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RECENT CALCINATION AND VITRIFICATION PROCESS ACCOMPLISHMENTS

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Abstract

Experience gained through the development and operation of calciners and glass melting systems has provided the information needed for selection of a high level waste solidification system. At the present time a spray calciner coupled to an in-can melter is sufficiently developed that design of an integrated system is underway for implementation at a U.S. commercial fuel reprocessing plant. A fluidized bed calciner operated with the addition of silica to produce a continuous inert bed (CIB) provides a second calciner which can also be used with the in can melter. A joule heated ceramic melter for converting calcine to glass shows great promise as a continuous one step process for converting liquid to glass. These systems will be demonstrated at the full scale capacities required for vitrifying HLLW from the reprocessing of 5 MT/day of spent power reactor fuel.

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INTRODUCTION

At Pacific Northwest Laboratory (PNL) processes are being developed for the vitrification of nuclear high level waste. This work is being carried out by Battelle-Northwest for the United States Energy Research and Development Administration. Several processes have been evaluated. These include spray and fluidized bed calciners and a wiped film evaporator for concentrating, evaporating and calcining liquid wastes and a continuous metallic melter, a joule heated ceramic melter and a metallic in-can melter (ICM) process for vitrification of the calcined or concentrated waste. Vitrification is accomplished by the addition of a glass frit additive which permits melting at 1050 to 1250°C.

The current Waste Fixation Program (WFP) is taking full advantage of the knowledge gained in the previous Waste Solidification Engineering Prototypes (WSEP) program.[1,2,3]

The intention of the WFP program is, to 1) carry out full scale development and operation of vitrification processes to demonstrate reliable operation and 2) provide the design for similar equipment to be installed in waste management facilities at nuclear fuel reprocessing plants. Based on accomplishments to date integrated processes have been selected for full scale testing and design. The mainline program is comprised of the spray calciner coupled to an in-can melter. A plant design has been started for this integrated close coupled process. The fluidized bed calciner as operated at PNL for vitrification purposes can be substituted in place of the spray calciner. A second vitrification process that is being developed for longer term application is the joule heated ceramic melter. ~~This is the joule heated ceramic melter.~~ The melter has the potential for direct liquid feeding.

The glass produced in the above processes is a zinc borosilicate. In all cases the additives are added as a glass frit in a separate solids stream. The high level waste compositions used in this program are typical of those anticipated by United States fuel reprocessors. Purex Waste-4b (PW-4b) was typical for the General Electric Morris Illinois Plant, PW-7a is the mixed HLLW-ILLW for the Allied General Nuclear Services, Barnwell, South Carolina plant and PW-8 is that from the Nuclear Fuel Services West Valley New York plant.

CALCINATION AND WASTE CONCENTRATION

A spray calciner, fluidized bed calciner and wiped film evaporator have been evaluated and are described below.

Spray Calcination

A spray calciner has been operated at PNL for several years and is ready for commercial application. Liquid is fed in at the top of the spray calciner chamber through a pneumatic atomizing nozzle. The atomized waste is sequentially evaporated, dried, and calcined as it falls through the cylindrical calciner chamber at a temperature of 750°C. Separation of calcine from the off-gases is effected by porous stainless steel filters. A periodic pulsed blowback with air in the reverse direction through venturies into the filters removes the powder collected on the filters.

The calcine produced is a dry ~~fluffy~~ powder with a particle medium diameter of 3 microns. The bulk density varies from .51 to 1.12 g/cc depending on feed type with a moisture content of <0.5 weight percent.(Table I) The nonalkali metal nitrates are completely decomposed and approximately 30% of the alkali metal nitrates are decomposed to oxides.

The ease of autom~~izing~~ating the spray calciner's process variables (feed rate, atomizing air flow rate, furnace temperature and filter blowback timing) has greatly simplified the spray calciner. Do to its simplicity in overall process operation (start up, shutdown, ~~maintenance~~ reliability, etc.), a trouble free operation is obtained.

The spray calciner has been operated for approximately 800 hours calcining a wide variety of feed compositions ~~(PW-6, PW-7, PW-7A, and PW-8)~~ with sodium content ranging from 0-2M simulating AGNS HLLW waste and high iron simulating NFS HLLW waste.

A 510 hour continuous run varying in feed rates and coupled to an Inconel Melter exposed two inadequacies: excessive nozzle wear and spray chamber fouling.[4] Nozzle wear on the air cap greatly affects atomization, thus having a ~~big factor~~ large effect on spray chamber fouling. Through extensive study and testing, nozzle wear and spray chamber fouling has been eliminated.

The nozzle tip has evolved from a stainless steel to a ceramic tip (Figure 1). Barium carbide has decreased nozzle wear, but a ceramic tip made of 96% alumina has not shown any detectable wear (< 0.5 mils) after nearly 50 hours on the spray calciner and over nine hundred hours on the nozzle test station. On the 1/4 inch orifice nozzle, a ratio of atomization air nozzle pressure

Metric units.

TABLE I

Operating Data for the Spray Calciner

Simulated Feed Types:

Type	ℓ/MTU	Na Content, M	g oxide/ℓ
PW-4b(GE)	378	0.0	108
PW-6 (early AGNS)	378	2.0	222
PW-7 (AGNS HLLW)	378	0.1	151
PW-7A(AGNS HLLW-ILLW)	378	0.586	179
PW-8 (NFS HLLW)	378	0.0	226
AGNS-ILLW	283	0.76	?
PW-8a (NFS HLLW-ILLW)	378	1.2	247

Feed Rates:

1 -inch chamber	0-
21 inch chamber	0-76ℓ/hr

Feed Nozzle:

Type: Internal mix : Spraying Systems Co Setups 42 and 72
Size: Feed opening 1/8" and 1/4"
Material: Ceramic (96% alumina) air cap SST fluid cap and body
Atomization: $\frac{\text{Atomization Air [illegible] Pressure}}{\text{Feed Pressure}} \geqq 2.0$

For droplet size ≦ 70 microns

Wear: <0.5 mls after a [illegible] of 45 hours in the spray calciner and over 900 hours in the nozzle test station.

Operating Temperature:

Furnace Temperature:	780°C
Spray Chamber:	700°C
Filter Housing:	350°C

Filter Data:

Type - 15 reinforced 316 SST sintered filters
Mean Pore Size - 65 μ
metric Dimensions - 2 in. OD x 2 ft. long x 1/16 in. thick
Total Filter Area - 15 ft^2
Filter ΔP under normal operating conditions ∿ 13 inches of water
Blowback system - air - 60 psig
cycle - 2 minutes
pulse -.25 seconds

Vibrators: Pneumatic vibrators by Cleveland Vibrator Co., Model 1300AC Vibra-Might

Frequency	2000-2700 vibrations per minute
Force	260-370 pounds

Properties (Dependent on Feed Type):

Bulk density, g/cc	0.5-1.1
Angle of Repose, degrees	∿40
Moisture Content, wt present	<0.5

TABLE I (CONTINUED)

NO_3 - Content, wt percent	<20.0
Particle Size, μ	<10 3 (mean)
[illegible]	
Longest continuous Run	510 hours
[illegible]	[illegible]

of greater than 2 to feed nozzle pressure is a prerequisite to atomize the feed to the required particle size of less than 70 microns.[5] Nozzle plugging has not been experienced; a sieve installed on the feed line is used to filter out large solids.

Spray chamber fouling has been completely eliminated by using two modified commercially available (Cleveland AC vibra-might) vibrators. They are mounted on springs in a housing and fitted with extension shafts which permitted mounting on the exterior shell of the spray furnace. The extension shaft passes through tunnels between the upper and lower zone and are located approximately 180 degrees apart. The spray chamber was fitted with impact pads 3/8 in. (~cm) ~~CM~~ thick of 310 stainless steel. The spray chamber was deliberately scaled by operating at high feed rates without vibration; ~~however,~~ the vibrators then removed the scale with only one 3 second pulse cycle. Studies conducted on the vibrators and spray chamber have ~~has~~ not shown any sign of fatigue or corrosion due to vibration or calcination.[6]

The maximum demonstrated spray calciner capacity is 76ℓ/hr of simulated waste in a 21 inch (0.83M) ID spray chamber. (Figure 4) Due to low capacity of the filters, the off gas was rerouted directly to the condenser. Higher capacity was jeopardized due to equipment not related to the spray calciner unit unable to handle the higher feed rates. During the capacity run it was noticed that the higher the feed rate the lower the percentage of calcined powder carried to the filter housing by the off-gas, decreasing from approximately 50 wt% at 50ℓ/hr to 30 wt% at 50ℓ/hr.

The spray calciner has been coupled to the In-Can Melter and has successfully transmitted the calcine through a 60 degree slope diverter line coupling the two units without the use of vibrators or any mechanical devices. This same integrated system was successfully demonstrated in the WSEP program with full levels of radioactivity.[3] Figure 2 shows a photograph of the WSEP calciner with both the continuous metallic melter furnace and the in-can melting furnace.

Studies on the blow back system for the sintered stainless steel filters have shown that the solenoid valves can be located as far as fifteen feet away from the venturies and pulsed approximately every hour. Longer intervals metric between pulses increased cake buildup from 1/16 to 1/8 inch (MM) thick over the entire filter. Upon blowback, the entire cake is disloged, reducing the pressure drop across the filters to a value comparable to a "clean filter". It was shown that ΔP across the filters increased slightly over the value of a "clean filter" when blown back every two minutes.

