position (about July 6, 1979), one of the Conax insulators on the south electrode instrument air line shifted its position and established a positive electrical connection between that electrode and the melter containment vessel through the instrument air line. In all probability, an electrical current flow was established at this time that started at the north electrode, went through the glass to the discharge throat, through the throat and up the riser channel, along the residual glass in the discharge trough, down the discharge face to the discharge lip, through the glass bridge to the Zirmul support block face cooler, down the face cooler tubing to the inner discharge tube lower flange, to the containment vessel, and finally through the Conax electrical short on the north electrode instrument air line to the north electrode

FIGURE 46. Glass Leakage from Discharge Lip

where it completed its electrical circuit. The impedance of this path was never measured but was probably fairly high (500 to 1000 ohms) due to the thin layer of glass in the trough and the relatively low temperature of the discharge section (700 to 800°C) and, consequently, the current flow was probably less than one amp.

On August 22, 1979, the inner discharge tube was being removed to clear it of an accumulation of glass. As the craftsman separated the inner discharge tube from the containment vessel flange, he received an electrical shock. Subsequent investigation revealed that the inner discharge tube was prevented from being removed from the melter because the Zirmul support block cooling pad was buried in the glass bridge that connected the discharge lip on the Zirmul support block face. The electrode potential at this time was 64 V, the potential between the inner discharge tube and the containment vessel was 27 V, and the short circuit current flow from the inner discharge tube to the containment vessel was 50 mA. There was no way to determine if a current flow existed from the discharge lip glass bridge through the "T" bar support to the outer discharge tube upper flange; but, if it did exist, it would probably have been less than the measured current flow through the cooling water lines discussed above.

The cooling pad was subsequently disengaged from the glass bridge and on October 3, 1979 a 2-cm (~1-in.)-thick accumulation of glass was removed from between the "T"-bar support and the outer discharge tube flange. Voltage measurements taken at this time are listed below:

<u>From</u>	<u>To</u>	<u>Potential</u>
North Electrode	South Electrode	65 V
North Electrode	Containment Vessel	41.5 V
South Electrode	Containment Vessel	23.3 V
Discharge Lip	Containment Vessel	4.4 V
"T"-Bar Support	Containment Vessel	3.4 V

A recording short-to-ground monitor (see Appendix D) was installed on October 23, 1979. At this particular time the monitor indicated the presence

of a short, or the sum of several shorts, approximately midway between the two electrodes, and had a resistive value of ~ 20 ohms.

Disassembly of the discharge trough and its supporting refractories showed that the glass that was observed flowing down the backside of the discharge cavity (September 19, 1978) did not originate at the riser channel or the hot end of the discharge trough as had originally been suspected, but came entirely from the discharge lip assembly. It was found that the Inconel discharge lip support plate (refer to Figures 35 and 46 for discussion), which was positioned between the discharge trough and the supporting Zirmul block, had caused some of the glass that flowed from the face of the discharge trough to the discharge lip to be drawn by capillary action under the trough block. This support plate was slotted to prevent warping due to temperature differences on the plate, and glass migrated through these slots to the top of the Zirmul support block. From here the glass flowed down the negative-sloped face of the Zirmul support block and dripped off of the "T"-bar support under the front edge of the Zirmul block and onto the discharge cavity floor.

Examination of the top of the Zirmul support block showed some migration of glass under the trough block toward the discharge end and some migration of glass from the discharge lip support plate back toward the melter tank, but the two migration patterns never met. Thus, the glass-leak down the Zirmul support block came totally from the discharge lip.

CORROSION MECHANISMS

Before a detailed investigation into the melter corrosion mechanisms was undertaken, a survey of the materials of construction of the melter and calcine system was made along with some offgas analysis. The objective of these investigations were: 1) identification of unique or key elements in the materials which were possibly detectable in streams exiting the system (i.e, the glass or offgas), 2) determination of the time or conditions when corrosion was taking place, and 3) identification of the source of trace elements found in the many sample analyses.

MATERIALS COMPOSITION INVENTORY

Materials of construction in the melter exposed to the corrosive environment were:

- Monofrax K-3 (tank refractory liner)
- Inconel-690 (electrodes and throat liner)
- Inconel-601 (melter lid and feed inlet cone)
- 304L SS (viewports and feed nozzle)
- LDS (moldable roof insulation)
- Zirmul (refractory above the normal melt level).

Inner surfaces of the spray calciner which contacted process vapors included:

- the 304L SS barrel cone
- the 321 SS flexible pipe connecting the melter to the calciner
- the 310 SS calciner barrel
- the 316 SS sintered metal filters.

The elemental analysis of these materials, as well as the theoretical composition of TDS feed plus 211 frit, are shown in Table 8.

Reviewing the table columns shows which elements are unique to the materials that corroded. With this in mind, feed and glass sample elemental analysis from previous runs can be reviewed to determine if elevated levels of these elements were present in the glass samples. This offers a means of tracking

TABLE 8. Calciner, Ceramic Melter and Offgas System Materials Composition

Element	Oxide	Calcine + Frit Oxide wt%	Typical Inconel 601 wt%(a)	Typical Inconel 690 wt%(a)	Typical 316 SS wt%(a)	Typical 321 SS wt%(a)	Typical 304L SS wt%(a)	Monofrax K-3 wt%	LDS Moldable Insulation wt%	Zirmul Refractory wt%
Al	Al ₂ O ₃	3.8	0.48	---	---	---	---	44.0	22.1	70.0
Ca	CaO	5.3	0.15	---	---	---	---	0.18	---	---
B	B ₂ O ₃	8.0	---	---	---	---	---	---	0.49	---
Cr	Cr ₂ O ₃	---	16.8	30.0	16-18	17-19	18-20	19.0	---	---
Fe	Fe ₂ O ₃	14.7	14.1	9.5	balance	balance	balance	5.85	---	---
Li	Li ₂ O	---	---	---	---	---	---	---	0.10	---
Na	Na ₂ O	15.4	---	---	---	---	---	0.20	5.36	---
Ni	NiO	1.7	60.0	60.0	10-14	9-12	8-12	---	---	---
Mn	MnO ₂	3.9	0.20	---	2.0	2.0	2.0	0.06	---	---
Mg	MgO	0.11	---	---	---	---	---	3.71	---	---
Si	SiO ₂	43.6	0.16	---	1.0	1.0	1.0	0.60	67.0	10.2
Ti	TiO ₂	---	0.34	---	---	---	---	0.16	---	---
Zn		---	0.20	---	---	---	---	---	---	---
P		---	---	---	0.045	0.045	0.045	---	---	---
S	Na ₂ SO ₄	0.4	---	---	0.03	0.03	0.03	---	---	---
Mo		---	---	---	2-3	3-4	---	---	---	---
Cu		---	0.30	---	---	---	---	---	---	---
C		---	---	---	0.08	0.08	0.03	---	---	---
Zr	ZrO ₂	---	---	---	---	---	---	---	---	19.5
Total		96.8	92.7	99.5	---	---	---	71.8	95.1	99.8

