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A LARGE-SCALE CONTINUOUS PROCESS TO VITRIFY NUCLEAR DEFENSE WASTE - OPERATING EXPERIENCE WITH NONRADIOACTIVE WASTE

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INTRODUCTION

The Department of Energy (DOE), with recommendations from the Du Pont Company, is proposing that a Defense Waste Processing Facility (DWPF) be constructed at the Savannah River Plant (SRP) to immobilize 25 million gallons of high level radioactive waste currently stored at SRP. The DWPF can be effectively implemented in two stages by first separating the high level waste into two fractions using a series of in-tank processing steps.[1]

A waste vitrification facility will immobilize the sludge component of the waste by dissolving it in a borosilicate glass matrix. The sludge fraction will contain over 60% of the total radioactivity in the waste and nearly all of the long lived radionuclides. A salt processing facility will remove cesium-137 and other radionuclides from the salt component of the waste. These radionuclides will then be processed in the vitrification facility so that greater than 99.99% of all the radioactivity in the waste will be immobilized in borosilicate glass.

Waste Form

Borosilicate glass, containing 28 wt % dissolved waste oxides, has been selected as the waste form for the design of the DWPF.[2] Large scale melter tests at Savannah River Laboratory have been made with a nonradioactive sludge composition designed to simulate the actual high level waste sludge. The compositions of the simulated waste oxides, borosilicate glass formers (frit), and final product used for the majority of the tests described in this report are given in Table 1. The physical properties of the simulated waste glass at the nominal operating temperature of 1150°C are given in Table 2.[3] Note the low viscosity (10 poise) and high iron content of this glass relative to most industrially produced glasses.

Large Scale Vitrification Process

At SRL, large scale development of the DWPF vitrification process began with the startup of the Calciner-Melter-Off-Gas system (CMOG) (Figure 1). An 18 wt % slurry of simulated waste sludge was dried in an induction-heated spray dryer. Glass frit was added to the dried waste and the mixture was gravity fed to the joule heated glass melter. The off-gas was passed through a series of abatement systems and then vented to the atmosphere. After six experimental runs in this operating mode, the system was modified to allow a 40 wt % aqueous slurry of glass and simulated waste hydroxides to be fed directly to the glass melter, and the

system was renamed the Slurry-Fed Melter Off-Gas system (SMOG). This version of the process, which is now the reference case for the DWPF, eliminates the spray dryer, thereby reducing the cost of the DWPF sludge processing facilty by 15%; primarily due to a reduction in height of the canyon building which will house the process.

Glass Melter Description

The Project 1941 melter (Figures 2 and 3), which was used for both the CMOG and SMOG tests, was an all electric, cylindrical melter with a 4 ft inside diameter. Joule heat in the main melter tank was provided by 4 top entering rod electrodes made of Inconel® 690 (trademark of Huntington Alloys, Inc.). These electrodes were 6 inches in diameter and air cooled. Glass in the riser section was heated by an Inconel® 690 resistance heater, as was the pour spout. Additional heat in the vapor space of the melter was supplied by 6 silicon carbide, resistance heaters. A drain valve, which consisted of a hollow Inconel® 690 resistance heater, was located in the center of the melter floor. The glass contact refractory was an 8 inch layer of Monofrax® K-3 (trademark of the Carborundum Co.). The vapor space refractories were Mullfrax® 202 (trademark of the Carborundum Co.). These refractories were encased in a one-inch-thick, water-cooled, stainless steel shell. An argon bubbler with two ports under the glass and one port in the vapor space, was used to measure the specific gravity and

height of the glass and also provided some mixing. The argon flow was controlled at 1 CFH for each port.

Overall Production History

The Project 1941 melter contained molten glass for 398 days at a nominal temperature of 1130°C. The operating history is summarized in Table 3. A total of 74 tons of simulated waste glass product was produced during ten experimental runs.

Initial startup of the 1941 melter was by auxiliary propane burners. The temperature was increased to 1150°C over a 12-day period at rates of 3°C to 10°C per hour (Figure 4). Ground glass (frit) was added on the 8th day and joule heating was established on the 9th day. Subsequent melters at SRL have been successfully started by other methods which are more easily adapted to remote operation:

- Joule heat, from the melter electrodes, generated in a relatively thin layer of a graphite/glass mixture.
- Lid heat, supplied by a bank of silicon carbide resistance heaters installed in the vapor space.

Calcine-Fed Melter Experience

During startup and 6 calcine-fed runs, the CMOG system produced 54 tons of simulated waste glass. Steady-state glass melting fluxes of 35 lbs/hr-ft^2 and 21 lbs/hr-ft^2 were demonstrated with and without supplemental lid heat, respectively. The DWPF design melt flux for this operating mode is 20 lbs/hr-ft^2.

The steady-state values of the primary melter operating variables are given in Table 4. The steady-state condition was verified by the constancy of these variables and by the stable condition of the cold cap.

The cold cap was monitored by a bundle of axially-spaced thermocouples installed in a thin-walled thermowell. By monitoring the axial temperature profile measured with this thermowell, increases in cold cap thickness were easily detected. A continuing increase in cold cap thickness indicated the feed rate exceeded the melter capacity and feed rates were reduced accordingly. When feeding the melter, a temperature gradient existed near the glass surface due to the cold cap. At a steady-state calcine-fed melt rate of 35 lbs/hr-ft^2, this temperature gradient extends to a depth of 5 inches below the nominal glass surface (Figure 5). To illustrate the effectiveness of a temperature profile for monitoring the cold cap thickness, temperatures measured at specific levels in the cold cap region are plotted versus time in Figure 6 during a brief period when the feed rate exceeded the melting capacity. The steady decline in temperatures with time, at and just below the glass surface, was a clear indication that a thicker and heavier layer of colder, unmelted material was accumulating on the glass surface. Reducing the feed rate caused the cold cap temperatures to quickly regain their previous steady-state values.

Slurry-Fed Melter Experience

Having successfully completed the demonstration of the calcine-fed vitrification process, three experimental runs were conducted in the slurry-fed mode of operation producing 20 tons of simulated waste glass. The primary modification to the glass melter was the addition of an insulated water-cooled feed nozzle and an off-gas pipe to the melter lid. In the slurry-fed operating mode, glass melting fluxes of 11.4 lbs/hr-ft^2 and 6.4 lbs/hr-ft^2 were demonstrated with and without supplemental lid heat, respectively. The steady-state values of the primary operating variables at these two rates are given in Table 4 for comparison with calcine fed operation.