SPRAY NOZZLE ASSEMBLY

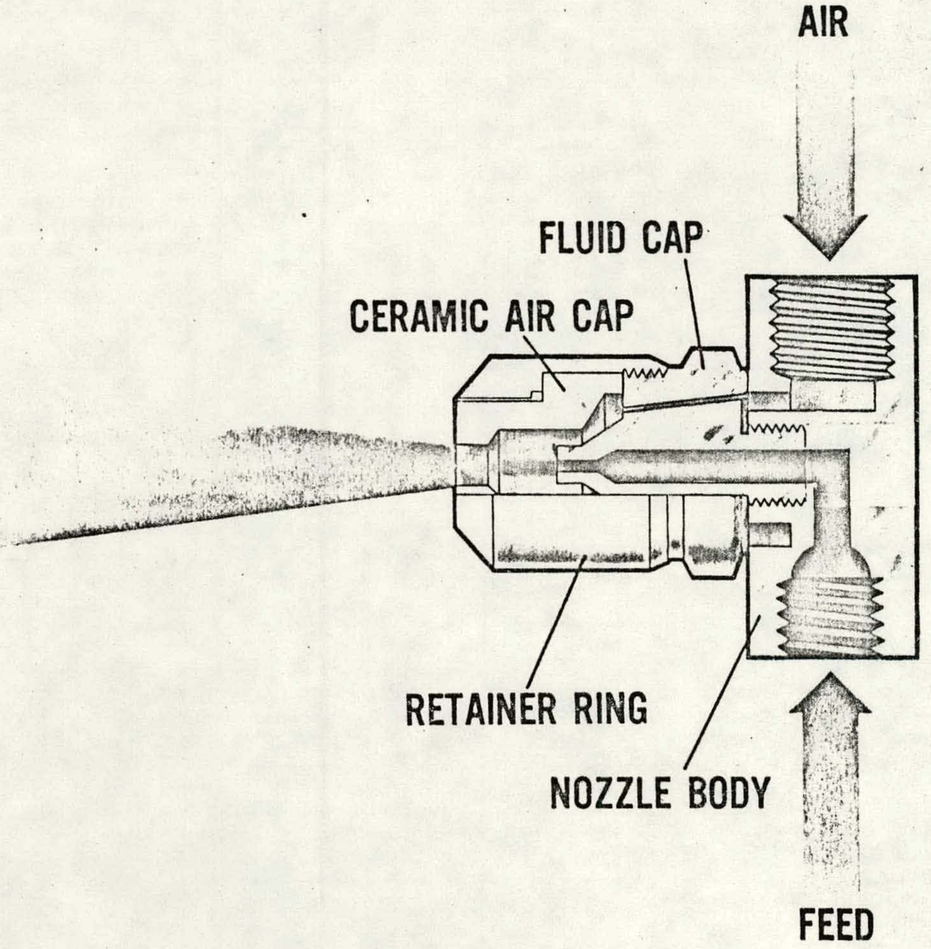
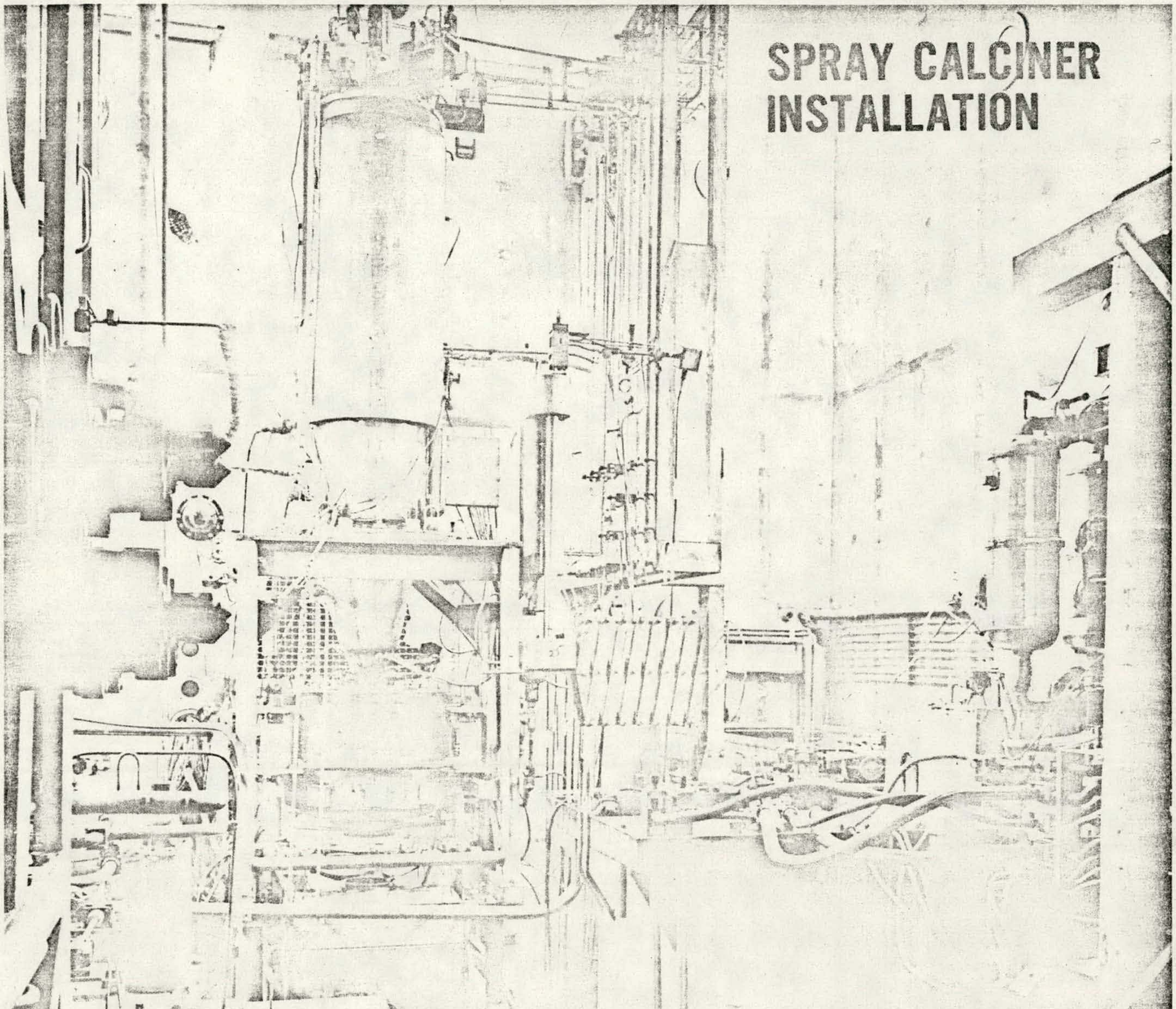


Figure — 1



SPRAY CALCINER INSTALLATION

Figure 2

An industrial scale spray calciner is in the design stage and will be in operation this year. The spray calciner will have the capacity to calcine the high level waste from a 5 metric tonne per day nuclear fuel reprocessing plant and containing up to 2M sodium.

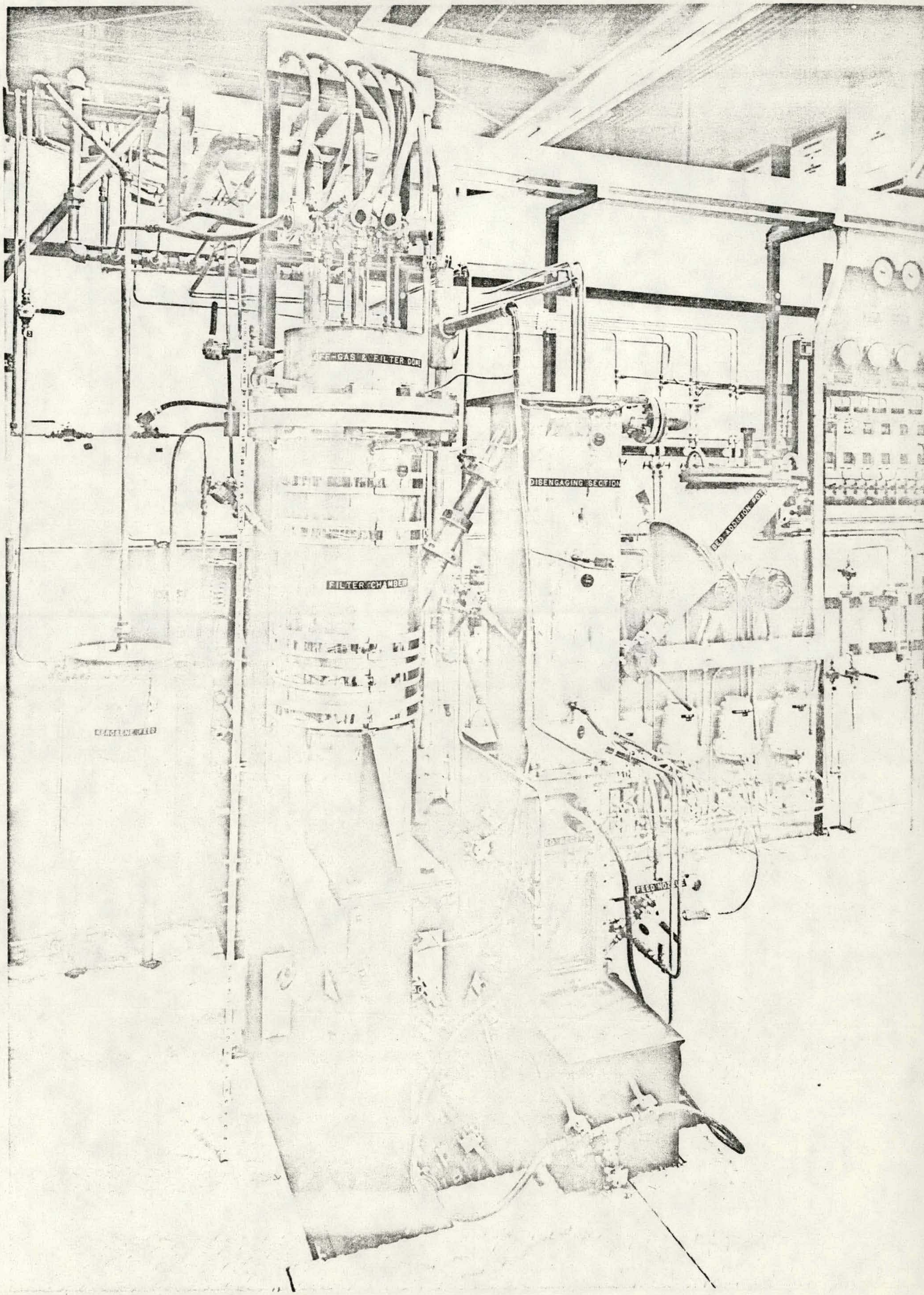
Fluidized Bed Calcination

A fluidized bed calciner (Figure 3) has been installed and operated at PNL since late 1974. Objectives have been to study the calcination of simulated high level commercial nuclear waste and its impact on the subsequent vitrification step. Significantly improved operating concepts have been developed which capitalize on the fluidized beds excellent heat transfer, heat distribution, and solids mixing properties. These unconventional operating techniques have reduced or eliminated problems such as decay heat consideration and particle size control which frequently trouble conventional type calcination techniques.

The pilot scale equipment (Figure 4) consists of a 1.7m (5.5 ft.) tall calciner vessel which has a 17.1cm (6.8 in.) square bed section and a 24.8cm (9.8 in.) square disengaging section. A perforated gas distributor plate is used. Product materials exit the calciner vessel via an overflow line, off-gas line or bed removal line all leading to a gas-particulate separator vessel. With the present design, gas and particulates are separated by a cyclone, gravity or sintered metal filters. The cluster of 17 filters offer 2.6m^2 (27.6 ft^2) of filtering surface nominally rated at 65 micron pore size. The filters are 7.0 cm (2.8 in.) in diameter, ten filters are 45.7cm (18 in.) long and seven are 91.4cm (36 in.) long. The filters are housed in a 52.4cm (20.6 in.) diameter vessel. Conventional blowback, including a high pressure air nozzle directed into venturi tubes in the end of each filter, is used as required to maintain satisfactory low pressure drop across the filters.

