BNWL-SA-6564

Technology Status of Spray Calcination/Vitrification of High-Level Liquid Waste for Full-Scale Application

by
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Presented at the 70th Annual Meeting
of the American Institute of Chemical
Engineers, New York, NY
November 13-17, 1977

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TECHNOLOGY STATUS OF SPRAY CALCINATION/ VITRIFICATION OF HIGH-LEVEL LIQUID WASTE FOR FULL-SCALE APPLICATION

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SUMMARY

Spray calcination and vitrification technology for stabilization of high-level nuclear wastes has been developed to the point that initiation of technology transfer to an industrial-sized facility could begin. This report discusses current process and equipment development status together with additional R&D studies and engineering evaluations needed. Preliminary full-scale process and equipment descriptions are presented. Technology application in a full-scale plant would blend three distinct maintenance design philosophies, depending on service life anticipated: 1) totally remote maintenance with limited viewing and handling equipment, 2) totally remote maintenance with extensive viewing and handling equipment, and 3) contact maintenance.

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TECHNOLOGY STATUS OF SPRAY CALCINATION/VITRIFICATION OF HIGH-LEVEL LIQUID WASTE FOR FULL-SCALE APPLICATION

1.0 INTRODUCTION

The overall objective of the Department of Energy high-level liquid waste (HLLW) program is to develop technologies to produce stable forms of wastes for ultimate isolation from the biosphere. The stabilized waste product must be capable of resisting thermal, chemical, mechanical, and radiation degradation for thousands of years. The Spray Calcination/In-Can Melter process removes water from the HLLW, converts the resulting solids to an oxide form, or calcine, and produces a stable glass product from the calcine. The glass should meet anticipated federal government waste acceptance criteria for storage and disposal. This paper discusses the process, equipment concepts, conceptual plant design concepts, and development status for a liquid waste vitrification facility. The development work was done principally at the Pacific Northwest Laboratory (PNL), operated by Battelle Memorial Institute for the Department of Energy (DOE).

The technology discussed in this paper is applicable, in general, to solidification of HLLW from nuclear fuel reprocessing plant operations. Application of this technology to commercial wastes in the United States will be delayed due to the recent U.S. decision to defer reprocessing of commercial spent fuel.

2.0 PROCESS DESCRIPTION

2.1 CALCINER FEED

A vitrification process has been developed and is undergoing a test program at PNL using simulated HLLW and intermediate-level (ILLW) that will be produced if Allied-General Nuclear Services' Barnwell Nuclear Fuel Plant (BNFP) reprocesses irradiated fuel. HLLW which originates from the first solvent extraction cycle, aqueous waste recycled from the second uranium, and the second and third plutonium cycles of the Purex process will be blended with the ILLW. Intermediate-level liquid waste originates from operations such as cask flushing, solvent cleanup, and analytical operations. The current BNFP flowsheet plans to blend HLLW/ILLW on a volume ratio of 2/1. Typical properties appear in Table 1.

TABLE 1. Properties of Liquid Wastes

	HLLW	ILLW
Storage Temperature, °C	60	25
Specific Gravity	1.3	1.1
HNO_3, molarity	4-7	2.5
Sulfate, molarity	-	0.001
Phosphate, molarity	0.003	0.24
Chloride, molarity	0.001	0.009
Suspended Solids, gram/liter	10	2
Volume, liters/MTU	570	280
Fission Products, grams/liter	45	$5(10^{-3})$
Actinides, grams/liter	10	17
Decay Heat, watts/liter	2.5	0.01

The blended waste will be fed directly to the calciner spray nozzle. The solidification facility will be designed to enable preconcentration of HLLW or ILLW in an evaporator if the total volumetric feed rate to the calciner limits the production capacity of the facility.

Table 2 shows the light water reactor fuel exposure design basis for the waste vitrification facility. It is based on anticipated fuel available to BNFP.

TABLE 2. Radioactive Exposure History of Waste

Burnup	29,000 MWD/MTU
Specific Power	30 MW/MT
Initial Enrichment	2.8% U-235
Onstream Time	80%
Age at Solidification	3 years

2.2 CALCINATION/VITRIFICATION

In the calciner, shown in Figure 1, the liquid feed is atomized by air in a top-mounted nozzle to produce liquid droplets about 70 microns in diameter. Convective and radiant heat transfers, dries, and calcines waste before the waste strikes the 800°C calciner walls. Over half of the calcine falls into the calciner outlet cone. The balance collects as a coating on sintered stainless steel filters located in the calciner gas outlet. This coating is periodically blown back, using high-pressure air through the filters, to dislodge the accumulated powder which falls into the calciner outlet cone.

Two parts by weight of glass-forming chemicals, or frit, are added continuously to the calcine in the discharge cone. The composition of frit for typical BNFP wastes is shown in Table 3.

The chemical composition of the frit has been formulated to give good homogeneity, reasonable viscosity, adequate durability, low leachability and long-term stability in storage.