(a) Metallic wt%

the corrosion and determining a time frame for the corrosion. For example, the Monofrax K-3 contains an average of 3.71 wt% MgO, and no other material in the table contains any Mg except the trace amounts of Mg that contaminated the feed and frit. Therefore, Mg levels in the glass samples above the trace values from the feed and frit could indicate K-3 corrosion. Because of the fluctuations in feed concentrations and small total volume of Mg corroded from the K-3, it would be difficult to determine the time-frame for the K-3 corrosion unless it took place very rapidly and a Mg peak could be found in the glass samples. At the beginning of a run on November 5, 1979, the glass samples contained 45% more MgO than could be accounted for in the feed and frit, which appears to indicate that there was K-3 corrosion at the beginning of the run or during the idling period preceding the run.

Aluminum levels above the levels from the frit and feed would indicate loss of one of the refractories since all three refractories contained large amounts of Al_2O_3 (from 22 to 70 wt%). Elevated levels of chromium in the glass could indicate stainless steel, Inconel or K-3 corrosion and, if accompanied by increased levels of nickel, would indicate metal corrosion.

VOLATILE SPECIES LEAVING THE FILTERS

Condensate and scrub solution samples from the 5-day run in November 1979 were analyzed on an ICP and ion chromatograph. A typical ICP condensate sample analysis is listed in Table 9.

The ratios of Al/Fe, Ca/Fe, Na/Fe and Ni/Fe in these samples agree closely with theoretical ratios from the feed indicating a uniform calcine mixture was penetrating the filters and none of these elements was volatile (concentrations higher than expected from calcine). Small amounts of Li and B relative to Fe indicate a larger DF (decontamination factor) for the larger frit particles. The Cr and Mo numbers are either contamination of the feed or frit, or corrosion products of stainless steel. The condensate samples were also analyzed for anions; the results are shown in Table 10.

The fluoride values appear to be roughly that of tap H_2O (~1 ppm), indicating either low fluoride contamination of the feed or low fluoride

TABLE 9. Typical Condensate ICP Analysis from the 5-Day November 1979 SRL Run

<u>Element</u>	<u>Elemental Concentration</u>	<u>Oxide Concentration</u>
---	g/l	g/l
Al	0.04	0.075
B	0.006	0.021
Ba	0.000	0.000
Ca	0.041	0.058
Cr	0.002	0.003
Fe	0.381	0.545
Li	0.001	0.001
Na	0.5	0.674
Mg	0.005	0.008
Mn	0.007	0.012
Ni	0.059	0.075
Si	0.030	0.063
Sr	0.000	0.000
Mo	0.002	0.003
TOTAL	---	1.54

volatility. It was first thought that fluoride may have contributed to the filter corrosion, but fluoride does not appear to be significant. The samples do show, however, chloride penetration of the filters, especially at the beginning of the run and decreasing as the run progressed. The nitrate numbers show the same trend; nitrate concentrations were high at the beginning of the run and decreased as the run progressed.

The pH numbers indicate the condensate was acidic at the beginning and end of the run (possibly in the form of HCl or HNO₃). Filter corrosion may have been more severe at the beginning of the run because the highest chloride and nitrate concentrations and the lowest pH values were observed then. Also, a white vapor (believed to be high in NaCl) was observed exiting from the view-ports of the coupled idling melter before the run started. These vapors, in

TABLE 10. Anion Concentrations from the Glassware Offgas Sampling System During the November 1979 5-Day Run

Sample Type	F ⁻ Concentration ppm(a)	Cl ⁻ Concentration ppm	NO ₂ ⁻ Concentration ppm	NO ₃ ⁻ Concentration ppm	SO ₄ ⁻ Concentration ppm	pH
Glassware Condensate (November 9, 1979)	<0.44	124.0	---	710.0	8.3	4.32
Glassware Condensate (November 7, 1979)	<1.5	15.0	---	8.6	36.0	8.46
Glassware Condensate (November 8, 1979)	<0.47	4.0	7.9	2.5	9.2	8.90
Glassware Condensate (November 9, 1979)	<0.15	2.9	5.8	5.5	~1.0	4.98

(a) Due to interference of a contaminant peak, the F⁻ values listed are approximate maximum values. Actual values are probably 10 to 50% of the values listed.

contact with the filters when a vacuum was placed on the filters to vent the melter, could explain the high chloride at the beginning of the run and the decrease in its concentration as the run progressed since large amounts of steam and atomizing air would tend to flush the filters while running.

Table 11 shows chloride weight percentages in the calcine and glass. There is a high degree of variability in the calcine chloride concentrations. The average is 1.83 wt%. The glass chloride concentrations were low at the beginning of the run, indicating that chloride may have volatilized from the melt during the idling period preceeding the run. At the end of the run, the glass concentrations were constant at 0.6 wt% while the feed concentrations continued to increase, which may indicate that the chloride solubility in the glass is limited to 0.6 wt%. The difference between the calcine and glass concentrations either accumulated in the calciner/melter or exited in the off-gas. If no accumulation is assumed, then an average of 50.4 wt% of the chloride exited in the offgas. This value does not agree with condensate analysis, however. If the chloride was exiting in the offgas, the concentration of the condensate collected would have been approximately 0.65 g chloride/l and analysis showed much lower values (see Table 10). It appears that despite the holes in the filters there was significant chloride accumulation, possibly as high as 190 g/h.