The most successful operating concept demonstrated with the calciner has been termed the continuous inert-bed process (CIB). A starting bed of inert material (SiO_2) is fluidized at about 30 cm/sec (1 ft/sec) superficial velocity while process heat is supplied by the combustion of oxygen and kerosene directly in the bed. As waste feed is introduced through an air atomized nozzle and the calcination reaction occurs the continuous addition of inerts to the bed is started. The calcine coats the particles, is spray dried, or coats and attrits from the material. Product is overflowed and/or elutriated from the bed to maintain the proper inventory. The degree of elutriation or overflowing depends on

FLUIDIZED BED CALCINER



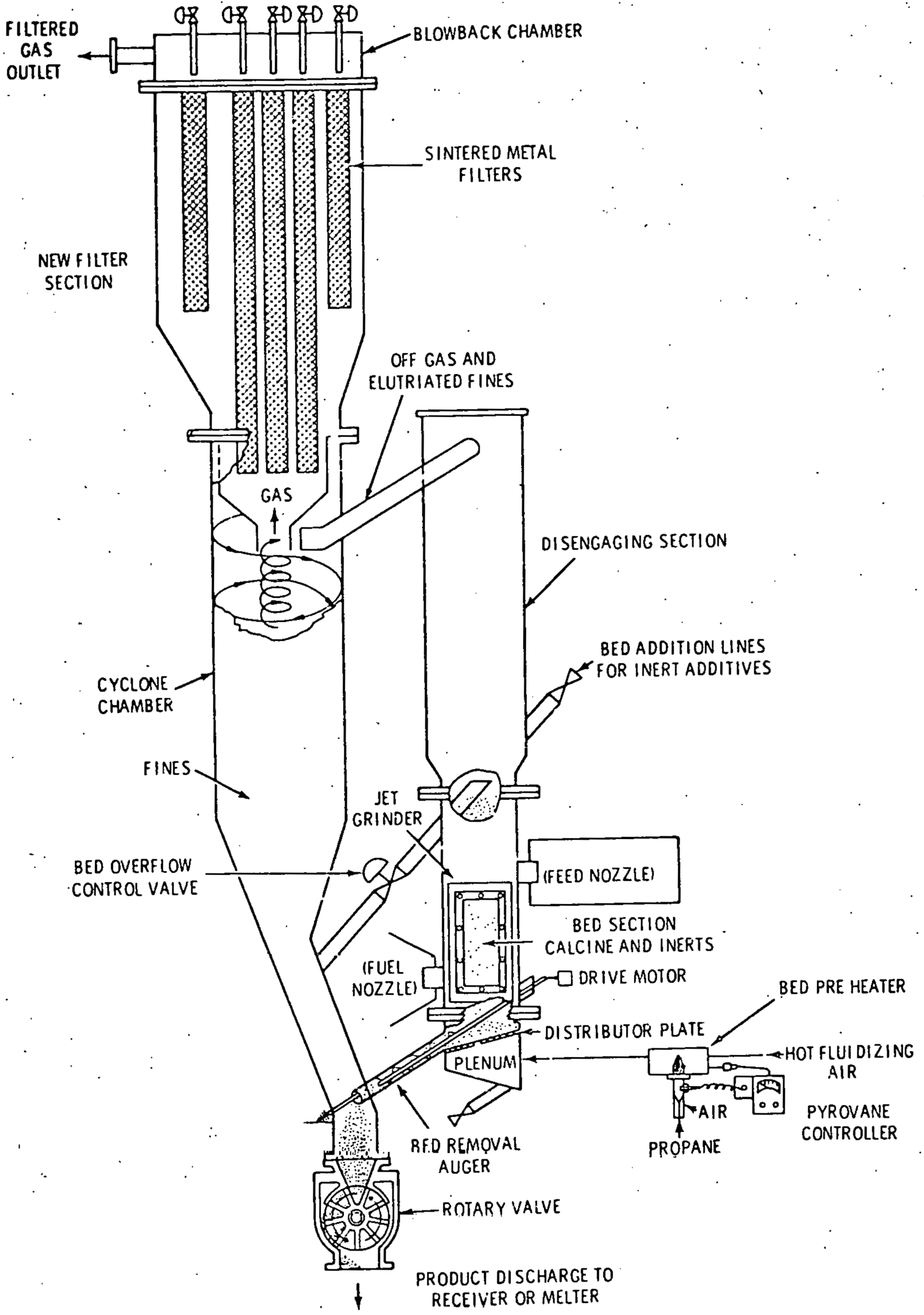


Fig. 4. **Fluidized Bed Calciner**

on the feed composition and amount of attriting force applied to the bed. By using jet grinders, high attrition type feed nozzles or operating conditions condusive to the generation of fines, the amount of calcine in the bed can be reduced significantly. The particle size of the inert material added is generally in a size range of 0.2 - 0.4 mm diameter. The rate of inert addition is dependent on the next processing step. At a minimum it would be equivalent to the bed attrition rate i.e. that necessary to maintain proper level. When vitrifying, the rate would be one to two times the weight of the calcine oxides being generated. Typically borosilicate glass frits are used at a frit to calcine ratio of 2.8:1. The inert material is readily incorporated in the frit.

Some advantages of continuous inert bed operation as compared to conventional operation are as follows:

1) low inventory of fission products is maintained in the bed, hence decay heat considerations are reduced.
2) general operability is significantly improved.
3) equilibrium is reached quickly hence development is simplified.
4) calcination of sodium waste is possible without additives.
5) process capacity is increased.
6) vitrification of the product is not compromised.
7) high temperature operation is practical.

Testing of this processing concept has shown it to be quite versatile over wide operating ranges. A summary of the conditions and performance to date has been summarized in Table II. The process appears readily accomodating to most waste compositions. The calciner has been coupled directly to an in-can melter and indirectly to a continuous ceramic melter with no operating problems observed. The use of sintered metal filters has been very satisfactory, no ill effects from the combustion heating has been noted. Iso ISO- kinetic sampling has shown concentrations of solids downstream of the filters to be less than 0.1 mg/scf of non-condensable off (metric gas. This represents a DF of 10^4 - 10^5 based concentration of calcined solids generated in the vessel divided by concentration in the off-gases.

TABLE II

OPERATING CONDITIONS TESTED WITH CONTINUOUS INERT BED CALCINATION

Feed Types	320 - 575 ℓ/MTU 0.01 - 1M Na 80 - 170 g oxide/ℓ
Feed Rates	20 - 40 ℓ/hr typical 80 - 120 ℓ/hr ft^2
Feed Nozzles	Commercial air atomized external mix Simple concentric tube type
Atomizing Air to Feed Volumetric Ratios	200 - 700
Vessel Operating Pressure	2 - 10 in. H_2O vacuum
Operating Temperature	500 - 800°C
Filter Pressure Drop	10 in. H_2O average 5 in. to 40 in. tested
Bed Properties	0.2 - 0.5mm dia. 14 - 50% calcine Avg. ∿ 20%
Product Properties	0.1 - 0.3 mm dia. Heavy fines or no fines dependent on feed, etc.

WIPED FILM EVAPORATION

metric

A horizontal wiped film evaporator, with 5 ft^2 of heat transfer surface was used to demonstrate the feasibility of utilizing the wiped film evaporator concept in the conversion of high level liquid wastes to a borosilicate glass product. Figure 5 illustrates the salient features of the evaporator.

Several simulated HLW formulations were concentrated to slurries containing up to 60 weight percent total solids. Figure 6 shows the performance of the evaporator when using a simulated PW-6 formulation as a feed stock.

The overall heat transfer coefficient for the evaporator ranged from 150 to 250 BTU/hr - °F - ft^2. While the coefficient increased with increasing feed rates, it appeared to be unaffected by the product composition, at least up to about 50 weight percent total solids, at which point the heat transfer surface began to scale at the discharge end of the unit. As the product total solids concentration increased above 50% the scaling increased and the heat transfer coefficient dropped rapidly. A short series of tests demonstrated that with jacket temperatures in the range of 300°C and sufficient rotor drive power to scrape the scale from the heat transfer surface, a free flowing powdered product could be realized directly from the evaporator discharge. While the product appeared to be dry, it actually contained 10-20 weight percent 17$\underline{M}$ nitric acid.

The evaporator was connected to several melting systems to evaluate the feasibility of operating the melters with evaporator concentrates rather than with dry calcine powders. Figure 7 shows the horizontal evaporator directly coupled to a metallic-type melter located immediately below the evaporator. Over 200 Kg of glass was produced from the metallic, the in-can, and the joule heated ceramic melting systems processing evaporator concentrates. While this direct coupled operation offers many advantages, e.g. high capacity, small size, and minimum product hold up, it is not without its problems, such as, premature calcination in the evaporator discharge nozzle, which blocks the flow of concentrate out of this evaporator, and high solids entrainment in the melter off gases.

The joule-heated ceramic melting system was the least affected by the evaporator concentrates, and future work with the wiped film evaporator will be in conjunction with the ceramic melter.