Two equipment options are being considered for making glass, either semicontinuous in-can melters or continuous melting in a ceramic-lined melter. In the semicontinuous option, the multizone melter furnace maintains the canister at 1050°C until calcine and frit in that zone have formed a homogeneous melt. Then electric power is terminated to the furnace section

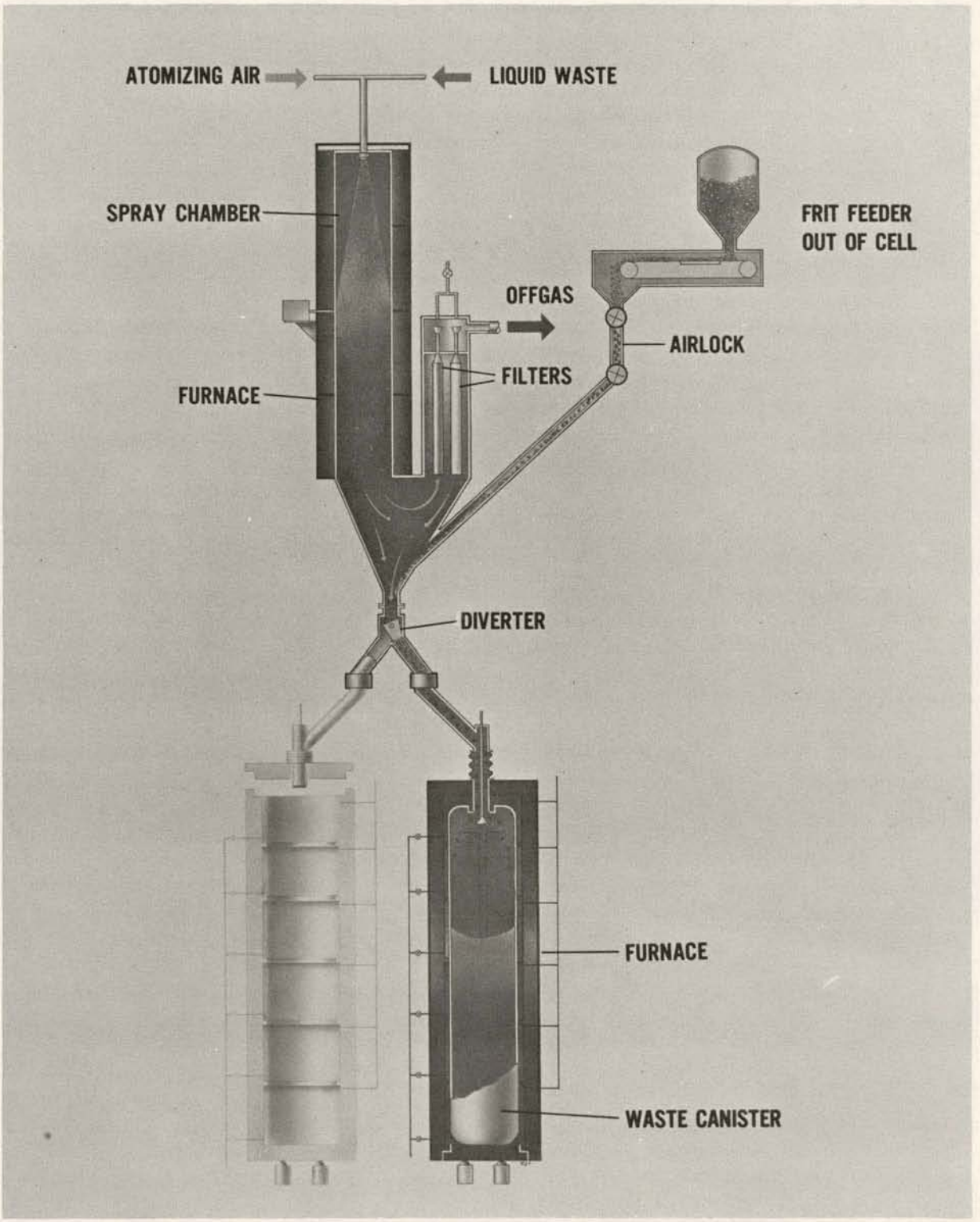

FIGURE 1. Spray Calciner/In-Can Melter

adjacent to the molten zone, and forced-air cooling is initiated. When the container is filled, the top melt zone is held at the processing temperature for several hours to allow residual gases trapped in the glass to be released.

TABLE 3. Frit Composition for BNFP Wastes

SiO_2	53%
B_2O_3	14%
TiO_2	9%
Na_2O	12%

and lesser amounts of Al_2O_3, K_2O, CaO, and CuO.

In the continuous option, frit and calcine will fall onto a molten (1200°C) pool of glass. The solids gradually flux into the melt to form vitrified waste. Periodically, the melter will be tilted to cause molten glass to overflow into a product canister.

After filling by either option, the canister caps will be welded in place, and the closure checked for quality before decontaminating the canisters for on-site interim storage.

2.3 OFF-GAS PURIFICATION

Calciner off-gases receive several stages of treatment to remove NO_x water, and particulates containing radionuclides. One of the more troublesome nuclides, if volatilized, would be ruthenium (Ru). Development work on the VERA spray calcination process in Germany and on fluid bed calcination at the Idaho National Engineering Laboratory (INEL) indicate that Ru can be limited to a 0.01% release under certain operating conditions if formic acid is added to the calciner feed. Apparently, formic acid creates a reducing atmosphere which suppresses Ru volatilization. With 1.5 moles of formic acid added for each mole of nitrate in the waste, the reaction products are expected to be CO_2, N_2 oxides of nitrogen and water.

