BNWL-1541
UC-70

WASTE SOLIDIFICATION PROGRAM
VOLUME 7
PHOSPHATE GLASS SOLIDIFICATION PERFORMANCE DURING FINAL RADIOACTIVE TESTS IN WASTE SOLIDIFICATION ENGINEERING PROTOTYPES

January 1971

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BNWL-1541

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Waste Disposal
and Processing

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VOLUME 7
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J. L. McElroy, J. N. Hartley, M. R. Schwab,
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ABSTRACT

Testing of high level radioactive waste solidification by the Brookhaven National Laboratory phosphate glass process has been successfully completed by Battelle-Northwest. More than 12 million curies of radionuclides were processed and collected in 6- and 8-inch diameter containers during the final five engineering-scale demonstration runs in WSEP at the Pacific Northwest Laboratory. Radioactivity processed ranged from 1 million to 3 million curies during the five runs. A maximum self-generating heat-rate of 11.9 kilowatts (198 W/liter) and 9.3 kilowatts (317 W/liter) was attained in 8-inch and 6-inch diameter pots, respectively. The solidified waste within a full 8-inch diameter pot represented 0.84 tonnes of PW-4m waste representative of power reactor fuel (irradiated at 45,000 MWd/tonne at a power level of 30 MW/tonne) and 0.36 tonnes for a waste representative of LMFBR core fuel irradiated to 100,000 MWd/tonne at 200 MW/tonne. High level aqueous radioactive waste was processed at overall rates of 13 to 26 liters/hr. The equivalent processing rates ranged from 0.20 to 0.58 tonnes/day of original fuel. From 5 to 9% of the total ruthenium fed to the solidifier was volatilized and/or entrained from the solidifier; entrainment of nonvolatiles varied from 0.04 to 0.07%. Volatilized and entrained material from the denitrator was further treated in the WSEP auxiliary process equipment, while the volatilized and entrained material from the melter was collected in a separate condensate receiver. The WSEP auxiliary process equipment consisting of an evaporator, an acid fractionator, mist eliminator, filters, condensers, and a caustic scrubber reduced the radionuclide concentration in the stack gas to well below 10CFR20 release limits. The radionuclide content in the final aqueous liquid effluent was decontaminated by a factor of 10^7 to 10^8 for nonvolatiles and 10^5 to 10^6 for radioruthenium to concentrations that initial studies indicate are acceptable for recycle to a fuel reprocessing plant or for low-level treatment processes. The phosphate glass product caused no significant changes to the solidified waste containers or no pressure increases within the containers after they were capped and welded.

This report is one of a series of reports from the Waste Solidification Demonstration Program being performed by Battelle-Northwest. Other current reports in this series are:

K. J. Schneider, editor, Waste Solidification Program, Volume 1, Process Technology for the Pot, Spray and Phosphate Glass Processes, U.S. AEC Report BNWL-1073, August 1969.

K. J. Schneider and V. P. Kelly, Waste Solidification Program, Volume 2, Design Features of the Waste Solidification Engineering Prototype, U.S. AEC Report BNWL-968, February 1969.

V. P. Kelly, Waste Solidification Program, Volume 3, Design Features of the Facilities and Equipment for the WSEP Product Evaluation Program, U.S. AEC Report BNWL-832, December 1968.

J. L. McElroy, C. R. Cooley, J. E. Mendel, W. V. DeMier, J. C. Suddath (ORNL), and J. O. Blomeke (ORNL), Waste Solidification Program, Volume 4, Pot Solidification Performance During the First Radioactive Tests in WSEP, U.S. AEC Report BNWL-814, December 1968.

J. L. McElroy, J. N. Hartley, K. J. Schneider, and R. F. Drager (BNL), Waste Solidification Program, Volume 5, Phosphate Glass Solidification Performance During the First Radioactive Tests in Waste Solidification Engineering Prototypes, U.S. AEC Report BNWL-1185, January 1970.

W. R. Bond, J. N. Hartley, J. E. Mendel, J. L. McElroy, K. J. Schneider, and M. R. Schwab, Waste Solidification Program, Volume 6, Spray Solidification Performance During the First Radioactive Tests in Waste Solidification Engineering Prototypes, U.S. AEC Report BNWL-1391, July 1970.

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PHOSPHATE GLASS SOLIDIFICATION PERFORMANCE DURING FINAL RADIOACTIVE TESTS IN WASTE SOLIDIFICATION ENGINEERING PROTOTYPES

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1.0 INTRODUCTION

During chemical reprocessing of spent nuclear fuels, essentially all of the fission products are accumulated as an aqueous waste. Traditionally, these "high-level" wastes have been stored in large, underground tanks. Since many of the nuclides will constitute a hazard for centuries,* storage in tanks is considered only a temporary or interim approach. More permanent disposal methods which improve isolation of these hazardous nuclides must be developed if full benefits of nuclear power are to be realized.

Responsible authorities in the United States and abroad generally agree that the best management approach involves converting the wastes to inert, refractory solids before storage. Such solids can then be isolated from human environment by storage in man-made vaults of high integrity or in geologically remote formations such as rock salt.

A considerable amount of development has taken place in the past 15 years and it is still progressing in order to develop techniques for solidification of high-level liquid wastes. Four processes for solidification of high-level liquid wastes have been developed in the USA. These processes have been developed to the point of radioactive demonstrations on an engineering

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* This is true for many fission product radionuclides; for some of the transuranic radionuclides, the hazard exists for thousands of centuries.

scale. The four processes are pot calcination, spray solidification, phosphate glass solidification, and fluidized bed calcination. Two waste solidification methods under development abroad include the FINGAL process in the United Kingdom and a pot vitrification process in France.

Such a diversity of effort reflects differences in needs for solidification when considering the chemical complexity of the many types of wastes to be processed, the different scales of operation required, and the different criteria set for the final products. In view of these factors, no single process is expected to be optimal for all applications.

Fluidized bed calcination was the first solidification process placed in routine radioactive operation. In this application, aluminum-bearing wastes from enriched uranium fuels have been processed at the Idaho Chemical Processing Plant (ICPP) by the Idaho Nuclear Corporation since 1963.

Pot calcination (developed by Oak Ridge National Laboratory), spray solidification (developed by Battelle-Northwest), and phosphate glass solidification (developed by Brookhaven National Laboratory), are being demonstrated at the Pacific Northwest Laboratory on an engineering scale with full radioactivity levels for the Atomic Energy Commission. The purpose of this waste solidification demonstration program is to provide the technological bases which will lead industry to adopt and implement, at the earliest possible time, the practice of solidifying the high level liquid waste which results from the reprocessing of nuclear fuel. This demonstration program is being carried out in the Waste Solidification Engineering Prototype (WSEP) by Battelle-Northwest, with cooperative efforts by Oak Ridge National Laboratory and Brookhaven National Laboratory.

The WSEP is a pilot plant designed to provide information necessary for technical, economic, and safety evaluations of the pot, spray, and phosphate glass processes. A detailed description of the WSEP and the Chemical and Materials Engineering Laboratory facility has been reported.(1) An up-to-date summary of the technology of the pot, spray, and phosphate glass solidification processes has also been reported recently.(2)

This report presents the results and analyses of the final five radioactive demonstration runs with the phosphate glass solidification system in WSEP. Results for the first six phosphate glass demonstrations were reported in Volume 5(3) of this series. Similar results for the first six radioactive demonstrations with the pot calcination system in WSEP and the first six spray solidification demonstrations were reported in Volumes 4 and 6 of this series.(4,5) Also included in this report are performance results of the associated auxiliary equipment and measurements on the solidified waste. Where pertinent, results are compared to previous nonradioactive data. Detailed descriptions of each demonstration run are presented in the Appendix (Section 9.0).

REFERENCES FOR SECTION 1

1. K. J. Schneider and V. P. Kelly. Waste Solidification Program Volume 2, Design Features of the Waste Solidification Engineering Prototypes, BNWL-968. Battelle-Northwest, Richland, Washington, February 1969.

2. K. J. Schneider, editor. Waste Solidification Program, Volume 1, Process Technology - Pot Spray and Phosphate Glass Solidification Process, BNWL-1073. Battelle-Northwest, Richland, Washington, August 1969.

3. J. L. McElroy, J. N. Hartley, K. J. Schneider, and R. F. Drager (BNL). Waste Solidification Program Volume 5, Phosphate Glass Solidification Performance During the First Radioactive Tests in Waste Solidification Engineering Prototypes, BNWL-1185. Battelle-Northwest, Richland, Washington, January 1970.

4. J. L. McElroy, C. R. Cooley, J. E. Mendel, W. V. DeMier, J. C. Suddath (ORNL), and J. O. Blomeke (ORNL). Waste Solidification Program Volume 4, Pot Solidification Performance During the First Radioactive Tests in Waste Solidification Engineering Prototypes, BNWL-814. Battelle-Northwest, Richland, Washington, December 1968.

5. W. R. Bond, J. N. Hartley, J. E. Mendel, J. L. McElroy, K. J. Schneider, and M. R. Schwab. Waste Solidification Program Volume 6, Spray Solidification Performance During the First Radioactive Tests in Waste Solidification Engineering Prototypes, BNWL-1391. Battelle-Northwest, Richland, Washington, June 1970.

2.0 SUMMARY

Solidification of high-level aqueous radioactive wastes containing 12 million curies was successfully completed in the final five demonstration runs using the phosphate glass solidification process in the WSEP. Major accomplishments in the demonstrations were as follows:

- Heat generation from fission products produced temperatures in the glassy solidified product at the maximum contemplated for the process as prescribed in WSEP. Adequate heating and cooling control of the receiver pots was demonstrated during filling to promote uniform filling and prevent excessive temperatures.

- Radioactive aqueous wastes were solidified and encapsulated in mild steel and stainless steel containers without pressurization, with minimal corrosion and without distortion of the container.

- Gases leaving the auxiliary effluent treatment equipment and the facility contained sufficiently low concentrations of radionuclides to easily meet government regulations and were directly released to the atmosphere.

- Initial studies have indicated that the aqueous effluents (the fractionator distillate and bottoms) from the auxiliary effluent treatment equipment contained sufficiently low concentrations of radionuclides to permit recycle to a fuel reprocessing plant; however, improved cleanup of these effluents is desirable to improve the efficiency of their reuse.

2.1 PHOSPHATE GLASS SOLIDIFIER PERFORMANCE

The principal variables investigated in the final five runs were heat generation rate in the solidified waste and three waste chemical compositions.

Maximum radioactive decay heat-rate densities of 198 W/liter in an 8-inch diameter receiver pot (11,900 watts of decay heat from 3.3 million curies) and 317 W/liter in a 6-inch diameter receiver pot (9,300 watts of decay heat from 2.6 million curies) were obtained satisfactorily with no adverse effects to the process.

High-level aqueous wastes simulating wastes from thermal power reactor fuels containing sulfate (PW-2)[a] and having a high exposure (PW-4m)[a] and from a liquid metal fast breeder reactor core fuel (LMFBR)[a] were processed at overall rates of 13 to 26 liters/hr. In general these rates were as expected, with the processing rate being limited by the capacity of the platinum melter. Although melter performance was good, transfer of heat to the melter fluid limited the maximum steady-state melt formation rate to approximately 1.4 liters/hr. The equivalent steady-state processing rate was 0.58 tonne/day[b] for PW-2 waste (from 20,000 MWd/tonne at 15 MW/tonne power reactor fuel) while for PW-4m waste (from 45,000 MWd/tonne at 30 MW/tonne power reactor fuel) the steady-state processing rate ranged from 0.34 to 0.47 tonne/day and for the LMFBR waste (from 100,000 MWd/tonne at 200 MW/tonne LMFBR core fuel) the rate was 0.20 tonne/day. The lower steady-state processing rate for LMFBR waste resulted from the larger quantity of additives required to process the waste.

(a) For detailed chemical compositions, see Appendix Table 9.1.

(b) Tonne is used throughout this report to represent a metric ton (1000 kilograms) of uranium plus plutonium in the original fuel.

Because of modest variations in chemical compositions of the feeds to the solidifier the overall volume reduction factors for PW-4m waste varied from 4.5 to 5.9 based on the original aqueous waste at 378 liters/tonne. This compares to an expected volume reduction of 5.0 for nominal PW-4m waste. The volume reduction factors for the single demonstrations of PW-2 and LMFBR compositions were 5.9 and 2.4 based on the original aqueous waste at 378 liters/tonne and compared to expected nominal volume reductions of 6.0 and 2.4, respectively.

General conditions for each run are summarized in Table 2.1.

Performance of the phosphate glass solidifier was satisfactory; however, the system is not optimized and some design improvements would be required to make it suitable for industrial use.

A denitrator-evaporator was used to concentrate the incoming feeds to temperatures ranging from 125 °C for PW-4m to 137 °C for PW-2. The tendency for solids to plug the denitrator dip tubes and the external airlift piping were minimized by operational techniques. The denitrator dip tubes were kept clear of solids buildup by periodically venting the tubes to allow liquid to rise in them and effectively wash out the tubes. The airlift piping was kept clear of solids buildup by periodic flushes and manipulations of the movable recirculation plug valve. Satisfactory control of the previously encountered foaming in the denitrator was accomplished by the addition of a silicone antifoam agent into the denitrator. Melter operation became less reliant on visual access as transfer of feed from the denitrator to the melter became more controlled due to the proper location of control thermocouples within the melter.

TABLE 2.1. Phosphate Glass Solidification Runs in WSEP

Run	Waste Type	Receiver Pot		Radioactivity Processed, MCi		Heat Generation Rate in Receiver Pot		Equivalent Tonnes to Receiver Pot		Equivalent Age[b] of Waste, years
		Diam., in.	Material	To Denitrator	To Melter	Total, kW	Density, W/liter	Actual	100% Fill[a]	
PG-7	PW-2	8	310 SS	3.4	2.8	9.8	146	1.05	0.94	0.46
PG-8	PW-4m	8	Mild Steel	2.5	2.3	8.8	132	0.84	0.76	1.0
PG-9	PW-4m	6	304L SS	1.3	1.0	4.2	158	0.41	0.49	0.9
PG-10	PW-4m	6	304L SS	3.6	2.6	9.3	317	0.35	0.38	0.25
PG-11	LMFBR	8	304L SS	3.7	3.3	11.9	198	0.38	0.36	1.5

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a. The equivalent tonnes of waste actually collected normalized to a fill height of 6 feet in the receiver pot. (A fill depth of 5 feet was planned in the two 6-inch diameter pots.)

b. Out-of-reactor time for power reactor fuel with the same heat generation rate. PW-2 irradiated to 20,000 MWd/tonne at 15 MW/tonne, PW-4m irradiated to 45,000 MWd/tonne at 30 MW/tonne and LMFBR core fuel irradiated to 100,000 MWd/tonne at 200 MW/tonne.

The successful rapid replacement of a filled solidified waste receiver pot with an empty receiver pot during back-to-back runs indicated that continuous operation of the phosphate glass solidifier is feasible because the changeover can be made in less time than is required to refill the melter after its contents have been drained to the receiver pot.

The amount of ruthenium that volatilized from the phosphate glass solidification process varied from 5 to 9% of the total amount fed to the solidifier; entrainment of nonvolatiles varied from 0.04 to 0.07%.

2.2 AUXILIARY PROCESS SYSTEMS PERFORMANCE

The conversion of high-level aqueous waste to solids by the phosphate glass solidification system results in a process off-gas containing a lower level of radioactivity. This off-gas is treated by the WSEP auxiliary system (i.e., condensers, evaporator, and fractionator, scrubber, and filters) where the effluent is separated into streams of cleaner nitric acid, water and noncondensible gases. The WSEP auxiliary system is similar to the high-level waste evaporation and acid recovery systems used in many fuel reprocessing plants.

To evaluate the performance of the WSEP auxiliary system, decontamination factors (DF's) were determined at each stage of the system. The overall DF's from the original aqueous waste through the auxiliary system to the recovered nitric acid in the fractionator were typically 10^3 to 10^4 for radioruthenium and 10^6 for radiocerium. Comparable DF's to the recovered water (accumulated fractionator distillate) were 10^5 to 10^6 for radioruthenium and 10^7 to 10^8 for radiocerium. Comparable radioruthenium DF's to the off-gas scrubber were 10^4 to 10^8. DF's from the original high-level waste to the off-gas leaving the scrubber were typically 10^8 for radioruthenium and 10^9 to 10^{11} for radiocerium. Comparable DF's for the final off-gas to the stack were greater than 10^9 to 10^{10} for radioruthenium and 10^{12} to 10^{13} for gross beta less radioruthenium.

Instantaneous ruthenium DF's (DF_i, ratio of the ruthenium concentration in the evaporator bottoms to the ruthenium concentration in the evaporator distillate) generally vary inversely with the nitric acid concentration in the evaporator bottoms and the nitric acid concentration in the overheads; however, during the last five phosphate glass solidification demonstration runs there was no apparent correlation with overhead acidity. The generally low DF_i's for ruthenium (about 10^3) are primarily attributed to vapor phase flow of ruthenium which is inefficiently scrubbed in the solidifier condenser as indicated by the presence of ruthenium in the solidifier condenser off-gas. The low DF_i's are also partly attributed to radionuclide contamination of the auxiliary system piping that cannot be satisfactorily flushed out between runs.

The radioruthenium concentration in the final aqueous effluent (fractionator distillate) was typically a factor of 3000 higher than allowable values in 10CFR20. Consequently, additional cleanup would be necessary before discharging to the environment unless the effluent is recycled in a fuel reprocessing plant. The nonvolatile radionuclide concentrations in the final effluent requires considerably less cleanup than the ruthenium.

Initial studies have indicated that the recovered nitric acid and water from the phosphate glass solidification process can probably be recycled to a fuel reprocessing plant.

Gas sampling techniques were initiated prior to the last series of phosphate glass runs which provided engineering scale data which in turn helped better define the type and extent of radioactivity present in the process off-gas. Gaseous effluents from the solidifier condenser, evaporator condenser, fractionator condenser, high efficiency filter, and off-gas scrubber were sampled for both particulate and volatile forms of radioactivity by routing a side stream through a glass fiber filter and KOH scrubber.

Gas sample data indicated that the DF's across the process condensers varied from 40 to 800 for radioruthenium and from 10 to 1800 for radiocerium.

The process off-gas leaving the scrubber contained a concentration of radionuclides above 10CFR20 discharge limits by factors up to 500 for ruthenium and 300 for nonvolatiles. The radioruthenium in the final stack gas is less than detectable in all cases after the off-gas leaving the scrubber is filtered twice more and combined with building ventilation air. All remaining beta radioactivity in the building stack gas is assumed to be ^{90}Sr and as with radioruthenium is well below 10CFR20 release limits.

Handling of PW-2, PW-4m and LMFBR phosphate glass solidification feed caused no unexpected operating problems in the feed tanks and the auxiliary evaporator. The primary solid in these wastes is a zirconium phosphomolybdate compound. This material is a hydrous, amorphous precipitate which has never been observed to cake in laboratory tests, even after several months of standing.

Although some minor malfunctions of auxiliary equipment occurred, no serious problems arose.

2.3 FILLED POT PERFORMANCE

The final series of five demonstration runs using the phosphate glass solidifier raised the total number of phosphate glass filled waste receiver pots to eleven. The performance of the waste receiver pots from these demonstration runs which began in November 1967 and ended in December 1969 is encouraging. None of the waste receiver pots has indicated any pressurization and none have suffered any measureable change in external pot dimensions through warpage, hot spots, or corrosion during processing or storage. Long-term effects up to five years after fill and beyond are not known but are being studied and evaluated in controlled environment tests in the Solids Storage Engineering Test Facility (SSETF).

Both stainless and mild steel receiver pots have proven to be satisfactory for filling with phosphate glass. Both materials have been seal welded remotely using WSEP developed techniques with existing equipment and leak checked to 1×10^{-7} atm cm^3/sec or better using a helium mass spectrometer.

Temperature profile measurements and calorimetrically determined heat generation have provided the basis for the effective thermal conductivity of the phosphate glass solidified waste and waste receiver pot. The following equation should be used to estimate the effective thermal conductivity (k_{eff}) of phosphate glass from PW-1, PW-2, PW-4m, and LMFBR wastes for the temperature range from 100 to 650 °C:

$$k_{eff} = 0.719 + 6.63 \times 10^{-4}\bar{T}$$

where $\bar{T}$ is the arithematic average temperature calculated from pot centerline and wall temperature in °C, and k_{eff} has the units

W/(m^2)(°C/m). At temperatures in excess of the remelt temperature (approximately 650 °C) the thermal conductivity increases more rapidly.

Gross axial radiation profiles and axial temperature profiles have shown that the fission products are uniformly distributed in the phosphate glass product. Continued observations of the filled receivers and core-drilled samples will be used to verify and further establish product uniformity. Excessive fission product migration and/or phase separation could result in hot-spots within the waste receiver pot.

Preliminary waste receiver wall thickness measurements after pot filling have given no evidence that would indicate a corrosion problem exists.

2.4 STATUS OF PHOSPHATE GLASS SOLIDIFICATION

The phosphate glass solidification demonstration runs in WSEP have been completed. Wastes from power reactor fuels irradiated up to 45,000 MWd/tonne and an LMFBR core fuel have been demonstrated. Sulfate and sulfate-free wastes and "clean" wastes containing far more fission product chemicals than reprocessing chemicals have been solidified. A fission product heat rate density of 195 W/liter is the maximum for a solidified phosphate glass waste in an 8-inch diameter receiver pot (when stored in 38 °C air) when the WSEP restriction of limiting the molten core radius to not more than 1/2 the receiver radius is considered. This restriction occurs before a 900 °C product centerline temperature is reached because of the low remelt temperature of 600 to 700 °C for the phosphate glass product. Therefore, PW-4m waste from light water reactor fuels irradiated to 45,000 MWd/tonne at a power level of 30 MW/tonne can be solidified within 0.75 years out of reactor. LMFBR core fuel irradiated to 100,000 MWd/tonne at 200 MW/tonne can be solidified at 1.7 years out of reactor.

Some individual radionuclides in the feed to the process (e.g., ruthenium) were not at the irradiation levels expected for the various waste types being demonstrated. However, data from all the WSEP radioactive phosphate glass solidification runs can be used to project results for full levels of all radionuclides. By applying the overall decontamination factors determined to date, several general conclusions can be made about the expected operation of the solidifier, the auxiliary evaporator, and the fractionator during processing of full level radioactive wastes:

- From 2 to 10% of the ruthenium will be volatilized from the solidifier. In the processing of nonsulfate wastes, most of this can be recycled to the fuel reprocessing plant high-level waste system. In the case of sulfate-containing waste, the sulfate-containing melter condensate portion of the solidifier effluent must be sufficiently decontaminated to permit its disposal as an intermediate-level waste (e.g., by incorporation with asphalt). The part of the solidifier effluent with little or no sulfate may be returned to the fuel reprocessing plant high-level waste system.

- Less than 1% of the total ruthenium fed to the solidifier will reach the acid fractionator and the nitric acid produced in the acid fractionator (approximately 200 to 300 liters/tonne of 8 to 14$\underline{M}$ acid) will contain 300 to 1500 μCi/mℓ of total β radioactivity. Radioruthenium will be the principal contaminant.

- The ruthenium DF from solidifier feed to the fractionator distillate can be expected to be about 10^6 with the ruthenium concentration in the fractionator distillate 37,000 to 800,000 times higher than the discharge limits quoted in 10CFR20* when solidifying these wastes aged 0.5 years. There will be about 200 to 400 liters of distillate per tonne of 378 liters/tonne fuel processed. Ruthenium-106 is the radionuclide in the final aqueous effluent with the highest concentration ratio to the limits in 10CFR20, followed by ^{90}Sr and ^{144}CePr. In general, an additional decontamination of 10^3 to 10^4 is needed to reduce all radionuclides, except ruthenium, in the fractionator distillate to below 10CFR20 values.

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- The recovered acid and water are sufficiently low in volume and radioactivity that they can probably be recycled for possible use in fuel element dissolution and/or for possible use in solvent extraction scrub streams. Effluent recycle is based upon having solidification processing capabilities with each fuel reprocessing plant.

- As an alternative to recycling, the radioactivity level of the fractionator distillate is acceptable for additional low-level treatment such as by distillation to 10CFR20 concentration limits for discharge of the water to the environment.

- Solidifier product from acidic wastes will have a volume of 46 to 108 liters/tonne of spent fuel for the types of thermal reactor wastes demonstrated. The smaller volumes will be representative of sulfate containing PW-2 wastes. These volumes represent 7.0 to 16.1 liters/1000 MWd_e.

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* Code of Federal Regulations, Title 10, Part 20, Appendix B, Table 2, Column 2. August 9, 1966.

Runs in WSEP demonstrated the phosphate glass solidification process at capacities in the range of 0.2 to 0.6 tonnes of fuel per day with the process essentially ready for application as an industrial method of solidifying wastes. The equipment design for phosphate glass solidification will be ready for application when the problems discussed below are resolved. Improvement of the denitrator-evaporator to melter liquid transfer mechanism and liquid level and specific gravity monitoring devices is needed. These denitrator-evaporator improvements could also possibly be brought about with a different evaporator design such as a wiped film evaporator. A different melter material is desirable as the platinum melter used is an expensive and weak structural link with poor heat transfer characteristics. Remaining investigations suggest:

- Testing of a wiped film evaporator as an improved denitrator-evaporator.

- Development of a less expensive melter material such as ceramic, chromium-aluminum oxide.

The receiver pots containing solidified waste are undergoing environmental testing to determine the effects of storage temperature in air or water, radiation, and feed type upon the physical and chemical properties of the solidified waste. Core drilled samples will be removed from the receiver pots and the samples will be measured for crystallinity, leachability, dispersibility, and fission product migration to determine the effects of time and environment. This information will characterize the product behavior during the initial years of interim storage when the product is undergoing the most change.