Figure

HORIZONTAL, REVERSE TAPER, WIPED FILM EVAPORATOR

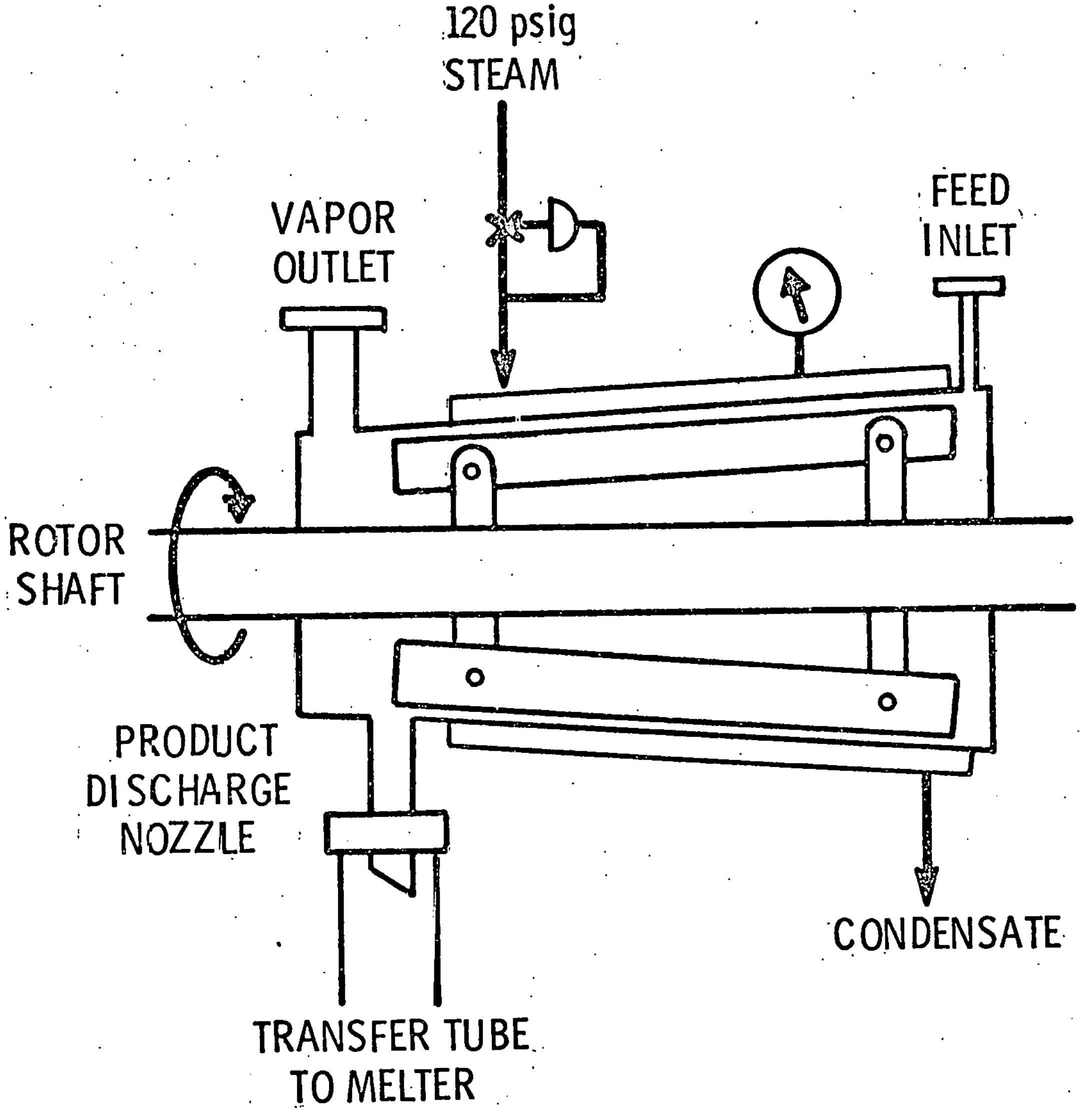


Fig 5

PADDLE SECTION

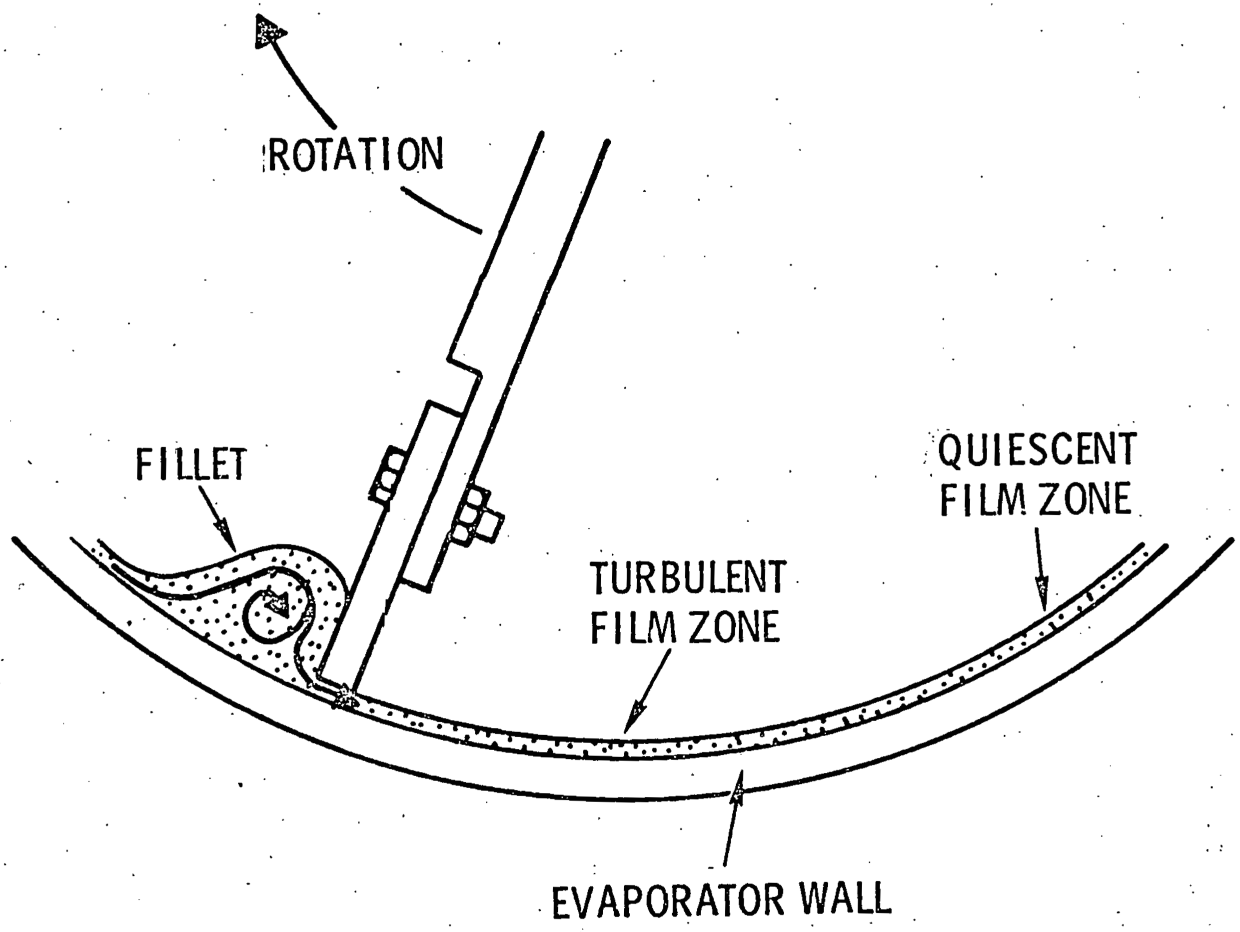


Fig 5 cont. Insert into Figure 5

EVAPORATOR PERFORMANCE CHARACTERISTICS

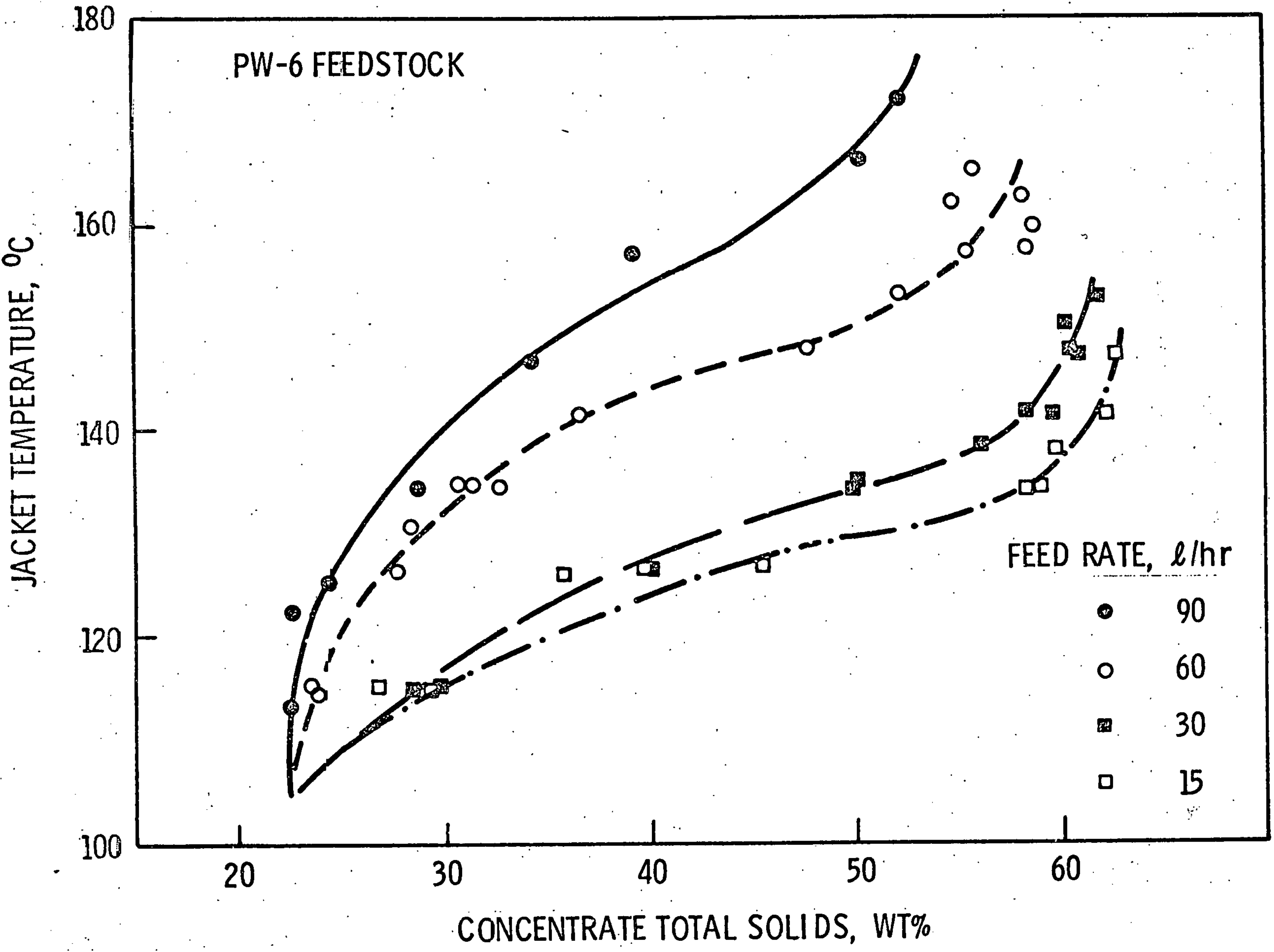


Fig 6

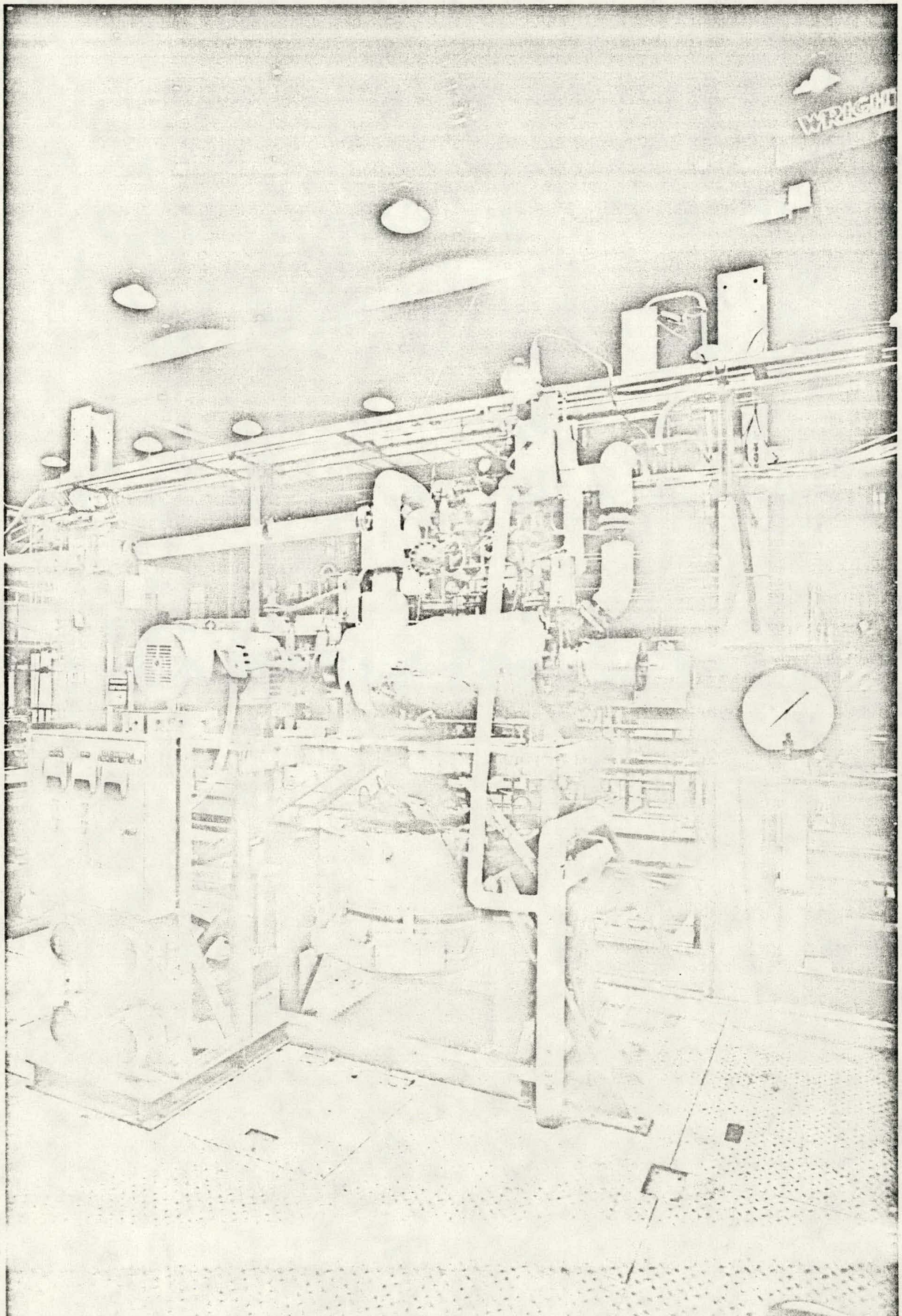


Figure 7

VITRIFICATION

An in can melter, continuous metallic melter and joule heated ceramic melter have been evaluated and are described below.