As condensable process off gases enter the first stage of off-gas treatment, shown in Figure 2, the gaseous decomposition products and atomizing air pass

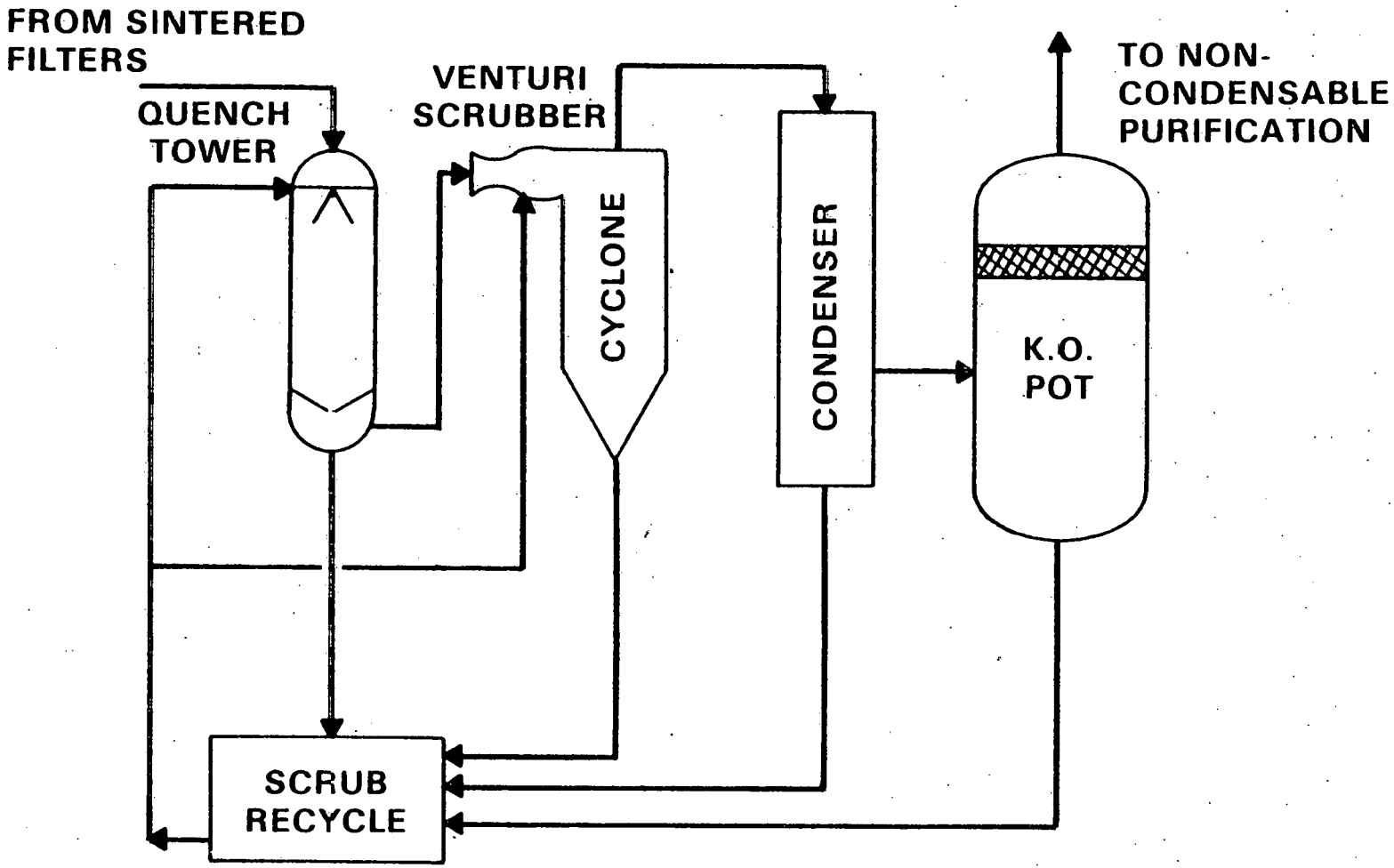

FIGURE 2. Purification of Condensable Off gases

through sintered metal filters having a mean pore size of 10 or 65 microns. From there the off gas enters two wet scrubbers. The initial contactor, a quenching spray tower, will cool the off-gas stream from about 350°C to 100°C, or below its dew point. A venturi scrubber downstream from the quench tower discharges into a cyclone for separation of liquids and solids from the gases. The gases exit from the cyclone to a condenser and a knockout pot (K.O.). The liquids removed in the quench tower, cyclone, condenser, and K.O. pot are collected and recycled to a quench tower and venturi scrubber. A portion of this combined recycle stream is purged to the high-level waste concentrator system.

The noncondensable off-gas stream leaving the de-entrainer in the condensable section will be heated to the appropriate temperature (based on the selected downstream Ru sorption media). Then it will be filtered. Silica gel or hydrous zirconium oxide will probably be used for sorption since Ru adsorbs efficiently on either material at less than 100°C. Figure 3 illustrates this process.

About six millicuries per year of Ru are expected to pass through the off-gas treatment system and be released to the calciner area stack, equating to an overall Ru decontamination factor* (DF) of about 10^{+9} for the solidification plant.