Cold Cap Observations

The nature of the cold cap while slurry feeding was considerably different than the calcine-fed cold cap. The steady-state, slurry-fed cold cap was much thinner, and supported a pool of boiling aqueous slurry on the top surface. Although in both operating modes the cold cap covered the glass surface completely, the slurry-fed cold cap always contained at least one vent hole (usually several 2 to 4 inches in diameter) through which molten glass was visible. In addition to monitoring the slurry-fed cold cap through the use of a bundle of axially spaced thermocouples as described previously, the cold cap was observed frequently through sight ports in the melter lid to ensure that some vent holes were

present. One sight port housed a TV camera connected to a television monitor.

The vent holes are caused by the evolution of gases in the upper levels of the melt pool resulting from the calcination of the waste components. Typical reactions involving gas evolution are:

$$2MnO_2 \rightarrow 2MnO + O_2$$

$$2Fe_2O_3 \rightarrow 4FeO + O_2$$

Carbon was added to the feeds in these tests to facilitate the reduction of these metals, causing the reactions to occur at lower temperatures and higher in the cold cap or glass melt. As a result, glass foaming was not a problem in these tests.

Comparing the axial temperature profile in the cold cap region for the slurry-fed and calcine-fed operating modes (Figure 7), the difference in temperature gradients in the molten glass beneath the cold cap revealed heat transfer to the bottom of the cold cap was more effective when slurry-feeding. The transition from bulk glass temperature to 800°C occurred over approximately 5" when calcine feeding and only approximately 2" when slurry feeding. This indicated that the boundary layer for heat transfer from the bulk glass to the bottom of the cold cap was thinner and therefore offered less resistance to heat transfer when slurry feeding.

The increased heat transfer to the bottom of the cold cap when slurry feeding may be due to more effective mixing of the

molten glass layer just below the cold cap due to increased gas evolution in this layer when slurry feeding. Since the metals in the waste fall onto the cold cap in the form of hydroxides in the slurry feed, as opposed to being partially calcined in the spray dryer, it was likely that more of the gas evolution from calcination occurred in the molten glass beneath the cold cap when slurry feeding. Also, some steam probably was evolved from the metal hydroxides in this layer. Finally, the slurry-fed cold cap was a damp cake covering the glass surface which was less permeable to the evolved gasses than was the dry powder cold cap formed when calcine feeding. Apparently, a significant portion of the evolved gas may migrate underneath the cold cap to a vent hole to be released to the vapor space. The increased evolution of gases, and the migration of these gases to vent holes, tend to increase mixing in the molten glass layer beneath the cold cap.

Although more heat is reaching the bottom of the feed pile when slurry feeding than when calcine feeding, typical slurry-fed rates for a given melter are much lower. This is because 5 or 6 times more energy is required at a given melt flux when slurry feeding due to the added energy required to evaporate and superheat the water from a 40 wt % slurry feed. In addition, calculations show that when operating this melter at an 8.0 lb/hr slurry-fed melt flux, more energy was reaching the feedpile from the lid of the melter and the lid heaters than from the molten glass below the

feedpile. Most of the joule heat produced in the glass was lost to the water cooled shell.

Melter Inspection

One of the major objectives of the experimental program was to characterize the corrosion rates of the materials which contact molten glass. Inconel® 690, a high Ni, high Cr metal alloy, was chosen for the metal components in the melter. An extensive corrosion testing program at SRL proved Inconel® 690 was the most corrosion resistant metal alloy available for our glass composition. The electrodes in the 1941 Melter were in good condition at the end of the program (Figure 8). The maximum wear rate measured on the Inconel® 690 electrodes and thermowells was 1/2 mil/day.

Extended tests with smaller glass melters at SRL have shown the Inconel® 690 wear rate to be 3/8 mil/day when idling the melter at 1150°C and 1-1/4 mil/day when feeding the melter. Using these values, combined with the fact the 1941 melter was idled 90% of the time, yielded a composite wear rate of:

3/8 mil/day (0.1) + 1-1/4 mil/day (0.9) = 0.5 mil/day.

The design bases is a 2 year life for all Inconel® components in the melter. These data showed that this criteria can easily be met.

The refractories inside the melter were in excellent condition after the melter was drained (Figures 9 and 10). Corrosion of the Monofrax® K-3 at the melt line was 600 mils in 398 days, or 1.5 mils/day. The maximum corrosion in the tank was 1000 mils or 2.5 mils/day measured on the sidewall just above the throat. Although

this low value probably reflected the amount of time spent idling, it was still well below the DWPF design criteria of 7.5 mils/day. Several consultants from the glass industry agreed that Monofrax® K-3 will easily last the required two years in continuous production. There were no places where pieces of refractory had fallen off due to cracking. This was partly due to the keyed configuration of each block in the 4 ft ID cylindrical tank, and partly because very little cracking of the blocks was found when the melter was disassembled. In fact, most of the blocks came out in one piece.

A spinel (or slag layer) approximately 7 inches thick accumulated on the melter floor. The primary components of this phase were of the form Fe_2O_3 [XO] where X = Ni, Mn, Ti, or Cr, with Ni being predominant. Spinel can be formed by three different methods: 1) refractory corrosion products forming insoluble crystals, 2) incorrect feed compositions due to poor mixing or process upset leading to higher levels of waste oxides in the glass, 3) temperature zones in the melter decreasing the temperature below the liquidus of the molten glass. Method 1 has been reduced as much as possible by choosing a corrosion resistant refractory. Method 2 can be controlled by a good quality assurance program; slurry feeding can help by ensuring the feed materials are well mixed. Method 3 was the major cause of spinel of deposition in the 1941 melter and is a function of melter design.

The liquidus of SRP waste glasses is in the range of 900 to 1000°C. The temperature on the floor of the 1941 melter was 920°C

when the bulk glass was 1150°C. Current and future melter designs will ensure glass temperatures above 1050°C everywhere in the melter when the bulk glass is at 1150°C. This criteria will be met by increasing thermal insulation in the melter floor, and by providing the ability to variably skew the power deposition in the melter to the top or bottom of the melter.

CONCLUSION

The developmental program underway at SRL (Figure 11) has demonstrated the vitrification process proposed for the sludge processing facility of the DWPF on a large scale. DWPF design criteria for production rate, equipment lifetime, and operability have all been met. The expected authorization and construction of the DWPF will result in the safe and permanent immobilization of a major quantity of existing high level waste.