In-Can Melting

The in-can melting process uses the storage canister as the melting crucible for vitrifying a mixture of calcined nuclear waste and glass forming frit. The canister is placed in a multi-zone furnace and coupled directly to the output of a calciner. The canister is heated to between 1050°C and 1100°C, and calcined waste and frit are fed to the canister at a rate which does not exceed the melting capacity of the system. The frit is metered continuously into the melter at a rate proportional to the calcine generation rate. The off-gas from the melting mixture is vented through the coupling section to the calciner off-gas system. Because heat is generated by the waste, the temperature below the melt level rises above the processing temperature as the can fills and the furnace zones are turned off as the melt level rises above them. Cooling is initiated in these zones, but the temperature is maintained above 750°C to prevent sensitization of the canister material.

After the canister is filled, the calcine and frit are diverted to another canister in another furnace. The canister contents are maintained at the melting temperature for several hours to assure complete melting. Then the canister is rapidly cooled to avoid sensitization, capped and seal welded, leak checked, decontaminated and moved to storage.

The advantages of In-Can Melting (ICM) are:

- ICM minimizes process steps and equipment,
- ICM does not require transfer or valving of melt,
- ICM assures that everything that enters the melter, with the exception of some volatile species, is fixed in the storage canister,

- ICM eliminates the problem of melter deterioration and disposal.
- ICM is not affected by the addition of reducing agents to the batch for phase separation control.
- ICM has potential for higher waste loadings and lower processing temperatures because the viscosity does not need to be low for draining.
- The ICM process is well developed:
  1. Two radioactive runs were made during the WSEP program at PNL (Figure 2).
  2. Fifteen months experience during current WFP in which over 1000KG of melt were produced in 14 runs.
  3. British HARVEST/FINGAL Process and French PIVER Process provide similar experience although they are liquid fed.

During the past 15 months over 1000 kg of vitrified simulated, nuclear waste were produced by fourteen engineering scale in-can melting runs at PNL. The canisters used in these tests were fabricated from four-foot long sections of 8 in. and 12 in. diameter, schedule 40 pipe made of 304L stainless steel. Many of the canisters contained internal, radial fins made from 1/4 in. thick, 304L stainless steel plate. These fins are placed in the can for improving the melting capacity of the in-can melting equipment, but they also improve heat dissipation during storage. The fin design determined to be most satisfactory through computer modeling, and engineering scale tests is the drop in assembly shown in Figure 8. The fins terminate 1/2 in. short of contacting the canister wall so that the temperature distribution around the circumference of the canister will be nearly uniform. If the fins contacted the wall, there would be hot spots along the lines of contact during storage.

Corrosion of the 304L stainless steel canister by the melt during the process does not appear to be significant. The results of laboratory corrosion tests, presented in Figure 9, indicate a 0.08 to 0.15 mm/day rate at 1050°C. Examination of the walls and fins from processed canisters verify these laboratory results. The 80 mg/cm² of Spall from the exterior surfaces of the canisters heated in air is significant, however, for it would soon amount to a considerable accumulation in the process furnace. A plasma sprayed coating of zirconia on the surface of the canister was demonstrated to be effective for preventing spall. The use of an inert cover gas during processing is also being evaluated, and will probably be recommended.

Sensitization of the canister material during processing does not appear to be a problem, except in that part of the canister which is located between the exterior of the furnace and the heated chamber. Coupling sections are being evaluated which will permit the complete canister to be within the hot zones of the furnace.

Because the mean linear coefficient of thermal expansion of the vitrified waste is approximately half that of the stainless steel, the glass restrains the canister from contracting during cooling; thus, introducing tensil stresses in the metal. These stresses have been measured and showed the canister wall had experienced yielding during cooling. Various canister designs and thermal cycles are being evaluated to reduce this stress, but some compressive force on the glass is good for its integrity. clarify effect on canister integrity (?)

The engineering scale in-can melting equipment at ~~the~~ PNL has been successfully operated while coupled directly to a spray calciner, a fluidized bed calciner, and a wiped film evaporator. Melting rates as a function of canister diameter, fins, and type of feed are presented in Table III. Calcine and frit melting rates of up to 30 kg/hr have been achieved with 8 in. diam. finned canisters. A computer model predicts rates in excess of 50 kg/hr for 12 in diam. finned canisters. Liquid feeds such as concentrate from the wip~~p~~ed film evaporator are not recommended for in-can melting because they greatly reduce the melting capacity and load the off-gas with entrained solids.

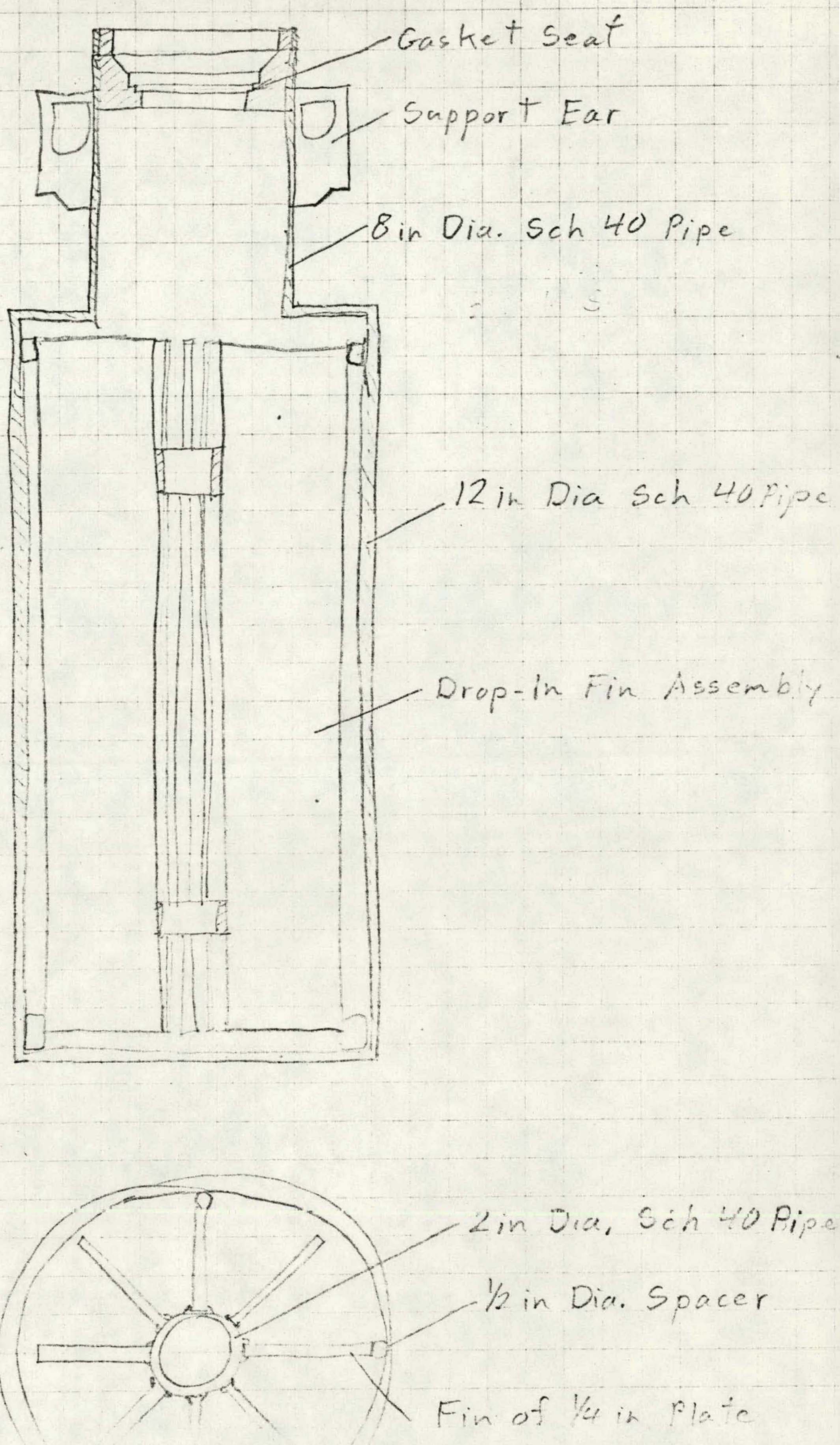


Figure 8 Typical In-Can Melter Test Canister

gure 4 Corrosion Rate Of 304L Stainless Steel In Simulated Nuclear Waste Glass Melt

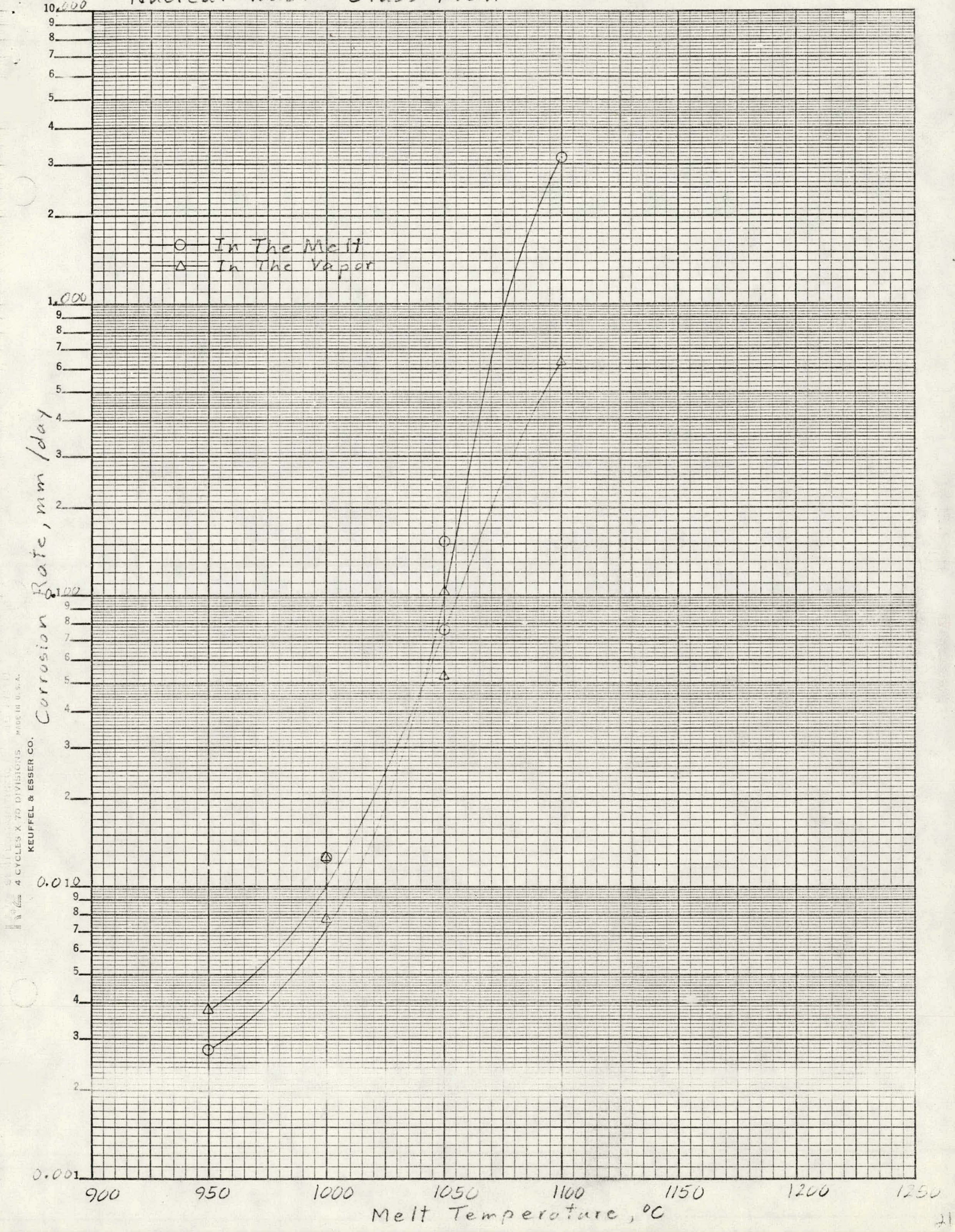


TABLE III

IN-CAN MELTING RATES

Can Diameter, Inches	No. of Fins	Batch Preparation	Calcine to Frit Ratio	Melting Rate kg/hr
8	0	Blended Powders	1:2	14
8	8	Blended Powders	1:3	20-30
12	0	Blended Powders	1:3	14.5-17.0
12	8	Metered Frit	1:2.9	24.0
Concentrated Liquid Feed				
8	8	WFE* Concentrate Metered Frit	1:2.2	12
12	8	WFE* Concentrate Metered Frit	1:2	13-19