About 1% of the iodine contained in the spent fuel will enter the solidification plant; 99% would be previously removed in the Separations Facility. Of this 1% to the waste facility, 98.5% will volatilize into the calciner off gas and be trapped on the silver zeolite beds downstream from the Ru adsorber. The remaining 1.5% will volatilize into the calciner off gas and be sent through two concentration steps before being vaporized into the main stack. If the final purification of this stream uses macro reticular resins, the total annual release is estimated to be six millicuries of I-129, equating to an overall DF across the solidification plant of about 100.

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*Decontamination Factor = $\frac{\text{Total Constituent Feed}}{\text{Total Constituent Effluent}}$

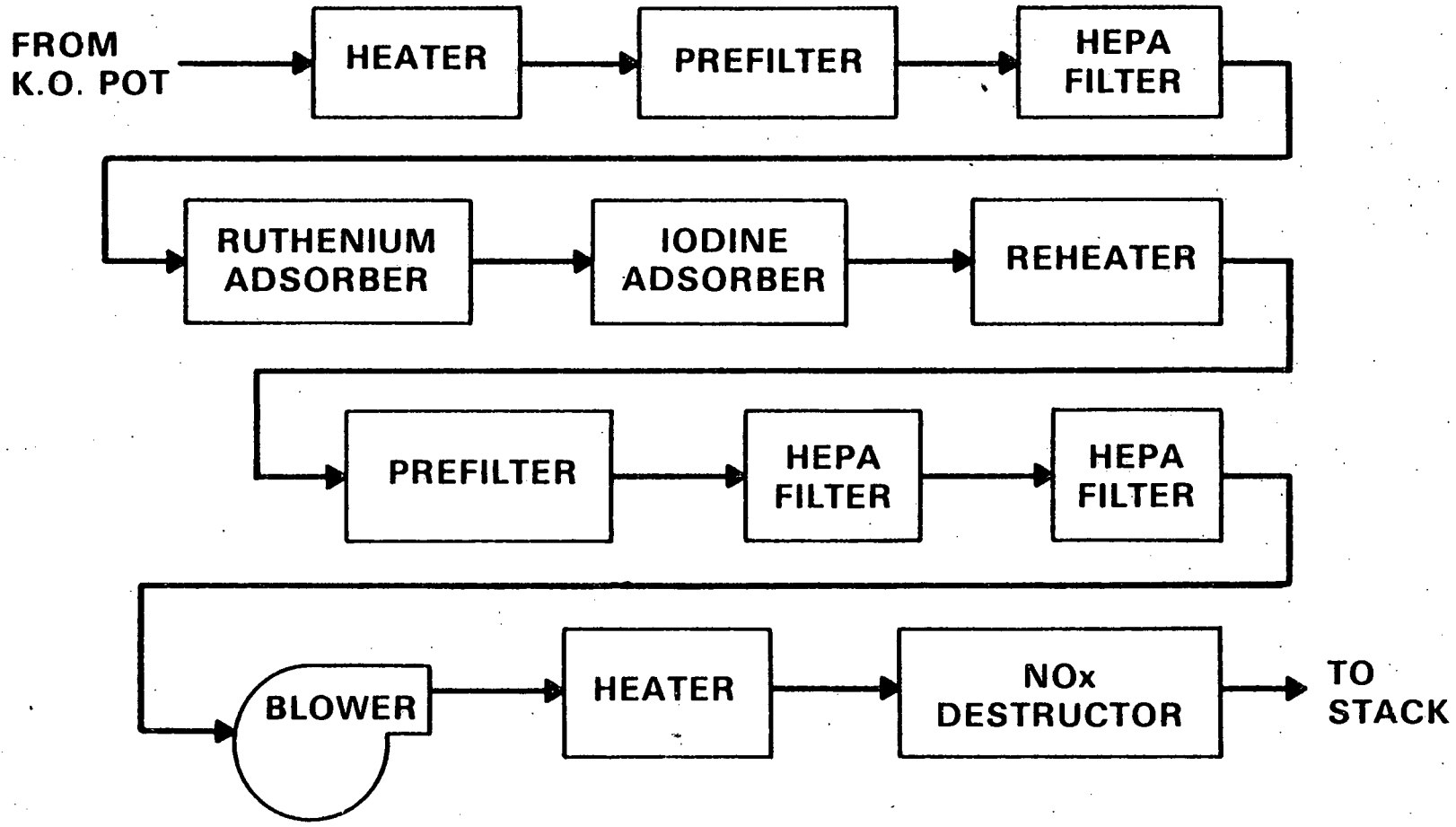

FIGURE 3. Purification of Non-Condensable Off gases

One roughing and two HEPA filter stages would be located upstream of the off-gas exhaust blowers to further remove radioactive particulates. Using Ce-144 as an indicator for efficient removal of particulates, the cerium passing through the off-gas treatment system and released to the stack is estimated to be 0.4 millicuries per year, equating to a DF of $2 \times 11^{+11}$.

In the final purification step, a stoichiometric quantity of ammonia will be added prior to passing the off gases over a heated catalyst bed (about 400°C). The reactor should convert over 99% of the NO_x to N_2 and water.