ACKNOWLEDGMENT

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2. J. A. Kelley. "Evaluation of Glass As a Matrix for Solidification of Savannah River Plant Waste," USERDA Report DP 1397, E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, SC (1975).

3. "Technical Data Summary for the Defense Waste Processing Facility, Stage 1," USDOE Report DPSTD-80-38-2, E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, SC (1981).

TABLE 1

Feed and Glass Composition

Component	Amount (Wt % of Solids) Glass Frit	Simulated Sludge	Simulated Waste Glass
SiO_2	57.9		40.9
B_2O_3	14.7		10.4
Na_2O	17.7		12.5
Li_2O	5.7		4.0
MgO	2.0		1.4
TiO_2	1.0		0.7
La_2O_2	0.5		0.4
ZrO_2	0.5		0.4
Chloride	0.2 max		
Fluoride	0.2 max		
$Fe(OH)_3 \rightarrow Fe_2O_3$*		59.1	16.8
$MnO_2 \rightarrow MnO$*		12.6	3.9
$Ca(OH)2 \rightarrow CaO$ *		4.3	1.3
$Ni(OH)_2 \rightarrow NiO$ *		6.7	2.1
$Al_2O_3 \cdot H_2O \rightarrow Al_2O_3$*		10.5	3.2
Zeolite**		6.7	2.0
Total	100%	100%	100%

* The original hydroxide components exist as oxides in the glass.

** Linde.

TABLE 2

Simulated SRP Waste Glass Properties at 1150°C

Viscosity (poise)	7.40
Thermal Conductivity (Btu-ft/hr-ft^{2}-^{o}F)	2.85
Electrical Resistivity (ohm-cm)	2.44
Thermal Diffusivity (cm^{2}/hr)	54.65
Density (g/cm^{3})	2.105

TABLE 3

Summary of Project 1941 Melter Experimental Program

	Calcine-Fed	Slurry-Fed
Total Operational Time (Months)	10	4
Experimental Runs	7	3
Days of Operation (Feeds On)	34	21
Glass Produced (Tons)	54	20
Production Rates ($lbs/hr-ft^2$)		
Without Supplemental Heat	20	6.4
With Supplemental Heat	35	11.4

TABLE 4

Calcine and Slurry-Fed State Operating Parameters

Criterion	Calcine-Fed		Slurry-Fed	
Slurry (wt% solids)	--	--	43	41.3
Mass Flux (lbs/hr-ft^2)	21	35	6.4	11.4
Bulk Glass Temp (°C)	1150	1150	1132	1136
Lid Temperature (°C)	130	525	590	625
Electrode Power (kw)*	45	75	80	50
Lid Heater Power (kw)	0	35	0	30
Melter Tank Geometry	Cylindrical, 34 inch melt depth, Radius = 2 ft. Surface Area = 11.78 ft^2			

* Measured average values for each electrode pair, e.g., 1/2 of total electrode power in the glass.

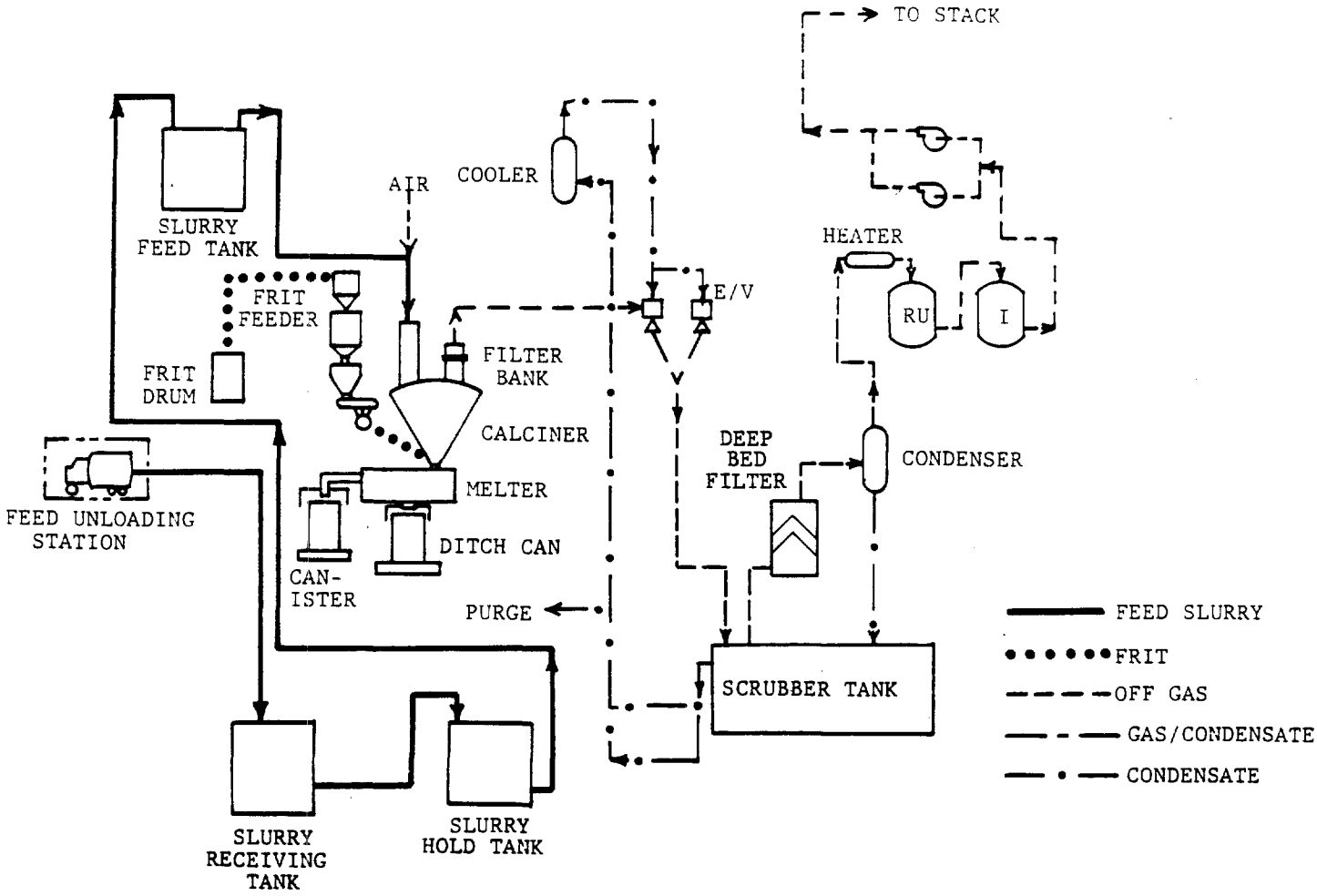

FIGURE 1. Waste Immobilization Process Development Facility Process Summary Diagram