TABLE 11. Chloride Concentrations in the Feed and Glass and Percent Difference

Date	Time	wt% Chloride in Calcine	Date	Time	wt% in Glass	wt% Without Frit	% Difference
11/5	0220	0.741	11/5	0330	<0.03	0.107	85.6
11/5	0730	0.647	11/5	0830	0.04	0.143	77.9
11/5	1300	0.741	11/5	1350	0.06	0.214	71.1
11/5	2145	0.706	11/5	2330	0.10	0.357	49.4
11/6	0200	0.823	11/6	0330	0.10	0.357	56.6
11/6	1000	0.706	11/6	0900	0.10	0.357	49.4
11/6	1400	0.894	11/6	1400	0.20	0.714	20.1
11/7	0015	0.941	11/7	0122	0.20	0.714	24.1
11/7	2000	0.706	11/7	2050	0.20	0.714	0
11/8	0621	3.76	11/8	0530	0.30	1.07	71.5
11/8	0840	3.65	11/8	0945	0.60	2.14	41.4
11/9	0005	4.47	11/8	2230	0.60	2.14	52.1
11/9	0200	5.06	11/9	0116	0.60	2.14	57.7
AVERAGE		wt% dry 1.83				0.859	% offgas 50.4

FILTER CORROSION

The normal operating temperature of the filters ranged between 200 and 500°C, filtering solids from the calciner offgas which was principally air with moisture and varying amounts of HCl, SO₃, NO_x, CO₂ and possibly boric acid. The presence of HCl, NO_x and SO₃ was confirmed by analyses of condensate leaving the filter unit which showed pH4 to pH8 with up to 125 ppm Cl, 710 ppm NO₃⁻ and 8 to 36 ppm SO₄⁻ (Table 10). The filter unit was backwashed with water prior to removal (Table 12).

Filter Examination

Sections of the 10-μm and 65-μm filter elements were examined metallographically and found to be uniformly corroded all the way through the cross section (see Figures 47, 48 and 49). The 65-μm filter was more severely

TABLE 12. Analysis of Water-Soluble Compounds in Filter Flush Water

Chemical	g/l ^(a)	Chemical	g/l ^(a)
Al	1×10^{-4}	Mn	2×10^{-5}
B	1×10^{-2}	Mo	5.7×10^{-3}
Ca	1.4 ^(b)	Na	11.7 ^(b)
Cr	4.3×10^{-3}	Pb	3×10^{-4}
Cu	1.5×10^{-4}	Si	2.9×10^{-3}
Fe	1×10^{-4}	Sr	3.1×10^{-3}
K	0.15 ^(b)	Ti	4×10^{-5}
Li	2.8×10^{-2}	Zr	4×10^{-5}
Mg	4.4×10^{-3}	Cl ⁻	18 ^(b)

(a) Approximately 70 l of flush water were used.

(b) Major constituents were Ca, K, Na and Cl⁻.

corroded than the 10- μ m filter. In an effort to identify the corrosive species, SEM examination of the specimens revealed only typical Fe, Cr and Ni with traces of impurities (see Figures 50 through 58). Chloride was noteworthy by its absence in the corrosion film, while essentially pure sodium chloride was present on the face of the filter (see Figures 50, 56 and 57). Another SEM examination for fluoride failed to reveal any residual fluoride contamination in the corrosion product (Figure 51). pH paper laid on a damp section of corroded filter gave a neutral reaction.

ICP analysis of the 316 SS sintered filters is shown in Table 13. The ratio of Fe/Ni, Cr/Ni and Mo/Ni are slightly less for the oxidized pieces of sintered metal relative to the unused sample, but no large Cr or Fe depletion was noted. X-ray diffraction analysis of the filters showed $\sim 3/4$ of the material was Fe₃O₄ (or substituted) spinel and the rest was austinite. This oxidation of a major portion of the original filter material caused the brittle behavior of the filters.

The corrosion that might be expected of 316 SS in moist air at 500°C or less for 1600 h would be about 1.0 μ m. The actual corrosion product, observed

FIGURE 47. 10-μm Filter Edge

79X

198X

395X

FIGURE 48. 10-μm Filter Center

EDGE

78X

78X

195X

390X

FIGURE 49. 65- μ m Filter Center

FIGURE 50. XRD Analysis of 65-μm Filter on the SEM Unit.
(Numbers refer to following analyses graphs.)

FIGURE 51. Dispersive Spectrometry Analyses Spots for Fluoride on the SEM Unit (No Fluoride Found)

with fair uniformity through the section, was 8 μm on the 10- μm filter and 18 μm on the 65- μm filter. Thus, it appears the filters have undergone an accelerated attack at their operating temperatures. Attempts to locate potential accelerating ions in the residual corrosion product were not successful. However, the difference in corrosion between the two filters is probably caused

FIGURE 52. Analyses for Point 1 on Figure 50

FIGURE 53. Analyses for Point 2 on Figure 50

FIGURE 54. Analyses for Point 3 on Figure 50

FIGURE 55. Analyses for Point 4 on Figure 50

FIGURE 56. Analyses for Point 5 on Figure 50

FIGURE 57. Analyses for Point 6 on Figure 50

FIGURE 58. Analyses for Point 7 on Figure 50

by the higher flow through the 65- μm unit since the filters were in parallel. Although most likely materials accelerating the corrosion of the filters would be the traces of HCl , NO_x , SO_3 and $\text{B}(\text{OH})_3$, these were not found and may have been hydrolyzed from the filter unit.

MELTER LID CORROSION

Samples of the lid were taken from Sections 1 and 2 illustrated on Figure 24 to determine corrosion mechanisms of the Inconel 601 alloy. Five samples were taken from Section 1; two samples from the underside of the lid; one sample of yellow material from the underside of the lid; and one sample each from the lower and upper feed inlet nozzle. Three samples from Section 2 were also analyzed: from the underside of the lid (mostly oxides), the metal adjacent to the oxide layer and a bulk sample. The results of the analysis are shown in Table 14. The ICP was used to determine which elements were in the sample (except chloride which was determined by X-ray fluorescence). X-ray diffraction was used to determine the forms in which the elements were present.

TABLE 13. ICP Analysis of the 316 SS Sintered Metal Filters (wt%)

Element	Oxide	New 65- μ m 316 SS(a) Sintered Filter	Corroded 65- μ m 316 SS(a) Sintered Filter	Corroded 10- μ m 316 SS(b) Sintered Filter
Al	Al ₂ O ₃			
B	B ₂ O ₃			
Ca	CaO			
Co	Co ₂ O ₃			
Cr	Cr ₂ O ₃	15.2	13.8	9.18
Cu	CuO			
Fe	Fe ₂ O ₃	57.6	53.3	42.6
K	K ₂ O			
Li	Li ₂ O			
Mg	MgO			
Mn	MnO ₂			
Mo	MoO ₃	2.19	2.02	1.52
Na	Na ₂ O			
Ni	NiO	11.2	13.5	9.24
Pb	PbO			
Si	SiO ₂	0.91	0.63	0.37
Ti	TiO ₂			
Zn	ZnO			
TOTAL		87.1	80.3	62.9

(a) As metal.