2.4 PROCESS WASTES

Process wastes would accumulate from the off gas purification system, regeneration of pool cleanup resins, cask decontamination and flushing, routine operational housekeeping, and support services. These solutions will be routed to a high-activity waste concentration (HAWC) system from which the bottoms will return to the calciner feed system. Figure 4 is the flowsheet for this process. The overheads from the HAWC will be condensed and re-evaporated in the low-activity waste concentrator (LAWC) system from which the bottoms will be recycled back to HAWC. Overheads from the LAWC will be condensed, monitored for radioactivity, and fed to a vaporizer. The vaporizer overheads will mix with the purified off gases and building ventilation air before the combined streams enter the stack.

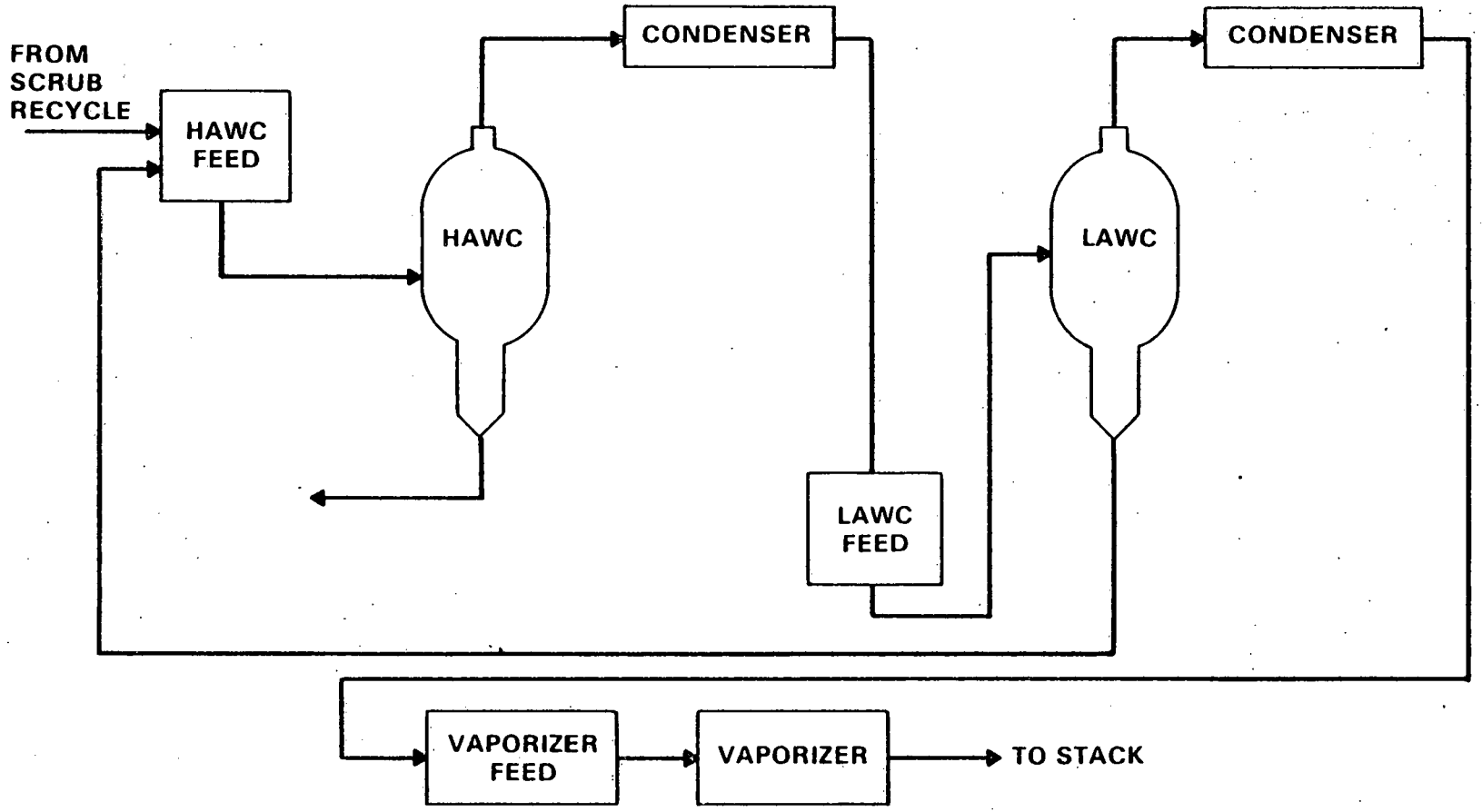

FIGURE 4. Process Waste Flowsheet

3.0 FULL-SCALE CALCINATION/VITRIFICATION EQUIPMENT

The full-scale calciner, shown in Figure 5, is basically a 3 ft diameter by 10 ft vertical cylinder surrounded by resistance-heated furnaces. The spray chamber mates to a conical discharge hopper. A filter chamber also mounts on the hopper, parallel with the main axis of the spray chamber. The furnace has multiple horizontal zones provided with variable maximum power densities to meet the demand at different elevations within the calciner. Thermocouples mounted in the furnaces control the calciner surface at the design temperature of 800°C.

The sintered stainless steel filters have about 150 ft^2 of total filter area. Each filter is a nominal 3 in. diameter by 3 ft long thimble. Periodically, a 1/4 sec pulse of 80 psig air blows back a fraction of the filters at a time to dislodge accumulated calcine fines.

Two pneumatically-driven vibrators periodically impart a short series of raps alternately to opposite sides at the midsection of the spray chamber. These vibrators assure minimum calcine accumulation on the walls, which otherwise would imped heat transfer.