* Wiped Film Evaporator

Joule Heated Ceramic Melter

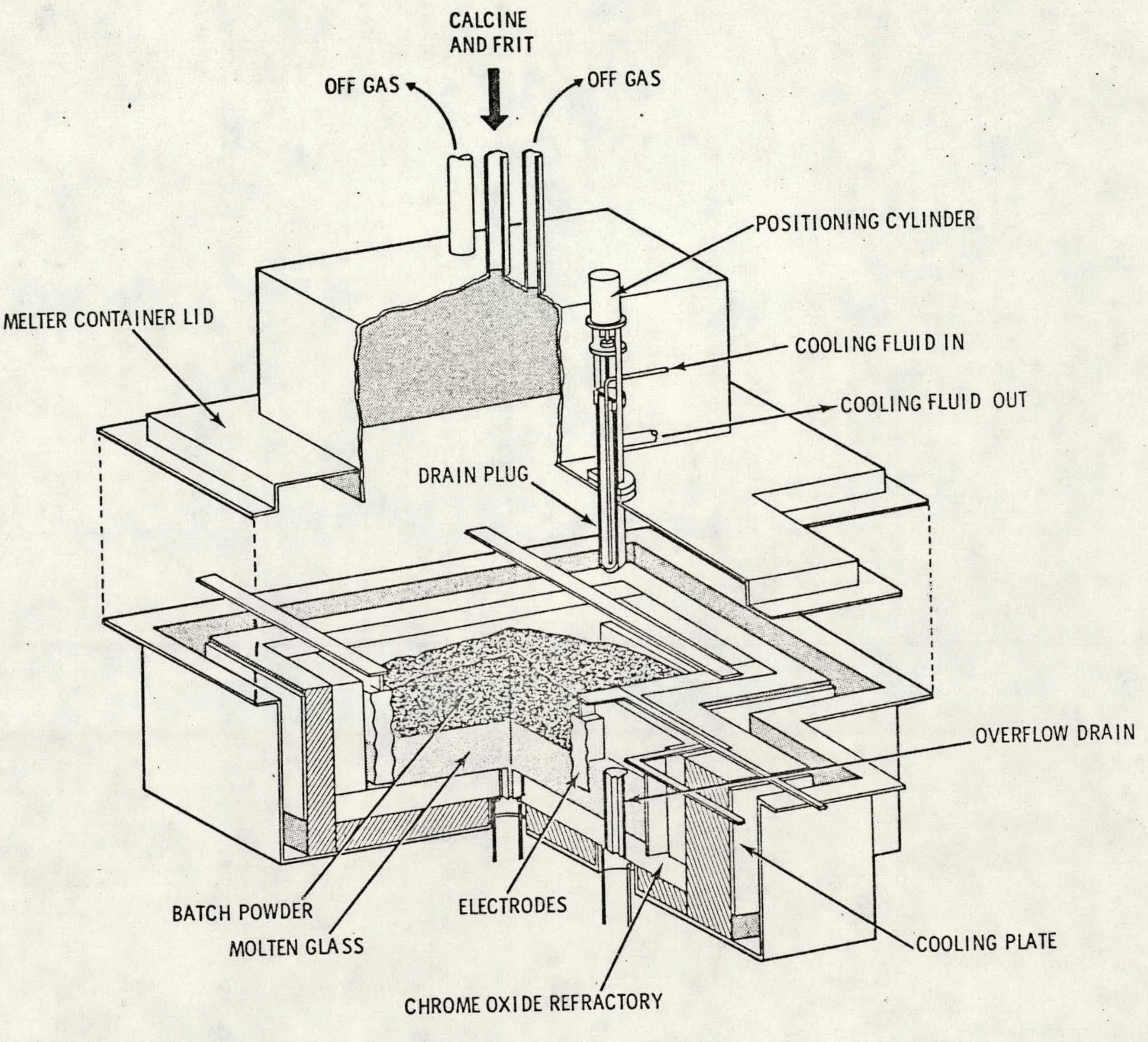
In this type of melter alternating current is transmitted from submerged electrodes through the molten glass where it is dissipated as heat. The molten glass is contained by high temperature, corrosion resistant ceramics. Using the molten glass itself as the "heating element" assures thorough melting at high throughput capacities while melting even difficult high iron oxide containing glasses.[ ]

Development of a joule heated ceramic melter started in late 1973.[ ] During 1974 four laboratory scale melters[ ] were constructed and tested. From early testing it was determined that melter startup and restart with a frozen tank was a factor which might limit its use. The scarifical element startup technique[ ] was developed and the initial startup and restart with a frozen tank has been repeatedly demonstrated. This technique employs coils of resistance wire which span the melting cavity between the main electrodes. These coils are used to heat the glass to the liquidous where the glass becomes conductive. After achieving continuity between the main electrodes through the glass, the coils are rapidly consumed by the molten glass. Using this technique heat up rates as low as 6°C/hr to as high as 300°C/hr have been demonstrated.[ ]

Corrosion tests of commercially avaialble refractories against the reference zinc borosilicate glasses were completed by Bates.[ ] Among several acceptable materials a fused cast high chrome oxide refractory was found to be superior. A sample of this material was rotated in the glass at 1250°C for 30 days and experienced only 0.05MM wear. This result suggested that refractory corrosion should not limit melter life.

The information from these corrosion tests and the laboratory scale melters was used to design an engineering scale melter in late 1974.[ ] In January 1975 the melter, shown schematically in Figure 10 was started up. The size of the melting cavity was 0.36M wide, 0.70M long and 0.3M deep. The unit was maintained at a nominal glass temperature in excess of 1150°C for 10.8 continuous months before it was shutdown. Simulated waste calcine, glass frit and simulated liquid waste solution were fed to this unit to evaluate its operability. A summary of the melter's performance is given in Table IV.

While feeding calcine and frit powder, the engineering scale melter repeatedly demonstrated smooth operation at a capacity in excess of 45 Kg/hr. The high melting capacity of this type of melter suggested that direct liquid feeding



~~FIGURE 4. SCHEMATIC OF CERAMIC MELTER~~

Melting cavity Dimensions 0.36m wide, 0.76 m long, 0.3 m deep

outside Dimensions 1.28 m wide, 1.36m long, 0.89 m high

Figure 10 Engineering Scale Ceramic Melter

TABLE IV

ENGINEERING SCALE CERAMIC MELTER PERFORMANCE

Time at Operating Temperature (Nearly Continuous)	-	10,8 months (7900 h)
Total Amount of Glass Produced	-	3600 kg
Capacity		
Calcine Feeding		
Maximum		60 kg/hr
Average all tests		46 kg/hr
Liquid Waste Feeding		
Maximum		29 ℓ/hr
Average all tests		20 ℓ/hr

of the HLLW might be feasible. Five separate tests were completed to evaluate this process. These tests showed that this unit was capable of processing 25ℓ/hr of simulated HLLW concentrated to 378ℓ/MTU. It was found that a portion of the glass frit needed to be slurried with the HLLW prior to feeding to insure rapid melting. In the most recent test the molten surface was completely covered with 20-40MM of the solution with no loss in processing rate. When the pool was covered with the waste solution, it was found that less than 0.5% of the waste was entrained in the off gas stream. From these tests it appears feasible to process liquid waste directly on this type of melter. This promises to provide a significant simplification in the vitrification process.

After 10.8 months of continuous operation the melter was shut down and examined. No observable, general refractory wear could be noted. The inconel® 690 electrodes experience a weight loss of less than 3.5%. These results suggest that an operating life in excess of two years may be readily achieved.

The engineering scale melter has proven to be a rugged piece of process equipment. It has recovered from electrical power outages (>25 minutes), sudden additions of liquid solution, periodic under- and over-powering and the presence of molten metal [ ] without loss of operability. The testing completed to date strongly suggest that this type of melter has excellant potential for use as an improved waste vitrification system.

Continuous Metallic Melter

The continuous metallic melter, shown schematically in Figure 11 is an Inconel 690® crucible in which calcine and glass frit are continuously melted, then batch dumped through a freeze valve into the receiving canister. Since 1965 over 2000 hours of operation have been logged at Battelle with this type melter. Over 1200 of the operating hours were ~~have been~~ logged during in-cell vitrification of actual high level waste during the WSEP Program[2]

The metallic melter is designed to operate at 1100 to 1200°C. Operating at a melt temperature of 1150°C with mechanical agitation, the melting capacity of the pilot unit shown is about .15 kg/hr Scaleup calculations for a stirred melter[9] indicate that a melter capable of vitrifying waste at a rate of over 60 kg/hr would be 23 inches in diameter and 29 inches high.

metric

During extended operation a cerium rich phase, which does not dissolve well in the glass at 1150°C, has been observed to accumulate on the melter floor. Although the existence of this phase is not ~~considered to be~~ detrimental to glass durability, the phase has a much higher viscosity than the glass and can cause melter drainage to be difficult. With mild agitation, 10 to 40 rpm, the phase can be kept dispersed. Excessive agitation, greater than 100 rpm, should be avoided because of increased melter corrosion. In fact corrosion resulting from agitation is believed to be the major factor limiting melter life([illegible]). Due to corrosion the projected life of an Inconel melter with 1/2 inch thick walls is 2 to 6 months.

During long term hot cell operations, the metallic melter has been shown to be a reliable, remotely operable unit, capable of producing currently acceptable waste glasses.

no ¶ However cerium phase separations and a desire for a higher melting capacity necessitates the use of mechanical agitation, with its attendant accelerated corrosion rate and added complexity. Therefore it has been decided to deemphasize development of this melter type, pending the identification of more corrosion resistant materials.