3.0 BACKGROUND, PROCESS DESCRIPTION, AND PROCESS TECHNOLOGY

3.1 BACKGROUND

The phosphate glass process for the continuous conversion of high-level radioactive wastes to phosphate glass was developed at the Brookhaven National Laboratory (BNL) on simulated waste solutions using laboratory scale, bench scale, and engineering scale pilot plant equipment.(1,2,3) Supplemental development work was performed at the Pacific Northwest Laboratories (PNL) by Battelle-Northwest (BNW)(4) including some radioactive laboratory studies.(5)

Nonradioactive laboratory studies were made to determine the most satisfactory glass compositions and to test materials of construction for the evaporator and melter.(4,6) Nonradioactive bench scale studies were made to obtain process information for design of a pilot plant. Pilot scale studies were made to provide more comprehensive information on the phosphate glass process, to develop operating and control parameters, to permit extensive testing of a platinum melter(7,8) and to confirm design features of WSEP equipment,(1) both prior to and during the radioactive WSEP runs. A total of seven nonradioactive design verification tests(9) were made by BNW with the WSEP equipment(10) for final confirmation of the WSEP equipment design and process operating parameters prior to the start of the radioactive demonstration program with the phosphate glass solidification equipment. The results of the first six radioactive demonstrations of the phosphate glass solidification process, Runs PG-1 through PG-6, were reported in Volume 5 of the Waste Solidification Program report series.(11)

Laboratory and bench scale studies were also made at BNL on the separation and decontamination of the sulfate component of the melter off-gas condensate by a low-pressure fractional distillation process.(1)

Nonradioactive laboratory and pilot plant demonstrations of the BNL vacuum distillation process with simulated sulfate-containing melter off-gas condensates were completed at PNL.(12,13)

The pilot scale vacuum distillation demonstration unit (DDU) shown in Figure 3.1 was installed in a radioactive cell at PNL and three radioactive tests were made with the radioactive, sulfate-containing melter condensate from WSEP Run PG-4.(14,15) In another study by BNW, several methods were explored for the treatment of intermediate level and low level radioactive condensates from waste solidification processes including the radioactive sulfate-containing condenstae from either the phosphate glass melter or from the vacuum still.(16)

3.2 PROCESS DESCRIPTION

The phosphate glass process is carried out in two continuous steps: a low temperature (120 to 140 °C) concentration step in which aqueous waste, chemically adjusted by the addition of phosphoric acid together with certain metal salts (when required) is continuously concentrated and partially denitrated to a thick slurry; and a high temperature (1000 to 1200 °C) glass forming step where final removal of water, nitrates and other volatile constituents is accomplished. The newly formed molten glass is then discharged to a receiver vessel where the glass is cooled to a monolithic solid. When the receiver is full, it is removed, sealed, and taken to storage. The effluent vapors from the denitrator-evaporator may be combined with those from the melter for further treatment if

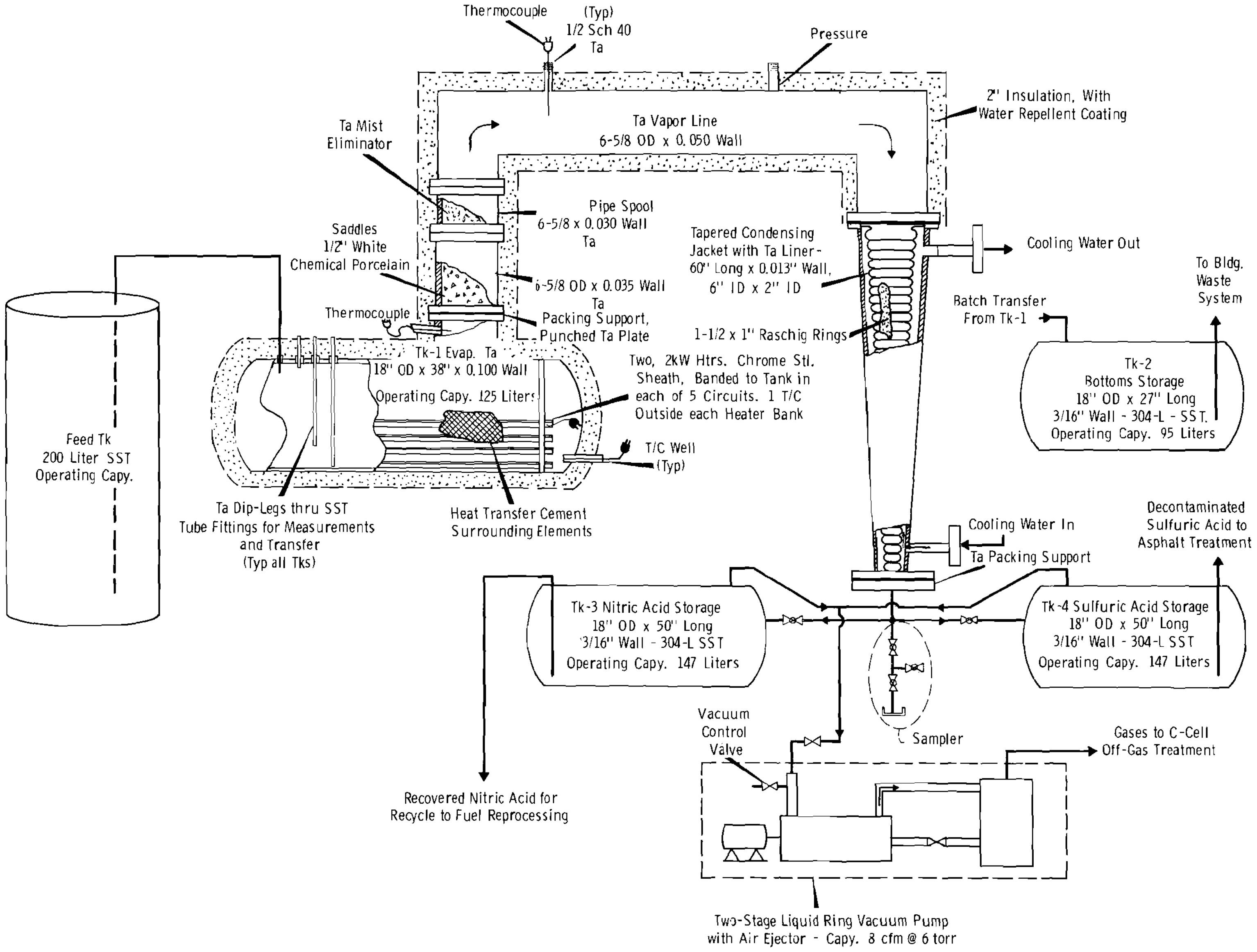

FIGURE 3.1. Sulfate Condensate Distillation Demonstration Unit (DDU)

sulfate is not present in the waste. Sulfate, if present in the waste, is volatilized from the melter, and the effluent must be treated separately. The phosphate glass process is shown schematically in Figure 3.2.

In the denitrator-evaporator, volume reduction factors ranging from two to seven are realized along with removal of 60 to 90% of the nitrate. Concentration-denitration is controlled at a point where the increased viscosity of the solution and solids settling in the solution do not become serious problems.

Although foaming did not occur in the denitrator-evaporator during the nonradioactive studies (except briefly at startup), severe foaming did occur during the first three radioactive demonstration runs due to trace quantities of dibutyl phosphate from the radioactive solutions used for feed makeup. However, after addition of an antifoam agent,(11) severe foaming did not occur during the final eight radioactive demonstration runs.

Transfer of the concentrated waste from the denitrator-evaporator to the melter feed system is initiated by air-lifting the concentrate from the bottom of the denitrator-evaporator to an airlift pot. A smaller portion of the solution in the pot flows over a weir into the melter, while the major portion flows back to the evaporator. The air-lifted concentrated feed is discharged into the melter via a solution feeder (a heat exchanger tube operated with a boiling water jacket). The solution feeder is needed to discharge the concentrated solution into the melter close to the surface of the molten glass pool to minimize spattering and entrainment. The heat exchanger design is used to maintain the viscous feed solution at a warm temperature without concentration and calcination occurring in the portion of the solution feeder inside the high temperature melter.

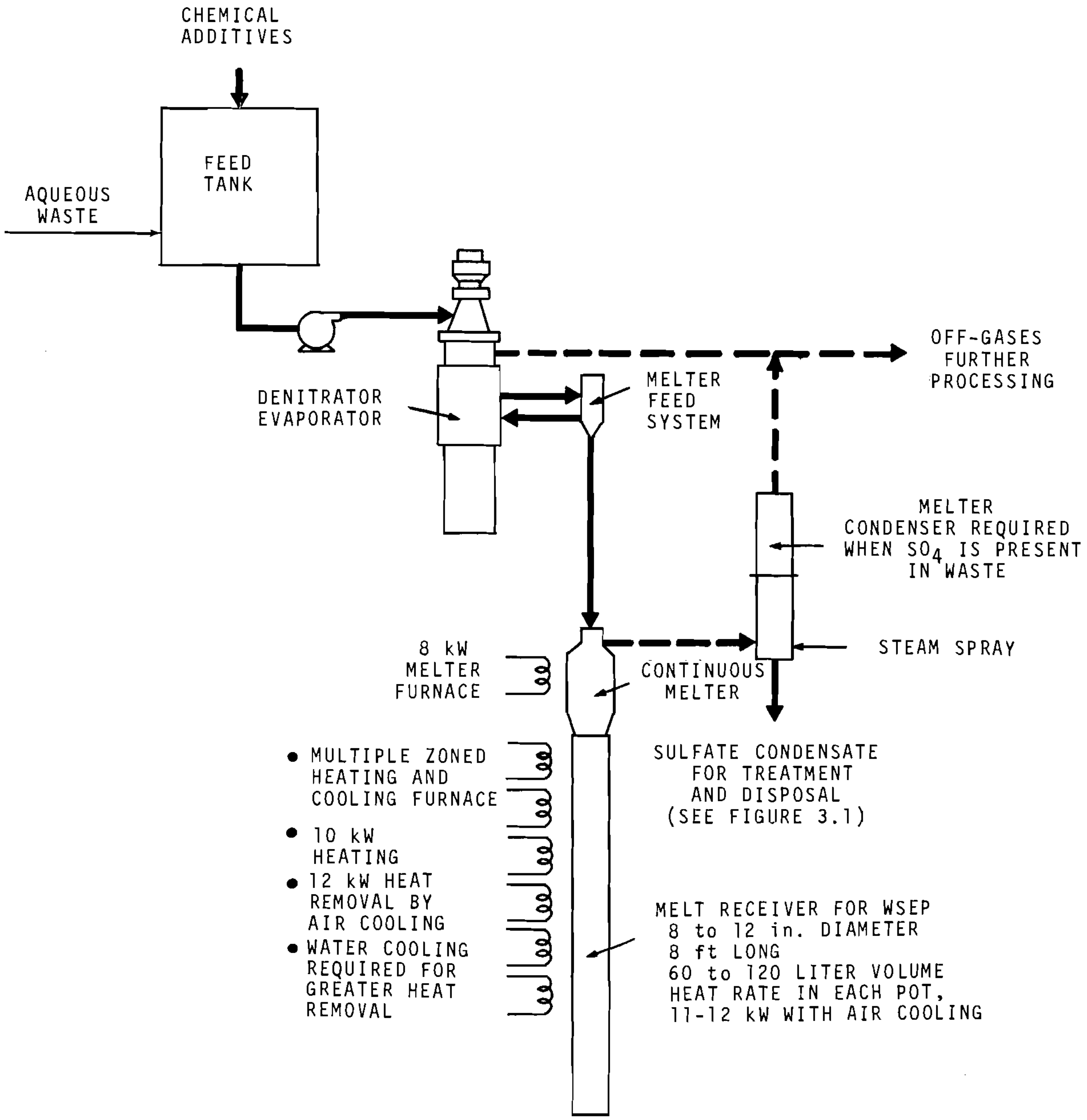

FIGURE 3.2. Phosphate Glass Solidification Process

TABLE 3.1. Composition of PW-2, PW-4m and LMFBR Wastes[a]

Component	PW-2	PW-4m	LMFBR
H^+	3.8M	4.5M	0.5M
Fe^{+3}	0.445	0.05	0.16
Cr^{+3}	0.024	0.012	0.046
Ni^{+2}	0.010	0.008	0.023
Al^{+3}	0.001	0.001	-
Na^+	0.93	0.10	0.10
U^{+6}	0.010	0.01	0.01
Pu^{+6}	0.001	0.001	0.001
$Am^{+6} + Cm^{+6}$		0.005	0.021
$NO_3^- + NO_2^-$	5.37	6.5	4.75
SO_4^{-2}	0.87	-	-
PO_4^{-3}	0.006	0.003	0.06
SiO_3^{-2}	0.010	0.010	0.010
F^-	<0.001	<0.001	<0.001
$M^+_{non\ FP's}$	2.42	0.5	1.0
FP's as M^+_{FP}[b]	0.91	1.7	4.1
Additive to Waste			
Na^+	-	1.4	2.9
Fe^{+3}	-	0.45	0.84
PO_4^{-3}	3.36	5.05	10.5
M^+_{add}	-	2.8	5.4
ΣM^+_T	3.33	5.0	10.5
$\Sigma M^+_T/P$	1.0	1.0	1.0
Total Radioactivity, Ci/liter			
At 0.5 yr	4,500	8,900	42,600
At 1.0 yr	2,550	5,200	21,300
At 5.0 yr	580	1,300	2,800
Heat Rate Density, W/liter			
At 0.5 yr	22.7	45	220
At 1.0 yr	12.2	28	120
At 5.0 yr	2	5.9	12

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a. Waste from one metric tonne of reactor fuel irradiated to 20,000 MWd/tonne at 15 MW/tonne for PW-2, 45,000 MWd/tonne at 30 MW/tonne for PW-4m, and 100,000 MWd/tonne at 200 MW/tonne for LMFBR; and contained in 378.5 liters (100 gal/tonne) of acidic waste solution.

b. M^+_{FP} is the summation of chemical equivalents of fission product cations. The elements Mo, Se, Tc, and Te are present as anions and are not included in M^+_{FP}. See Tables 3.2 and 3.3 for Fission Product (FP) distribution for PW-4m and LMFBR, respectively.

containing high concentrations of fission product rare earths to adjust the properties of the phosphate glass waste product for optimum production rate and product quality. High concentrations of multivalent metal cations generally increase the melting point of phosphate glass waste products.(4,11) Sodium is added to wastes to minimize the melting point of the waste product for maximum melter throughput. Iron is added to wastes containing high concentrations of the rare earth fission products to prevent the precipitation of a rare earth-rich phase from phosphate melts.(4) Laboratory studies at BNL established an optimum ratio of 3 moles of sodium per mole of iron for the phosphate glass waste products from the PW-4m and LMFBR wastes.(17)

In Table 3.1, the fission product radioactivity and heat generation rates are given for each waste after 0.5, 1.0 and 5.0 years of aging. The distribution and radioactivity of the principle fission product radionuclides from 1 tonne of exposed fuel aged 6 months are presented in Table 3.2 for the PW-4m waste and in Table 3.3 for the LMFBR waste. The fission product distribution for a PW-2 waste (i.e., from a fuel exposed to 20,000 MWd/tonne at 15 MW/tonne) was reported previously.(4,11)

As shown in Tables 3.2 and 3.3, the concentration of rare earth fission products in these wastes is approximately proportional to the total reactor fuel exposure. As shown in Table 3.1 and 3.4, the sodium and iron additives to the PW-4m and LMFBR wastes are in direct proportion to the fission product content of these wastes. Solid waste products with fission product concentrations as high as 50 wt% have been made in many silicate glasses;(4) however, the 22 wt% fission product calculated for the PW-4m and LMFBR phosphate glass waste products is about the optimum fission product loading for a homogeneous phosphate

TABLE 3.2. Fission Products from Power Reactor Fuel Exposed to 45,000 MWd/tonne at 30 MW/tonne After 6 Months Out-of-Reactor[a]

Element	Average Atomic Weight	Curies	Grams	g-moles	M	WSEP Oxide	Oxide mole., wt	Oxide, M	g Oxide per liter Waste	M^+[b]
Se	79	---	68	0.87	0.0023	SeO_3	127	0.0023	0.29	-0.0046
Rb	86	---	462	5.37	0.014	K_2O	94	0.0071	0.67	0.014
Sr	89	1.54×10^5	1201	13.49	0.036	SrO	104	0.036	3.70	0.071
Y	89	2.00×10^5	624	7.01	0.018	RE_2O_3	328	0.0092	3.03	0.055
Zr	93	1.80×10^5	5045	54.25	0.143	ZrO_2	155	0.14	22.21	0.57
Nb	95	3.54×10^5	9	0.09	0.0002	ZrO_2	155	0.0002	0.03	0.0008
Mo	98	---	4841	49.40	0.130	MoO_3	144	0.13	18.79	-0.26
Tc	99	---	1153	11.65	0.031	MoO_3	144	0.031	4.43	-0.062
Ru	102	4.45×10^5	3154	30.92	0.082	Fe_2O_3	160	0.041	6.54	0.24
Rh	103	4.56×10^4	519	5.04	0.013	CoO	75	0.013	1.00	0.013
Pd	106	---	1701	16.05	0.042	PdO	123	0.042	5.21	0.08
Ag	109	---	68	0.62	0.0016	Ag_2O	232	0.0008	0.18	0.0016
Cd	111	---	103	0.93	0.0024	CdO	128	0.0024	0.30	0.0048
In	115	---	2	0.02	-	SnO_2	151	-	-	0.0002
Sb	123	1.01×10^4	23	0.19	0.0005	Sb_2O_3	292	0.00025	0.073	0.0015
Sn	123	---	78	0.63	0.0017	SnO_2	151	0.0017	0.25	0.0068
Te	128	1.28×10^4	704	5.50	0.014	TeO_3	176	0.014	2.55	-0.029
Cs	135	4.09×10^5	4003	29.65	0.078	Cs_2O	282	0.039	11.04	0.078
Ba	138	---	2134	15.46	0.041	BaO	153	0.041	6.24	0.082
La	139	---	1729	12.44	0.25	RE_2O_3	328	0.12	41.90	0.77
Ce	141	1.40×10^6	3518	24.95						
Pr	141	---	1610	11.42						
Nd	145	---	5453	37.61						
Pm	147	1.20×10^5	127	0.86						
Sm	150	---	1023	6.82						
Eu	153	1.79×10^4	273	1.78						
Gd	156	---	127	0.81						
Tb	159	---	2	0.01						
Dy	162	---	---	---						
Total per tonne:		3.36×10^6	39754	343.72	0.91			0.68	128.47	2.00
Total per liter:		8.88×10^3	105	0.91	-					

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[a] Taken partially from H. H. VanTuyl, ISOGEN-A computer code for Radioisotope Generation Calculations, Reference 3 of Section 7

[b] M^+ = metal equivalents. The elements treated as anions are shown as negative M^+.

TABLE 3.3. Fission Products from a Fast Reactor Core Fuel Exposed to 100,000 MWd/tonne at 200 MW/tonne After 6 Months Out-of-Reactor(a)

Element	Average Atomic Weight	Curies	Grams	g-moles	M	WSEP Oxide	Oxide mole., wt	Oxide M	g Oxide per liter Waste	M^+(b)
Se	79	---	166	2.1	0.006	SeO_3	127	0.006	0.76	-0.012
Rb	86	---	609	7.1	0.019	K_2O	94	0.0095	0.89	0.019
Sr	89	3.48×10^5	1,310	14.7	0.039	SrO	104	0.0039	4.06	0.078
Y	89	4.90×10^5	677	7.6	0.020	RE_2O_3	328	0.010	3.28	0.060
Zr	93	1.21×10^6	7,584	81.5	0.21	ZrO_2	155	0.21	33.32	0.86
Nb	95	2.35×10^6	60	0.63	0.002	ZrO_2	155	0.002	0.31	0.0080
Mo	98	---	8,800	89.8	0.24	MoO_3	144	0.24	34.13	-0.47
Tc	99	---	2,384	24.1	0.064	MoO_3	144	0.064	9.22	-0.13
Ru	102	3.60×10^6	8,535	83.7	0.22	Fe_2O_3	160	0.11	17.68	0.66
Rh	103	---	2,490	24.2	0.064	CoO	75	0.064	4.80	0.13
Pd	106	---	6,660	62.8	0.17	PdO	123	0.17	20.42	0.33
Ag	109	---	756	6.9	0.018	Ag_2O	232	0.009	2.088	0.018
Cd	111	7.3×10^3	440	4.0	0.010	CdO	128	0.010	1.28	0.020
In	115	---	42	0.36	0.001	SnO_2	151	0.001	0.15	0.0040
Sb	123	6.9×10^4	160	1.3	0.003	Sb_2O_3	292	0.0015	0.44	0.0090
Sn	123	6.1×10^4	436	3.5	0.009	SnO_2	151	0.009	1.36	0.036
Te	128	5.8×10^4	1,666	13.0	0.034	TeO_3	176	0.034	5.98	-0.068
Cs	135	5.35×10^5	10,830	80.2	0.21	Cs_2O	282	0.11	29.89	0.21
Ba	138	---	3,540	25.6	0.068	BaO	153	0.068	10.40	0.14
La	139	---	3,058	22.0	0.51	RE_2O_3	328	0.25	83.64	1.53
Ce	141	6.28×10^6	7,110	50.4						
Pr	141	---	3,125	22.2						
Nd	145	---	10,168	70.1						
Pm	147	9.5×10^5	1,015	6.9						
Sm	150	1.5×10^4	2,470	16.4						
Eu	153	1.34×10^5	407	2.7						
Gd	156	---	323	2.1						
Tb	159	---	30	0.19						
Dy	162	---	20	0.12						
Total per tonne:		1.61×10^7	84,871	726.22	1.92			1.42	264.10	4.11
Total per liter:		4.26×10^4	224	1.92	-					

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a. Taken partially from E. A. Copinger, "Waste from Chemical Processing of Fast Reactor Fuels," Reference 2 of Section 7.

b. M^+ = metal equivalents. The elements treated as anions are shown as negative M^+

TABLE 3.4. Theoretical Composition of PW-4m and LMFBR Phosphate Glass Waste Products

			PW-4m				LMFBR			
Ion	WSEP Oxide	Oxide, molec. wt	Solution, M	Oxide, M	g Oxide per liter Waste	M^+	Solution, M	Oxide, M	g Oxide per liter Waste	M^+
H	-	-	4.5	-	-	-	0.50	-	-	-
Fe	Fe_2O_3	160	0.05	0.025	4.00	0.15	0.16	0.080	12.80	0.48
Cr	Cr_2O_3	152	0.012	0.006	0.91	0.036	0.046	0.023	3.50	0.14
Ni	NiO	75	0.008	0.008	0.60	0.016	0.023	0.023	1.72	0.046
Al	Al_2O_3	102	0.001	0.0005	0.051	0.003	-	-	-	-
Na	Na_2O	62	0.10	0.050	3.10	0.10	0.10	0.050	3.10	0.10
U	UO_2	270	0.01	0.01	2.70	0.020	0.01	0.01	2.70	0.020
Pu	UO_2	270	0.001	0.001	0.27	0.002	0.001	0.001	0.27	0.002
Am + Cm	UO_2	270	0.005	0.005	1.35	0.010	0.021	0.021	5.67	0.042
$NO_3^- + NO_2^-$	-	-	6.5	-	-	-6.50	4.75	-	-	-
PO_4	P_2O_5	142	0.003	0.0015	0.21	-0.003	0.06	0.032	4.54	-0.060
SiO_3	SiO_2	60	0.010	0.010	0.60	-0.020	0.010	0.010	0.60	-0.020
F^-	F_2	22	<0.001	<0.0005	0.011	-0.001	<0.001	<0.0005	0.011	-0.001
				0.12	13.81	0.34		0.25	34.92	0.83
Additives										
Na	Na_2O	62	1.40	0.700	43.4	1.40	2.90	1.45	89.90	2.90
Fe	Fe_2O_3	160	0.45	0.22	36.0	1.35	0.84	0.42	67.20	2.52
PO_4	P_2O_5	142	5.05	2.52	358.5	-5.05	10.50	5.25	745.50	-
				3.45	437.9	2.75		7.12	902.6	5.42
Fission Products			0.9081	0.68	128.5	2.00	1.92	1.42	264.1	4.11
Totals				4.25	580.2	5.09		8.79	1201.6	10.36
Measured Product Density, g/liter					2900				2900	
Theoretical Volume Reduction (Liquid to Solid):					5.0				2.4	
Theoretical Product Volume, liter/tonne					76				158	
Theoretical Product Composition:				Mole %	wt%			Mole %	wt%	
FP				16	22			16	22	
Waste				19	25			19	25	
Additives				81	75			81	75	

melt. Simulated PW-4m phosphate glass waste products have been prepared with higher fission product concentrations by adding less sodium and iron but this generally resulted in higher product melting temperatures with corresponding lower production rates and precipitation of rare earths from the phosphate melts occurred. Consequently, the 22 wt% fission product content in the waste products in Table 3.4 represents one of the limits which prescribes how much solid waste product will be produced from these wastes and also establishes the maximum heat generation rates for the PW-4m and LMFBR phosphate glass waste products. The thermal maximum heat generation rates for these phosphate glass waste products is discussed in Section 7 of this report.

The high concentrations of rare earth fission products in the PW-4m and LMFBR wastes gave adjusted feed solutions which contained nominally 50 vol% suspended solids, about twice that present in the PW-1 and PW-2 adjusted feed solutions. The volume percent of undissolved solids in actual feed samples is given in Table 3.5 and varied appreciable due to the difficulty in obtaining representative samples without accumulating excess solids while recirculating through the sample bottle.