A gravimetric feeder is adjusted to provide frit in proportion to the production of calcine. Analysis of feed and knowledge of oxide conversion ratios enables the operator to select the appropriate frit feed rate to produce an acceptable glass. The operator is able to observe weight or level of calcine, frit, and glass accumulating in the product container.

From each calciner, the frit and calcine mixture flows through a diverter mechanism which can discharge to either of two batch melters, or through a single shutoff valve to a continuous melter. Either method provides continuous operation of the calciner. Both the batch and continuous melters can accommodate product canisters of various diameters.

The current PNL design for a radioactive glass canister has a 6 in. diameter opening and a breech-locked cap with integral handling pintel. Internal (drop-in) fins are provided for the canisters to enhance heat transfer. Optimum materials of construction of full-scale canisters are

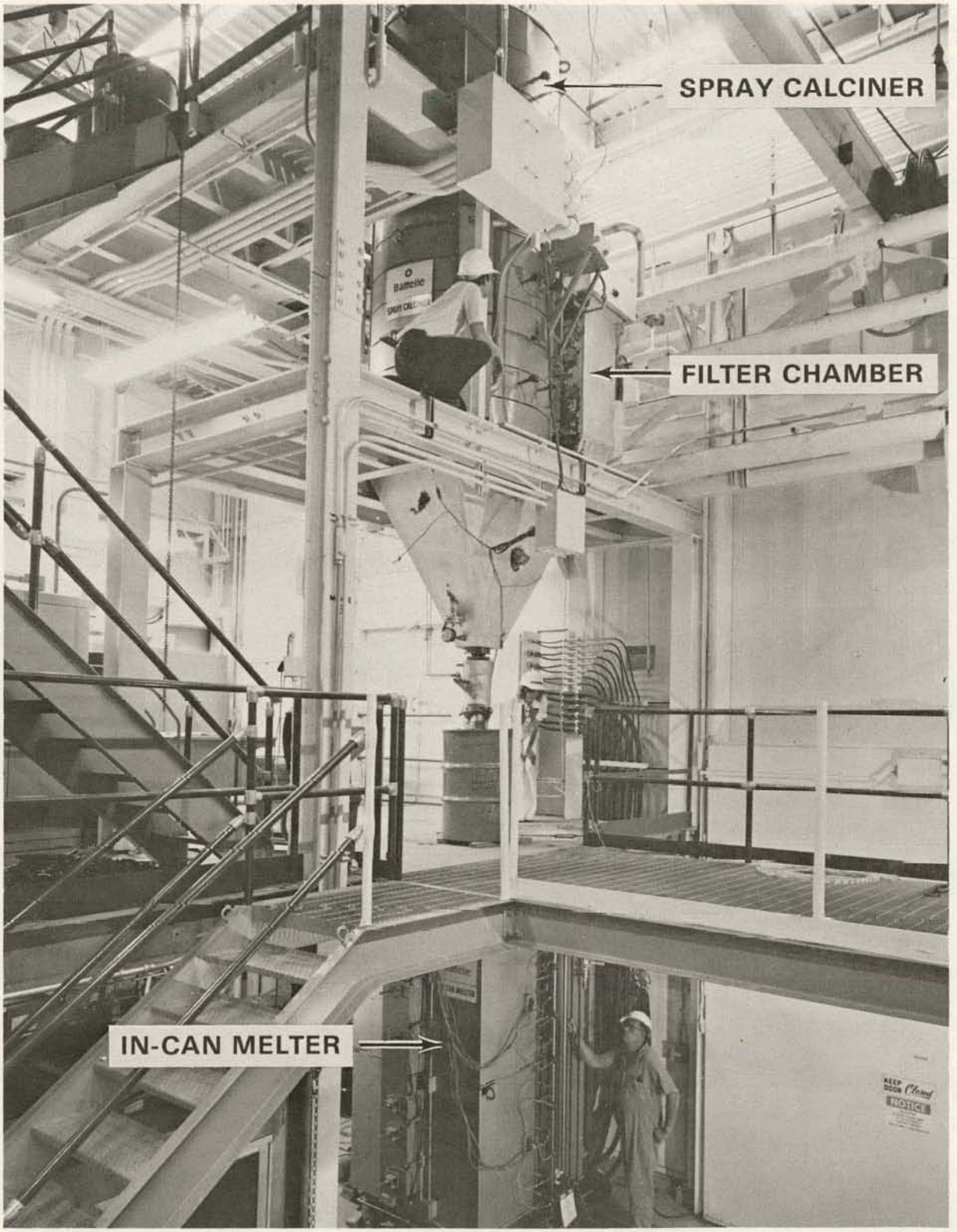

FIGURE 5. Full-Scale Spray Calciner/In-Can Melter

still being investigated. Economics, chemical and physical stability of materials under filling and storage conditions, and waste acceptance criteria will impact this decision. Materials under consideration include 304L stainless steel, Inconel 600, Incoloy 801, and possibly carbon steel.

Racks are provided for interim in-cell storage of canisters after their caps have been welded in place. Canisters will then move through decontamination, quality testing, and into the transfer fixture serving the Waste Transfer Pool.