(b) X-ray diffraction indicated the elements were present as ~3/4 oxides and ~1/4 metals. The compositions, however, are shown as metals for comparison with the new 316 SS sintered sample.

The samples from the underside of the lid were composed primarily of oxides of Ni, Cr and Fe. Significant amounts of NaCl were also found. In addition, a sample of a yellow material from the underside of the melter lid was found to be NiCl₂. The other components present appeared to be material from the batch feed which had adhered to the lid.

TABLE 14. ICP Analysis of the Inconel-601 Melter Lid (Composition in wt%)

Element/ Oxide	Section 1					Section 2		
	Underside of Lid(a)	Underside of Lid(a)	Yellow Material Underside of Lid	Lower Feed Inlet Nozzle(a)	Upper Feed Inlet Nozzle(a)	Underside of Lid(a)	Metal Adjacent to Oxide Layer(b)	Bulk Sample(b)
Ni/NiO	48.5	59.0	---	45	3.5	64.5	70.4	60.0
Fe/Fe ₃ O ₄	11.9	14.1	---	14.8	17.2	14.3	7.54	14.7
Cr/Cr ₂ O ₃	30.4	26.5	---	17.1	4.5	20.6	0.43	16.8
NaCl	4.0	1.8	---	10.5	32.0	---	---	---
NiCl	---	---	100	---	---	---	---	---
Other(c)	5.2	---	---	10.6	42.8	0.6	21.6	8.5

(a) As oxides.

(b) As metals.

(c) Primarily materials from melter batch.

The material from the lower portion of the feed inlet nozzle was very similar to that on the lid. However, the material contained a significantly higher NaCl content. The material from the uppermost portion of the inlet nozzle contained significantly lower concentrations of Cr₂O₃ and NiO, and was extremely high in NaCl. This sample also contained a significant amount of sulfur.

The metal adjacent to the oxide layer from the Section 2 sample was depleted in Al, Fe and Cr. Approximately 83% of the Al, 49% of the Fe and 97% of the Cr was depleted relative to the bulk sample. Although the missing Al, Fe and Cr should have shown up in the oxide layer, the ratios of Cr/Ni, Fe/Ni and Al/Ni were nearly the same for the bulk sample and oxide layer, indicating no enrichment of these elements in the oxide layer. Since the Cr was depleted from the metal adjacent to the oxide layer, it appeared the Cr did not pacify the Inconel by forming an insoluble chromate film on the surface. The Ni appeared to be left intact.

During melter operation, portions of the lid reached fairly high temperatures, ~500 to 850°C. Since the melting point of NaCl is 801°C, NaCl vapors in the melter would have condensed in the lid as a solid or molten salt. Chloride vapors may also have been present in small amounts. Inconel-601 has poor resistance to high-temperature chlorine attacks. This is especially true when water is present, and small amounts of water would have been present from

decomposition of the calcine and from the calciner atmosphere. Small amounts of chloride were seen randomly dispersed in the melter lid photomicrographs.

Those areas of the lid which were not exposed to the high temperatures experienced less corrosion because of slower reaction rates at lower temperatures.

Inconel-601 is also subject to corrosion by fluorine and sulfur at high temperatures (INCO 1965). Both were present in the melter atmosphere. Scanning electron micrographs of the melter lid have identified sulfur attack on the Inconel. Three lid samples were analyzed. One is shown in Figures 59, 60 and 61, and another is shown in Figures 62 and 63. The last is shown in Figures 64, 65 and 66.

Photo 1 of Figure 59 is a "normal" SEM micrograph. The photo shows two phases (one dark and one light) near the edge of the sample exposed to the glass and one homogeneous phase deeper into the metal (right side of the micrograph). Photo 2 is of the same area in Photo 1 but shows only where Fe is present. In both photos, except in the dark phase of Photo 1, Fe is present throughout the sample.

Photo 3 of Figure 60 is the same area as Photo 1 but shows only where nickel is present, and nickel is present everywhere except in the dark phase of Photo 1. Photo 4 of Figure 60 and Photo 5 of Figure 61 show that the dark phase of Photo 1 is chromium sulfide. Chromium has been depleted out of the area surrounding the dark phase of Photo 1, and the Cr is homogeneously distributed beyond the point where the sulfur penetration stops.

Figure 62 and 63 show the same pattern. The Cr has agglomerated in the dark phase leaving the surrounding area depleted in Cr. The sulfur is also concentrated in the dark phase of Photo 6. The Cr has not been attacked where sulfur is not present.

Figures 64, 65 and 66 show three phases present in the Inconel. These figures are included to show the presence of a Ni-S phase which was not seen

PHOTO 1
SURFACE EXPOSED TO
MELTER ATMOSPHERE

PHOTO 2
SURFACE EXPOSED TO
MELTER ATMOSPHERE
(SHOWS WHERE Fe
IS PRESENT)

FIGURE 59. Photomicrographs of the Inconel 601 Melter Lid

PHOTO 3
SHOWS WHERE Ni
IS PRESENT

SURFACE
EXPOSED TO
MELTER
ATMOSPHERE →

PHOTO 4
SHOWS WHERE S
IS PRESENT

SURFACE
EXPOSED TO
MELTER
ATMOSPHERE →

FIGURE 60. Photomicrographs of the Inconel 601 Melter Lid

**SURFACE
EXPOSED TO
MELTER →
ATMOSPHERE**

in the other two samples. The three phases include a Cr-S phase in the leading edge of the corrosion zone, followed by a Ni-S phase, and a Ni-Fe phase throughout the zone.

Figures 65 and 66 identify the phases. Figure 65 (Photos 1 and 2) show a Ni-Fe phase to be the lightest-colored phase of Figure 64. Figure 65 (Photo 1) and Figure 66 (Photo 1) show that the medium-dark phase of Figure 64 is Ni and S. There was almost no Fe in the Ni-S phase. Figure 66 (Photos 1 and 2) and Figure 65 (Photo 2) show that the darkest phase of Figure 64 is composed of S and Cr with a small amount of Fe.