Laboratory scale tests were made on each batch of actual feed prior to each WSEP demonstration run. The results of these tests determined the suitability of the feed for processing in the phosphate glass solidifier. Boiling points, melting point, corrosiveness of the melt, foaming tendencies of the denitrated solution, and visual volatilization were noted. The results of these tests are shown in Table 3.5.

TABLE 3.5. Results of Preliminary Radioactive In-Cell Laboratory Tests with Adjusted Phosphate Glass Feeds

	WSEP Run No.				
	PG-7	PG-8	PG-9	PG-10	PG-11
Feed Type	PW-2	PW-4m	PW-4m	PW-4m	LMFBR
Heat Generation Rate in Feed, W/liter	10.5	14.8	9.0	16.4	14.6
Feed Boiling Point, °C	∿107	Spattering started at ∿95 °C	∿100	Not Available	Bubbling ∿90 °C
Suspended Solids in Adjusted Feed, vol%[a]	20 to 30	50 to 60	10 to 50	10 to 50	50 to 90
Foaming below 150 °C (denitrator-evaporator conditions)	No severe foaming to 146 °C	Severe spattering coated crucible walls with viscous droplets	No foaming, rapidly formed viscous syrup which bubbled and spattered	No foaming, rapidly formed viscous brown syrup which bubbled and spattered	No foaming, some spattering. Bubbles at 145 °C collapsed to viscous brown sludge
Foaming above 150 °C (melter operating conditions)	Viscous bubbles at 170 to 200 °C filled crucible then collapsed at ∿220 °C	Viscous bubbles filled 1/2 crucible from 170 to 220 °C. Greyish-white bubbles filled crucible from 400 to 525 °C, subsided and only residue at 750 °C	Viscous bubbles to 800 °C, some slumping at 850 °C, viscous melt at 900 °C, glassy fluid melt at 950 °C	Viscous sludge to 800 °C turning to shiny viscous residue at 850 °C, viscous molten glass at 900 °C, to fluid melt at 950 °C	Sludge moist at 200 to 220 °C, crumbly, light colored. Turned dark grey, dull dry solid to 750 °C, slumped at 800 °C, all melted at 850 °C and fluid melt at 900 °C
Volatilization[b]	None visible after holding at 900 °C for 1 hr	No fumes observed at 1000 °C for 1 hr	No fuming observed during 2 hr at 1000 °C	No fumes observed during 2 hr at 1000 °C	No fumes observed during 1 hr at 900 °C
Melt Corrosivity to Product Receiver Material	Well oxidized after 20 hr at 750 °C but no visible penetration of 310 SS coupon	Heavily oxidized after 20 hr at 750 °C but no visible penetration of mild steel coupon	Not Available	Not Available	Oxidized after 24 hr at 650 °C but no visible penetration of 304L SS coupon
Product Appearance[c]	Green-black smooth, glassy	Brown-black smooth, glassy	Green-black smooth, glassy	Black smooth, glassy	Black smooth, glassy
Initial Melting Point,[d] °C	825	900	900	900	850

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a. Range of undissolved, settled solids in adjusted feed samples taken before, during, and after each run.

b. Test for excess phosphate as seen by evolution of white P_2O_5 vapors from melt at 50 to 100 °C above initial melting point.

c. After cooling.

d. Temperature at which all melt is in bottom of crucible and all melted. Samples usually began slumping from the crucible walls about 50 °C below melting point.

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4.0 PHOSPHATE GLASS SOLIDIFICATION PERFORMANCE

The final five radioactive demonstration runs with the phosphate glass solidification process were completed in the WSEP. The major objectives were to demonstrate the solidification of PW-4m and LMFBR waste types, to increase the concentration of radionuclides for prediction of maximum allowable heat generation rates in a receiver pot and to determine the performance of the phosphate glass process coupled with the auxiliary off-gas treatment equipment. Major variables of the runs are shown in Table 4.1. Data presented in Section 4 are from References 1 through 4.

Engineering scale performance of the phosphate glass solidification process with highly radioactive feed again generally confirmed earlier development work.(5) The predicted capacities of the process and the distribution of radioactivity in the effluents were in the range indicated by nonradioactive work at BNL and PNL.

There were no major problems during this second series of runs. Plugging problems prominent during the solidification of PW-1 wastes in the first series of runs were significantly reduced and eliminated due to the continued successful application of the remotable features of the new airlift pot and the introduction of a new dip tube venting technique which permitted washing of the tubes by letting liquid rise inside them for short periods. The new waste types were also less prone to plugging because solids were kept more readily in suspension. The feasibility of a screw type pump to deliver concentrated feed from the denitrator to the melter more uniformly and with more control was also established. Satisfactory control of foaming was again achieved by the addition

TABLE 4.1. Major Run Variables

Run	Mode	Pot Diam., in.	Waste Type	Radioactivity Processed, Ci	Equivalent Tonnes to Pot[a]	W/tonne in Waste[b]	Equivalent Age, yr.
7	A	8	PW-2	2,800,000	1.05	9,400	0.46[c]
8	A, B	8	PW-4m	2,300,000	0.84	10,500	1.0[d]
9	A	6	PW-4m	1,000,000	0.41	10,200	0.9[d]
10	A	6	PW-4m	2,600,000	0.35	26,600	0.25[d]
11	A	8	LMFBR	3,300,000	0.38	31,300	1.5[e]

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a. Tonne is a metric ton of original fuel.
b. Heat generation rate based on analytical results.
c. Based on 20,000 MWd/tonne at 15 MW/tonne.
d. Based on 45,000 MWd/tonne at 30 MW/tonne.
e. Based on 100,000 MWd/tonne at 200 MW/tonne.

of a silicone antifoam agent into the denitrator. Of significance was the successful completion of back to back Runs PG-9 and PG-10 which confirmed the feasibility of continuous operation with the phosphate glass process.

Solidification of wastes during the second series of radioactive demonstrations produced a phosphate glass with a heat generation rate as high as 11,900 watts in an 8-inch diameter pot and a heat generation rate density as high as 317 W/liter in a 6-inch diameter pot which is the highest attained for a WSEP product to date. A higher thermal conductivity for the product in a molten or near molten state was also noted. However, molten core restrictions, as defined in WSEP (see Section 4.2), may diminish any gains to be realized from it. The molten core restriction was surpassed in two of the pots but no adverse effects have been noted to date.

4.1 OVERALL PROCESSING RATES

Overall processing rates (based on melter feed time up to denitrator dilution) were 0.2 and 0.58 tonne/day for LMFBR and PW-2 wastes, respectively, and ranged from 0.34 to 0.47 tonne/day for PW-4m waste. These rates represent production of glass products at 32 and 37 liters/day for the LMFBR and PW-2 wastes and from 29 to 31 liters/day for the PW-4m waste. The internal heat generation rate within the phosphate glass melt in the melter was as high as 2 kilowatts. The total net power requirements were 2 to 4 kilowatts for the melter. A significant (30%) increase in processing rates was obtained over previous runs and was chiefly attributable to a new furnace installed prior to Run PG-7. Even with the increase in internal heat and the resulting decrease in melter power requirement, the melter remained the capacity limiting unit of the process. Processing rates are summarized in Table 4.2.

TABLE 4.2. WSEP Phosphate Glass Solidification Processing Rates

PG Run No.	Mode	Feed Conc., liters/tonne fuel	Pot Diam., in.	Pot Internal Heat Rate, W[(a)]	Total Feed to Denitrator, liters	Feed Time, hr	Steady-State Feed Time, hr	Average Feed Rate During Startup, liter/hr	Average Feed Rate During Steady State, liter/hr	Average Overall Feed Rate, liter/hr
7	A	644	8	9,800	806	44.2	36.9	24.9	16.9	18.2
8	A, B	722	8	8,800	660	49.5	42	16.5	12.8	13.3
9	A	1,023	6	4,200	579[(b)]	22	16.7	30.8	24.9	26.3
10	A	1,198	6	9,300	580	24	17.5	30.8	21.7	24.2
11	A	1,916	8	11,900	907[(c)]	47	42	35.4	17.5	19.3

PG Run No.	Total Run Time,[(d)] hr	Total Equivalent Feed to Melter,[(f)] liters	Total Equivalent Feed to Melter, tonnes of fuel	Steady-State Processing Rate to Receiver Pot[(g)]: equivalent tonnes/day	Steady-State Processing Rate to Receiver Pot[(g)]: liters melt/day	Total Volume of Product Produced, liters
7	61.8[(e)]	675	1.05	0.58	37	67.3
8	55.2	610	0.84	0.39	31	66.7
9	27.4	423	0.41	0.47	31	26.6
10	30.0	414	0.35	0.34	29	29.3
11	58.7	726	0.38	0.20	32	60.0

---

a. Total internal heat rate in pot at end of run.
b. Consists of 481 liters at a concentration of 1,023 liters/tonne and 98 liters at 1970 liters/tonne.
c. Consists of 708 liters at a concentration of 1,916 liters/tonne and 199 liters 3,832 liters/tonne.
d. Includes startup time, steady-state operating time and shutdown time.
e. Includes a 4 hr period when feed was shut off.
f. Amount of material fed to the melter in terms of the volume fed to the denitrator-evaporator.
g. Based on melter feed time up to denitrator-evaporator dilution and tonne equivalents to pot up to denitrator-evaporator dilution.

The general factors affecting rates were only qualitatively investigated. The limiting factor affecting the melter processing rate is the transmission of heat into the melter to produce a fluid melt. Other factors affecting the rate are feed composition and feed rate control to the melter. The processing rate is not limited by the denitrator-evaporator since it can evaporate at greater than 35 liters/hr of distillate to provide a three-fold greater concentrate rate than the melter can handle.

4.2 RADIONUCLIDE HEATING EFFECTS IN THE PRODUCT RECEIVER

Since high concentrations of radionuclides in solidified waste produce high internal temperatures even when the receiver pot is cooled, the maximum allowable temperatures must be determined. The temperatures are dependent on the concentration of the radionuclides in the solid product (the irradiation history of the fuel and the age of the waste), the receiver size, the thermal conductivity of the solid product, and the cooling environment in which the receiver is placed.

The maximum allowable product temperatures established for WSEP are a product temperature of 900 °C and/or a receiver pot wall temperature of 427 °C. If a molten core exists in the receiver pot, the radius of the molten core is not to exceed one-half the receiver pot radius. The 900 °C restriction limits corrosion to the stainless steel thermowells used to house the thermocouples at the centerline of the pots. (The wells will probably not be used in production model receiver pots.) The 427 °C wall temperature limits excessive air oxidation of the container and allows remote handling of the pot without excessive special precautions. Limiting the molten core radius prevents molten waste from contacting the pot wall and thus reduces the corrosion potential. It also minimizes the consequences from changes within the product, such as fission product migration and gas formation.

The temperatures caused by the internal heat generation rate in the five pots are listed in Table 4.3. During the second series of radioactive demonstrations of the phosphate glass process in WSEP, the internal heat rate density of the PW-4m product was increased to a maximum of 317 W/liter in PG-10 which caused the average internal centerline temperature to reach 731 °C and the wall temperature to reach 387 °C while stored in air. In no cases were restrictions limiting centerline and wall temperatures to 900 and 427 °C, respectively, exceeded. Because the phosphate glass product has an approximate 700 °C remelt temperature, the maximum heat rate density is limited by the molten core radius restriction and will be approximately 180 to 200 W/liter for an 8-inch diameter receiver pot and 320 W/liter for a 6-inch diameter pot stored in air. The heat rate density of 198 W/liter in the 8-inch diameter receiver pot of Run PG-11 produced an average intermediate (midway between the pot centerline and wall) zone temperature of 796 °C while stored in air, consequently, the molten core restriction was definitely surpassed in this receiver. An average intermediate temperature of 674 °C was recorded in the 6-inch diameter receiver of Run PG-10. Since the intermediate thermowell is closer to the wall of the receiver for the 6-inch pot (less than 1 inch distance), the molten core restriction was most likely surpassed in this run also, or at least equaled. However, there were no adverse effects noted in the PG-10 and PG-11 receivers with respect to storage and handling.

During the runs the receiver pot furnace was held at about 600 °C. This furnace temperature was used to assure that the pot wall temperature remained sufficiently high so that the

TABLE 4.3. Pot Receiver Temperatures Caused by Internal Heat Generation

PG Run No.	Pot Diam., in.	Pot Material	Total Heat Rate, W(a)	Total Heat Rate Density, W/liter	Average Centerline Temp,(b) °C	Average Centerline to Wall Temp Difference,(b) °C
7	8	310 SS	9,800	146	754	389
8	8	Mild Steel	8,800	132	628	325
9	6	304L SS	4,200	158	566(c)	204(c)
10	6	304L SS	9,300	317	731	344
11	8	304L SS	11,900	198	803	443

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a. Based on analytical results.
b. Receiver pot stored in air except where otherwise noted. Temperatures are the averages of temperatures recorded in zones 3, 4, and 5.
c. Receiver pot stored in furnace with forced air cooling outside the susceptor.

steady drip of melt entering the receiver pot at rates as low as 1 liter/hr would cause no stalagmites. During Run PG-11 glass stalagmites formed in the upper portion of the receiver where no heat was available to permit the melt to slump. This situation developed because the melter had become tilted and was discharging melt so that it would strike the upper receiver wall and upper thermowell. Batch drains were subsequently employed and posed no problems as far as stalagmite formation was concerned. Any receiver wall temperature increases due to batch drains, were reduced by turning heat off to the affected zone or by turning cooling air on or by combinations of both. Pot wall temperatures of about 600 °C are recommended when melt is to be continuously discharged via the melter weir. Figure 4.1 is a schematic of a receiver pot which shows the elevation of the pot thermocouples and zones. One air blower rate at 275 scfm was sufficient to control the receiver pot centerline temperature below 900 °C and the pot wall below 425 °C during Run PG-10 which contained the highest heat rate density (317 W/liter) tested. The maximum centerline temperature recorded during processing was 960 °C during Run PG-9 and occurred during a batch discharge when the melter drain freeze valve was inadvertently permitted to thaw. This temperature was quickly reduced by applying cooling air to the outside of the furnace susceptor* and turning off the furnace heat in the affected zone. The maximum wall temperature recorded during processing was 740 °C and also occurred in Run PG-9 in the same zone due to the inadvertent batch drain. A typical receiver pot temperature profile for a continuous drain operation using data from Run PG-8 is shown in Figure 4.2. For a batch drain operation, data from Run PG-11 is shown in Figure 4.3.

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* Direct cooling of the pot wall (inside the susceptor) was available, but was not used.

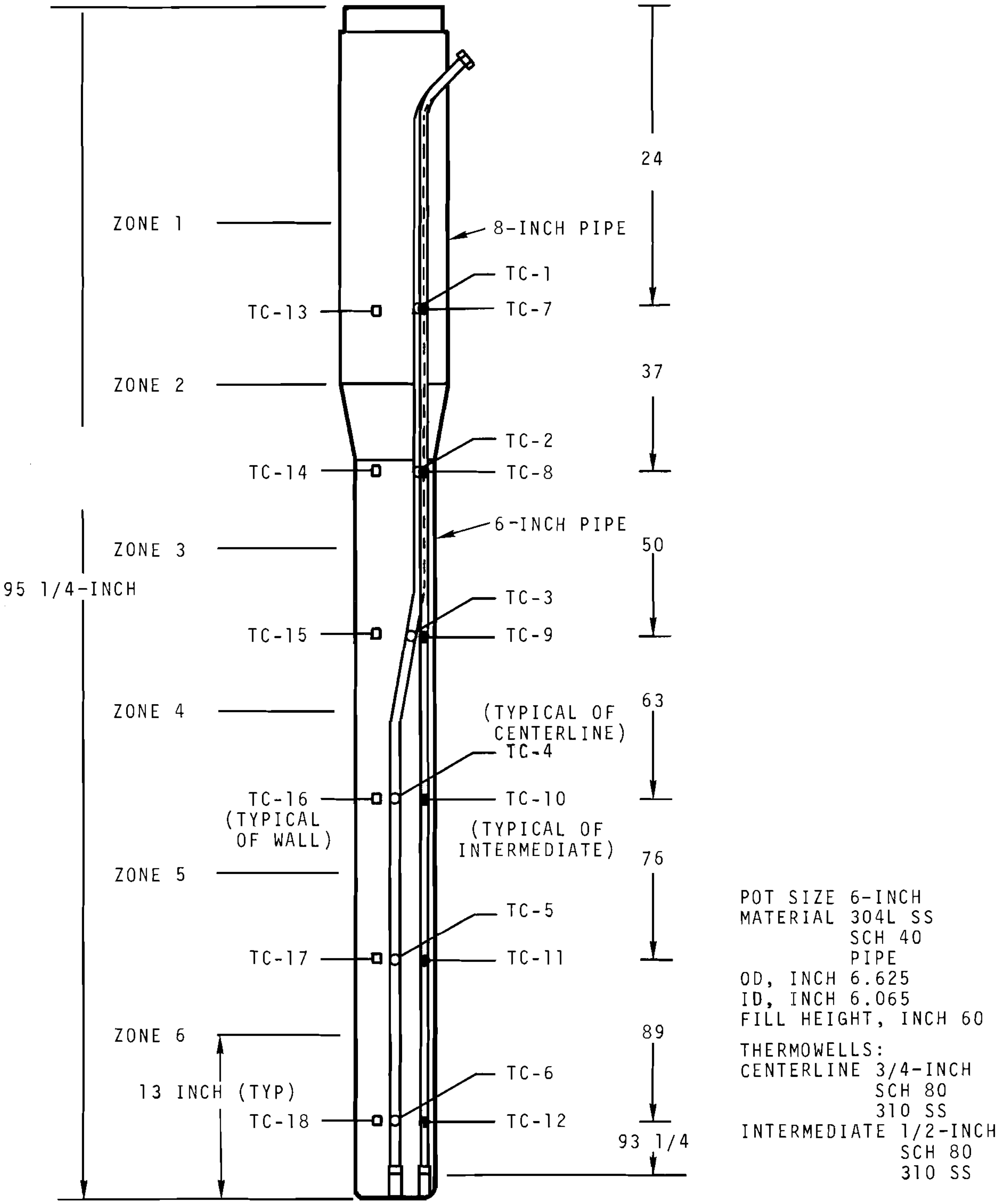

FIGURE 4.1. Phosphate Glass Receiver Pot Thermocouple Arrangement

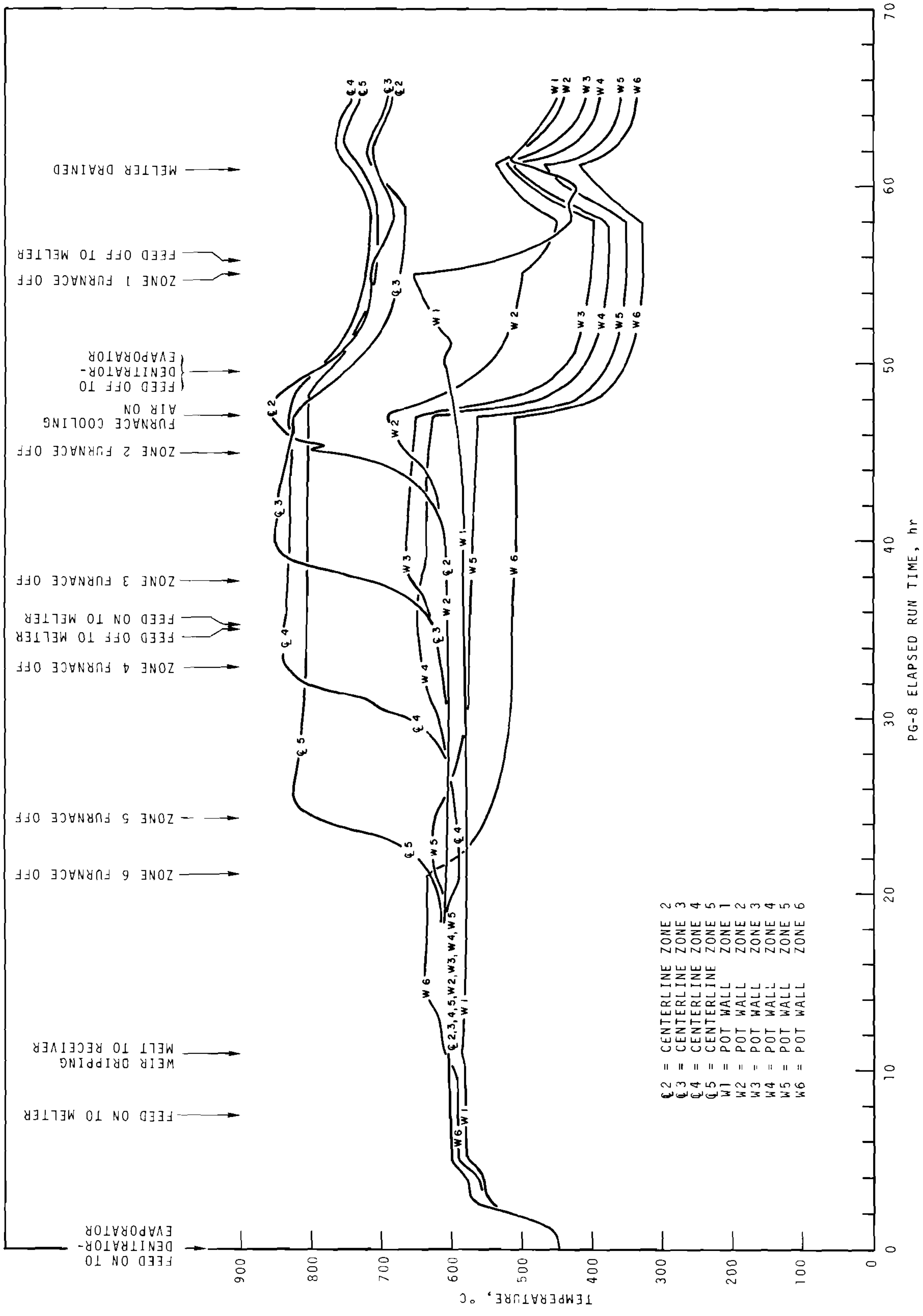

FIGURE 4.2. Run PG-8 Receiver Pot Temperatures

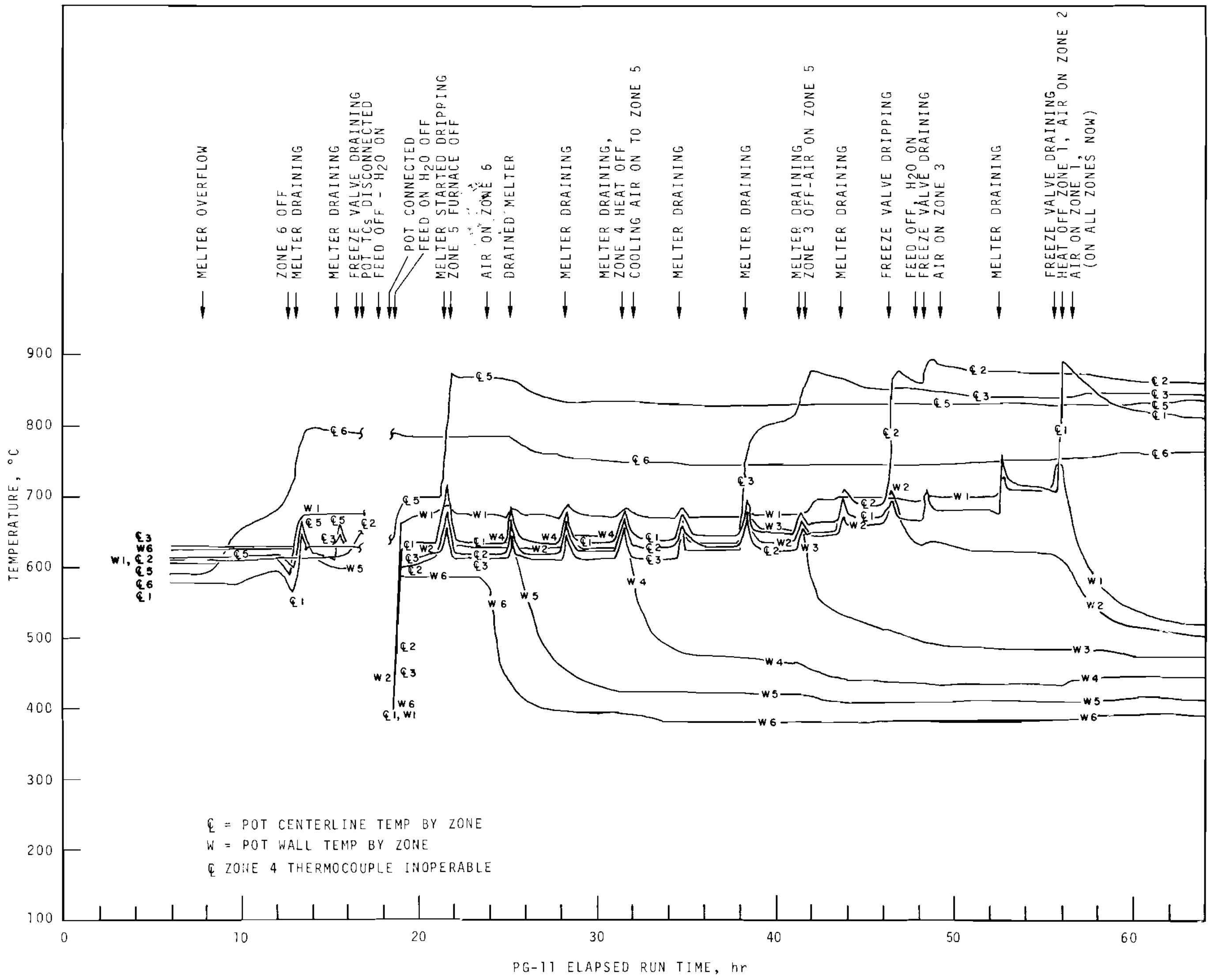

FIGURE 4.3. Run PG-11 Receiver Pot Temperatures

4.3 WASTE VOLUME REDUCTION

Because of the variations in chemical compositions of the different wastes processed during solidification, the overall volume reduction factors varied from 2.4 to 5.9 (based on the ratio of aqueous waste at 378 liters/tonne to product). Volume reduction factors are summarized in Table 4.4. Also shown for comparison with observed values are the calculated volume reductions that were expected. Observed values of volume reduction differed from calculated values in Runs PG-7, 8, and 10 by about 8, 12, and 10%, respectively. Observed values in Runs PG-9 and 11 were identical with calculated values. The average difference for the six runs was about 6%. Differences in this area can usually be attributed to difficulties in analyzing feed for some of the oxide forming metallic cations such as aluminum in the presence of phosphate. Comparison of laboratory measured densities with calculated bulk densities shows good agreement with only the products of Runs PG-7 and 10 differing by 6.9 and 3.3%, respectively. Differences here, if not caused by errors in measuring the product volume could be caused by voids which can form in either slow cooling or extra viscous melt.