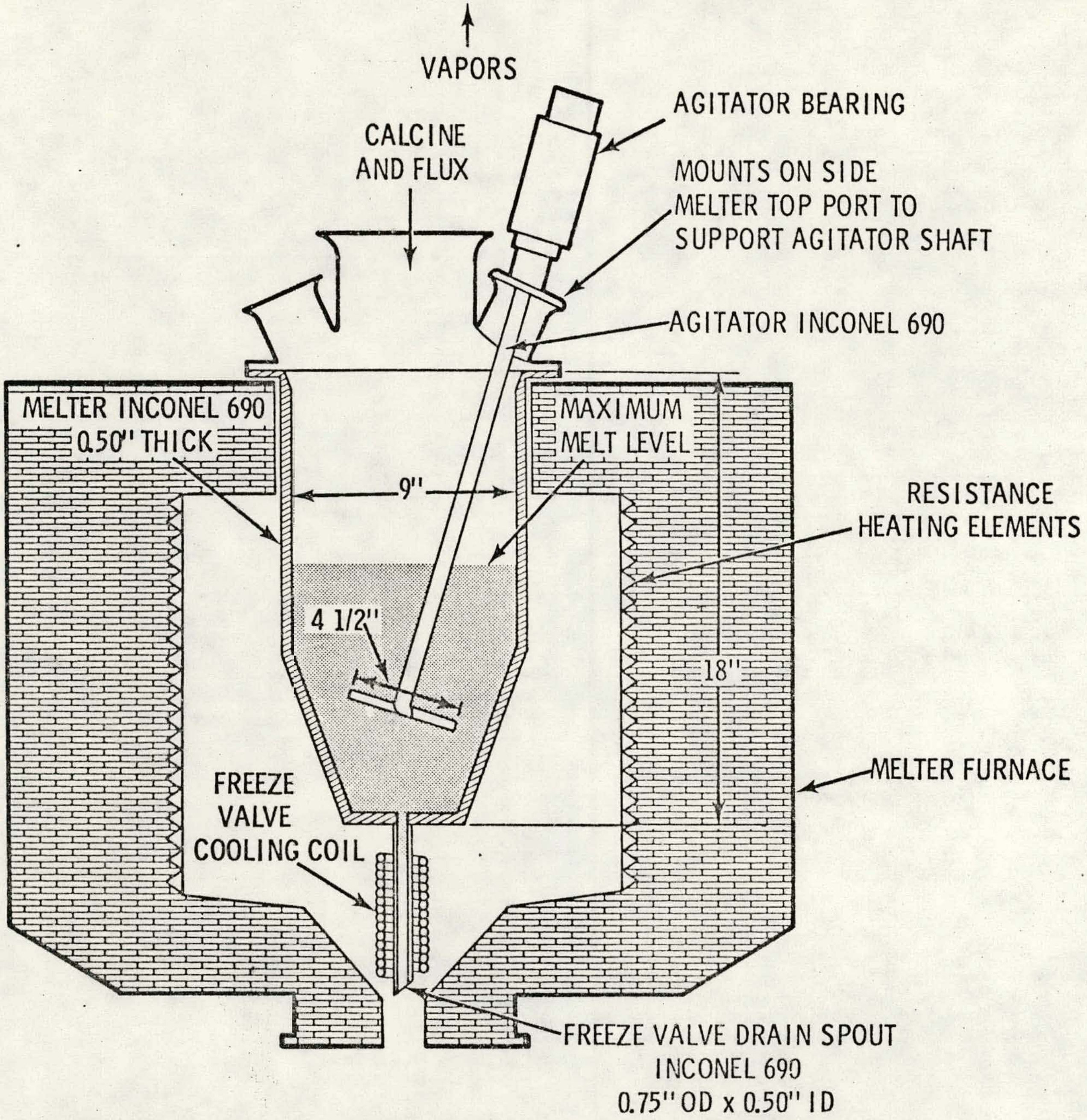


FIGURE 11. SCHEMATIC OF METALLIC MELTER

Integrated Processes for Close Coupled Calcination and Vitrification

Current U.S. regulations require solidification of commercial high level wastes within 5 years of reprocessing. Dur to the high cost of liquid waste storage tanks, earlier solidification is planned and waste solidification facilities are needed by the early 1980's.

To meet this need, current vitrification processes were studied and two well developed processes were chosen. The selected process consists of the spray calciner or fluidized bed calciner (CIB) coupled to the in-can melter. Due to its versatility the spray calciner/in-can melter is currently being designed for use at the West Valley Nuclear Fuel Services Reprocessing plant.

Direct Calciner and Melter Coupling

The calciner and melter are closely coupled to avoid the problems encountered in calcine storage and transport. In addition, the calciner and melter are easily operated as one unit since the spray calciner has no holdup and startup and shutdown does not produce any adverse effects. The fluidized bed calciner operated by the CIB technique is also relatively unaffected by startup and shutdown. For most plants, two in can melters are proposed. Thus, any failure of one unit would be followed by immediate switching to the second canister.

Storage of heat generating calcine is quite a different problem from storage of liquid due to the difficulty of calcine transport and the difficulty of heat removal to avoid calcine sintering and agglomerating in the storage bin. To avoid further cell height increase, calcine storage should be located below the calciner and a calcine transport system should be added to elevate and transfer the calcine to the melter. The alternative, a gravity flow system, would require increasing cell height about 4-6M.

When heated sufficiently, calcine will off-gas, sinter and agglomerate. Depending on calcine sodium content, agglomeration occurs over a range of 300 to 900°C. Since agglomerated calcine may be difficult to remove from a bin, it is anticipated that the maximum allowable routine storage temperature would be below 800°C. Based on this centerline temperature and on recent thermal conductivity measurements of simulated commercial HLW calcine[ ], the following bin thickness ~~has~~ have been calculated for calcine generating 90 watts of heat per kg. This corresponds to waste approximately two years out of reactor. To store fluidized bed calcine from reprocessing of 5 MTU/day for 14 days abour 2.7M^3 of storage is required.

clarify height + width

	Maximum Calcine Thickness CM	Bins Required for 14 days Storage
slab shaped bin, externally water cooled (2.5mH. x 1.2mW)	10	10
slab shaped bin, free air convection cooled	7	15
cylindrical bin, externally water cooled (2.5mH.)	14	70
cylindrical bin, free air convection cooled	9	170

Since improved plant operational efficiency can also be obtained by increasing both HLLW storage capacity and vitrification equipment capacity, it is recommended that the calciner and melter be direct coupled to avoid the complexities of intermediate calcine storage.

Vitrification Plant Design

Work in the WSEP program and the WFP have been directed to technology development and demonstration of the total waste solidification system. The various equipment pieces in the process from waste storage through canister decontamination and off gas treatment have been developed and design is currently underway for a vitrification facility to begin operation in the early 1980's.

The vitrification process under design consists of a spray calciner or a CIB-operated fluidized bed calciner coupled to an in-can melter. The conceptual integrated process is shown in Figure 12. As part of the design effort, a full size developmental spray calciner/in-can melter is being prepared for operation this year to verify remote equipment design and scale up factors.

The following discussion of a full scale plant design is based on several factors.

- HLLW-ILLW received from reprocessing 5 MT/day of 33,000 MWD burnup fuel
- A waste concentration of 567ℓ/MTU
- 75 Kg calcine per MTU
- Borosilicate glass containing 33 weight percent calcine

Equipment in the vitrification process is designed with the goal of totally remote operation and maintenance with manipulator use restricted to infrequent maintenance. The processing equipment shown in Figure 13 can be contained in a cell 8 M wide by 6 M deep with a working depth of 12 M.

SPRAY CALCINER/IN-CAN MELTER PROCESS

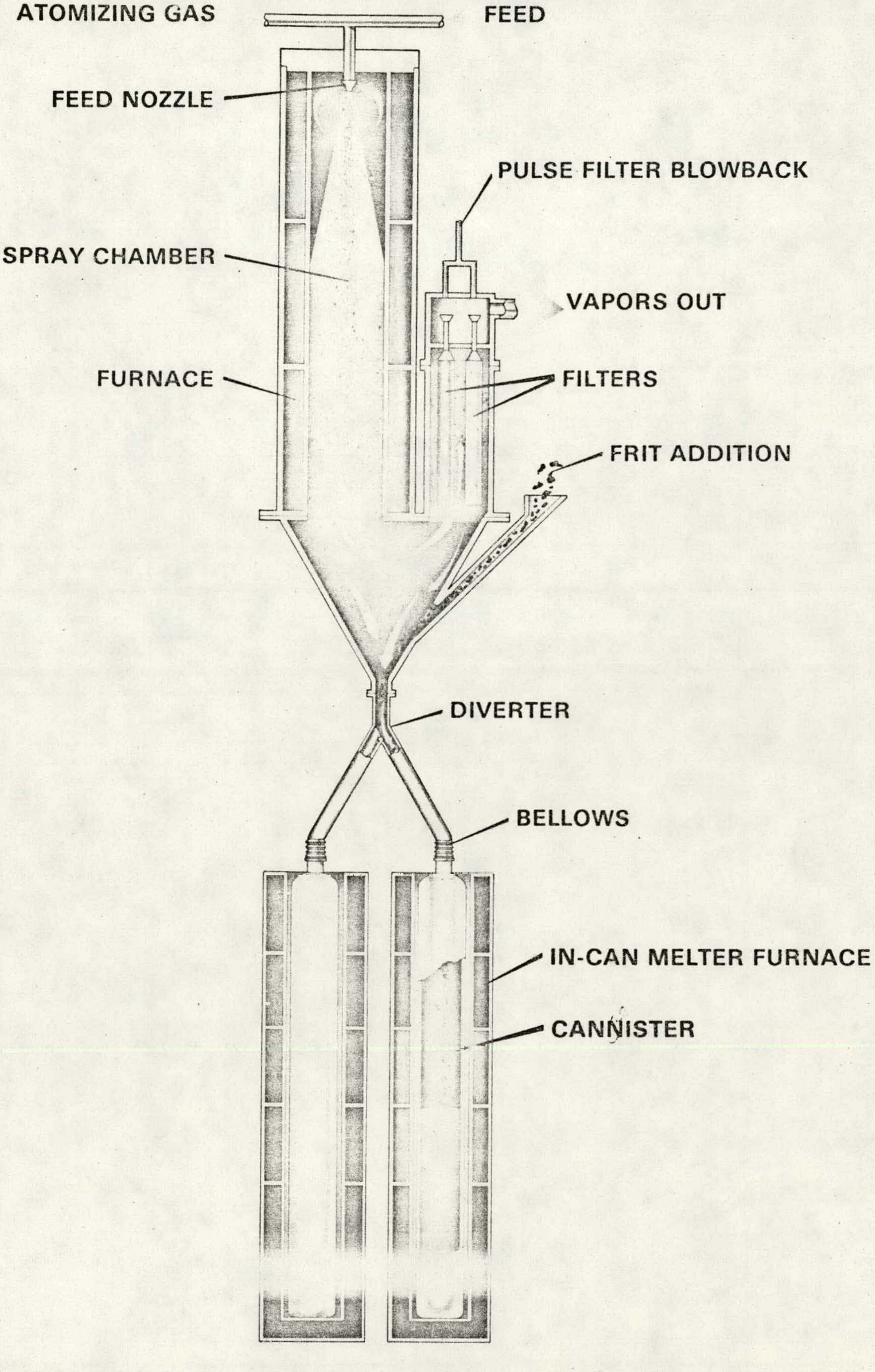
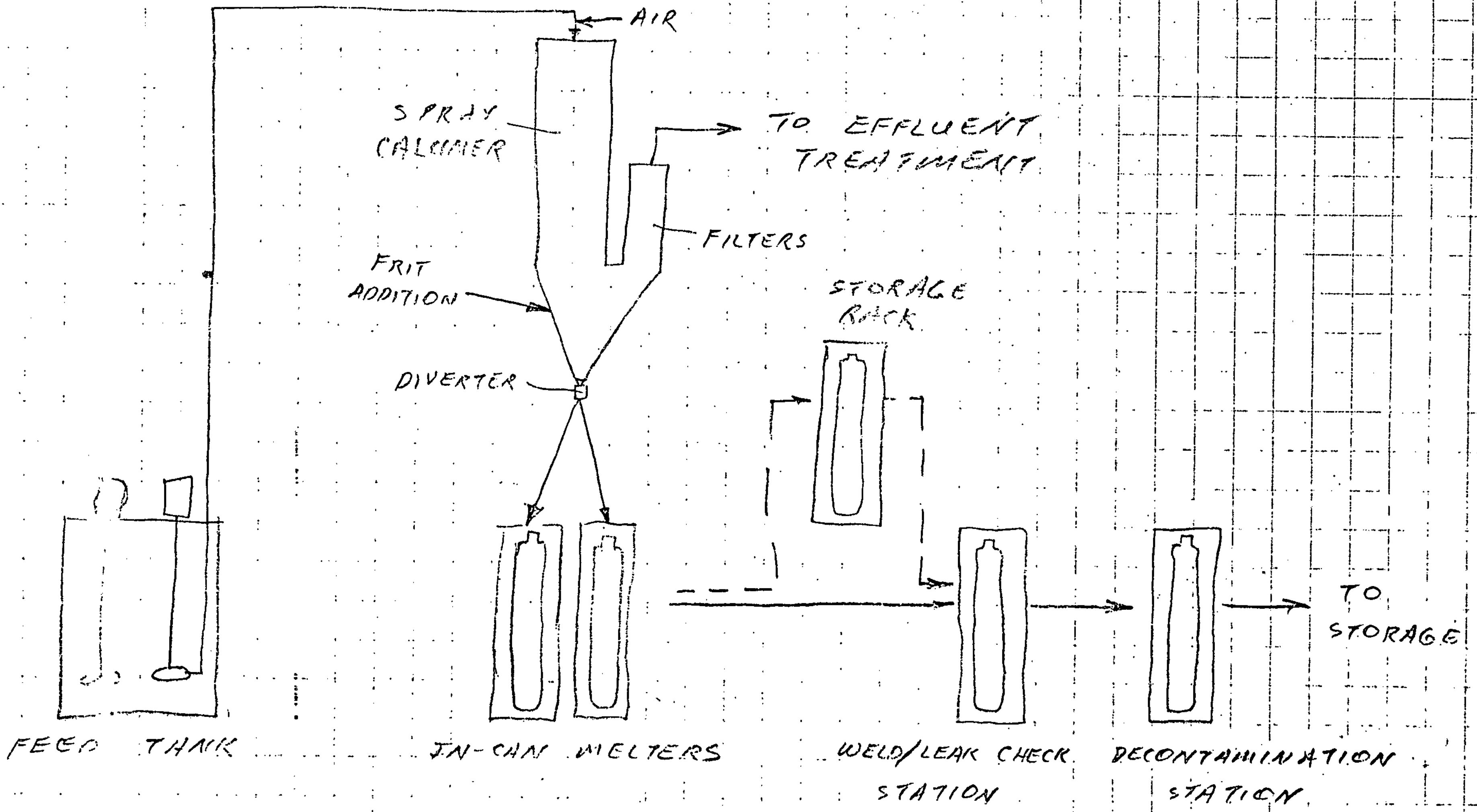