As stated previously, the Cr at the outermost surface of the Inconel exposed to the glass is present as an oxide. When the chromium sulfide is converted to chromium oxide, the sulfide may be freed to attack more Cr. If

PHOTO 6

**SURFACE
EXPOSED
TO MELTER
ATMOSPHERE**

PHOTO 7
SHOWS WHERE Cr
IS PRESENT

**SURFACE
EXPOSED
TO MELTER
ATMOSPHERE**

FIGURE 62. Photomicrographs of the Inconel 601 Melter Lid

SURFACE
EXPOSED
TO MELTER
ATMOSPHERE →

PHOTO 8
SHOWS WHERE S
IS PRESENT

FIGURE 63. Photomicrographs of the Inconel 601 Melter Lid

←
MELT
SURFACE

→
CORROSION
LEADING
EDGE

SHOWS
3 PHASES
Ni-S
Ni-Fe
Cr-S

FIGURE 64. Photomicrograph of Inconel 601 Melter Lid

**MELT
SURFACE**
←

**CORROSION
LEADING EDGE**
→

**PHOTO 1
INDICATES
THE
PRESENCE
OF Ni**

**MELT
SURFACE**
←

**CORROSION
LEADING EDGE**
→

**PHOTO 2
INDICATES
THE
PRESENCE
OF Fe**

FIGURE 65. Photomicrographs of Inconel 601 Melter Lid

**MELT
SURFACE**
←

**CORROSION
LEADING EDGE**
→

**PHOTO 1
INDICATES
THE
PRESENCE
OF S**

**MELT
SURFACE**
←

**CORROSION
LEADING EDGE**
→

**PHOTO 2
INDICATES
THE
PRESENCE
OF Cr**

FIGURE 66. Photomicrographs of Inconel 601 Melter Lid

this is true, a band of sulfur may have moved through the Inconel leaving a trail of chromium oxide in its path. However, it is also possible that the sulfide is oxidized to SO_2 gas which could leave the metal oxide matrix. This mechanism would require addition of sulfur to the Inconel from the glass melt if the attack were to continue.

MELTER TANK CORROSION

Experimental Procedure

Two samples of the refractory from the east wall of the melter, just above the discharge throat, were examined to determine the reason for the corrosion of the K-3 brick. The locations of these samples are shown in Figure 26. Sections 2 and 6 of Brick K-6 were examined.

Figures 67 and 68 show the brick samples 2 and 6. Also shown are the portions of the bricks which were used for examination. Four portions of brick number 2 were examined. Two sections of brick number 6 were investigated.

The cut sections of each brick were mounted and polished for photomicroscopy. The samples were then examined using an SEM with a microprobe attachment which allowed the determination of the compositions of individual phases.

Structure and Composition of the K-3 Refractory

The structure and morphology of the refractory and the area of corrosive attack to the brick may be seen in an examination of Section 2C of Sample 2 (Figure 69). The K-3 refractory is produced by fusing (melting) and casting a mixture of Al_2O_3 and Cr_2O_3 . Also present are MgO , Fe_2O_3 and small amounts of SiO_2 and alkali oxides. The composition of the brick is shown in Table 15. As the cast melt solidifies, a low-porosity outer layer forms. The inside of the brick, however, contains a significant void volume, which can be clearly seen in Figure 69.

TOP SURFACE

~.55X

LEFT FACE

~.55X

RIGHT FACE

~.55X

BOTTOM SURFACE

~.55X

FIGURE 67. Brick Sample No. 2 from Melter Refractory K-6

TOP SURFACE

~.55X

LEFT FACE

~.55X

RIGHT FACE

~.55X

BOTTOM SURFACE

~.55X

FIGURE 68. Brick Sample No. 6 from Melter Refractory K-6

FIGURE 69. Section C from Brick Sample No. 2

The reaction zone in which the brick is corroded can also be seen in this figure. The zone appears as a band of light-colored material on the right side of the sample. This side of the sample was the surface exposed to the glass.

TABLE 15. Composition of K-3 Refractory and Approximate Compositions of the Brick Phases and Corrosion Products

Oxide Component	Brick			Corrosion Products	
	K-3 wt%	Al Phase of K-3 ~wt%	Cr Phase of K-3 ~wt%	Spinel Crystals ~wt%	Glass ~wt%
Cr_2O_3	27.3	20	50	30-60	Trace
Al_2O_3	60.2	80	20	Trace	30-50
MgO	6.1	--	10	Trace	--
SiO_2	1.8	--	--	Trace	50-70
Fe_2O_3	4.2	--	30	20-50	5-10
Na_2O	0.3	--	--	--	20
NiO	--	--	--	10-20	--
MnO_2	--	--	--	10-30	Trace

Figure 70 shows an enlargement of a section of the brick at the reaction layer. The as-manufactured brick (to the left of the light-colored reaction band) consists of two phases which appear light and dark gray; the light portions are a chromium-rich phase.

Figure 71 shows a microprobe analysis of this material. The peak heights correspond to relative weight percents of the elements. Because the microprobe cannot detect elements below sodium on the periodic table, O, which is a major portion of the brick, is not seen. The figure shows that this phase contains Cr, Fe, Al and a minor amount of Mg. An analysis of the light areas in Figure 70 is shown in Figure 72. This phase is primarily Al along with Cr and a minor amount of Fe. Analyses of these two phases in a number of locations on different samples showed these compositions to be consistent throughout the brick. Their approximate compositions are given in Table 15.

Corrosion Products and Mechanism

The light-gray material at the glass-brick interface in Figure 70 has a different composition than either of the brick phases. The composition of this corrosion product is variable, containing Cr, Fe, Mg, Ni and small amounts of Al and Si. The crystalline form of the product indicates a spinel structure. The microprobe analyses of this material from three locations are shown in

FIGURE 70. Reaction Zone at Brick-Glass Interface

Figures 73, 74 and 75. These figures give some indication of the variability of the composition encountered. The approximate range of the composition of the material is shown in Table 15.

As Figures 70 and 76 show, this corrosion product consists of discrete crystallites with little or no intercrystalline bonding. These crystallites are formed in two steps: 1) initially the glass attacks and dissolves the surface of the refractory, 2) then, because Cr has a very low solubility in borosilicate glass (~ 0.5 wt%), the dissolved Cr immediately precipitates out of the glass into these crystals. The Mg, Ni and a portion of the Fe in the crystals comes from the glass, and the Al from the refractory remains in solution in the corroding glass. Spinel precipitation may be enhanced by the Al_2O_3 dissolved from the brick. Noted previously in SRL glasses, alumina additions cause increased spinel precipitations.