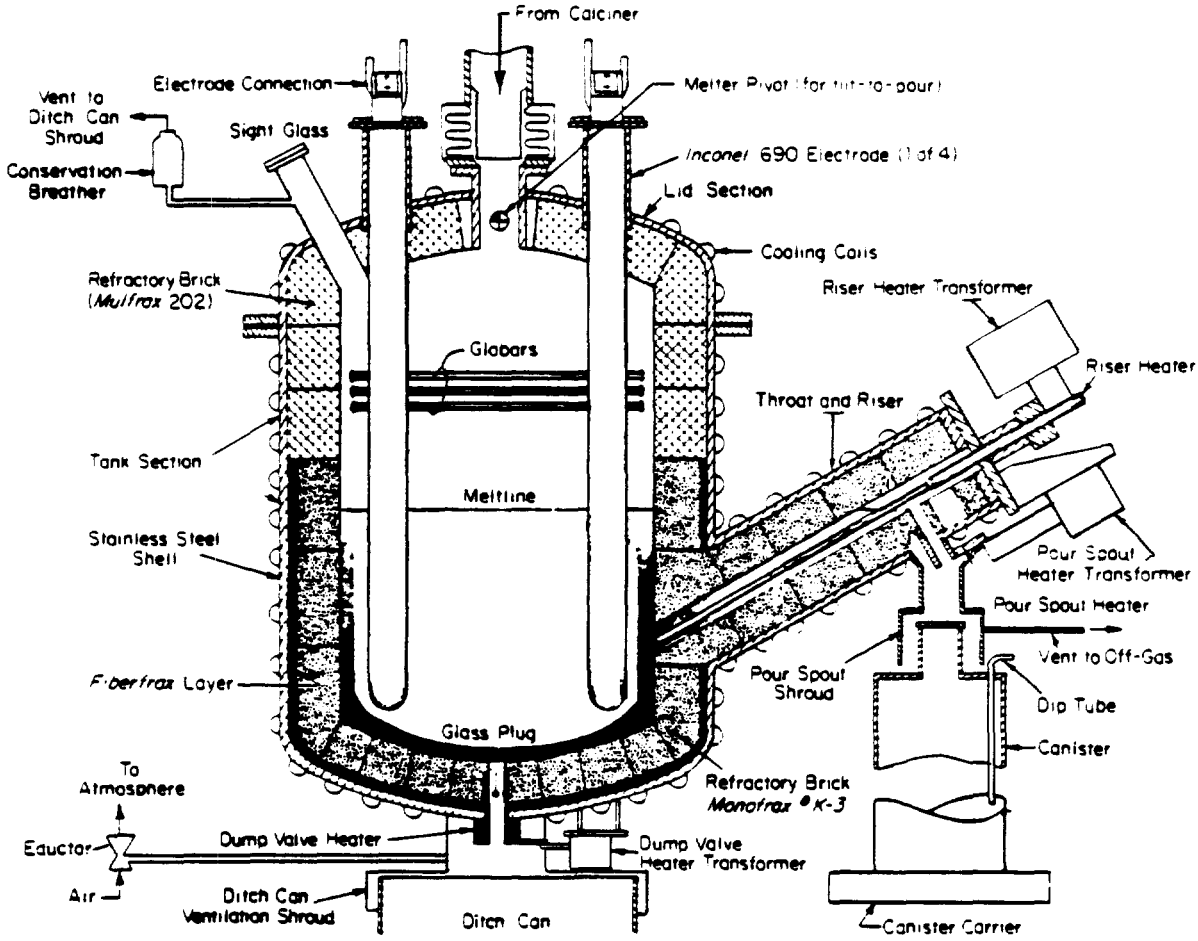

FIGURE 2. TNX Full-Scale Continuous Melter

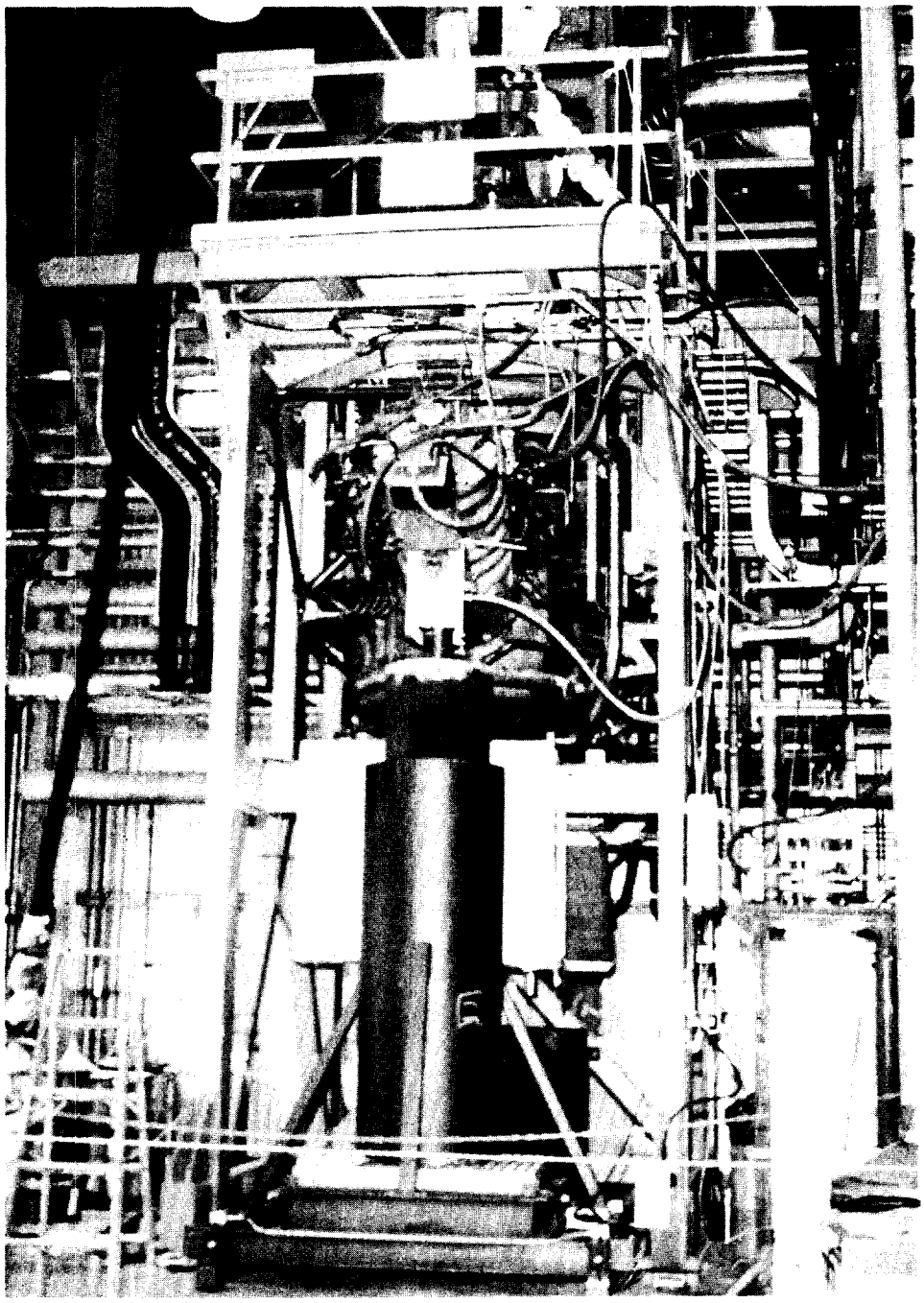

FIGURE 3. TNX Full-Scale Continuous Melter