4.0 FULL-SCALE PLANT DESIGN

Conceptual plant layouts modeled on the Barnwell Nuclear Fuel Plant have been developed to blend the following maintenance concepts to give high reliability with reasonable capital investment:

1) remotely-operated cells typical of the head-end processing cells at the Barnwell Separations Facility;

2) ease of viewing and high manipulative equipment capability and valve cubicles currently being designed for the New Waste Calciner Facility at INEL; and

3) contact maintenance cells, typical of Barnwell and Idaho extraction cells.

The remote-maintenance cells house all equipment which may require infrequent maintenance or replacement within the service life of the plant. These cells house redundant calciner and melter systems and some of the purification equipment in the condensable portion of the off-gas system. Remote viewing will be provided by windows and periscopes. An overhead crane(s) with appropriate attachments enables removal and replacement of in-cell components. Master-slave manipulators may be provided to do light-duty decoupling or equipment alignment movements if adaptability to crane fixtures alone proves too difficult to accomplish.

The equipment and valve cubicles will provide rapid changeout of highly radioactive components which potentially require frequent mainentence. Such components are control valves, flow elements, transfer pumps for feed and process waste streams, as well as iodine adsorbers, Ru traps, and HEPA filters in the off-gas purification system. The cubicles will be fitted with an overhead crane, powered manipulator, viewing windows, in-cell mobile TV, impact wrenches, and possibly an occasional master-slave manipulator.

Within the cubicles, equipment modules such as those developed at INEL may be used. A typical pump module is shown in Figure 6. These designs feature a single mating plane for all flanges and disconnects on each component module. Other design improvements at INEL have been to limit

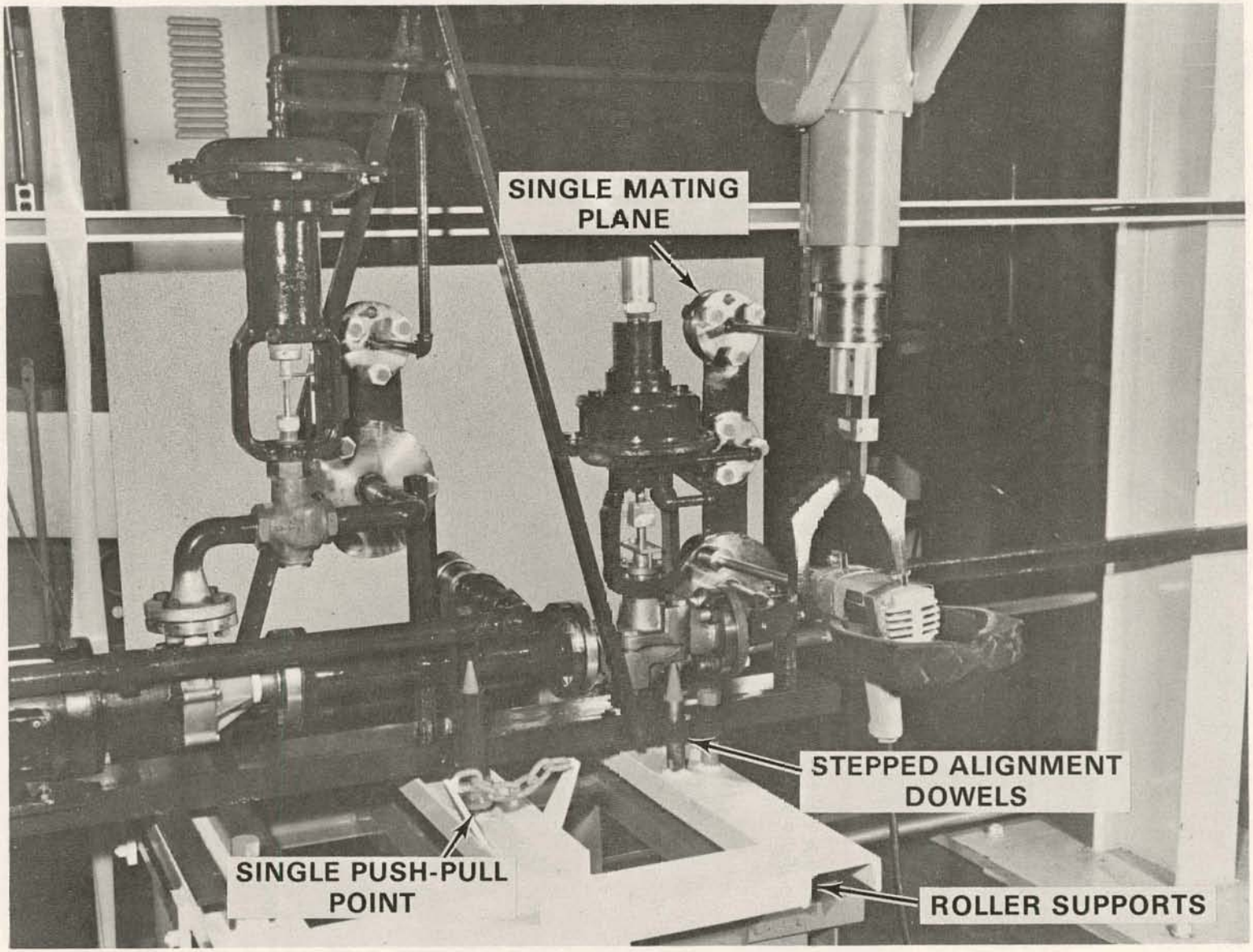

FIGURE 6. INEL Pump Module

size selection of bolts, flanges, and other coupling fixtures. By providing stepped alignment dowels, roller supports and cradles for each module, and a single push/pull point, these design developments assure ease of withdrawal and accurate alignment during reinstallation of a replaced or repaired module. Easily manipulated instrument, electrical, and piping connections provide tight, environs-proof seals. Changeout of any single module in the cubicle should be possible in approximately two hr.