Because these crystals are not bonded to the brick or each other, they can only form a protective layer if they are held in place by the glass layer at the surface of the brick in which they are located. As previously noted,

FIGURE 71. Microprobe Analysis of Light-Gray (Cr-Rich) Phase of K-3 Refractory

FIGURE 72. Microprobe Analysis of Dark Gray (Al-Rich) Phase of K-3 Refractory

FIGURE 73. Microprobe Analysis of Reaction Zone Crystallite

FIGURE 74. Microprobe Analysis of Reaction Zone Crystallite

FIGURE 75. Microprobe Analysis of Reaction Zone Crystallite

this glass is enriched in Al_2O_3 from the refractory and is depleted in Fe, Mg and Ni which have precipitated in the spinel. A comparison of the compositions of the glass outside of and within the corrosion layer is shown in Figures 77 and 78. The approximate composition range of the glass within the corrosion layer is given in Table 15. At lower temperatures (below $\sim 1150^\circ\text{C}$), the higher Al_2O_3 glass between the crystallites is viscous enough that a protective layer adheres to the brick protecting the surface of the brick from excessive attack.

At higher temperatures, above 1150°C , the glass phase becomes much more fluid. This is especially critical with the SRL TDS-211 glass composition (Table 15). The high alkali level in this composition results in a glass phase in the corrosion layer which will be more fluid at a particular temperature than would be the case if a lower alkali composition were used. The normal convective action in the melter may then sweep this protective layer away, allowing further attack to occur. Sloughing away of the protective layer would also be enhanced during periods of high temperature reboil.

FIGURE 76. Reaction Zone at Brick-Glass Interface

FIGURE 77. Microprobe Analysis of Glass Outside of Glass-Refractory Reaction Zone

FIGURE 78. Microprobe Analysis of Glass Within Reaction Zone

Once removed from the brick's surface, the crystalline corrosion products do not dissolve in the glass. Very little Cr was found in glass samples poured during a 5-day test in November 1979. It might be expected that the crystals would deposit out of the glass onto the melter floor. This was confirmed when floor samples were analyzed for Cr content. Results of these analyses are shown in Table 16. Compared to a chromium oxide level in the glass of ~0.1 wt%, the sludge on the floor was found to have ~2 to 7 wt% chromium oxide in various locations.

Very little corrosion was found on the melter floor and at the edges where spinel buildup had occurred because the spinel formed a protective layer on the brick which prevented interaction of fresh glass and refractory. Also, only minimal corrosion was found on the sides of the tank behind the electrodes because there was very little convection in these locations which would remove corrosion products and expose fresh brick.

Due to the porous structure of the center of this type of brick, it is expected that once the impervious outer layer has been lost, corrosion might occur more rapidly. Figures 79 and 80 show cross sections of the surface of the brick which faced the inside of the tank. It can be seen that in these locations, where significant corrosion had occurred, the porous portion of the brick had been reached by the glass.

TABLE 16. Chromium Oxide Content of the Melter Glass and Sludge from Various Floor Locations

<u>Cr₂O₃ wt%</u>	<u>Location^(a)</u>
1.9	4
2.3	10
7.3	14
3.4	16
0.7	21
0.1	Bulk Glass

(a) For floor locations corresponding to these numbers see Figure 25.

6.3X

FIGURE 79. Section A of Brick Sample 2

The major refractory corrosion/erosion probably occurred during the periods in which the melter was operated in excess of 1150°C . These periods occurred during April and June of 1979 (see Figure 73). Previous corrosion tests showed minimal attack at temperatures at or below this value. Also, the

6.3X

FIGURE 80. Section B of Brick Sample 2

corrosion found in the tank after the October 1978 shutdown and drain was minimal. Temperatures during this campaign were kept much lower and never exceeded 1150°C except during very short (<1 day) periods.

An interesting feature of the corrosion of K-3 by the glass can be seen in Figure 69 where a crack is present in the lower portion of the brick along the A-B-C line. This crack is filled with glass. At the end of the crack nearest to the interior of the melter (A), corrosion identical to that found at the brick's surface is seen. As the crack goes deeper into the brick, however, the corrosion layer decreases until at between B and C no corrosion can be seen. The fact that no corrosion occurred in the area of C is supported by the chemical analyses of the brick phase in contact with the glass at this location. These analyses were found to be identical to those found for the bulk sample. The glass, however, was found to be very enriched in Al_2O_3 , which may suggest that this concentration was high enough to prevent further interaction with the refractory. The brick's appearance at this location is shown in Figure 81. The analysis of the glass, chromium phase and aluminum phase, is shown in Figures 82, 83 and 84.

Corrosion Testing

Initial corrosion testing of K-3 in TDS-211 glass gave no indication that the degree of attack found in the melter would occur. There may be a number of reasons for this. Testing temperatures did not exceed $1150^{\circ}C$. Higher temperatures are needed before the protective layer becomes easily removed. Also, the tests were done in Al_2O_3 crucibles. The crucibles were found to have partially dissolved in the glass during the tests. This dissolved alumina may have inhibited the corrosion reaction. The corrosion rates found in these tests were ~ 3.5 mm/yr. A second series of experiments were done at $1300^{\circ}C$ in platinum crucibles. These tests showed ~ 50 to 100 mm/yr corrosion rates. These are closer to the rates which would be required to explain the attack on the melter. Figure 85 shows a photomicrograph of a brick section used in the higher temperature experiments. It can be seen that the corrosion appears to be similar to that found on the melter bricks.

One of the reasons that these types of tests did not give an accurate prediction of the attack which was found is that these were static tests. The type of corrosion/erosion found in the melter requires that the protective layer of spinel crystals and glass be removed. This occurred in the melter

FIGURE 81. Enlargement of Area C of Brick Section 2-C

through the convection in the tank. In static corrosion tests, the protective layer would not be sloughed away and the corrosion rate might appear to be much lower. In order to predict the attack, a test with moving glass or refractory at high temperatures would have been needed.