Fig 12

Fig. 13 SPRAY CALCINER/IN-CAN MELTER VITRIFICATION PROCESS



Feed Tank and Canister Sizing

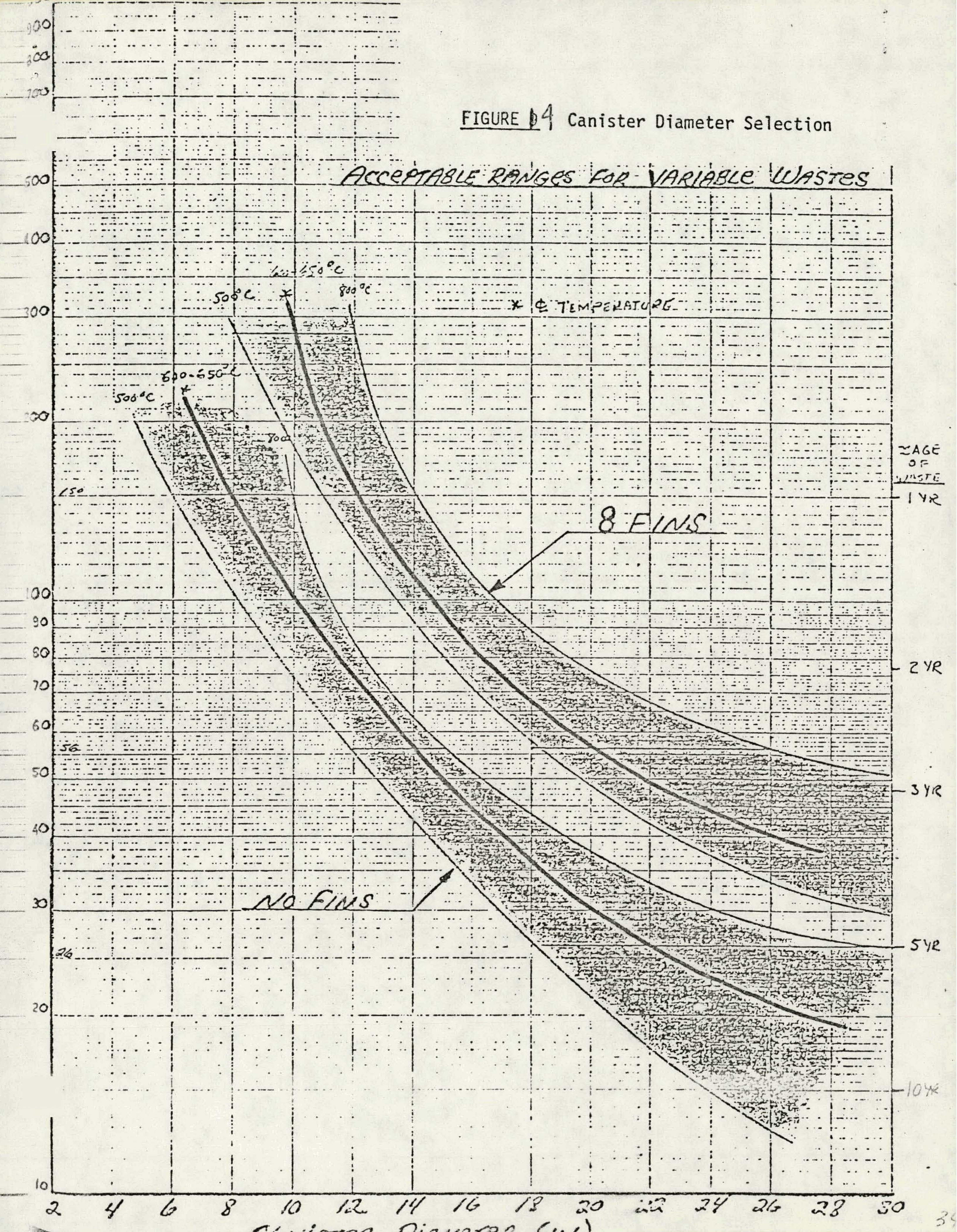
The waste slurry is contained in an agitated, cooled feed tank capable of containing sufficient waste to fill a glass canister. Many factors contribute to determining the size of the glass canister and hence the feed tank volume. However, for 1 year out of reactor reference waste a canister of glass containing 8 internal drop-in fins can be as large as 35 CM cm in diameter and hold the waste from 4 MT of fuel in a nominally 3 meter long canister. The diameter is limited by the requirement that the centerline temperature of the glass be less than 800°C during air storage. At two years out of reactor the canister could be 51 CM cm diameter (Figure 14) and contain waste from 8 MT of fuel. Thus, the feed tank would contain 2500ℓ of waste depending mainly on the heat generation rate.

Calciner - The nominal waste flowrate to the calciner is 130 ℓ/hr including 10% recycle from the effluent scrubbing system. At this feedrate a single spray calciner or fluidized bed calciner about 1 M in diameter by 3 M tall converts the liquid waste to a dry powder for melting. Glass former added to the lower unheated part of the calciner flows by gravity to the melter below. Totally remote features such as incorporation of the spray calciner feed nozzle into a remote connector enhance the maintainability of the system.

Effluent Treatment - Vapors passing through the sintered stainless steel calciner filters contain less than 0.1% of the nonvolatile feed constituents and less than 2% of the radioruthenium. These radionuclides are removed by wet scrubbing techniques, concentrated, and returned to the calciner. Designing the effluent treatment system for waste several years out of reactor offers little savings over design for 1 year out of reactor waste.

In-Can Melter - Since calcination is a continuous process and melting is batch, two melters are coupled to the calciner via a diverter valve. Each melter furnace is 1.2M in diameter by slightly over 3 M tall and is capable of processing 60 CM by 3 M canisters. In operation, calcine and frit are fed to one melter until the desired melt level is reached at which time the feed is diverted to the other canister. After the melter operation is complete the furnace is disconnected from the fill head and translated far enough for canister removed by crane. An empty canister is inserted in the furnace and reconnected to the fill head. Use of a 4.5M length canister instead of 3 M may improve melter capacity and will allow 50% more waste per canister, but will require a 1.5 M increase in cell height.

FIGURE 14 Canister Diameter Selection



Canister Operations - Although the canisters are designed to be safe during air storage, water cooled storage and work locations are provided to prevent excessive heating of the cell air. The cooled canisters are closed and seal welded then leak checked with a mass spectrometer prior to decontamination by water spray and transfer ~~discharge~~ to the water storage basin.

Joule Heated Ceramic Melter PROCESS

A vitrification facility utilizing a ceramic melter would be similar to the previously described facility. Since the height of the melter is significantly less than that of a calciner the required cell height would be reduced to about 8 M while other cell dimensions would be relatively unaffected. With the exclusion of the calciner, other major cell equipment, including the feed system, off gas treatment, and canister operation would be similar.

From the experiments completed with the current ceramic melter it appears ~~to be~~ practical to feed the HLLW from a reference 5 MTU/day reprocessing plant directly to the melter when concentrated to 378ℓ/MTU. This process consolidates the evaporation-calcination and vitrification steps into a single piece of process equipment and thus provides a significant simplification in the conversion process. Near term development plans are to construct on improved melter design which will be capable of processing greater than ≥ 50ℓ/hr of HLLW. Methods of boosting the capacity are under study and will be tested if promising (e.g. ionic heating the aqueous solution in the melter, microwave heating, or preconcentration by a wiped film evaporator). The direction of development which will be pursued is dependant upon the success of the boosting schemes. If successful, the melter will be designed for remote operation and tested. If boosting is not a promising approach, the melter will be scaled up and tested. The objective of this development program is to have a viable design by 1978 which can be used in a full scale reprocessing plant. ¶Consolidation of all wastes from a fuel reprocessing plant appears economically attractive. A flow sheet has been proposed which would accomplish this goal. The HLLW, ILLW and α waste (incinerated ash) streams would be combined and converted to a glass. The glass would then be drained into a canister filled with cladding hulls and would form a matrix around the hulls. Evaluation and laboratory testing of this scheme is in progress. Should this process appear feasible, the ceramic melter would play a central role. A joule heated ceramic melter would be designed to process the much higher glass throughputs required and also provides the needed melt draining control into the clad filled canisters. Initial testing and evaluation of this scheme is planned for early 1977. If this process proves worthwhile, a demonstrated system will be ready for use by 1979.

Summary

Experience gained through the development and operation of calciners and glass melting systems has provided the information needed for selection of a high level waste solidification system. At the present time a spray calciner coupled to an in-can melter is sufficiently developed that design of an integrated system is underway for implementation at a U.S. commercial fuel reprocessing plant. A fluidized bed calciner operated with the addition of silica to produce a continuous inert bed (CIB) provides a second calciner which can also be used with the in-can melter. A joule heated ceramic melter for converting calcine to glass shows great promise as a future continuous one step process for converting liquid to glass. These systems will be demonstrated at the full scale capacities required for vitrifying HLLW from the reprocessing of 5 MT/day of spent power reactor fuel.

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References