The unit volumes of phosphate glass from PW-4m waste in a receiver pot (Table 4.5) were 79, 65, and 84 liters/tonne of fuel for Runs PG-8, 9, and 10, respectively. For LMFBR waste, the unit volume was 158 liters/tonne of fuel and for the PW-2 waste used in Run PG-7 the unit volume was 64 liters/tonne. The fission product oxide content of the products varied from 15 to 25 wt%. Comparison of the calculated fission product contents in the products with that from the nominal fission product content shows that the actual fission product oxide content differs from -24% to +25%. Differences are primarily due to variations in the rare earth content of the wastes.

TABLE 4.4. Waste Volume Reductions

PG Run No.	Feed Type	Denitrator-Evaporator Average Liquid Temp, °C	Overall Volume Reduction[a]	Estimated Volume Reduction[b]	Denitrator Concentration Factor[c]	Melter Concentration Factor[d]	Measured Density of Product, kg/liter
7	PW-2	136	5.9	6.4	2.7	2.2	2.9
8	PW-4m	123	4.8	4.3	1.4	3.4	2.9
9	PW-4m	126	5.9	5.9	1.44	4.1	2.8
10	PW-4m	123	4.5	5.0	1.47	3.1	3.0
11	LMFBR	121	2.4	2.4	0.7[e]	3.37	2.9

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a. Ratio of initial aqueous waste at 378 liters/tonne of fuel to that of the final phosphate glass product.

b. Estimate is based on 2.8 kg/liter density of product/total nonvolatile oxide weight in feed at 378 liters/tonne.

c. Volume ratio of initial aqueous waste at 378 liters/tonne of fuel to that of the concentrate from the denitrator-evaporator.

d. Volume ratio of the concentrate from the denitrator-evaporator to that of the final phosphate glass product.

e. This waste cannot exist at 378 liters/tonne. This number is purely for comparison purposes.

TABLE 4.5. Capacity of a Receiver Pot

PG Run	Pot Diameter, in.	Total Internal Heat Rate, W	Total Product Weight, kg	Unit Volume of Solid, liter/tonne	Equivalent Tonnes of Fuel/Pot	Equivalent Tonnes of Fuel/Pot, if Pot Were Filled to a Nominal 6-foot Depth	Actual Fission Product Oxide Content, wt%	Nominal Fission Product Oxide Content, wt%	Deviation from Nominal Fission Product Oxide Content, %
7	8	9,800	182	64	1.05	0.94	15	14.4	+2.6
8	8	8,800	196	79	0.84	0.76	25	19.8	+25
9	6	4,200	76	65	0.41	0.49	15	19.8	-24
10	6	9,300	85	84	0.35	0.38	20	19.8	+2.8
11	8	11,900	172	158	0.38	0.36	23	19.7	+19

TABLE 4.6. Volatilization and Entrainment from the Melter and General Melter Operating Parameters

PG Run	Feed Type	Furnace Temperature, °C	Average Internal Melt Temperature, °C	Melter Sparger Flow, scfh	Total Curies to Melter	Total Curies Ruthenium to Melter	Total Ruthenium Volatilized, %(a)	Total ^{144}Ce-Pr Entrained, %(a)	Denitrator Concentrate Rate to Melter, liters/hr
7	PW-2	1225	1148	0.2	2,800,000	13,000	8	0.05	3.8
8	PW-4m	1230	1150	0.2	2,300,000	9,800	4	0.04	3.9
9	PW-4m	1225	1135	0.2	1,025,000	9,000	5.7	0.068	4.3
10	PW-4m	1250	1200	0.2	2,600,000	(b)	(b)	0.044	4.5
11	LMFBR	1215	(c)	0.2	3,275,000	30,000	7.4	0.05	4.0

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a. Percentage of total fed to the melter, as determined by that found in the total condensate from the melter.
b. Radioruthenium was not present in the feed.
c. Thermocouple was defective.

4.4 VOLATILIZATION OF RUTHENIUM AND OTHER VOLATILES

An important objective of the five phosphate glass solidification runs was to characterize the path and behavior of volatile fission products which are present in the waste. In the first series of runs made with PW-1 and PW-2 wastes, the only fission product present in significant quantities which volatilized was ruthenium. The behavior of this fission product was again closely followed in this last series of demonstration runs. In addition, the fission products of selenium, tellurium, antimony, and tin were also designated worthy of study because they are present in more significant quantities in LMFBR wastes. During the demonstration runs, using PW-2 and PW-4m wastes, ruthenium was again found to be the only fission product volatilized. Cesium evolution was more typical of cerium entrainment results than of ruthenium volatilization results and is therefore not considered to be significantly volatile. Ruthenium was also volatilized in the run using LMFBR waste. During the run with simulated LMFBR waste 2.6% of the ^{129m}Te in the feed to the melter volatilized. Analysis of the effluents from a "cold" run made at BNL has shown that from 1 to 10% of the tellurium and 50 to 100% of the selenium can be expected to volatilize from the melter.(6) However, the quantity of selenium in the waste will be insufficient for its volatility to be a significant problem. The fission products of antimony and tin are not expected to volatilize. Most of the ruthenium that is volatilized and entrained during the denitration-concentration step is collected in the WSEP auxiliary evaporator; that which is volatilized and entrained from the melter is collected in the melter condensate receiving tank.

As expected, ruthenium was volatilized from the melter in quantities that were in agreement with previously determined results. These results and melter parameters are shown in Table 4.6. From 4 to 8% of the total ruthenium entering the melter was volatilized based on ^{106}Ru analysis. Entrainment was less than 0.1% for all runs and ranged from 0.04 to 0.07%. Entrainment was always determined with respect to ^{144}Ce-Pr.

Volatilization and entrainment of ruthenium from the denitrator-evaporator was less than 1% for all runs in which radioruthenium was added and ranged from about 0.5% to about 0.9%. Radioruthenium was not added to the feed used in Run PG-10 therefore no volatilization numbers are reported. Entrainment from the denitrator was consistently less than 0.1% and ranged from 0.001 to 0.06%. Volatilization and entrainment from the denitrator is shown in Table 4.7 along with other parameters. Feed composition had no apparent affect on either volatilization of ruthenium or entrainment. Figures 4.4 and 4.5 shows the accumulations of ruthenium and cerium, respectively, in the denitrator-evaporator and melter condensate receivers as a function of elapsed run time. The boiloff rates did not affect the entrainment markedly because the rates were below the capacity of the denitrator (viz. 35 liters/hr capacity). Foaming that occurred in the denitrator during the early part of Run PG-7 did not appear to increase losses from the denitrator and apparently had no effect on entrainment.

4.5 PERFORMANCE OF THE DENITRATOR-EVAPORATOR

The denitrator was started with an initial volume of approximately 35 liters of 6$\underline{M}$ nitric acid. During the initial concentration period feed was continuously added to the boiling contents of the denitrator-evaporator while the denitrator-evaporator volume was kept essentially constant, and no material

TABLE 4.7. Volatilization and Entrainment from the Denitrator-Evaporator

PG Run	Mode	Feed Type	Denitrator Concentrate Volume, liters/ tonne	Denitrator Consentrate Composition, $\underline{M}$(a)						Additives	Foam Present	Average Feed Rate, liters/hr	Boiloff Rate, liters/hr	Percent ^{106}Ru Volatilized(c)	Percent ^{144}Ce-Pr Entrainment(c)
				Fe^{+3}	Al^{+3}	Na^{+}	RE	PO_4^{-3}	Ru(b)						
7	A	PW-2	139	0.88	0.41	3.78	0.57	11.4	0.0092	6$\underline{M}$ HNO_3 Antifoam B	yes	18.2	17.6	0.8	0.001
8	A, B	PW-4m	270	0.29	0.56	2.18	0.83	8.12	0.0050	6M HNO_3 Antifoam B	no	13.3	12.7	0.62	0.029
9	A	PW-4m	262	0.10	0.61	1.93	0.17	6.54	0.0029	6M HNO_3 Antifoam B	no	26.3	26.2	0.88	0.063
10	A	PW-4m	258	0.11	0.74	2.15	0.42	7.81	0.015	6M HNO_3	no	24.2	21.2	(d)	0.036
11	A	LMFBR	540	0.38	0.49	2.34	0.64	7.12	0.006	6$\underline{M}$ HNO_3 Antifoam B	no	19.3	19.0	0.48(e)	0.001(e)

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a. All molarities are at denitrator-evaporator average operating conditions. See appendix for feed concentration in the feed tank.
b. Chemical ruthenium.
c. Percent of total activity fed to the denitrator, which was found in the condensate from the denitrator.
d. Radioruthenium was not added to feed.
e. Based on denitrator condenser condensate stream samples.

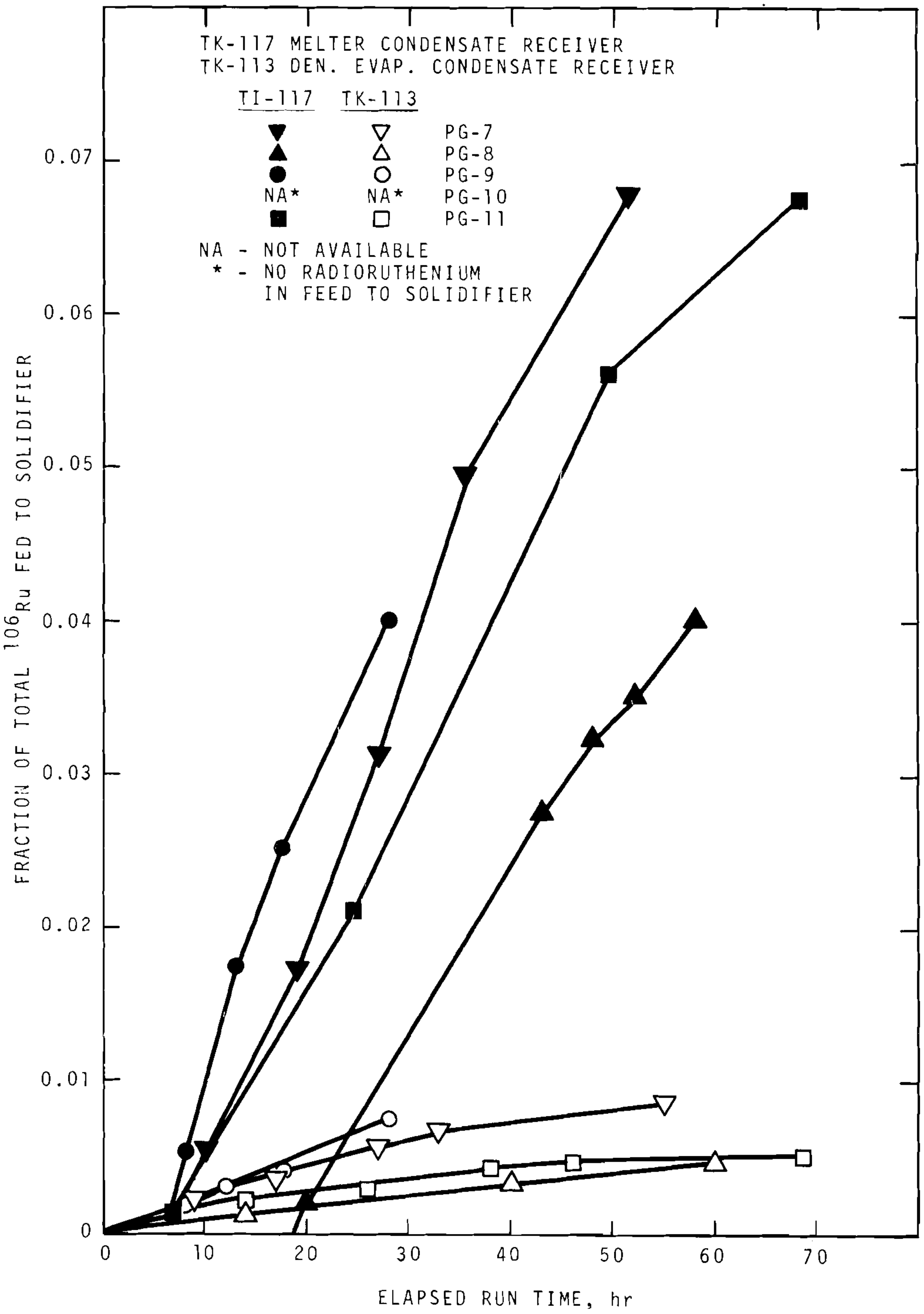

FIGURE 4.4. Accumulation of Ruthenium in the Phosphate Glass Solidifier Condensate

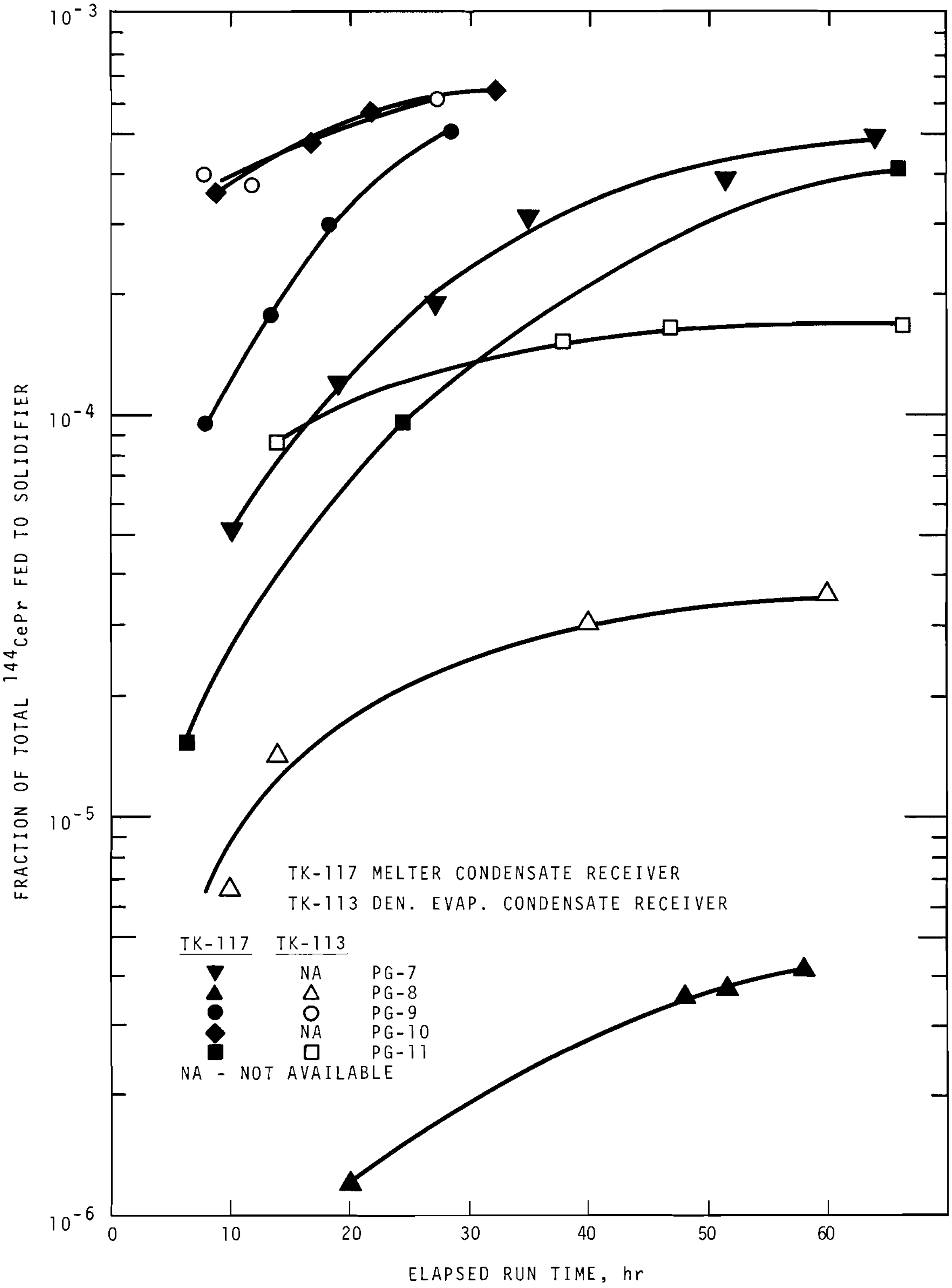

FIGURE 4.5. Accumulation of Cerium in the Phosphate Glass Solidifier Condensate

was fed to the melter. During this concentration period the feed rate to the denitrator averaged almost 25 liters/hr for PW-4m waste and ranged from 16.5 to 31 liters/hr for PW-4m waste depending on the feed concentration. The average startup rate for the LMFBR waste was 35 liters/hr. The startup period required from about 5 to 7.5 hours for all demonstration runs. The steady-state feed rates averaged 17 liters/hr for PW-2 and varied from 13 to 25 liters/hr for PW-4m wastes. LMFBR steady-state processing rates were 17.5 liters/hr. Processing rates are summarized in Table 4.2. Operating parameters are shown in Table 4.8. The shutdown period involves dilution of the contents of the denitrator-evaporator with 6M nitric acid as feeding to the melter is continued. No waste is fed to the denitrator during this period.

The denitrator concentrate boiling temperature during the processing of PW-4m waste was held at about 123 °C for both Runs PG-8 and 10 and 126 °C for Run PG-9. These were higher than the 121 °C required for the processing of LMFBR waste but much lower than the 136 °C required for the PW-2 waste used in Run PG-7. Because of the higher fission product content in the higher burnup PW-4m and LMFBR fuel, lower temperatures were required to prevent the concentrate from getting too high in specific gravity and viscosity. The denitrator concentration factor* for PW-2 waste in Run PG-7 was 2.7 and was lower than the average value of 3.3 determined for PW-2 wastes in the first series of runs. The presence of extra sodium in PG-7 from an inadvertent addition of EDTA and the presence of extra rare earths were the reasons for the lower concentration factor. The concentration factor for PW-4m waste was typically 1.4 and reflects the increased fission product loading of the spent

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* Volume ratio of initial aqueous waste at 378 liters/tonne of fuel to that of the concentrate from the denitrator-evaporator.

TABLE 4.8. Denitrator-Evaporator General Operating Parameters

PG Run	Feed Type	Average Liquid Temp, °C	Average Vapor Temp, °C	Startup Volume, liters	Average Concentrate Volume, liters	Average Density,[a] kg/liter	Agitator, rpm	Average Steam Pressure to Tube Bundle, psig[c]	Average Steam Temp, °C	Average ΔT Steam-Liquid, °C
7	PW-2	136	116	40	44	1.92	200	62	154	18
8	PW-4m	123	111	40	47	1.7	200[b]	47	146	23
9	PW-4m	126	110	33	40	1.74	(d)	56	151	25
10	PW-4m	123	112	39	48	1.74	(d)	43	144	21
11	LMFBR	121	108	31	47	1.7	(d)	46	145	24

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a. At operating temperature
b. Use discontinued after 13 hr of elapsed run time
c. Saturated steam
d. Not used

fuel because of the higher burnup (45,000 MWd/tonne at 30 MW/tonne). The 0.7 value presented as the concentration factor for LMFBR waste is due to an even higher burnup (100,000 MWd/tonne at 200 MW/tonne for core fuel only). It must be realized that these values are based on wastes at theoretical concentrations of 378.5 liters/tonne. This was a realistic figure selected for wastes containing lower fission product concentrations; however, for the wastes with increased fuel burnup it becomes apparent that the selected theoretical waste concentration is not representative and will lead to the anomaly encountered above. However, it still is convenient for purposes of comparison, particularly when attempting to describe reasons for differences that may exist within the same waste type. The extent of denitration was not determined during the final five runs. Two attempts were made to obtain concentrate samples at the entrance to the solution feeder by a suction device; however, both attempts were unsuccessful.

4.5.1 Plugging

Plugging of the specific gravity and liquid level (weight factor) tubes was significantly minimized as a problem during the processing of purex wastes, principally due to the incorporation of a self-cleaning technique. The technique consisted of venting the tubes to the denitrator-evaporator periodically to allow solution to rise inside the tubes and cleanse them. Venting the tubes for a 10 minute period of every 15 minutes of operation proved satisfactory for this purpose.

Operational parameters in the denitrator-evaporator, such as liquid and vapor temperatures, liquid volume, feed rates, and specific gravity are shown in detail for each demonstration in the Appendix as Figures 9.5 through 9.8.

4.5.2 Foaming

Foaming in the denitrator was either completely suppressed or else extremely well controlled during this final series of runs with the exception of the first part of Run PG-7. It was quickly determined, however, that the reason for the incomplete suppression of foam in this run was due to the use of stale antifoam agent. The problem was eliminated when fresh antifoam was used in the remainder of the run. The primary indicator of foaming, equal liquid and vapor temperatures, was not present in any run as the average minimum difference between liquid and vapor temperatures was never below 11 °C. No loss of feed from the denitrator occurred during any of the runs. Antifoam agent was generally added to the denitrator at about 2.7 to 2.8 liters/hr as a solution containing 6.75 grams of antifoam per liter and was very effective in these amounts. The feed used in Run PG-10 was made only from a radiocerium solution and consequently did not contain the foam inducing agent dibutyl phosphate (DBP). Because of this, no antifoam agent was added during this run nor was it found necessary. This was also established in experiments and in practice during the first series of runs.

4.5.3 Agitator Operation

Erratic operation of the agitator was first noted in Run PG-8 and required its curtailed use during a major portion of Run PG-8 and in all subsequent runs. Primarily, its use was suspended during the startup and steady-state-portions of the runs when boiling was normally present. It was still used during dilution periods when boiling is normally absent since it was felt that some agitation is necessary to keep solids in suspension. No obvious deleterious effects were noted during the runs when the agitator was not used nor were any obvious differences evident. The erratic operation appeared to be due to dragging of the agitator shaft. This is almost conclusively believed due to breakdown of the shaft bearing lubricant from the radioactive environment.

4.5.4 Effect of Internal Heat Generation in the Denitrator-Evaporator

The heat requirement to denitrate and concentrate the waste entering the denitrator is about 12 kilowatts at a feed rate of 15 liters/hr based on evaporation of water. Concentrating the feed which contained from 10 to 22 W/liter for PW-4m waste, 15 W/liter for PW-2 waste and 17 W/liter for LMFBR wastes increased the heat rate density in the denitrator until in Run PG-10 the heat rate density was 104 W/liter in the denitrator concentrate. This maximum heat-rate density theoretically accounted for about 26% of the net heat requirement. (See Table 4.9.) The effects of this available heat was not readily apparent in terms of denitrator-evaporator steam requirements; however, the internal heat was sufficient to maintain the concentrate near the boiling point without external heating.

TABLE 4.9. Denitrator-Evaporator Internal Heat Generation Effects

PG Run	Feed Type	Average Feed Rate, liters/hr	Heat Rate Density in Feed W/liter[a]	Denitrator Average Holdup Volume, liters	Average Heat Rate Density in Denitrator Concentrate, W/liter	Internal Heat Generation[b] % of Denitrator Heat Requirement
7	PW-2	18.2	14.6	44	67.4	20
8	PW-4m	13.3	14.2	47	37.9	17
9	PW-4m	26.3	9.9	40	38.6	7
10	PW-4m	24.2	22.3	48	103.7	26
11	LMFBR	19.3	16.6	47	58.9	18

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a. Based on feed analysis

b. Based on evaporation of water

4.5.5 Melter Feed System

The transfer of concentrated waste from the denitrator-evaporator to the melter was achieved principally by the modified airlift pot used during Runs PG-5 and PG-6 of the first series of runs and for a short period in PG-11 by a slurry pump. With the airlift, the denitrated and concentrated waste is airlifted from near the bottom of the denitrator to the airlift pot from which part of the hot concentrate recirculates back to the denitrator and part overflows into the melter feed line. An alternate device was installed prior to Run PG-11 and is shown in Figure 4.6. The slurry pump uses the Archimedes screw principle and consists of an air driven auger which rotates within a snug fitting tubular casing. A tachometer is fitted to the drive assembly and provides speed indication which is used as a measure of pumping rate.