FIGURE 82. Microprobe Analysis of Glass Phase in Area C of Brick Section 2-C

FIGURE 83. Microprobe Analysis of Cr-Rich Phase in Area C of Brick Section 2-C

FIGURE 84. Microprobe Analysis of Al-Rich Phase in Area C of Brick Section 2-C

FIGURE 85. K-3 Specimens Used in 1300°C Test of Corrosion in TDS-211 Glass

REFERENCES

Bonner, W. F., H. T. Blair and L. S. Romero. 1976. Spray Solidification of Nuclear Waste. BNWL-2059, Pacific Northwest Laboratory, Richland, WA 99352.

INCO. 1965. Resistance of Huntington Alloys to Corrosion. International Nickel Company, Inc., New York.

APPENDIX A

ELECTRICAL CONDUCTIVITY OF TDS-211
GLASS AND MELTER FLOOR SLUDGE

TABLE A.1. Electrical Conductivity of TDS-211 Glass and Melter Floor Sludge

<u>Temperature</u> <u>(°C)</u>	<u>10³/Temperature</u> <u>(μ in.)</u>	<u>Conductivity</u> <u>(ohm-cm)</u>
A. <u>TDS-211 Glass</u>		
1099	0.729	1.02
1002	0.784	0.47
900	0.853	0.21
858	0.884	0.17
B. <u>Melter Sludge</u>		
		0.91
1198	0.680	1.19
1097	0.730	0.38
998	0.787	0.14
		0.19

FIGURE A.1. Electrical Conductivity of TDS-211 Glass and Melter Floor Sludge

APPENDIX B

THE "SKIN-EFFECT" ON THE CURRENT
FLUX DENSITY DISTRIBUTION

THE "SKIN-EFFECT" ON THE CURRENT FLUX DENSITY DISTRIBUTION

It has been proposed that "skin-effect" may cause the electrical current flow between the electrodes of the CFCM melter to be mainly in peripheral areas of the molten glass normal to the current path. The electrode circuit is supplied from the secondary windings of a transformer rated 250 kVA at 480 V to 120 to 316 V. The transformer primary circuit is controlled by a phase-angle-fired Silicon-Controlled Rectifier (SCR) rated 250 kVA at 480 V single phase.

At 100% of rating, the SCR output frequency is 60 Hz. As the load current is reduced, harmonic frequencies of the fundamental are present. These harmonic frequencies become more prominent as load current is reduced. A spectrum analyzer was used to show these harmonic frequencies at two load values. Copies of these data are included in this appendix.

"Skin-effect" results in a conducting medium when alternating current is caused to flow. The magnetic flux surrounding the conductor resulting from the alternating current induces a electromotive forces (emf's) in the conductor. These emf's are greater at the center than at the periphery of the conductor and tend to establish currents that oppose the main current at the center and assist it at the periphery. The result is that the main current is forced to the outside portion of the conductor.

For a conducting medium, such as molten glass, "skin-effect" can cause the main current to flow in an outer shell normal to the current flow. The thickness of this shell can be approximated by

$$d = \frac{1}{[f\pi\mu\gamma]^{\frac{1}{2}}} \text{ (Meters)}$$

where γ is the conductance in Mhos per meter, μ is the permeability in Henries per meter, and f is the frequency in Hertz.

The conductance of glass at 1200°C was found to be:

$$\gamma = 333.3 \text{ Mho/Meter}$$

Because of the impurities in glass, some of which are iron, a permeability was assumed to be:

$$\mu = 10^{-4} \text{ Henries/Meter}$$

Solution for depth of penetration is as follows:

$$d = \frac{1}{\sqrt{f} [\pi (333.3)(10^{-4})]^{\frac{1}{2}}} = \frac{3.09}{\sqrt{f}}$$

The following tables (B.1 and B.2) show penetration depth and percent of load in shells of different thickness:

The first column shows the harmonic frequencies^(a) which are present when the SCRs are operated at low power levels. The second column indicates penetration depths at those frequencies. Percent power was derived from spectrum analyzer prints, copies of which are included. The mV values were summed and converted to percent power. Since each unit of penetration contains 86.5% of the remaining power, column four shows these values. The last three columns show the percent of power at the designated frequencies which are contained in shells of 5, 10 and 15 cm thickness. Sums at the feet of the last three columns are the percent of total power contained in those shells.

It can be seen that a shell of 10-cm depth carries about 50% of the current when power levels are 15% of rated SCR output. This could indicate that peripheral heating of the molten glass would predominate.

Also, the electrical resistivity of glass varies as the reciprocal of the temperature. One path which is the hottest, and therefore lowest in

(a) See Figures B.1 and B.2.

TABLE B.1. Data for 6.4 kW (13%)

Hz	Penetration (cm)	% Power	86.5% x % Power	% of Power at Depth		
				5 cm	10 cm	15 cm
60	40.0	24.9	21.5	2.7	5.4	8.0
180	23.0	21.3	18.4	4.0	8.0	12.0
300	17.8	14.9	12.9	3.6	7.2	10.9
420	15.1	11.2	9.7	3.2	6.4	9.6
540	13.3	7.8	6.7	2.5	5.0	6.7
660	12.0	4.7	4.1	1.7	3.4	4.1
780	11.1	4.4	3.8	1.7	3.4	3.8
900	10.3	3.9	3.4	1.7	3.3	3.4
1020	9.7	3.1	2.7	1.4	2.7	2.7
1140	9.2	2.2	1.9	1.0	1.9	1.9
1260	8.7	<u>1.7</u>	1.5	<u>0.9</u>	<u>1.5</u>	<u>1.5</u>
		100.1		24.4	48.2	64.6

TABLE B.2. Data for 2.2 kW (5%)

Hz	Penetration (cm)	% Power	86.5% x % Power	% of Power at Depth		
				5 cm	10 cm	15 cm
60	40.0	19.5	16.9	2.1	4.2	6.3
180	23.0	17.8	15.4	3.3	6.7	10.0
300	17.8	15.0	13.0	3.7	7.3	11.0
420	15.1	13.0	11.2	3.7	7.4	11.1
540	13.3	10.8	9.3	3.5	7.0	9.3
660	12.0	8.0	6.9	2.9	5.8	6.9
780	11.1	4.8	4.2	1.9	3.8	4.2
900	10.3	3.0	2.6	1.3	2.5	2.6
1020	9.7	2.8	2.4	1.2	2.4	2.4
1140	9.2	2.6	2.2	1.2	2.2	2.2
1260	8.7	<u>2.6</u>	2.2	<u>1.3</u>	<u>2.2</u>	<u>2.2</u>
		99.9		26.1	51.5	68.2

resistance, will become the dominant path for current flow. The heat developed in a current path is

$$W = I^2R$$

Where W is watts, I is current in amperes, R is resistance in ohms. Therefore, the heat in the low resistance path will dominate.