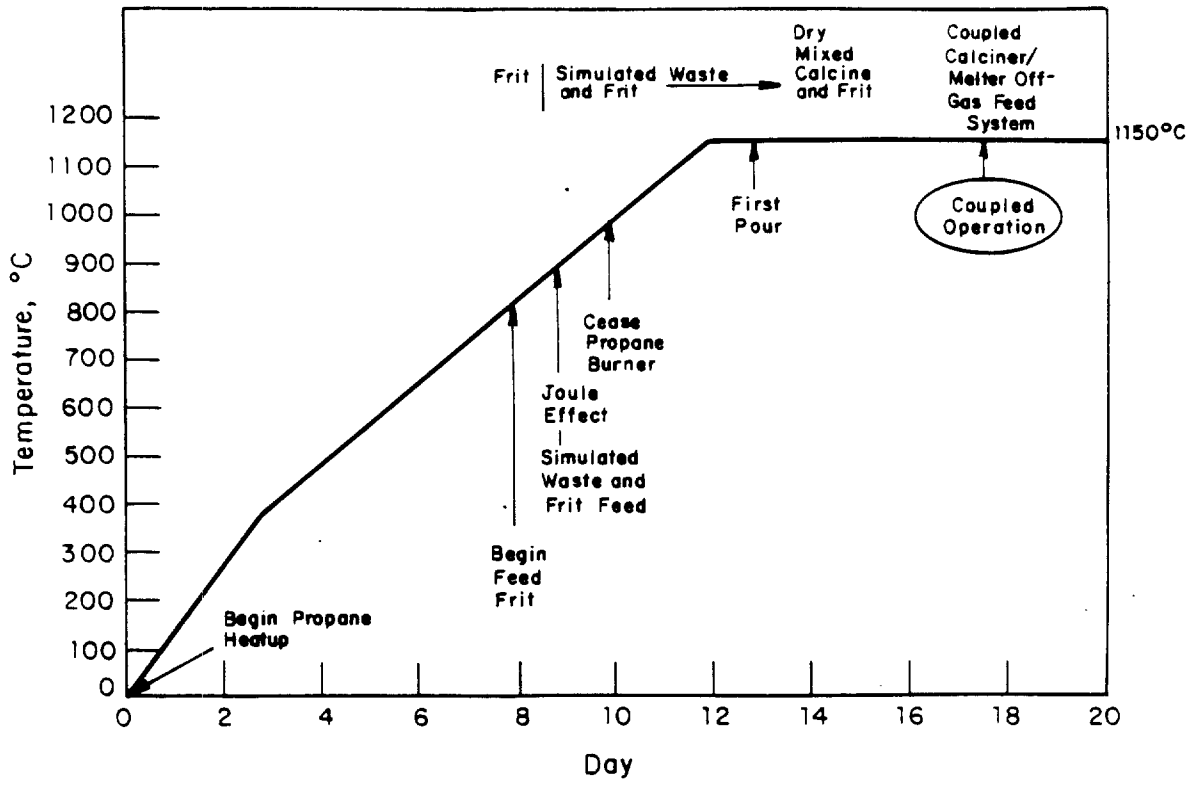

FIGURE 4. Temperature Rise During Startup of Continuous Melter

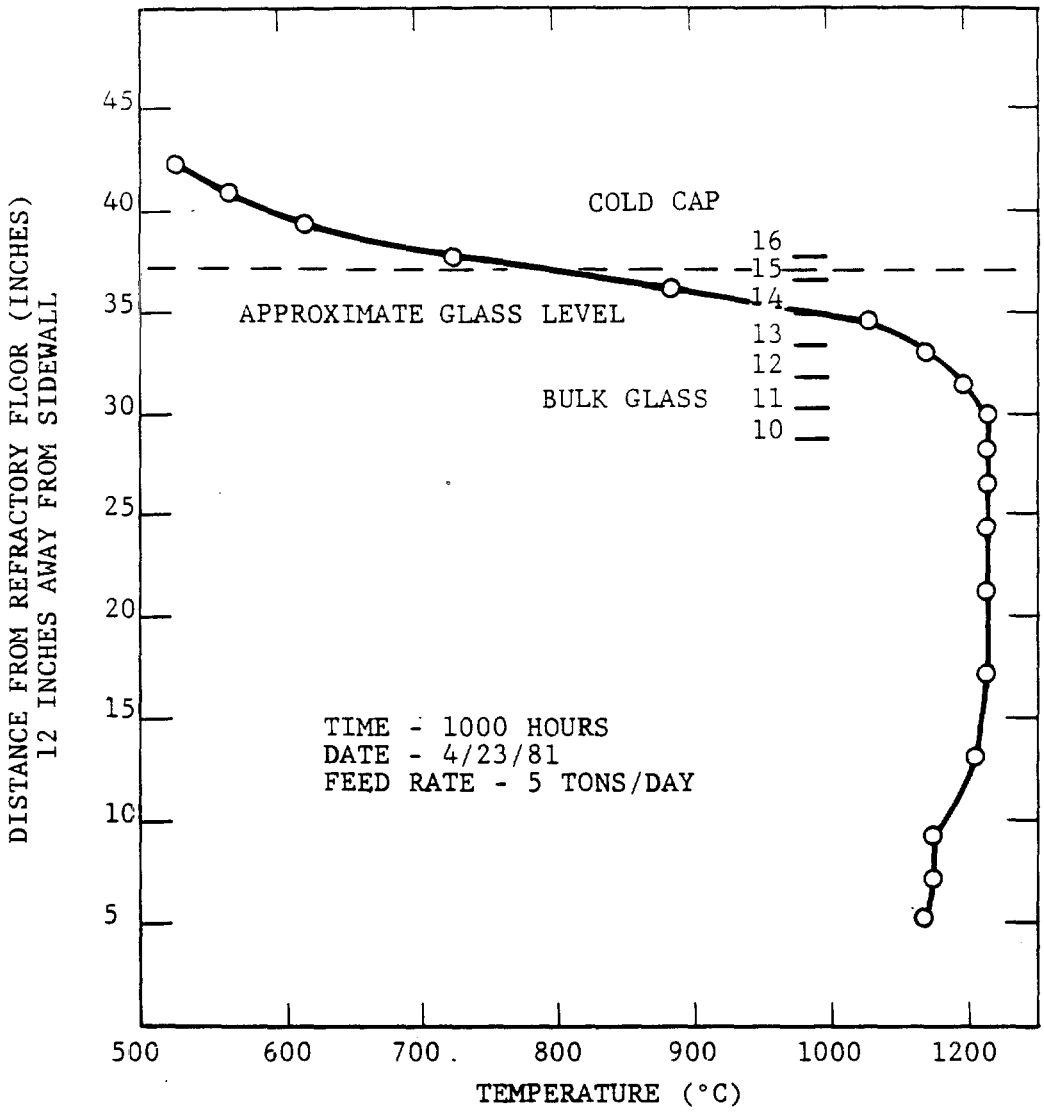