The transfer of concentrated waste from the denitrator-evaporator to the melter was limited to an average of about 4 liters/hr because of the capacity of the melter to transfer heat into the incoming concentrated feed. This rate was significantly higher (30%) than in the first series of runs. A new melter furnace was installed prior to this second series and was operated at a higher temperature and was mainly responsible for the increased rate. Airlift pot operation was usually very satisfactory during the second series of runs with the exception of Run PG-7. Plugs developed in the recirculation line about eight times during the run and at least twice in the airlift weight factor dip tube. These plugs in turn led to loss of control of the feed rate to the melter. Control of feed rate to the melter was also affected to a lesser extent whenever changes occurred in the internal denitrator-evaporator liquid level and pressure. As the runs progressed, these disruptions

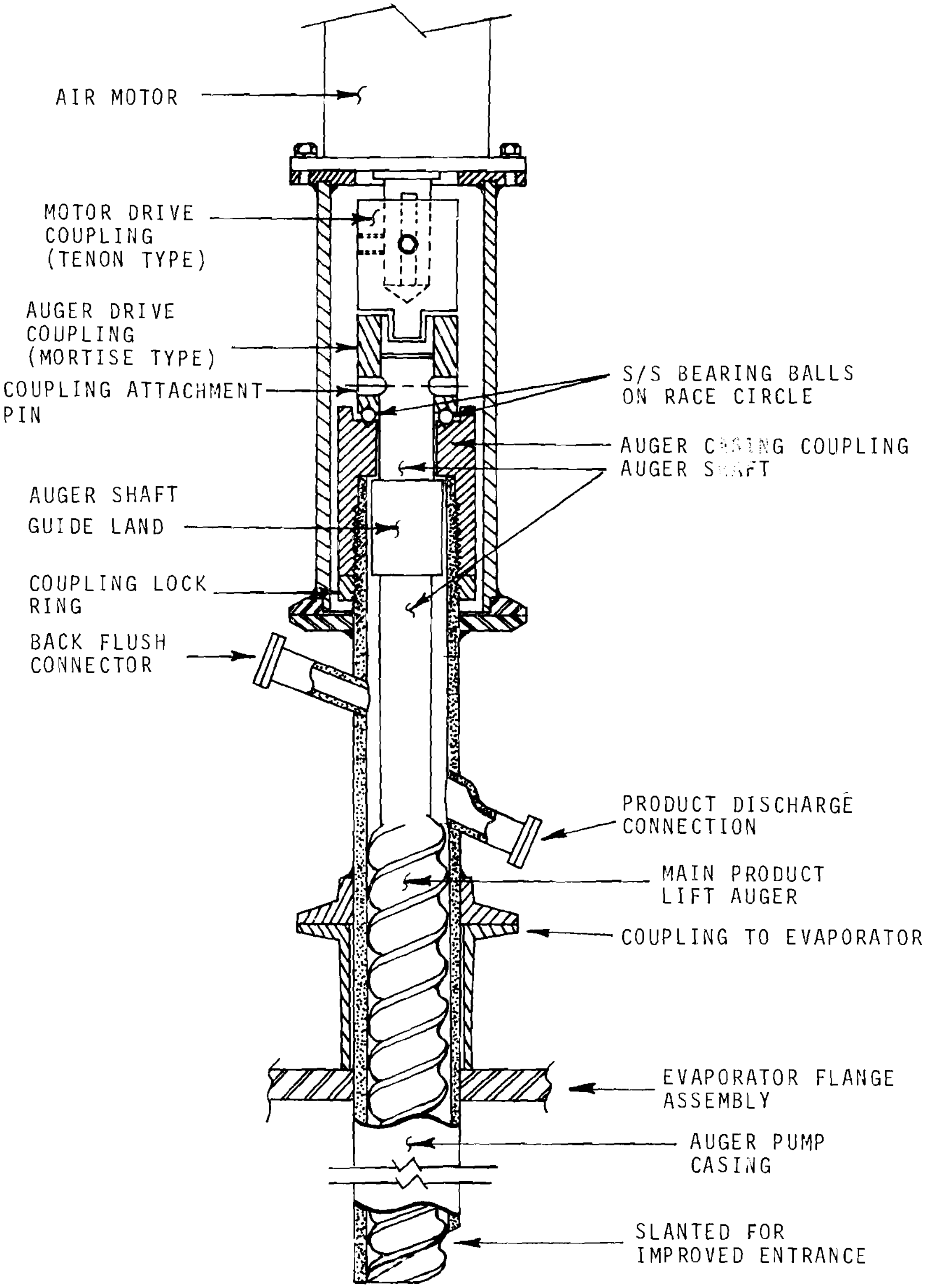

FIGURE 4.6. Schematic Sketch of Radioactive Slurry Pump for the Phosphate Glass Solidification Process

were anticipated and their effects were minimized through the use of a vent control jet to help stabilize process pressures. The major plugs in the recirculation line were always removed either by inserting the airlift cleanout rod into the recirculation line or by backing out the recirculation plug valve and flushing the line with nitric acid. The airlift pot weight factor dip tube plugs were removed by flushing the line with nitric acid. Partial plugs in the weight factor line were perhaps more serious because it obscured the development of plugs in the recirculation line by failing to signal a rise in the liquid level in the airlift pot. The cause of the plugs in the airlift pot may have been due to the presence of residual PW-1 material from Runs PG-6 and 7 which was never completely removed prior to Run PG-7. These problems were significantly reduced or eliminated in all subsequent runs by the routine application of sprays and flushes and by use of the remotable features of the airlift pot. Airlift pot temperatures averaged about 4° lower than feed processing temperatures in the last four runs. Other operating parameters of the airlift pot are shown in Table 4.10.

During the early part of Run PG-7 the airlift pot was vented to the melter via the melter feed line and was the procedure used on all previous runs. This procedure was changed later in Run PG-7 and also in the remainder of the runs by venting the airlift to the denitrator-evaporator. Smoother operation seemed to result from the change.

An alternate method of transferring feed to the melter via a screw pump was tried in Run PG-11. Although airlift pot operation was satisfactory during the last four runs, very close watch on operating parameters was necessary to assure good performance. The airlift is very sensitive to changing conditions

TABLE 4.10. Airlift Pot Operating Parameters

PG Run	Mode	Feed Type	Average Density Denitrator Bottoms, kg/liter	Average Concentrate Temperature		Average Air Supply Pressure, psig	Average Airlift Air Supply Rate, scfh	Average Airlift Pot Jacket Steam Pressure, psig
				Denitrator, °C	Airlift Pot, °C			
7	A	PW-2	1.92	136	92[(a)]	6.2	0.7	17
8	A, B	PW-4m	1.7	123	122	5	1.3	13.7
9	A	PW-4m	1.74	126	120	5.2	0.9	15.3
10	A	PW-4m	1.74	123	118	5.6	2.1	9.6
11	A	LMFBR	1.7	121	118	6	2.3	9.5
		Average		123.2(b)	119.5(b)	5.6	1.46	13.0

---

a. Airlift pot thermocouple believed faulty during Run PG-7 and was replaced following the run.

b. Excluding Run PG-7

and it is easy to overadjust to compensate for these changing conditions. Plugging of various parts of the airlift pot with quick settling solids, as experienced in Runs PG-5 and PG-6 in which PW-1 waste was used, was also a problem which was reduced in magnitude by timely use of the remotable features of the unit. Further reduction of the plugging problems associated with the use of PW-1 wastes may be forthcoming since recent developments(7) in glass compositions made it apparent that the PW-1 waste flowsheet could be adjusted by the addition of sodium and phosphoric acid to make it similar to a PW-4m feed which was processed with no difficulty. (This will also result in an increase in the unit volume of the solid). The screw pump was developed to provide an added degree of control and to lessen the constant surveillance that is necessary with the airlift pot. The screw pump was in operation for 8 hours when its air driven motor failed, causing the use of the pump to be terminated. The air motor was either inherently defective due to prolonged use in developing the pump or became defective because of radiation damage. During its brief performance several advantages of the use of a pump of this type were apparent. These advantages included:

- More stable melter operation as indicated by stable temperatures in the melter.
- Higher than average temperatures in the melter at a melter feed rate of 3.5 liters/hr indicated that an increased feed rate could be accommodated.
- Less sensitive to changes within the denitrator.
- More positive control with little likelihood of overcompensating.

Further use of the screw pump is recommended with emphasis on determining its useful life during operating conditions.

Operating parameters of the pump and the motor and solution characteristics are shown in Figure 4.7. The pump operated between 600 and 650 rpm with 40 psig air pressure and delivered concentrated feed to the melter at about 3.5 liters/hr. Performance of the pump began to decrease as an increased air pressure was required to maintain a desirable rpm. Air motor failure finally occurred as the air pressure reached 85 psig.

4.6 PERFORMANCE OF MELTER

Denitrator concentrate at 120 to 135 °C is converted to a melt at temperatures up to 1200 °C. When the concentrate enters the melter (at the nominal rate of about 4 liters/hr), final evaporation and denitration takes place and the solids are melted. During normal operation, the melt was continuously overflowed from the melter via an internal melter weir at an average rate of about 1.3 liter/hr. At the end of each run the melt was batch discharged through the drain freeze-valve. Throughout most of the runs, feed from the denitrator entered the melter as a gummy and bubbly material but caused no major difficulties. Melter operation during the five runs proceeded smoothly except during short periods of foaming which sometimes followed excessive surges of feed to the melter.

In these five runs, no initial sealing of the melter internal weir with nonradioactive glass was provided. Instead the melter vacuum was reduced from the normal 6 inches of water to 2 inches of water to minimize sucking air through the unsealed weir tube while concentrate was fed to the melter. When melt was observed dripping from the weir, the weir tube was known to be sealed and the vacuum was increased back to the normal 6 inches of water.

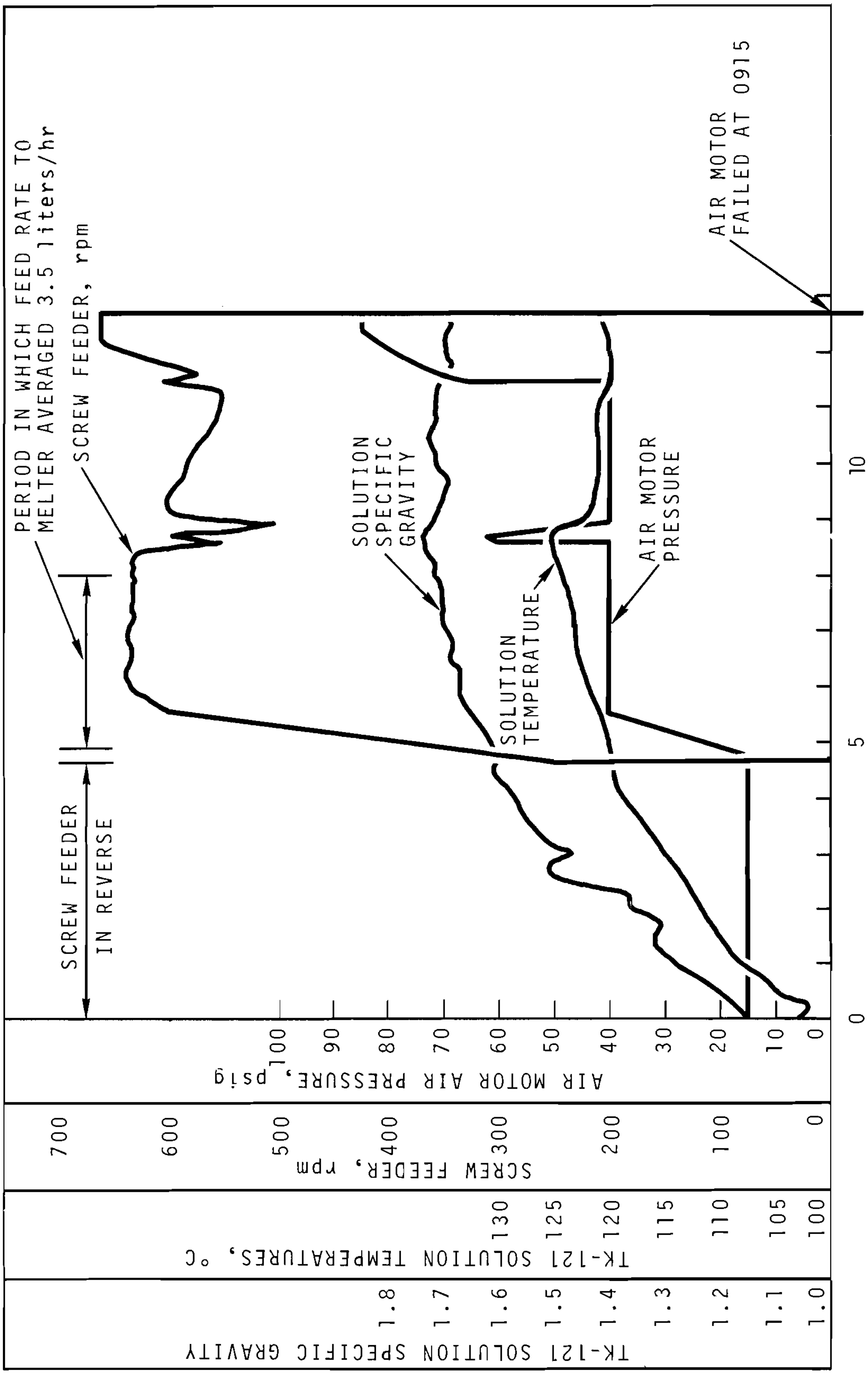

FIGURE 4.7. Screw Feeder Operating Parameters During Run PG-11

The melter furnace was operated at an average temperature of 1230 °C during all five runs, and the resulting average internal melt temperature ranged from 1150 to 1200 °C as measured near the bottom of the melter. Figure 4.8 shows typical melter temperature profiles during Run PG-11 where both the screw feeder and airlift were used. No appreciable temperature difference was distinguishable among phosphate glass melts from PW-4m, LMFBR, and PW-2 wastes except that the melt temperature increased as the internal heat rate density increased. The net heat requirement to produce glass was about 2 kilowatts. This was less than expected from the design verification tests. The average melt level in the melter was about 6 inches. Melt level control was attempted by controlling the feed rate to the melter. This was done by adjusting air supply to the airlift as a function of temperature readings within the melt. However, melt levels did not always correspond to those indicated by control thermocouple readings. The control thermocouple is about 1 inch above the cold feed layer and melt. If the melt level is approximately at the weir overflow level, a decreasing melter feed control temperature indicates an increasing level of melt in the melter. An internal melter thermocouple, located 1/2 inch below the weir overflow, was monitored continuously and provided for better interpretation of internal melter operating conditions. The upper control temperature was monitored to detect sudden changes in feed rate to the melter. The control temperature located below the weir overflow level responded less rapidly to system changes and was used to estimate the magnitude of the feed rate changes necessary to restore the melt to the proper temperature. The upper melt control temperature averaged between 925 and 1015 °C during the six runs. An optimum would have been about 850 °C for steady continuous operation. The melter was operated under an average vacuum of 6 inches of water. The drainage of melt to the receiver was cyclic during most of the runs due to the airlift not feeding the melter at a steady rate.

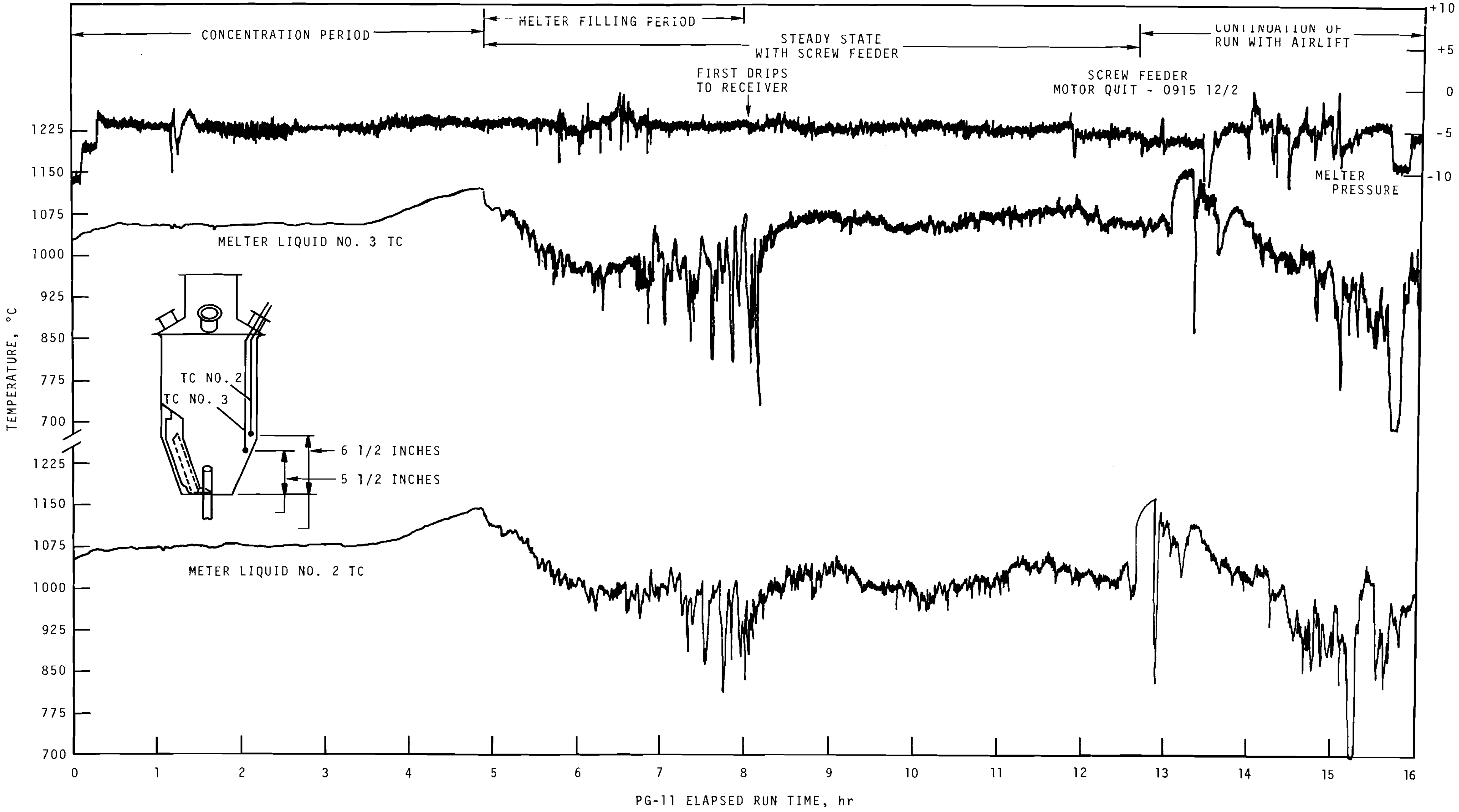

FIGURE 4.8. Typical WSEP Melter Temperatures

Foaming in the melter occurred during all the runs, but was usually held to inconsequential limits. In all cases, the foam level largely depended on the feed rate to the melter. When a prolonged surge of feed entered the melter, a surge of foam followed. At one period during Run PG-7, an excessive foam level existed which resulted in the release of vapors from the melter. Successful control of foaming and melt level at other times was accomplished by manually maintaining as steady a feed rate to the melter as possible and by always keeping some feed entering the melter. There were no obvious differences in foaming tendencies among the three wastes processed in these runs.

An average melter processing capacity of about 4 liters/hr of concentrated feed was obtained during this final series of runs and represents an increase of 30% over the average capacity of the melter during the first six runs. The installation of a new furnace prior to the start of the second series of demonstration runs was most probably the reason for the increased capacity. Part of the increase may also have been due to the greater internal heat generation rate of the melt but no conclusive results can be cited to establish the validity of this assumption. Heat losses from the melter and furnace unit obscure analysis of the effects of this internal heat.

The installation of a new furnace prior to the start of this series of runs became necessary when several elements (Hevi-Duty Kanthal A-1) of the old furnace became open. The elements were visibly distorted and severely bowed outward toward the center of the furnace (Figure 4.9). The elements also sagged and may have made contact with neighboring elements. The furnace had been in use for 861 hours. The furnace was removed and replaced with a nearly identical, but modified furnace that had been used briefly in cold spray solidifier

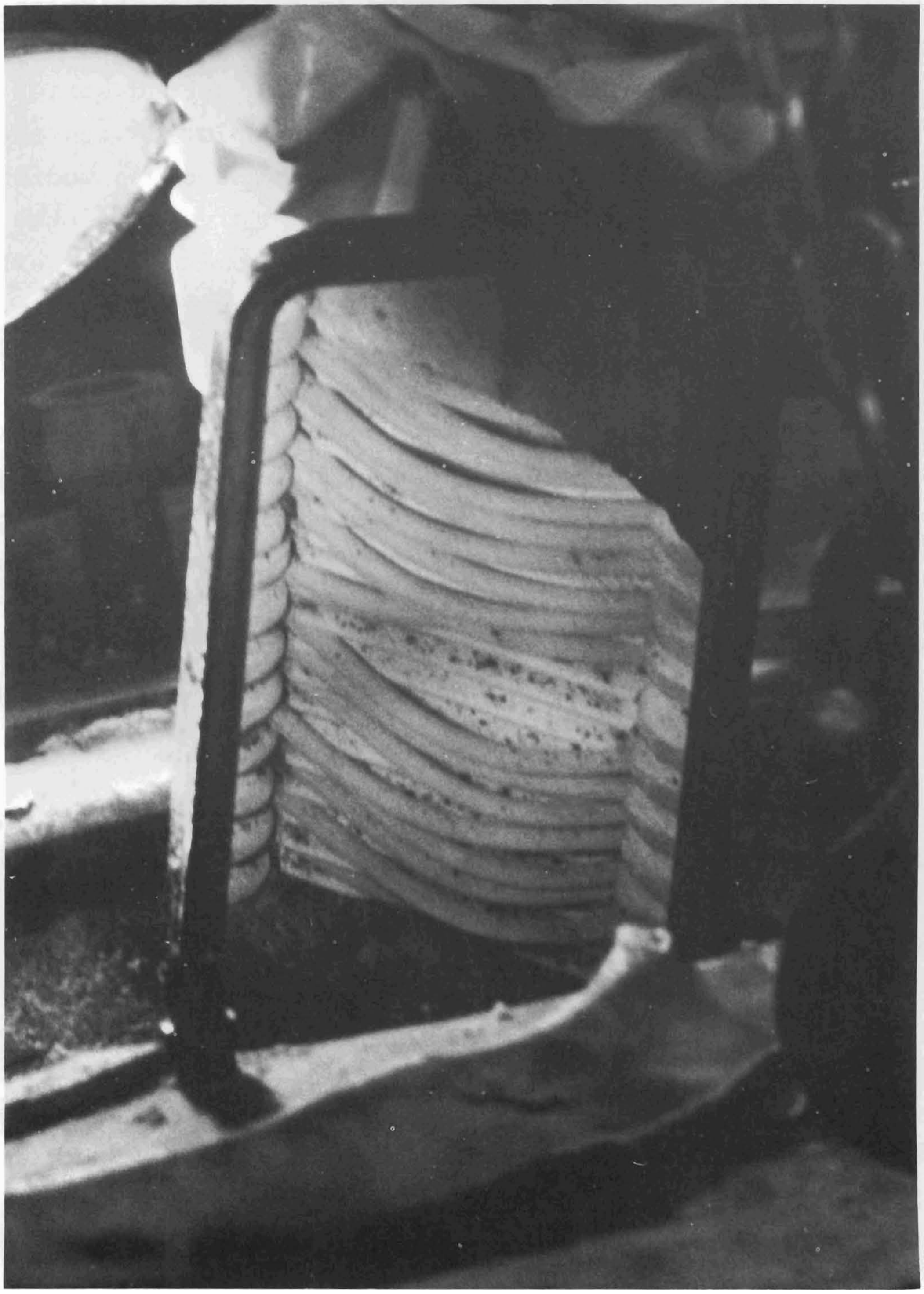

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FIGURE 4.9. Distorted Elements of the First Phosphate Glass Melter Furnace After 861 Hours of Operation

development tests. At this time there is no explanation for the failure of the elements. Inspection of the old furnace was limited to remote viewing with a mirror. The second series of phosphate glass demonstration runs was completed with the modified furnace with no difficulty. The furnace was modified by installing vertical ceramic rods in front of each of the sets of Kanthal A-1 elements to limit their bowing. The effects of thermal cycling of the new furnace was lessened in these last runs by limiting the furnace heating and cooling cycles tc 200 °C/hr.

The platinum melter was examined at the time the furnace was being replaced. The sides of the melter were slightly concave (Figure 4.10). The lower two-thirds of the melter appeared to have larger grain growth than the upper portion. Both of these conditions have been noted in a melter used for over 2800 hours under similar, but nonradioactive, conditions at BNL.(8)

The various off-gas fittings of the melter were examined for cake formation. The seal pot vent line had a cake at the flanged connection (Figure 4.11). The cake covered approximately half the opening and tapered off toward the inside of each line. Cake formation at this joint suggests that the joint was not absolutely tight. Inflow of cooling air with subsequent condensation of vapor at this point provided a site for cake formation. The remainder of the line was clear as was the melter off-gas line. The cake was greenish-gray in color and was easily removed.