SPECTRUM ANALYZER PRINTS

T. W. Jeffs

Melter Data:

40 V-RMS
93 Amps
2.2 kW

Spectrum Analyzer Constants:

Scale: 5 mV ϕ Freq: 250 Hz Window: 10 Hz Attenuator: 80 db

FIGURE B.1. Frequencies Resulting from Phase-Angle-Fired SCR for ECM

Melter Data:

55 V-RMS

118 Amps

6.4 kW

Spectrum Analyzer Constants:

Scale: 5 mV

Q Freq: 250 Hz

Window: 10 Hz

Attenuator: 80 db

FIGURE B.2. Frequencies Resulting from Phase-Angle-Fired SCR for ECM

APPENDIX C

UPWARD DRILLING

UPWARD DRILLING

Upward drilling is a unique corrosion phenomenon related to the underside of submerged horizontal refractory surfaces where the normal refractory corrosion rates are accelerated by the presence of trapped gas bubbles.

Several investigators^(a) have suggested that the refractory corrosion process is controlled at first by a chemical process, but that this quickly changes to a slower diffusion-controlled process as a reaction product layer accumulates at the refractory-glass interface. When gas bubbles are in contact with the interface, convective currents are very active in the thin meniscus surrounding the bubble, and the reaction product layer is constantly replaced with fresh glass. Thus, the controlling corrosion process shifts toward the faster chemical reaction process.

A strong association between upward drilling rates and metal line, or flux line, attack^(b) suggests a similarity in the mechanism of the two corrosion phenomena. Surface tension of the molten glass is seen to generate the same meniscus at the flux line as is present around trapped gas bubbles, and, again, vigorous convective activity in the meniscus is observed in laboratory experiments.^(c)

(a) Busby, T. S. 1979. Glass Tech. 20(4):117-131.

(b) Begler, E. R. and P. O. Herndon. 1970. Bull. Am. Ceram. Soc. 49(7):633-637.

(c) Buckner, R. 1967. Glastech. Ber. 41(12):513-522.

APPENDIX D

SHORT-TO-GROUND MONITOR

1

2

3

4

SHORT-TO-GROUND MONITOR

Figure D.1 is a schematic drawing of the short-to-ground monitor that was installed on the CFCM on October 23, 1979.

FIGURE D.1. Schematic of Short-To-Ground Monitor

Assumptions:

- Because of the 250-kVA Isolation Transformer, the power at the electrodes is "floating" from ground.
- The three voltage-indicating devices, V_0 , V_{19} , and V_{20} , are high impedance ($50\text{ k}\Omega$), true RMS meters.
- RL is an electrical leakage path with a resistance value of RL ohms that is assumed to originate at Point P in the melter liner.

- RT is a test resistor with a resistance value of RT ohms and is manually connected between the containment vessel and the north electrode with a normally open, momentary-contact, push-button switch.

Now assuming TS is left open, and:

- Assuming there is no electrical path from the glass tank to the containment vessel, i.e., $R_L = \infty \Omega$, then V_{19} and V_{20} will both indicate 1/2 the value of V_0 .
- Assuming there is an electrical path from the glass tank to the containment vessel, and the point where it leaves the melter tank (P) is exactly equidistant from the N and S electrodes, then V_{19} and V_{20} will again both indicate 1/2 the value of V_0 .
- Assuming there is an electrical leakage path, and P is located N% of the distance separating the electrodes away from the N electrode, then

$$V_{19} = \frac{N V_0}{100}, \text{ and } V_{20} = \frac{(100-N)V_0}{100}$$

Therefore, V_{19} = the electrical potential with respect to the N electrode in the glass at Point P.

Now, assuming there is an electrical leakage path somewhere in the floor of the melter of some unknown resistance, then:

$$V_{19} \text{ (With TS Open)} = \text{the potential at P} \quad (1)$$

Then, if TS is closed, the potential at P, Equation (1), will remain constant and will force an electric current to flow through R_L , through the containment vessel, and through RT to the N electrode, and since:

$$E = IR \quad (2)$$

$$V_{19} \text{ (With TS Open)} = I (R_L + R_T + R_V)$$

RV is the electrical resistance of the containment vessel and, if RT is sufficiently large, RV can be omitted and Equation (2) then becomes:

$$V_{19} \text{ (With TS Open)} = I (RL + RT)$$

or

$$I = \frac{V_{19} \text{ (With TS Open)}}{(RL + RT)} \quad (3)$$

Also, when TS is closed, V_{19} is measuring the voltage drop across RT, and again since:

$$E = IR$$

$$V_{19} \text{ (With TS Closed)} = I [RT]$$

or

$$I = \frac{V_{19} \text{ (With TS Closed)}}{(RT)} \quad (4)$$

When TS is closed, the current that flows through RL and RT is identical,
or

$$(3) = (4)$$

or

$$\frac{V_{19} \text{ (With TS Open)}}{(RL + RT)} = \frac{V_{19} \text{ (With TS Closed)}}{RT}$$

$$\frac{V_{19} \text{ (With TS Open)}}{V_{19} \text{ (With TS Closed)}} = \frac{RL + RT}{RT}$$

$$R_L = \left(\frac{V_{19} \text{ (With TS Open)}}{V_{19} \text{ (With TS Closed)}} - 1 \right) R_T \quad (5)$$

The choice of the value of R_T is dependent on the sensitivity desired and the power dissipation rating of the resistor. With a small resistor (10 ohms), the ratio of the V_{19} readings is larger and the sensitivity of the measurements increases; however, depending on the value of R_L , 20 to 50 watts may be dissipated in R_T . With R_T at 100 ohms, the sensitivity of the measurement decreases as does the power dissipated in R_T . The installed monitor used a 25Ω , 20-watt, wire-wound power resistor for R_T and, on occasion, dissipated 50 watts. For momentary tests, this overloading of the resistor did not compromise its operation.

Voltage sensors V_0 , V_{19} and V_{20} are continuously recorded on a multipoint recorder, and the relative trend of V_{19} and V_{20} indicates the approximate location of an electrical path to the containment vessel. Periodically TS was depressed, just long enough for V_{19} and V_{20} to print, and the resistance value of the electrical path to the containment vessel was then manually calculated from Equation (5).

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