FIGURE 5. Axial Temperature Profile 1941 Melter CMOG Run 6

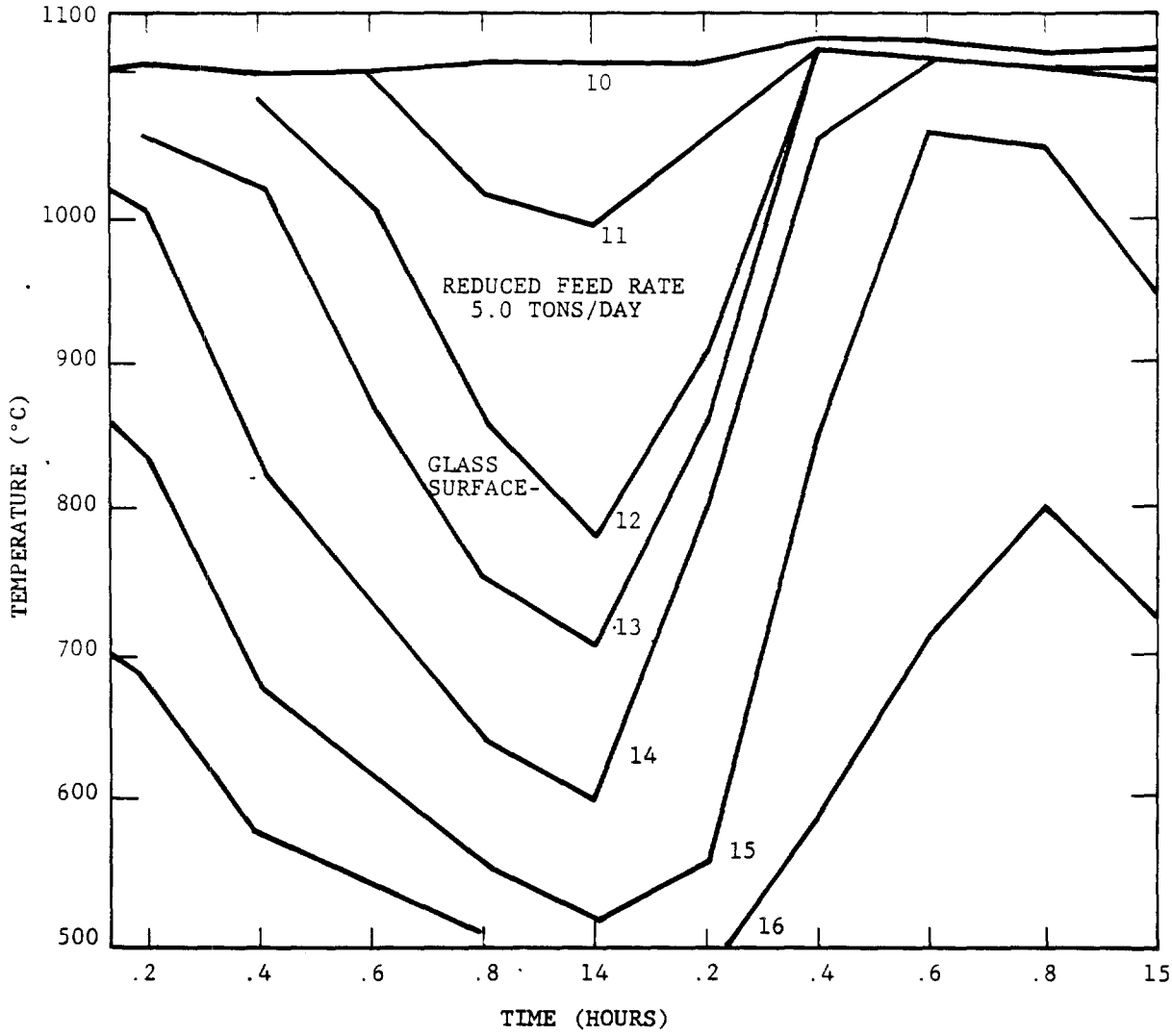

FIGURE 6. Cold Cap Growth Monitor

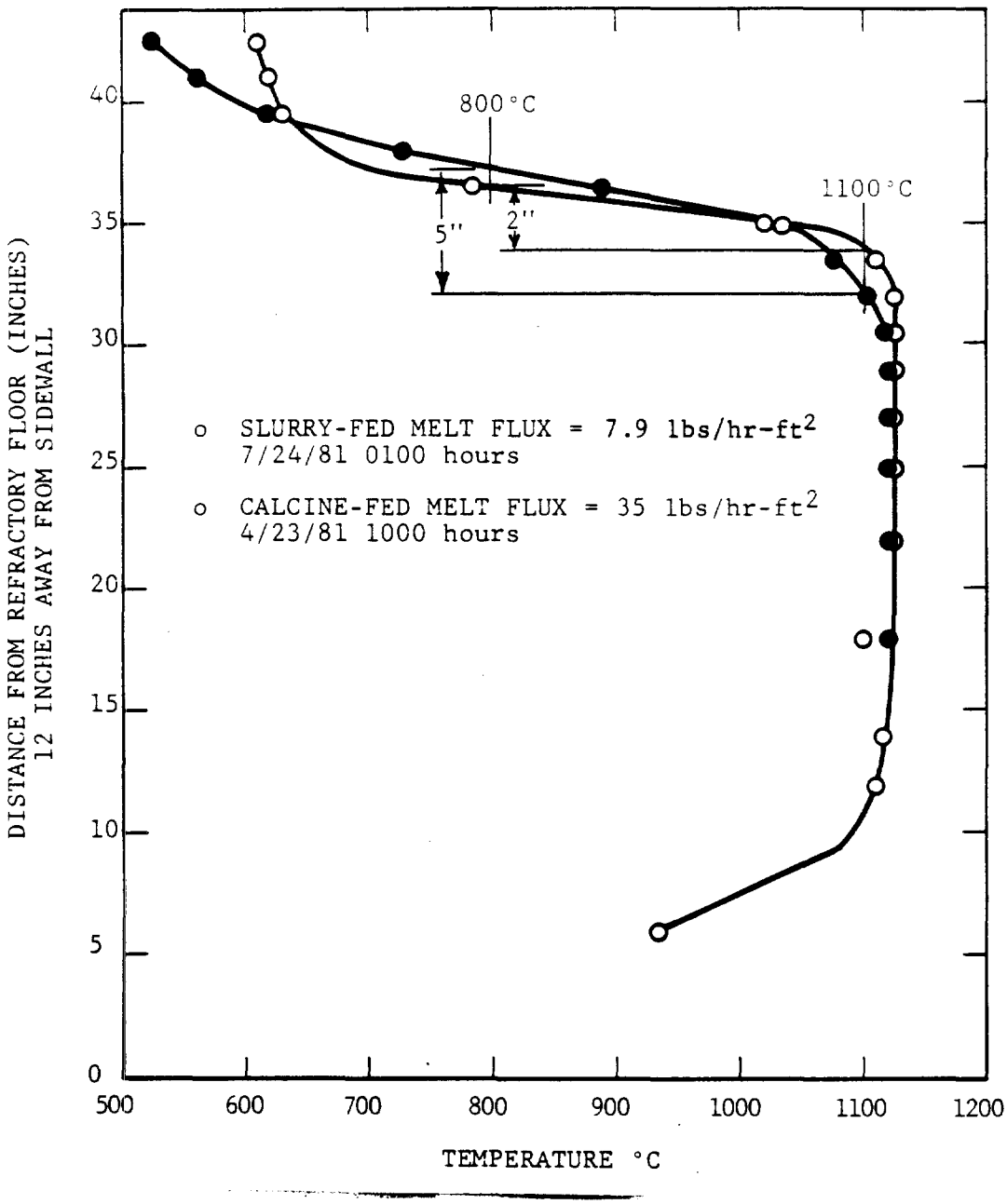