4.6.1 Drain Systems

During all the demonstrations with the exception of the latter part of Run PG-11, melt was discharged to the receiver

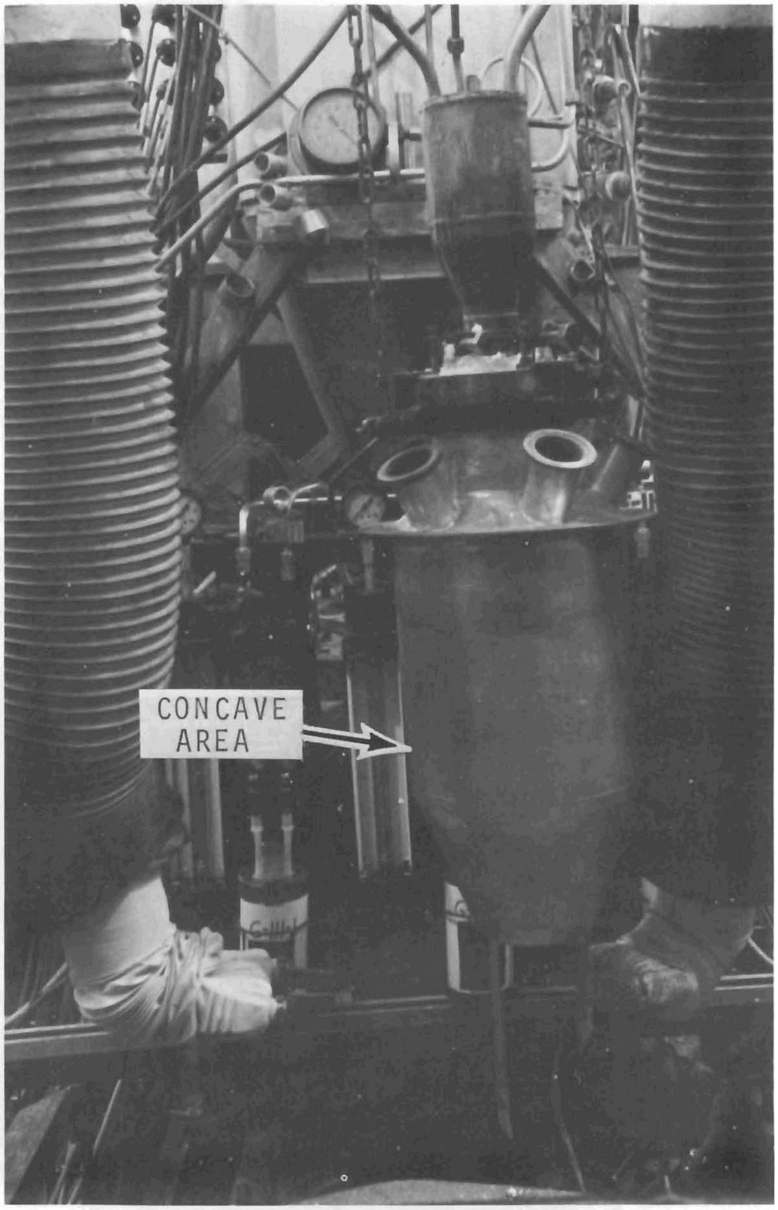

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FIGURE 4.10. Phosphate Glass Platinum Melter

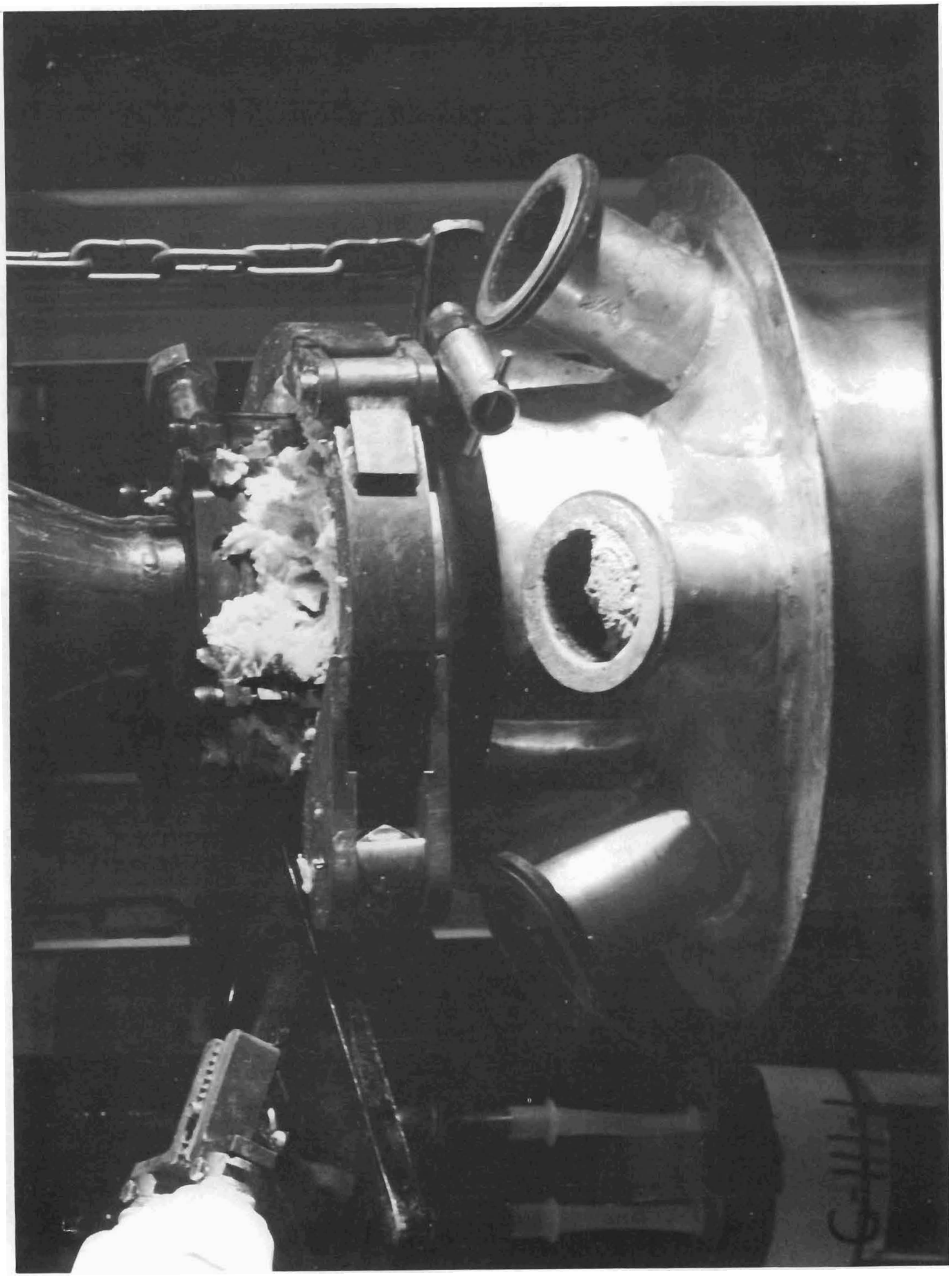

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FIGURE 4.11. Cake Accumulation in the Melter Outlet to the Seal Pot

pot via the unheated internal overflow weir. At the end of each run, batch discharge of melt was accomplished through the drain freeze-valve to empty the melter completely to minimize the potential for stretching the melter due to different coefficients of thermal expansion of the glass and the platinum melter. During Run PG-11 a tilted melter made it necessary to drain the melter in batches for a large portion of the run. A propane-air torch was used to directly heat the drain freeze-valve to drain the melter at the end of Runs PG-7 and PG-8. The batch drains during PG-11, as were the final drains in PG-9 and PG-10, were effected by turning off cooling air and allowing the frozen products in the drain valve to thaw. The valve was sealed by turning cooling air on again.

4.6.2 Off-Gas Line, Melter Condenser, and Steam Spray

Off-gases generated in the high-temperature glass-making step in the melter consisted mainly of water, nitrates, and sulfate (when present in the waste), and to a lesser extent, phosphates. In addition, some volatilized ruthenium, selenium and tellurium, and entrained materials are present. This stream is routed through a platinum-5% irridium off-gas line to the melter-condenser. The temperatures of the gases passing through this line were maintained in the range of 400 to 475 °C in the five WSEP runs to prevent condensation and thereby minimize corrosion in the line.

The gas temperatures at the inlet of the melter condenser were essentially the same as those of the off-gas line shown in Table 4.11. The gas temperatures at the outlet of the condenser ranged from 50 to 55 °C, and were generally higher than the temperatures of the collected condensate which were 41 to 47 °C. Condensate flow rates ranged from 2.0 to about 3.0 liters/hr.

TABLE 4.11. Performance of Melter Condenser

PG Run	Mode	Waste Type	Inlet Gas Temp, °C	Outlet Gas Temp, °C	Outlet Cond. Temp, °C	Steam Spray Pressure, psig	Steam Flow, liters/hr	Average(a) Rate of Melter Cond. Flow, liters/hr	Recovery of Melter Volatilized Sulfate, %
7	A	PW-2	400	50	41	2.65	7.8	2.0	99
8	A, B	PW-4m	475	50	44	0	0	2.5	(b)
9	A	PW-4m	400	53	47	0	0	2.69	(b)
10	A	PW-4m	440	55	46	0	0	2.98	(b)
11	A	LMFBR	470	53	46	0	0	2.54	(b)

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a. During period of continuous feeding to melter.

b. Sulfate is not present in PW-4m and LMFBR wastes.

Recovery of volatilized sulfate from PW-2 waste was 99% in Run PG-7. Steam spray additions to the bottom chamber of the melter-condenser during PG-7 were made through a modified, full-cone, Nionel spray nozzle* to help recover volatilized sulfate from the melter off-gas vapors and to help inhibit corrosion of the stainless steel melter condensate drain line by diluting the condensate and reducing condensate temperatures. Sulfate was not present in significant quantities in the wastes used in the other runs; consequently it was not necessary to use steam additions in these runs.

4.7 GENERAL PERFORMANCE AND OPERATING HISTORY

4.7.1 Waste Composition Effects

During WSEP phosphate glass solidification of highly radioactive aqueous wastes to solids, relatively few processing problems occurred. One run each with PW-2 and LMFBR wastes, and three runs with PW-4m waste demonstrated performance with waste representing that from reprocessing spent fuel irradiated from 20,000 to 100,000 MWd/tonne at power levels ranging from 15 to 200 MW/tonne, respectively. The only problems were plugging of the airlift air line and of the airlift pot recirculation line during Run PG-7. Relatively few processing difficulties were encountered while concentrating and solidifying PW-4m and LMFBR wastes.

The sulfate in the PW-2 waste reduces the viscosity of and homogenizes the evaporator concentrate. Also, evolution of sulfur oxide gases from the melter helps to increase mixing and heat transfer rates. Melt foaming was not appreciably affected by the chemical flowsheet.

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* Spraying Systems Co.-- Wide Spray Hydraulic Atomizing Nozzle Type 1/4 NW4W with 0.060-inch diameter orifice modified by removing internal parts and drilling to obtain about a 1/8-inch diameter orifice.

General waste composition ranges and additives for the five phosphate glass runs are shown in Table 4.12. Feed compositions for the five runs, as well as other pertinent data on the feeds, are listed in Table 9.1 of the Appendix. Feeds to the phosphate glass solidification process were prepared using actual Purex high-level waste and concentrated radiorare-earth (mostly ^{144}Ce-Pr) solutions to provide the desired self-heat generation rate in the glass product. However, because the stock solutions sometimes contained excess aluminum and rare earths compared to the standard PW-2, PW-4m, and LMFBR waste compositions, the actual composition of the wastes processed varied somewhat from the desired composition. The PW-2 wastes used in Run PG-7 contained almost 50% more sodium than the nominal value in the flowsheet. This excess sodium concentration probably caused the denitrator-evaporator slurry to become somewhat more nonhomogeneous, (e.g., forming heavier solids, which settle out at a more rapid rate). The excess aluminum in the Purex waste was used as a substitute (34 to 100%) for the iron during all the runs. An excess of rare earths in all runs except PG-9 required additional H_3PO_4 be added to the waste to maintain the M/P equal to 1.0.

Chemical additives were added directly to the feed.

4.7.2 Related Equipment

Performance of the primary pieces of phosphate glass equipment has been discussed in the preceding sections. The operating history of this equipment is summarized in Table 4.13. Discussion of other related equipment is presented below.

TABLE 4.12. General Waste Composition Ranges[(a)]

Constituents	PW-2 Waste, M		PW-4m Waste, M		LMFBR, M	
	Nominal	Actual	Nominal	Actual	Nominal	Actual
H^+[(b)]	3.93	1.27	4.5	0.9-2.4	0.5	4.6
Na^+	0.93	1.39	0.1	0 -0.2	0.1	1.04
Fe^{+3}	0.45	0.32	0.05	0.07-0.1	0.16	0.09
Al^{+3}[(c)]	0.001	0.15[(c)]	0.001	0.4-0.5[(c)]	0	0.70[(c)]
SO_4^{-2}	0.87		0	∿0	0	0
NO_3^-	5.37	6.1	6.5	7.0-7.7	4.75	17.5
$(Y + RE)^{+3}$	0.12	0.21	0.274	0.015-0.53	0.47	0.72
Additives						
Na^+	0	0	1.4	1.4	2.3	2.3
Fe^{+3}	0	0	0.45	0.-0.1	0.84	0.46
PO_4^{-3} (H_3PO_4)	3.3	4.2	5.1	5.06-5.25	10.23	10.6

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a. All values are quoted at 378 liters/tonne.

b. Excludes H^+ from dissociation of H_3PO_4 additive.

c. Aluminum used as an iron substitute.

TABLE 4.13. Phosphate Glass Equipment Operating History

Equipment	Construction Material	Temp, °C	Pressure, in. water or flow	Chemical	Operating Hours	Remarks
Phosphate Glass Rack (5C-Rack)	Fe, SS, Nionel	∿50	-2 to -10	Liquid Nitrates, Sulfates, and Phosphate Slurries	1125	--- --- ---
Melter	Platinum	800-1270	-2 to -10	Phosphate Melts	1035	After 110 hr of CPG(a) operation, the inadequately heated melter vent nozzle corroded and partially collapsed because of expansion stresses. The melter was replaced after 783 hr. Walls were slightly concave.
Melter Sparger No. 1	Platinum	800-1200	0 to 1.2 scfh	N_2	1	Used only on trial basis during CPG-7.
No. 2	Platinum	800-1200	0 to 0.8 scfh	N_2	445	Used only during in-cell hot operation.
Melter Level Dip Tube	Platinum	800-1200	0 to 0.5 scfh	Air	725	Used only during in-cell hot operation.
Melter Furnace No. 1	Hevi-Duty Kanthal A-1 Elements	800-1270	Trace	N_2 Purge in Jacket	861	N_2 purge is to prevent oxidation of electrical wiring in furnace jacket. Elements failed at end of this time.
Melter Furnace No. 2	Hevi-Duty Kanthal A-1 Elements	800-1270	Trace	N_2 Purge in Jacket	252	
Melter Weir Heater	Kanthal A-1 Elements	600-1000	---	---	260	The weir heater burned out periodically and it never worked during the hot Runs PG-1 through PG-6.
Melter Freeze Valve Heater	Kanthal A-1 Elements	600-1000	---	---	48	The F.V. heater burned out periodically and during PG-5 it failed and was not replaced.
Melter Off Gas Line	Platinum-5% Iridium	150-600	-2 to -10	Sulfate and Nitrate Vapors	1035	--- --- ---
Melter Off Gas Line Heater	Nichrome Heating Wire	200-600	---	---	763	A hand wrapped heater was used for CPG-7, (a) the present heater was installed for radioactive operation
Melter Condenser (E-117)	Inner Shell, Tubes Drain-Nionel Outer Shell-SS	40-180	-2 to -10	Sulfate and Nitrate Vapors	1035	After 200 hr service, the SS line on the 5C rack was changed to nionel. For the in-cell runs (hot), the nionel drain line jumper has been used 473 hr.
Melter Solution Feeder	Platinum	100-120	---	Purex Type Wastes	1035	--- --- ---
Denitrator Airlift Pot No. 1a	304L SS	120-140	-5 to +5	Purex Type Wastes	310	Removed and replaced after CPG-7 due to excessive corrosion caused by adding 5 liters of 17.5M H_2SO_4 to the denitrator via the pot.
No. 1b	304L SS	120-140	-5 to +5	Purex Type Wastes	319	Removed and replaced after PG-4(b) due to inadequate remotable features.
No. 2	304L SS (Ti-Airlift Air Line)	120-140	-5 to +5	Purex Type Wastes	393	Installed prior to PG-5 to provide remotable feature.
Denitrator Evaporator (TK-121)	A-55 Ti	40-140	-2 to -10	Purex Type Wastes	1125	Evaporator airlift return line was corroded through following CPG-7 when 5 liters of 17.5M H_2SO_4 was added to the denitrator via the airlift pot.
Denitrator Tube Bundle	A-55 Ti	40-140	0 to 100 psig steam	Purex Type Wastes	1125	--- --- ---
Denitrator Agitator	SS Shaft, SS and Ti Impellers	40-140	---	Purex Type Wastes	914	After 330 hr the SS impeller was changed to A-55 Ti. The agitator ran backwards for PG-1 to 3. Used only intermittently after 914 hr due to radiolytic break down of bearing grease.
Denitrator Over Flow Pot	304L SS	30-50	-2 to -10	Dilute HNO_3	873	--- --- ---
Denitrator Seal Pot	304L SS	30-50	-2 to -10	Dilute HNO_3	873	--- --- ---
Denitrator Vacuum Breaker	304L SS	30-50	-2 to -10	H_2O	300	Removed from the racks after CPG-7.
Melt Receiver Pots	304L SS	100-900	Trace	Solidified Melt	185	No visible warping or bending. No detectable corrosion of stainless steel pots.
	Mild Steel				320	Mild Steel pots became externally corroded during water storage when reductants were not added to the water.
Receiver Furnace	Hastelloy X	100-900	---	Waste Pots	2348	Also used as pot calciner furnace. Delaminated insulation was completely replaced with Ceroform at 1025 hr just before radioactive service.
Screw Feeder	304L SS	115-125	---	Purex Type Wastes	63	Use discontinued after 13 hr run when drive motor failed.
Screw Feeder Motor		∿50 °C	0 to 90(c)	Cell Air	138	Failed after 13 hr in hot cell.

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a. CPG = "Cold" phosphate glass runs.
b. PG = "Hot" phosphate glass runs.
c. Air pressure, psig.

Seal Pots

Secondary vent lines from the denitrator-evaporator and melter were provided for relief of pressure if it increased to atmospheric level during operation. Water-seal pots in each of the two lines allow the pots to vent and overflow directly into the melter condensate tank.

The melter seal pot is an 8-inch diameter by 22-inch long section of pipe which is closed at each end and contains inlet and outlet piping designed so that maximum pressure differentials of up to 8 inches of water are required to allow gas to flow from the melter to the condensate tank. Seal water cannot flow backwards to the melter.

The denitrator-evaporator overflow seal pot is a 6-inch diameter by 17-inch long section of pipe which is closed at each end and contains inlet and outlet piping designed so that maximum pressure differentials of up to 12 inches of water are required to allow gas to flow to the condensate tank. The overflow seal pot was never needed for emergency venting of the denitrator during the five runs.

Receiver Pot Furnace

The six-zone induction-heated receiver pot furnace which has a temperature-controlled susceptor to transfer heat to or from the melt receiver wall performed well. Each zone was controlled to within ±10 °C of the set point without gross influence from adjacent zones while heating all zones to approximately 600 °C to permit slumping of the melt within the receiver. Zones below the melt level were unheated and were usually cooled. Indirect cooling by forced air around the outside of the susceptor was sufficient for the five phosphate glass runs and the furnace should be adequate for cooling pots containing up to 13 kilowatts of phosphate glass. This furnace is also the primary solidification furnace for the pot calcination process.

Process Condenser

The same process condenser is used for the vapors from all solidification processes in WSEP. A 304L stainless steel sleeve was installed at the inlet of the titanium condenser to prevent corrosion at this point after local sulfate corrosion occurred during early DVT runs. Corrosion coupons were installed in the liner prior to radioactive operation. These were made of A-55 titanium, 304L and 316L stainless steel, and Nionel. The coupons were inspected at the end of the first series of six pot calcination runs(3) and again after the first six and the second five phosphate glass runs. Although no increase in corrosion to either the liner or the coupons was visible, some deposits (up to 1/8 inch thick) were on the samples and in the liner. Laboratory analysis of the deposits indicated that they were probably entrained calcine, rather than ruthenium which was suspected.

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5.0 AUXILIARY PROCESS SYSTEMS PERFORMANCE

Conversion of high-level aqueous wastes to a solid results in one or more effluent streams with lower levels of radioactivity. These effluent streams must be reduced to nontoxic levels before the total benefits of solidification are truly realized. Therefore important to any waste solidification system are the auxiliary systems (primarily decontamination equipment) located downstream of the solidification systems. Demonstration of effluent cleanup (decontamination) is a significant part of the WSEP Program. This objective was established to investigate the parameters affecting the performance of the decontamination equipment and involves the following items:

- Providing data on decontamination of solidifier off-gases prior to their discharge to the atmosphere.
- Characterizing the secondary aqueous effluent streams from waste solidification.
- Evaluating the needs and methods for treating the secondary effluent streams.
- Establishing the performance characteristics of the individual decontamination equipment, i.e., condensers, evaporator, acid fractionator, filters, and scrubber.

Auxiliary equipment in support of a waste solidification system must be designed to assure that sufficient decontamination of secondary effluent streams is done so that these streams are acceptable for recycle to the fuel reprocessing plant or for final release to the environment.

Initial studies have indicated that the recovered nitric acid and water streams from the phosphate glass solidification processes can probably be recycled to a fuel reprocessing plant.(1) The recovered acid which is slightly contaminated can be recycled for possible use in fuel element dissolution and/or for possible use in solvent extraction scrub streams. Effluent recycle is based upon having solidification processing capabilities with each fuel reprocessing plant. If the solidification capabilities were not integrated with but were remote from the fuel reprocessing plant, the solidification plant would need a complete but smaller capacity version of the effluent waste treatment and acid recovery facilities. Shipping of high level aqueous waste and reusable effluents between the two plants would also be required. These conditions are believed to be impractical and unsafe.

Process auxiliaries that are necessary for a solidification system consist of equipment for (1) preparing aqueous waste solutions for feeding the solidifier, (2) decontaminating the solidifier off-gas, and (3) decontaminating the solidifier condensate and recovering nitric acid.

In the WSEP auxiliary system, vapors from the solidification system which are not acceptable for discharge without further treatment are first routed through a condenser to the evaporator. The solidifier condensate is concentrated in the evaporator (along with incoming feed in some cases). The vapors from the evaporator are first decontaminated from entrained aerosols in the evaporator tower by impengment plates, bubble caps, and a mist eliminator and then they are condensed. The evaporator condensate is further decontaminated and concentrated in the acid fractionator where nitric acid is recovered. The vapors from the fractionator are again condensed and about 80% of the fractionator distillate is recycled to the evaporator as acid stripwater while the remaining 20% is collected as an intermediate- to low-level waste stream. The remaining gases are treated by high efficiency filtration, scrubbing, and additional filtration before discharge to the atmosphere. Figure 5.1 illustrates the WSEP auxiliary process system.

The effluents resulting from the phosphate glass solidification process can be generalized as follows:

1) The immediate effluent (solidifier off-gases) has been decontaminated by factors of 7 to 20 so that it remains as an intermediate-level waste.
2) The decontamination of process off-gases by the WSEP auxiliary system is adequate for the final gaseous effluent stream, but is inadequate for the final aqueous effluent stream which is above 10CFR20 release limits by factors as high as 6×10^3.
3) The volumes and radionuclide content of the immediate effluent (evaporator bottoms) and recovered acid (fractionator bottoms) are relatively small and can be recycled to the solidifier feed and to a fuel reprocessing plant, respectively.