The contact maintenance cells include surge, blend, adjustment, and feed tanks for the high-level and intermediate-level liquid wastes transferred from the Separations Facility. The contact-maintenance cells also include process waste treatment equipment, such as HAWC and LAWC. Other facilities continguous to the processing structure are: a storage pool with a 5-yr capacity for canisters of glass; a blower station to supply and to exhaust ventilation air; and a support area having change, lunch-room, and low-level radiochemical analytical facilities. Facilities for support service personnel, including maintenance, health and safety, engineering, and supervision, will be in the waste solidification building.

The main waste processing building will include remote decontamination and packaging areas for large components. A low-level decontamination area outfitted with hoods and ultrasonic cleaners will disassemble and further decontaminate components before repair work is performed.

Table 4 estimates the engineering/procurement/construction schedule for a full-scale solidification facility:

TABLE 4. Solidification Facility Schedule

Start of Engineering	0.0 yr.
Start of Procurement	+1 yr.
End of Development Work	+2 yr.
Start of Construction, End of Procurement	+3 yr.
Start of Cold Checkout	+6 yr.
Start of Hot Operation	+7 yr.

Current development programs need to be completed at least midway through the period planned for plant equipment procurement.

5.0 PROCESS DEVELOPMENT STATUS AT BATTELLE

5.1 HISTORICAL

Preliminary cold development culminated in the 1967-1970 operation of the Waste Solidification Engineering Prototype (WSEP) program at PNL. During 580 operating hours of the spray calciner, 13 canisters of glass were produced. Liquid waste feed was formulated from: 1) HA column waste from reprocessing chemically-declad defense fuel to provide the fission product spectrum, 2) nonradioactive chemicals, and 3) a radioactive rare earth fraction, mainly Ce, to provide decay heat.

5.2 SPRAY CALCINER/IN-CAN MELTER

Since the WSEP operation, cold testing of the spray calciner/in-can melter has continued, which has resulted in the following process and equipment improvements.

A medium efficiency cyclone (as an alternate to sintered metal filters) has been used for calciner off-gas treatment which is capable of removing 94% of feedstock solids. A 36-inch diameter calciner can accept a liquid feedrate of over 200 ℓ/hr (equivalent to a 5 MTU/day reprocessing plant). The system has demonstrated its ability to calcine and vitrify waste compositions representing anticipated U.S. fuel processes, including wastes containing over 95% $NaNO_3$ equivalent solids. The calciner is operable with commercially available gravity flow or pressurized, liquid-feed nozzles. Vibrators assure low calcine inventory in the calciner. Calciner startup or shutdown can be accomplished in less than an hour. A continuous 10-day run has produced glass at a 5 MTU/day rate for simulated HLLW-ILLW wastes. The In-Can Melter system has been controlled with only furnace thermocouples and gamma detectors sensing canister fill levels; none of the typical pilot plant equipment, i.e., auxiliary viewpoints, internal thermocouples in the canister, were used. About 99.5% of the particulates (by mass) penetrating the sintered filters have been measured to be in the size range of 0.5 to 6.0 microns; the larger particles were only present immediately after filter blowback.

5.3 CERAMIC MELTER

In 1973, development of a ceramic-lined melter, in which the current passes through the melt, was initiated at PNL. Building upon experience with similar equipment in the glass industry, a full-scale melter has formed glass for over two years from blends of frit/calcine.

Ultimately, the high energy input to a ceramic melter may make possible direct liquid feeding, thus eliminating the need for an upstream calciner. PNL's present melter has operated using liquid-feed at 100 ℓ/hr. The throughput is apparently limited by the rate of evaporation of the water layer present above the calcine/frit layer, which, in turn, floats on the glass layer. The surface area of the present melter (11 ft^2) could be increased to meet a design feed requirement of 200 ℓ/hr. Future development work should establish whether liquid-fed ceramic melters can successfully limit Ru volatility and provide stable operations.

6.0 ADDITIONAL DEMONSTRATION AT PACIFIC NORTHWEST LABORATORY

Additional demonstration and process optimizations are desirable to show that the full-scale process is suitable for remote operation in a hot cell, as well as to assure process licensability. The following programs have been planned or in progress at PNL.

1) Industrial Design (nonradioactive) - to demonstrate full-scale calciner/melter design for remote operation; and to provide accident, safety, operability, and maintainability studies.

2) Waste Vitrification Program (radioactive) - to demonstrate current vitrification process for actual HLLW producted from spent nuclear fuel, using remotely-operated, pilot-scale equipment.

3) Full-Scale Spray Calciner and Melter (nonradioactive) - to gain extended operating experience and to determine tolerance for upset conditions.

7.0 CONCLUSIONS

Spray calcination/vitrification technology development is considered to be well into the final confirmatory stages. Technology transfer can begin which will enable full-scale demonstration of the process using high-level liquid wastes from fuel reprocessing operations.

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