FIGURE 7. Axial Temperature Profiles for the Calcine-Fed and Slurry-Fed Melters

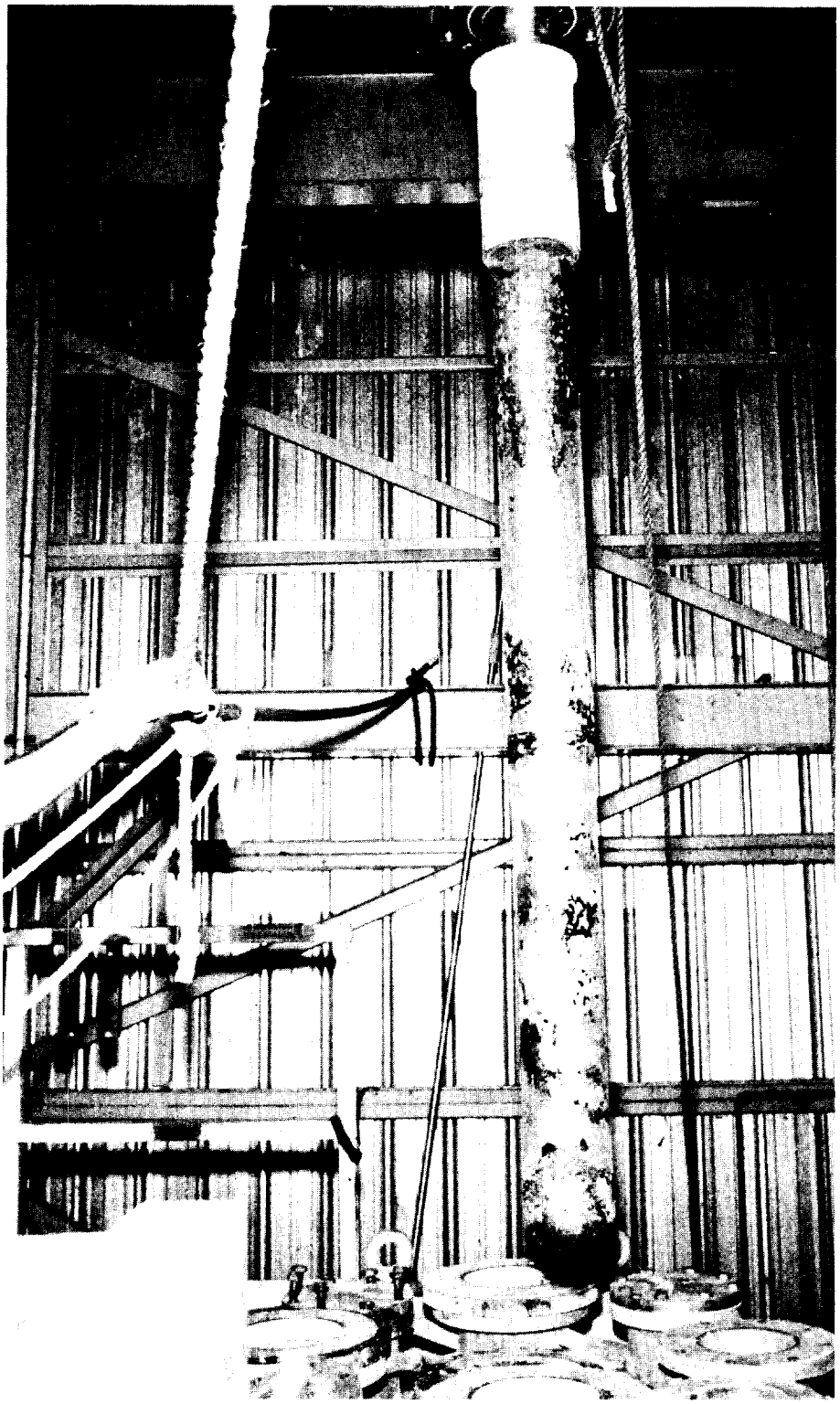

FIGURE 8. Rod Electrode