A summary of information on typical effluents resulting from the phosphate glass solidification process is presented in Table 5.1. During the last series of phosphate glass solidification runs (PG-7 through PG-11), from 5 to 14% of the radioruthenium fed to the solidifier was volatilized from the solidifier, while less than 0.1% of the nonvolatile radioactive species were entrained. These values were typical of the first series of phosphate glass runs. During this last series of runs as with the first series, the melter condensate which contained most of the volatilized and entrained materials

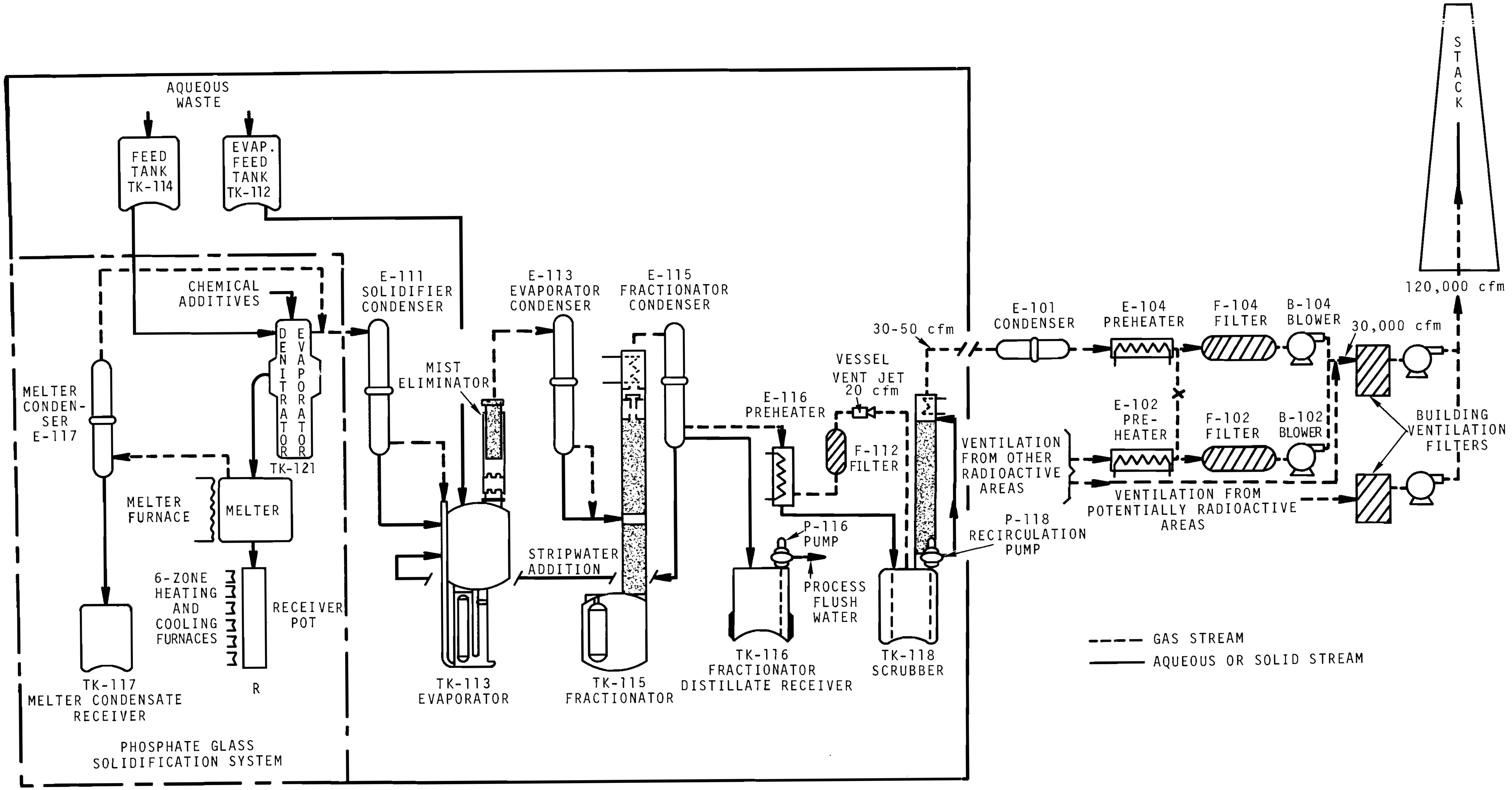

FIGURE 5.1. WSEP Auxiliary Process System

TABLE 5.1. Typical Effluents During Mode A Operation[a] (based on the last five phosphate glass runs)

Stream	Solution	Volume,[b] liters/ liter feed	Radioactive Ruthenium, Ci/Ci in feed	Gross Radioactivity Less Ruthenium, Ci/Ci in feed	Potential Disposal
Evaporator Bottoms	5$\underline{M}$ HNO_3	0.7[c]	4.8×10^{-3}	1.3×10^{-5}	Recycle to solidifier feed or to fuel reprocessing plant waste concentrator
Acid Fractionator Bottoms	9$\underline{M}$ HNO_3	0.3	5.2×10^{-4}	1.3×10^{-6}	Reuse in fuel reprocessing plant
Fractionator Distillate	0.01$\underline{M}$ HNO_3	0.6	2.2×10^{-7}	2.6×10^{-9}	Reuse in fuel reprocessing plant
Scrubber Bottoms	2$\underline{M}$ NaOH	0.7[d]	6.3×10^{-7}	NDG	Intermediate level treatment or combine with high level waste
Final Off-Gas from Scrubber	Air	2200	1.4×10^{-9}	2.3×10^{-12}	To building ventilation filters and atmosphere
Final Off-Gas to Stack	Air	---	$<9 \times 10^{-10}$	$<7 \times 10^{-13}$	To atmosphere

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NDG No detectable gain in radioactivity.

a. Run PG-11 data was used as representative of Mode A operation (see Appendix Table 9.5).

b. Volumes include additions to system (see Appendix, Table 9.4). Fractions do not sum to 1.0 since actual data was used.

c. The starting volume in the WSEP evaporator varied from 300 to 500 liters. This solution can remain in the evaporator for several runs.

d. The starting volume in the scrubber varied from 400 to 500 liters. This solution can remain in the scrubber for several runs.

was collected separately. An average of only 0.71% of the radioruthenium and 0.042% of the nonvolatiles were in the denitrator off-gas which was condensed and collected in the auxiliary evaporator for further treatment.

During commercial processing of aqueous wastes using the phosphate glass solidification process, the melter off-gas can be combined with the denitrator off-gas and decontaminated by the auxiliary system. Also, the melter off-gases could be condensed and recycled to the denitrator feed or directly to the evaporator.

5.1 OPERATING MODES

The need to demonstrate how the treatment of effluents from solidification can be integrated into a fuel reprocessing plant using existing equipment such as waste evaporator and acid recovery system or done separately prompted the selection of three different operating modes in WSEP. These are designated in WSEP as Mode A, B, and C; and are described in References 2 and 3. Figure 5.2 shows the three operating mode options for WSEP. To date, Mode A and B were tested with the phosphate glass solidification process; Mode C was not tested.

Applications of the modes in a fuel reprocessing plant are visualized as shown in Figure 5.3. During Mode A operation, the evaporator bottoms is an additional effluent stream which must be recycled back to the solidifier feed or to the waste concentrator in a fuel reprocessing plant. In Mode B and C operation, the evaporator bottoms are mixed with incoming waste. Typical effluent data for Mode A operation for the auxiliary system during the last series of phosphate glass was summarized in Table 5.1. The only Mode B Run was Run PG-8.

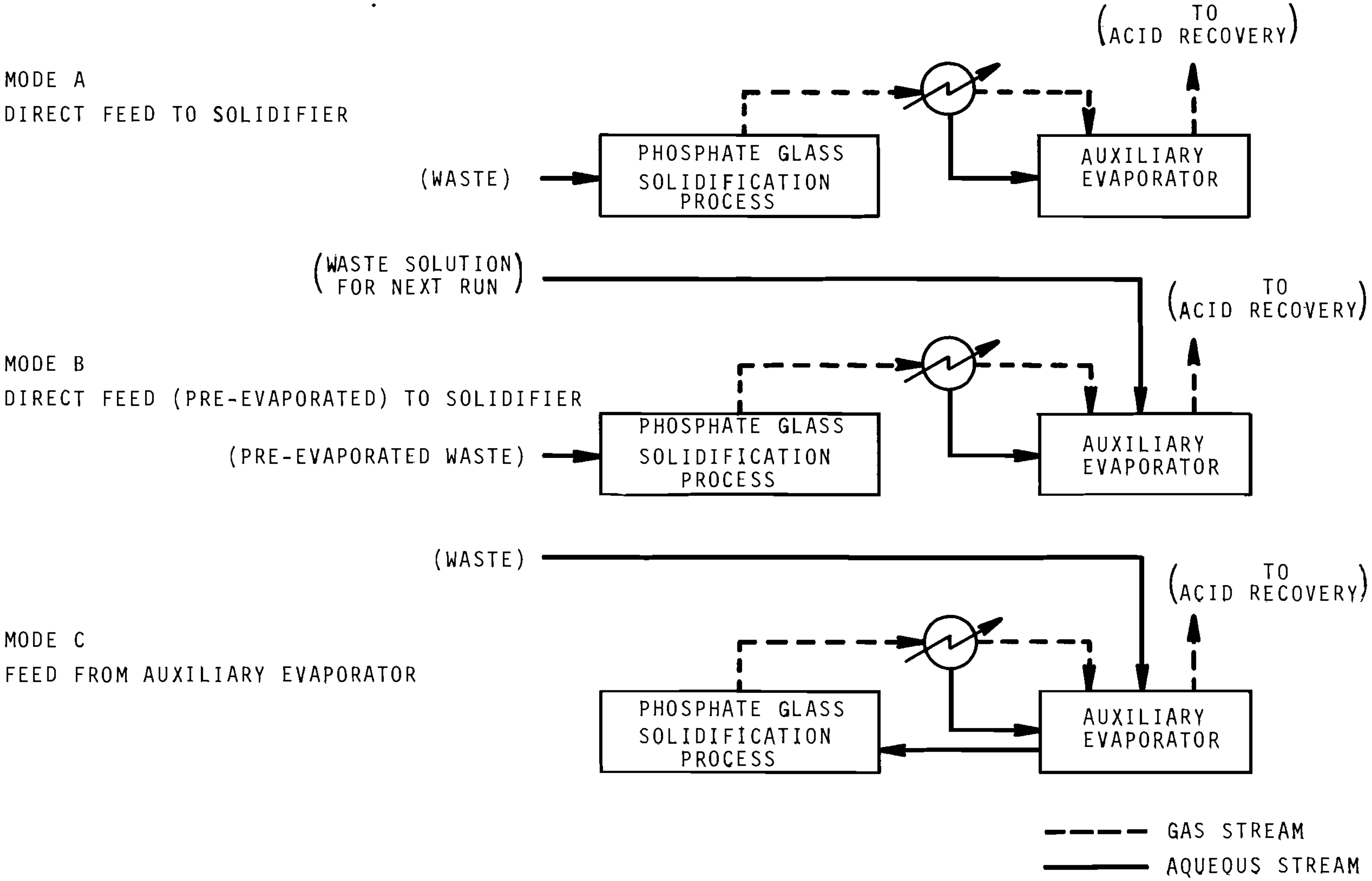

FIGURE 5.2. WSEP Process Mode Options

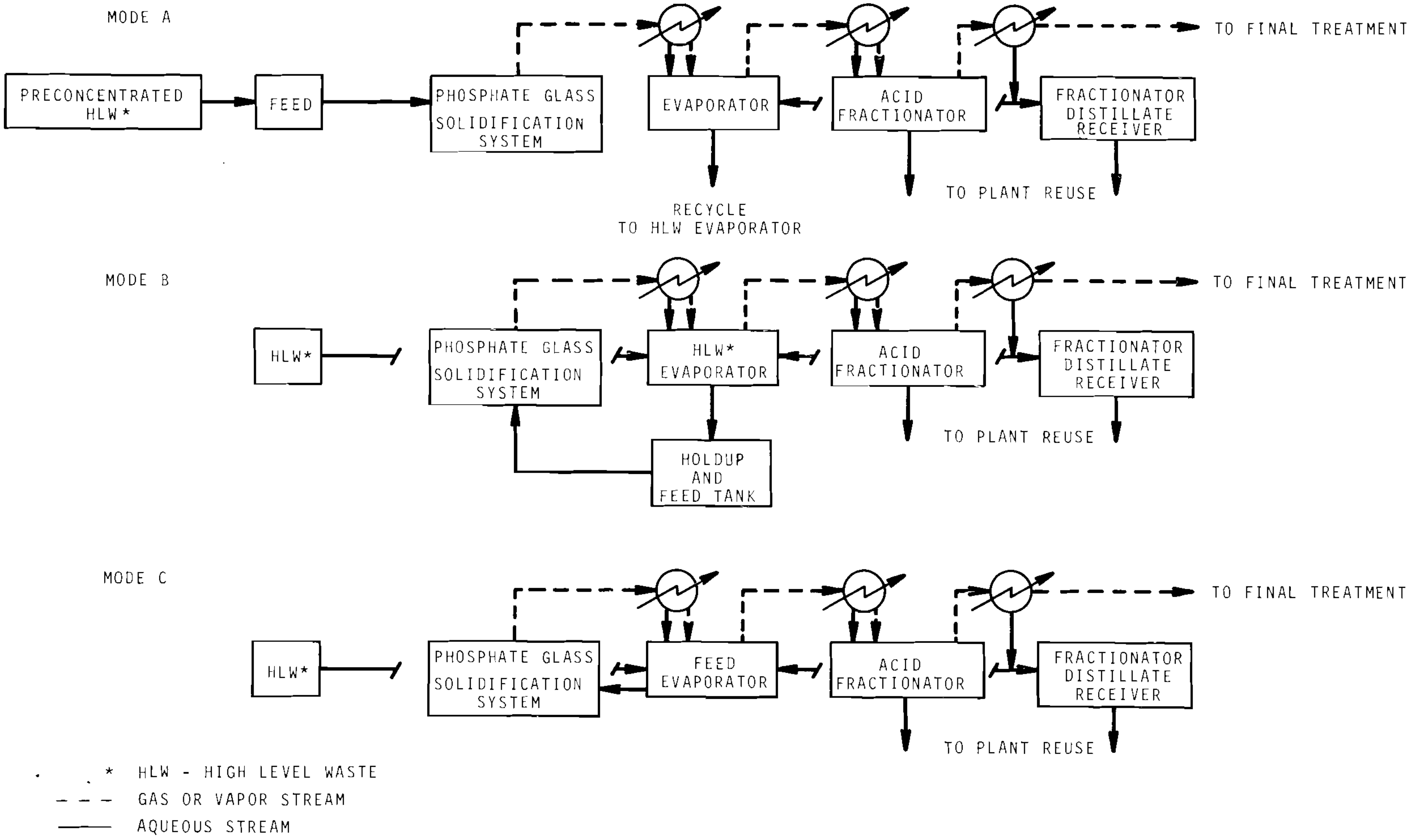

FIGURE 5.3. Operating Mode Applications in a Fuel Reprocessing Plant

Although waste solution is fed to the evaporator during Mode B and C, ruthenium in the evaporator effluent is more dependent on other factors such as acid concentration in the evaporator bottoms, evaporator boilup rate, and fraction of ruthenium volatilized from the solidifier. Thus, the difference in the ruthenium concentration in the evaporator and fractionator effluent streams with different operating modes is generally less than the difference between the ruthenium concentration in the evaporator and can be minor.

The ruthenium concentration in the fractionator bottoms and distillate will probably allow these streams to be reused in a fuel reprocessing plant. The acid fractionator bottoms can probably be reused in fuel dissolution and in the first cycle solvent extraction scrub solution, and thus will not require further cleanup. The acid fractionator distillate can also probably be reused in the first cycle of the fuel reprocessing plant. To be released to the environment, the fractionator distillate stream (final aqueous effluent) would require additional decontamination.

Mode C operation was not demonstrated during the phosphate glass runs because it would have required continuous boiling of the phosphate containing feed. The degree of feed pre-evaporation which would be gained by Mode C operation is not needed because of the capacity of the denitrator-evaporator.

5.2 RUTHENIUM CONTROL

The process effluents from phosphate glass solidification are contaminated primarily by volatilized ruthenium. The complexity of ruthenium can be seen in Reference 4 by the many ranges of values for ruthenium volatilization in nitric acid solutions. Some correlations do exist for very specific solutions, but the volatilization for a constant bottoms acidity ranges as much as five orders of magnitude, and depends largely on the net oxidizing potential due to the presence of other ingredients in the solution. Ruthenium tetroxide (RuO_4) has been established(4,5) as the principal volatile form of ruthenium from boiling nitric acid solutions. Several general relationships apply to minimizing the volatilization of ruthenium:(4,6)

- Maintaining a low concentration of HNO_3 in the bottoms and resulting overheads.
- Lowering the temperature of distillation by means of vacuum distillation.
- Adding reducing agents (e.g., sugar and phosphite) into the solution.

A combination of these methods may prove advantageous.

During the last series of phosphate glass solidification runs, the WSEP auxiliary evaporator was operated with a bottoms acidity of less than 6$\underline{M}$ HNO_3 and a overhead acidity of less than 1$\underline{M}$ HNO_3, thus reducing the potential for ruthenium volatilization. Volatilization of ruthenium was typically kept below 2% of that present in the evaporator bottoms. It may be desirable to decrease the ruthenium volatilization from the evaporator by the continuous addition of a reductant to the evaporator. Reductants have been shown to decrease ruthenium volatility,(6-9) but no such reductants were added to the evaporator during the last series of phosphate glass runs.

During the last five phosphate glass solidification runs, from 0.48 to 0.88% of the radioruthenium fed to the solidifier was volatilized from the denitrator and accumulated in the auxiliary evaporator. Figure 5.4 presents the accumulation of radioruthenium in the WSEP auxiliaries as a function of run duration for Mode A operation.

The auxiliary evaporator serves as a decontamination stage between the phosphate glass solidifier and the nitric acid fractionator. The evaporator was operated with a bottoms acidity of 4 to $5\underline{M}$ HNO_3. Stripwater (fractionator distillate) was recycled back to the evaporator to strip nitric acid while maintaining the evaporator overheads between 0.2 and $0.4\underline{M}$ HNO_3. Auxiliary evaporator operating conditions for Runs PG-7 through PG-11 are shown in the appendix in Figures 9.9 through 9.13. These include: volume, specific gravity, solution temperature, stripwater addition rate, and overhead acidity. Typical auxiliary evaporator operating conditions are shown in Figure 5.5. Other operating data for the evaporator as well as other auxiliaries is presented in Table 9.2 in the Appendix.

Performance of the auxiliary system was mainly assessed by determining the decontamination factors at each stage in the system. Data on decontamination factors across the evaporator and fractionator are presented in Table 5.2 to show the effects of evaporator bottoms and overhead acid concentration on ruthenium DF's. Cumulative ruthenium DF's (DF_c)(a) across the evaporator varied from a low of 15 to a high of 580 and averaged about 50. The lowest DF_c occurred in the Mode A portion of Run PG-8 while the highest DF_c occurred in the Mode B portion of Run PG-8. The increase in the

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(a) Total curies of ruthenium in evaporator bottoms at end of run from any source/total curies of ruthenium gained in the fractionator.

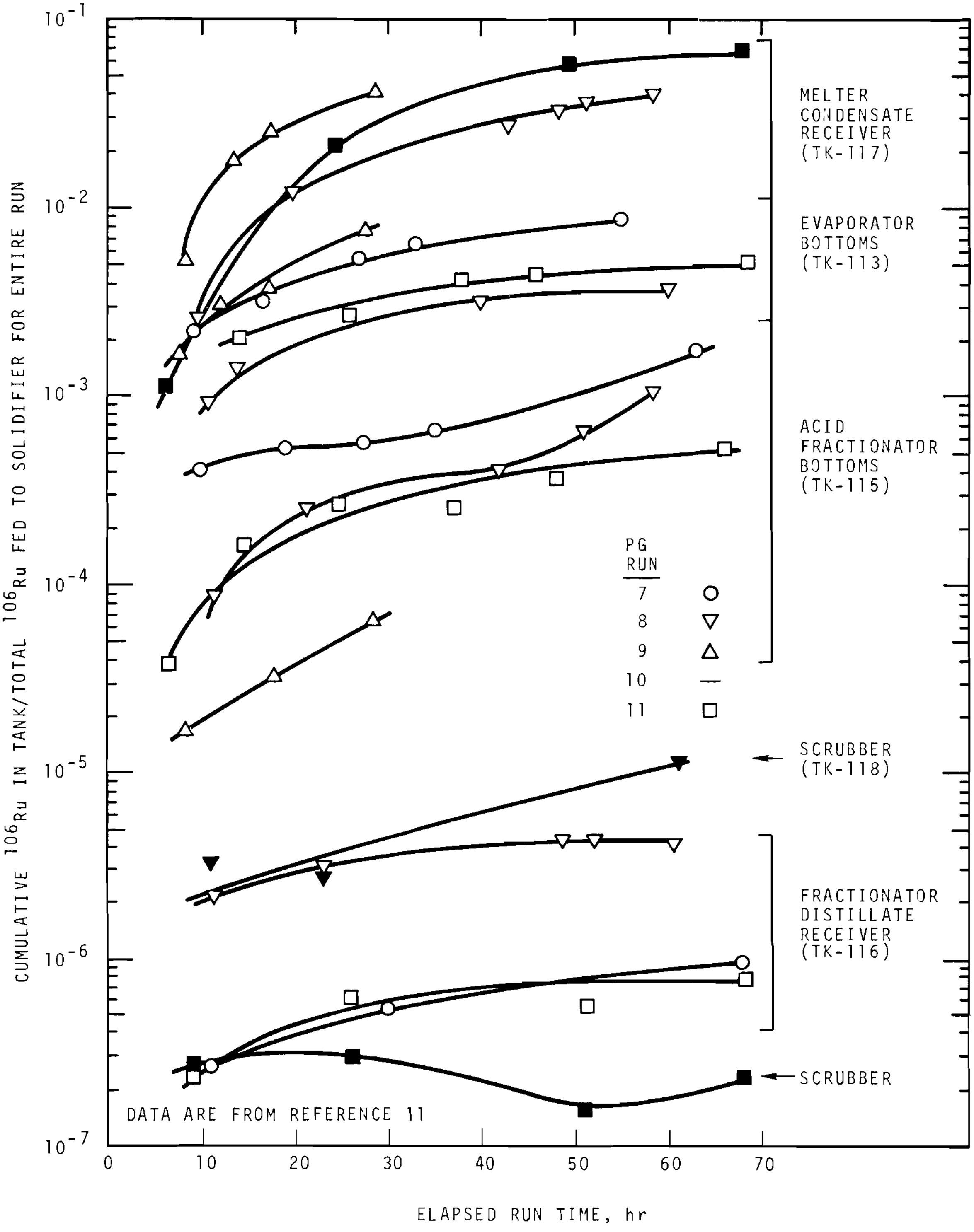

FIGURE 5.4. Radioruthenium Accumulation in the WSEP Auxiliaries

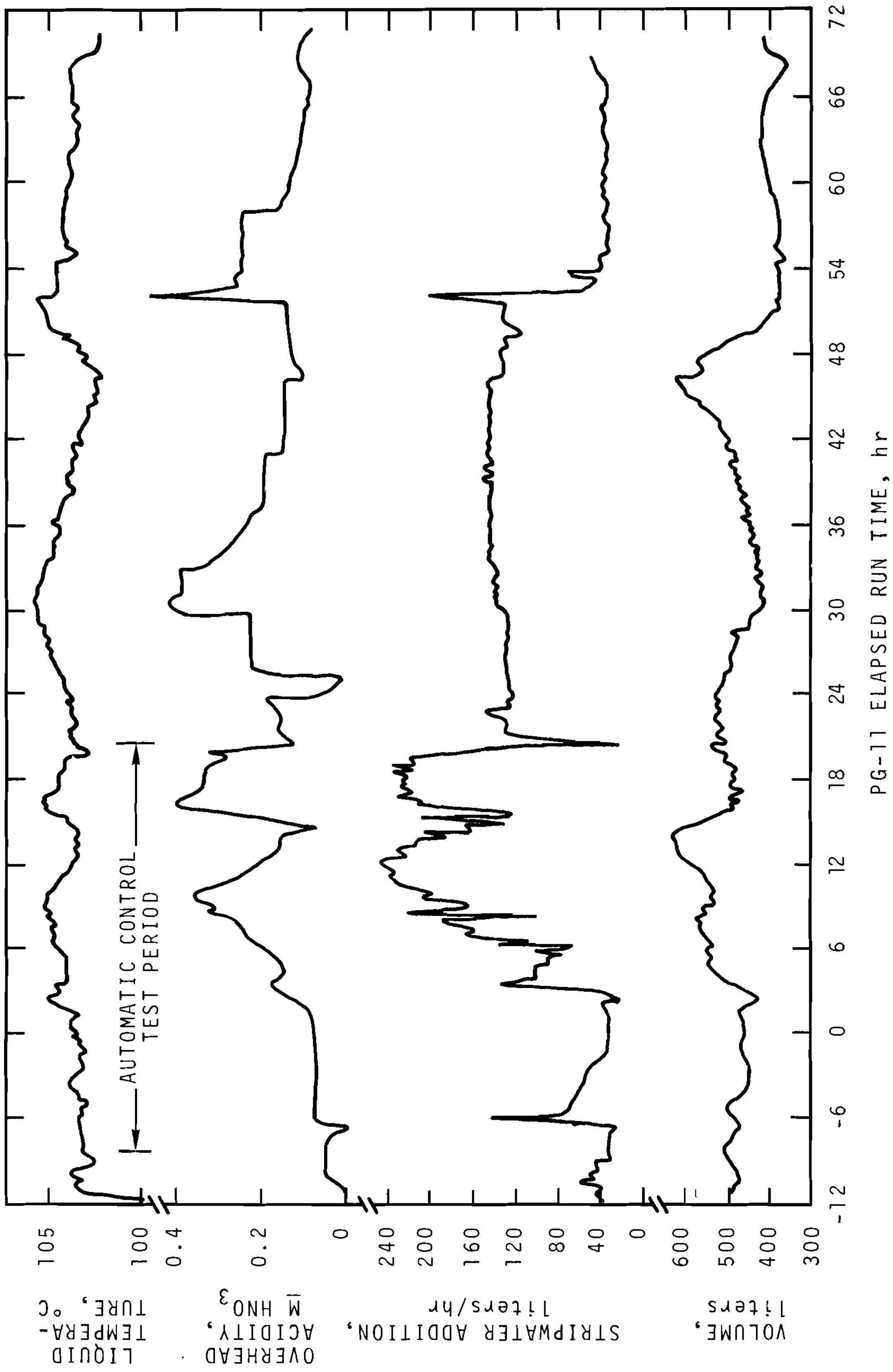

FIGURE 5.5. Typical WSEP Auxiliary Evaporator Operating Parameters

TABLE 5.2. Radioruthenium and Radiocerium Decontamination Factors Across WSEP Auxiliary Evaporator and Fractionator

		Evaporator							Fractionator			
				Average Acidity, M HNO_3		Cumulative Radioruthenium	Cumulative Radiocerium	Instantaneous Radiocerium	Average Acidity, M HNO_3		Cumulative Radioruthenium	Cumulative Radiocerium
PG Run	Mode	Solution in Evaporator	Additive	Bottoms	Distillate	DF(a)	DF(a)	DF(b)	Bottoms	Distillate	DF(c)	DF(c)
7	A	Nitric Acid Plus Denitrator Condensate	Stripwater	5	0.4	4.9×10^1	2.7×10^4	10^5	7	0.02	1.5×10^3	8.3×10^3
8	A	Nitric Acid Plus Denitrator Condensate	Stripwater	5	0.3	1.5×10^1	NA	10^2 to 10^3	9	0.03	1.5×10^1	$>2.4 \times 10^3$
8	B	Nitric Acid, Denitrator Condensate and HL Waste	Stripwater	5	0.3	5.8×10^2	1×10^5	10^2	8	0.02	5.8×10^2	9.5×10^4
9	A	Nitric Acid Plus Denitrator Condensate	Stripwater	5	0.2	1.4×10^2	1.9×10^3	10^2 to 10^3	8	0.02	2.0×10^3	NA
10	A	Nitric Acid Plus Denitrator Condensate	Stripwater	4	0.3	2.9×10^2	1.9×10^3	10^2 to 10^3	9	0.02	8.0×10^3	NA
11	A	Nitric Acid Plus Denitrator Condensate	Stripwater	4	0.2	4.8×10^1	1.9×10^4	10^4 to 10^5	9	0.02	2.7×10^3	9.1×10^2

NA Not Available

a. Total curies of component in evaporator at end of run/total curies gained in the fractionator.

b. Instantaneous concentration of component in evaporator/instantaneous concentration in the condensed evaporator overheads.

c. Total curies of component in fractionator at end of run/total curies gained in fractionator distillate receiver.

ruthenium DF_c during the Mode B portion of Run PG-8 is due to the method of calculating the DF. During the Mode B portion of Run PG-8, about 700 liters of 1WW containing 1.3×10^5 curies of total radioactivity were transferred to the evaporator in 50 liter batches, hourly. During the Mode B operation the accumulation of radioruthenium in the fractionator did increase by a factor of 17 indicating an appreciable increase in ruthenium volatilization from the evaporator bottoms but this still was within the range of Mode A data attained from the other runs. This increased ruthenium volatilization was due to the increased ruthenium concentration in the evaporator bottoms and increased boilup rate during Mode B.