FIGURE 9. Melter Tank Sidewall

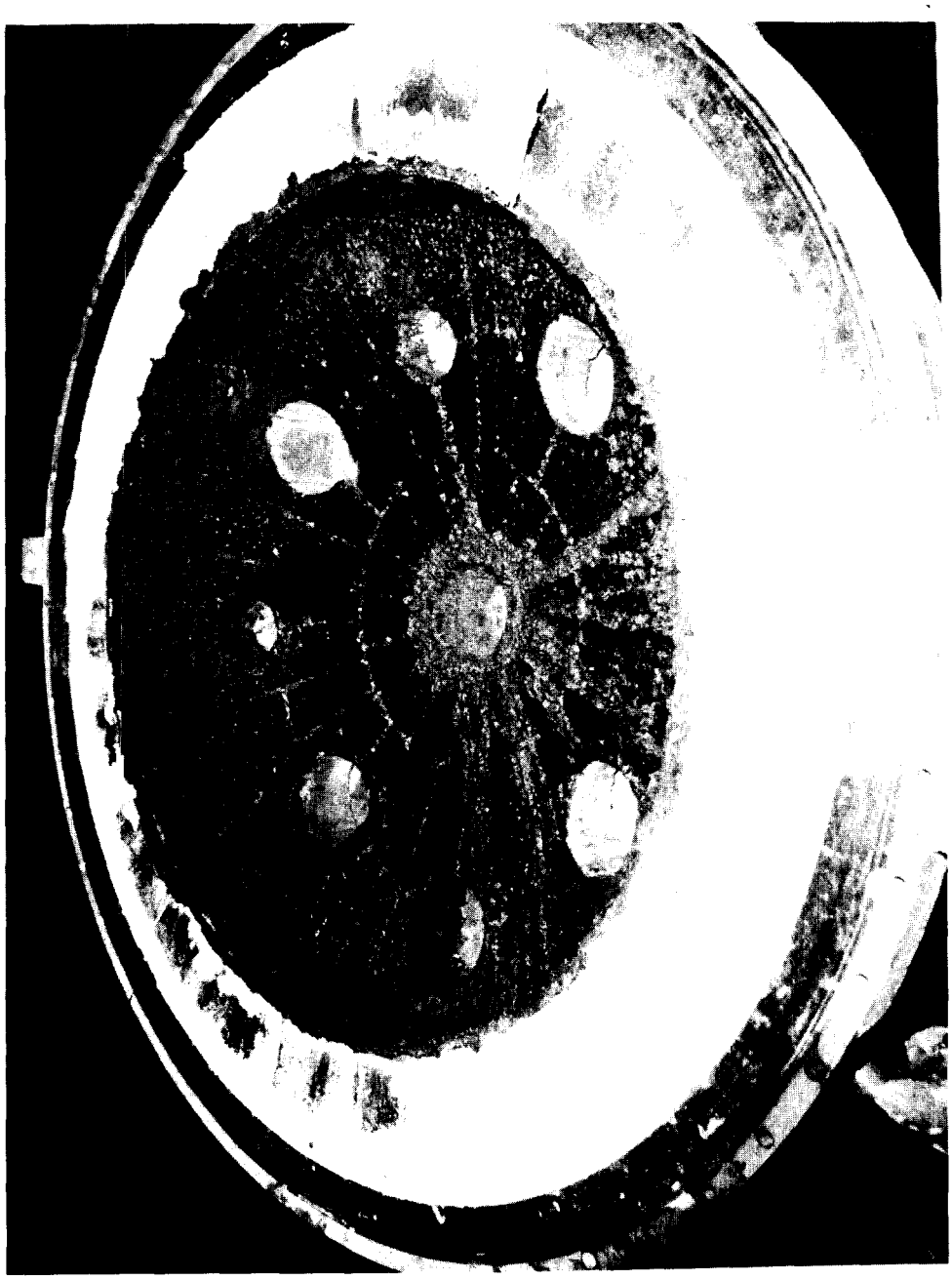

FIGURE 10. Melter Lid

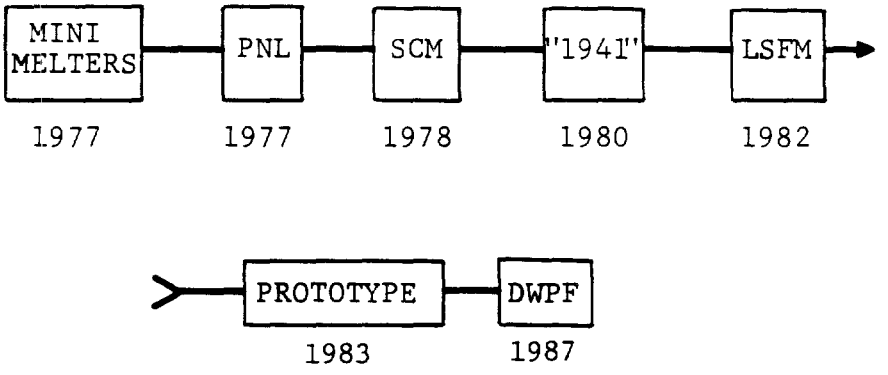

FIGURE 11. DWPF Melter Development