The radionuclide distribution for these last five phosphate glass runs is summarized in Table 5.3. From 0.2% during the Mode B portion of Run PG-8 to 7% during the Mode A portion of Run PG-8 of the equivalent radioruthenium present in the evaporator bottoms at the end of the run accumulated in the fractionator bottoms. In general, these values were typical of previous WSEP runs.(2,3,10) These values indicate that the accumulation of ruthenium in the fractionator is not a direct function of the ruthenium present in the evaporator since the accumulation of ruthenium in the fractionator does not follow ruthenium increases in the evaporator. This suggests that gas phase carryover of ruthenium from the solidifier condenser off-gas is more important than the volatilization of ruthenium from the evaporator.

The problem of ruthenium volatilization from the WSEP auxiliary evaporator was investigated by defining instantaneous DF's (DF_i's)(b) across the evaporator. Generally, these DF_i's for the first series of phosphate glass solidification and pot calcination runs varied inversely with the nitric acid concentration in the

TABLE 5.3. Radionuclide Distribution in WSEP Auxiliaries for Phosphate Glass Solidification Runs PG-7 Through PG-11

	Fraction of Equivalent Feed Radioactivity in Effluent Streams[a] for Total Run									
	^{106}Ru (Radioruthenium)					^{144}CePr (Radiocerium)				
PG Run	7	8[e]	9	10[c]	11	7	8	9	10	11
Melter Condensate Receiver (TK-117)	7.0×10^{-2}	4×10^{-2}	4.7×10^{-2}	NA	6.6×10^{-2}	4.1×10^{-4}	4.0×10^{-4}	5.4×10^{-4}	3.1×10^{-4}	4.1×10^{-4}
Evaporator (TK-113)	8.5×10^{-3}	6.2×10^{-3}	8.8×10^{-3}	NA	4.8×10^{-3}	8.2×10^{-6}	2.9×10^{-4}	6.3×10^{-4}	3.6×10^{-4}	1.3×10^{-5}
Fractionator (TK-115)	1.6×10^{-3}	1.4×10^{-3}	7.6×10^{-5}	NA	5.2×10^{-4}	1.7×10^{-6}	NDG	8.0×10^{-7}	4.9×10^{-7}	1.3×10^{-6}
Fractionator Distillate Receiver (TK-116)	1.0×10^{-6}	2.8×10^{-6}	6.5×10^{-7}	NA	2.2×10^{-7}	2.4×10^{-10}	3.7×10^{-10}	2.8×10^{-8}	3.2×10^{-9}	2.6×10^{-9}
Scrubber (TK-118)	6.5×10^{-9}	1.3×10^{-5}	NDG	NA	6.3×10^{-7}	NDG	1.6×10^{-7}	NDG	NDG	NDG
Off-Gas from Scrubber[d]	1.1×10^{-7}	9.9×10^{-9}	3.5×10^{-9}	NA	1.4×10^{-9}	7.1×10^{-10}	2.7×10^{-11}	6.9×10^{-12}	3.5×10^{-12}	2.3×10^{-12}
Off-Gas to Stack[d,e]	$<1.6\times10^{-10}$	$<3\times10$	$<3.0\times10^{-10}$	NA	$<9\times10^{-10}$	$<3.0\times10^{-13}$	5×10^{-12}	1.2×10^{-13}	5.2×10^{-14}	$<7.3\times10^{-13}$
Ratio (Fract. Dist. Radioactivity to 10CFR20)	2.5×10^{3}	5.6×10^{3}	1.6×10^{3}	NA	2.2×10^{3}	55	89	3.5×10^{3}	2.2×10^{3}	1.5×10^{3}
Ratio (Scrubber Off-Gas Radioactivity to 10CFR20)	4.8×10^{3}	3.3×10^{2}	1.4×10^{2}	1.4×10^{2}	1.5×10^{2}	3.0×10^{3}	1.1×10^{2}	18	9	10
Ratio (Stack Off-Gas Radioactivity to 10CFR20)	$<4\times10^{-4}$	$<1.8\times10^{-4}$	$<4\times10^{-4}$	$<4\times10^{-4}$	$<4\times10^{-4}$	$<1.0\times10^{-4}$	2.8×10^{-4}	1.4×10^{-4}	1.4×10^{-4}	$<7.7\times10^{-4}$

Data are from References 11, 12 and 14.

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a. Total curies of component gained in auxiliary tank/Total curies of component fed to solidifier for total run
b. Run PG-8 was a Mode A and Mode B run.
c. No radioruthenium was present in feed.
d. Total curies of component in off-gas/Total curies of component fed to solidifier
e. Based on total noncondensible gas flow of 20 scfm
NA Not Available
NDG No Detectable Gain

evaporator bottoms and resulting distillate as shown in Figure 5.6.(2,10) This indicated that ruthenium volatility increases with increasing acidity in the evaporator bottoms. However, during the last series of five phosphate glass solidification runs there was no apparent correlation of DF_i and the distillate acidity. These generally low DF_i's for ruthenium are attributed to vapor phase flow of ruthenium from the solidifier which was only partially scrubbed in the solidifier condenser as indicated by the presence of ruthenium in the solidifier condenser off-gas. From 1.5×10^{-4} $\mu Ci/cm^3$ of ^{106}Ru during Run PG-10 where no radioruthenium was present in the feed to 2.1×10^{-2} $\mu Ci/cm^3$ of ^{106}Ru during Run PG-8 was present in the solidifier condenser off-gas.

The DF's across the solidifier condenser for radioruthenium were generally about 40 (about 2.5% of the ruthenium in the solidifier off-gas remained unscrubbed and in the condenser off-gas). Average concentrations of radionuclides in the process off-gas are summarized in Table 5.4 while DF's across the WSEP process condensers and process off-gas filter are summarized in Table 5.5. This vapor phase flow of ruthenium apparently had less effect on DF_i's during the first six phosphate glass and pot calcination runs. Another possible cause of the generally low DF_i's and no correlation between DF's and evaporator distillate acidity could be the contamination of the auxiliary system by the continual buildup or adsorption of ruthenium on the stainless steel piping and other auxiliary equipment. Stainless steel has been shown to adsorb ruthenium(12) onto its surface.

Most of the ruthenium that volatilizes from the evaporator is condensed by the evaporator condenser and accumulated in the fractionator. From 4.9×10^{-6} to 3.0×10^{-5} $\mu Ci/cm^3$ of ^{106}Ru were present in the evaporator condenser off-gas. Ruthenium DF's across the evaporator condenser averaged 330. This was a factor of about 8 increase over the denitrator solidifier condenser.

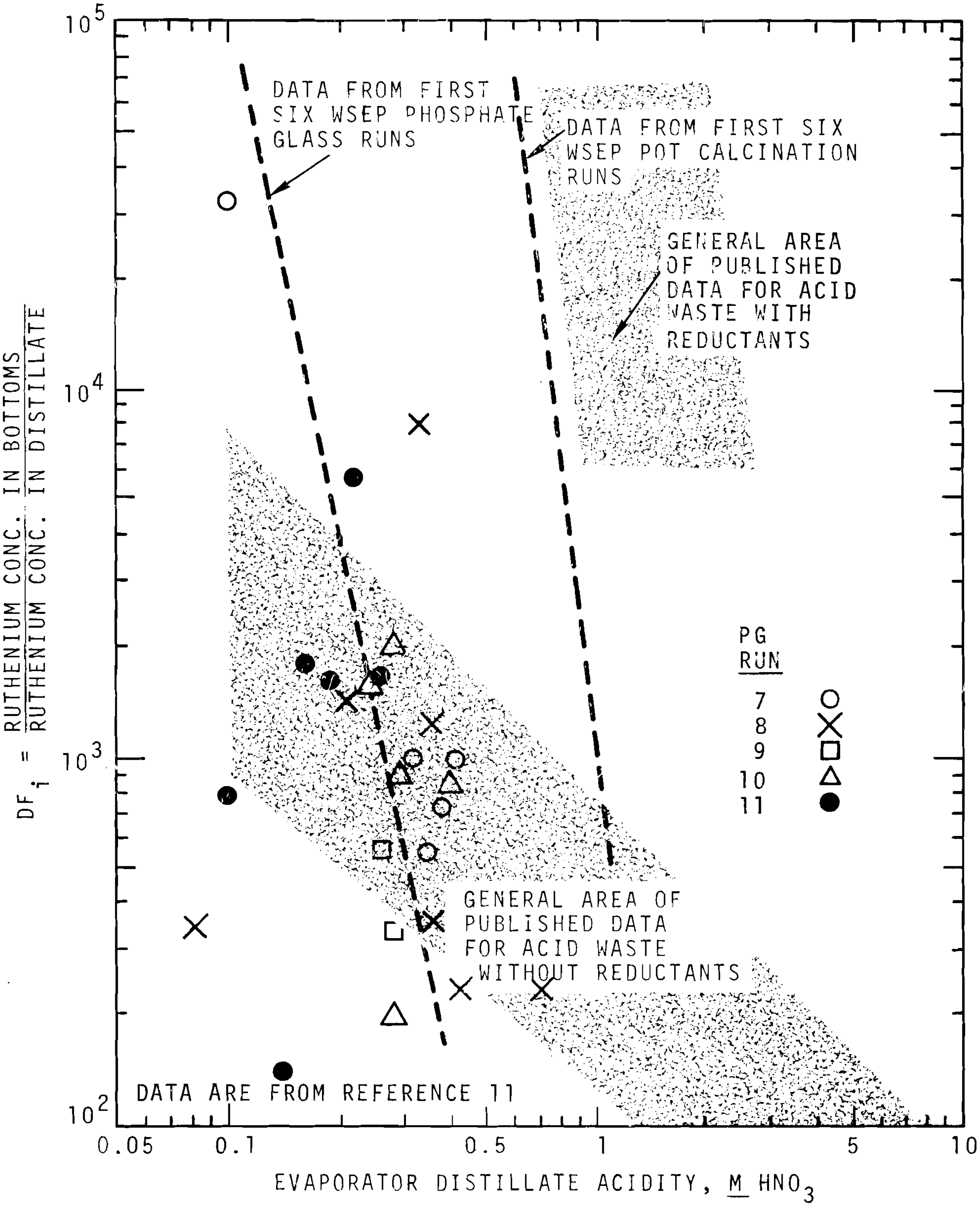

FIGURE 5.6. Volatilization of Radioruthenium from the WSEP Auxiliary Evaporator

TABLE 5.4. Average Concentration of Radionuclides in the Process Off-Gas for the Phosphate Glass Solidification Runs PG-7 Through PG-11

Run No.	Mode	Denitrator Condenser (E-111) Off-Gas, μCi/cm^3			Evaporator Condenser (E-113) Off-Gas, μCi/cm^3			Fractionator Condenser (E-115) Off-Gas, μCi/cm^3		
		^{106}Ru	^{137}Cs	^{144}CePr	^{106}Ru	^{137}Cs	^{144}CePr	^{106}Ru	^{137}Cs	^{144}CePr
7	A	3.2×10^{-3}	2.1×10^{-5}	1.1×10^{-4}	3.0×10^{-5}	9.8×10^{-7}	3.6×10^{-4}	---	---	---
8	A,B	2.1×10^{-2}	3.2×10^{-4}	1.3×10^{-3}	1.6×10^{-5}	3.9×10^{-7}	1.1×10^{-5}	1.9×10^{-7}	7.5×10^{-8}	2.5×10^{-6}
9	A	2.9×10^{-3}	3.2×10^{-5}	1.0×10^{-4}	6.0×10^{-6}	2.5×10^{-6}	2.1×10^{-5}	9.0×10^{-8}	6.7×10^{-8}	1.4×10^{-5}
10[(a)]	A	1.5×10^{-4}	8.9×10^{-5}	1.5×10^{-3}	4.9×10^{-6}	3.3×10^{-7}	1.6×10^{-5}	9.3×10^{-8}	8.3×10^{-8}	3.8×10^{-5}
11	A	2.2×10^{-2}	1.0×10^{-4}	3.7×10^{-4}	2.1×10^{-5}	8.2×10^{-7}	1.6×10^{-4}	9.6×10^{-7}	1.1×10^{-7}	1.7×10^{-5}

Run No.	Mode	Off-Gas from Filter (F-112) to Scrubber, μCi/cm^3			Final Process Off-Gas from Scrubber, μCi/cm^3		
		^{106}Ru	^{137}Cs	^{144}CePr	^{106}Ru	^{137}Cs	^{144}CePr
7	A	---	---	---	9.6×10^{-7}	1.0×10^{-6}	1.2×10^{-6}
8	A,B	---	---	---	6.5×10^{-8}	4.1×10^{-8}	4.4×10^{-8}
9	A	2.2×10^{-8}	3.4×10^{-8}	2.2×10^{-7}	2.7×10^{-8}	1.0×10^{-8}	5.5×10^{-9}
10[(a)]	A	5.6×10^{-8}	3.7×10^{-8}	4.6×10^{-8}	2.4×10^{-8}	8.2×10^{-9}	5.7×10^{-9}
11	A	---	---	1.9×10^{-8}	3.0×10^{-8}	5.0×10^{-8}	3.9×10^{-9}

---

a. No radioruthenium in feed to solidifier

TABLE 5.5. Decontamination Factors Across the Process Condensers and Process Off-Gas Filter

	Average DF(a)									
	^{106}Ru					^{144}CePr				
PG Run	7	8	9	10	11	7	8	9	10	11
Denitrator Condenser (E-111)	45	40	36	41	2000	63	60	1800	450	10
Auxiliary Evaporator Condenser (E-113)	200	200	150	320	800	66	70	440	390	30
Fractionator Condenser (E-115)	NA	NA	370	NA	200	NA	NA	380	NA	NA
High Efficiency(b) Filter (F-112)	NA	NA	1.7-9.4	2.1-7.1	NA	NA	NA	130-800	330-1700	4000

---

a. DF = Average concentration of component in off-gas to condenser/average concentration of component in condenser off-gas.

b. DF = average concentration of component in off-gas to filter/average concentration of component process off-gas leaving the filter prior to entering the scrubber.

NA Not Available.

A total of 7.6×10^{-3} to 5.4×10^{-1}% of the equivalent ruthenium fed to the solidifier accumulated in the fractionator. The fractionator nitric acid concentration was maintained at about 7 to 9$\underline{M}$, and the resulting fractionator overheads acidity ranged from 0.006 to 0.02$\underline{M}$ HNO_3 using a tower internal reflux ratio varying from about 0.1 to 0.5. The ruthenium DF_c across the fractionator varied from a low of 15 in the Mode A portion of Run PG-8 to 8.0×10^3 in Run PG-10 where no radioruthenium was fed to the solidifier. The ruthenium DF_i's across the fractionator ranged from less than 100 to greater than 1000 and were typically greater than 100. The low DF_i's probably were caused by contaminated fractionator distillate stream samples. These samples are intermediate-level samples that were handled in-cell which could result in some contamination of the samples.

Ruthenium that escapes the WSEP acid fractionator is mostly condensed by the fractionator condenser and then either recycled back to the evaporator as stripwater or accumulated in a separate distillate receiver or both. Typically 90% of the fractionator distillate was recycled back to the evaporator while the remaining 10% was accumulated in the fractionator distillate receiver. The distillate receiver accumulated from 2.2×10^{-5} to 2.8×10^{-4}% of the equivalent ruthenium fed to the solidifier during the last five runs. The fractionator distillate (final aqueous process effluent) from the last five runs average about 3×10^{-6} Ci/liter of radioruthenium. This concentration is above 10CFR20 release limits by a factor of 3000. Typical auxiliary tank volumes including the acid fractionator are shown in Figure 5.7. Average stripwater rates to and boiloff rates from the evaporator are listed in the Appendix Table 9.2.

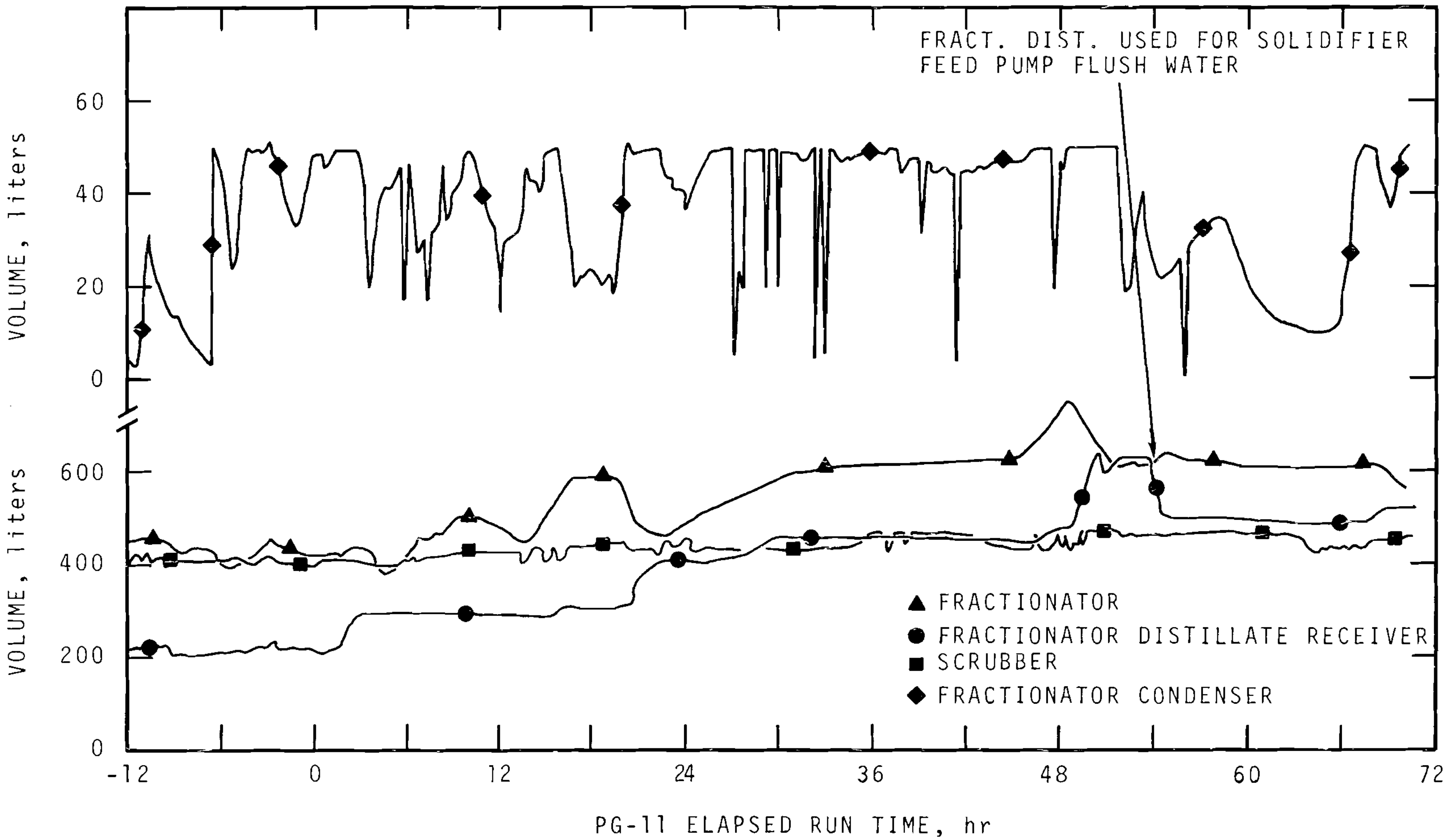

FIGURE 5.7. Typical Auxiliary Tank Volumes

Approximately 10 scfm of noncondensible gases leaving the fractionator condenser are filtered through a high efficiency filter before entering the off-gas scrubber. The filtering efficiency for radioruthenium based on gas samples ranged from 40 to 90% during Runs PG-9 and PG-10. Most of the remaining radioruthenium in the process off-gas was removed in the off-gas scrubber where from 6.5 x 10^{-7}% of the equivalent radioruthenium fed to the solidifier during Run PG-7 to 1.3 x 10^{-3}% during Run PG-8 accumulated in the scrubber bottoms. Accumulation of radioruthenium in the scrubber during Runs PG-8 and PG-11 is shown in Figure 5.4.

The final process off-gas leaving the off-gas scrubber contained concentrations of radioruthenium that were factors of 140 to 4800 above 10CFR20(17) release limits. However, the final process off-gases are filtered twice more and discharged into the main building ventilation system where they are mixed with about 120,000 scfm of air before entering the stack. This large dilution by the main building ventilation flow and the additional filtration reduced the ruthenium concentration to below detection limits for the available counting equipment. During the last five phosphate glass solidification runs, the radioruthenium in the stack gases was at least 2500 times less than the 2 x 10^{-10} μCi/cm^3 10CFR20(17) release limit. This value is conservative because it assumes all radioruthenium emitted to the off-gas is from WSEP processing. Other sources of radionuclides in the facility are ventilation air from eight other high level radioactivity cells and process vent effluents from other in-cell activities.

The primary factor influencing the evaporator and the fractionator DF's is the fraction of the volatilized ruthenium and the mechanism by which the ruthenium is removed in the towers and overhead condensers. A mechanism based on the diffusion of the airborne ruthenium from the gas stream to the wetted walls of a downdraft condenser was assumed in the mathematical modeling of the WSEP auxiliary off-gas train.(16) The diffusion model for the condenser suggests that the inadequately scrubbed ruthenium leaving in the solidifier condenser off-gas has at least as much influence on the DF's across the evaporator and the fractionator as does the quantities of ruthenium volatilized and/or entrained from the evaporator and the fractionator bottoms under normal operating conditions. The mathematical model of the behavior of the airborne ruthenium suggests that prior to the high efficiency filters and the scrubber in the auxiliary off-gas train, the auxiliary equipment is not ideally suited for the removal of ruthenium.

Gas sample data from the denitrator condenser off-gas as previously discussed, suggest that additional or modified equipment is needed to remove more of the gaseous and particulate ruthenium from the denitrator off-gas. The use of improved gas-liquid contacting equipment (e.g., a condenser packed with efficient contacting surfaces) for gas removal and a high efficiency filter for particulate removal should substantially improve the ruthenium DF's. Such a system was designed and used in the last series of spray solidification demonstrations.

In conclusion, the ruthenium decontamination factors for the effluent from phosphate glass solidification are largely influenced by the scrubbing efficiency of the towers and overhead condensers for removal of ruthenium vapors and by internal contamination of the auxiliary system.

5.3 CONTROL OF OTHER RADIONUCLIDES

With phosphate glass solidification a relatively small amount (less than 0.06%) of nonvolatile constituents were entrained from the denitrator-evaporator and accumulated in the auxiliary evaporator. Cumulative decontamination factors (DF_c) for nonvolatiles represented by ^{144}CePr across the WSEP evaporator ranged from 1.9×10^3 to 1.0×10^5. Instantaneous decontamination factors (DF_i's) for nonvolatiles across the auxiliary evaporator based on ^{144}CePr ranged from about 10^3 to 10^5. These data agree quite well with data from the first series of phosphate glass(1) and pot calcination(9) and spray solidification(2) runs.

Typical entrainment from the WSEP auxiliary evaporator was less than 0.66% of the nonvolatiles present in the evaporator. The overall DF's for nonvolatiles represented by ^{144}CePr from the original aqueous waste through the auxiliary system to the recovered acid in the fractionator were typically 10^6. Comparable DF's to the fractionator distillate were typically 10^9. Accumulation of nonvolatile radionuclides in the WSEP auxiliaries is shown in Figure 5.8.

The WSEP phosphate glass solidifier off-gases contained about 10 scfm of air from inleakage. The presence of this noncondensable gas phase significantly affects decontamination and efforts to keep air inleakage minimized should be applied to commercial applications. The air flow through the system probably caused some increase in ruthenium carryover through the auxiliaries. Overall, the nonvolatile constituents in the noncondensable gas flow were sufficiently removed by the auxiliary system to levels that were insignificant compared to radioruthenium.

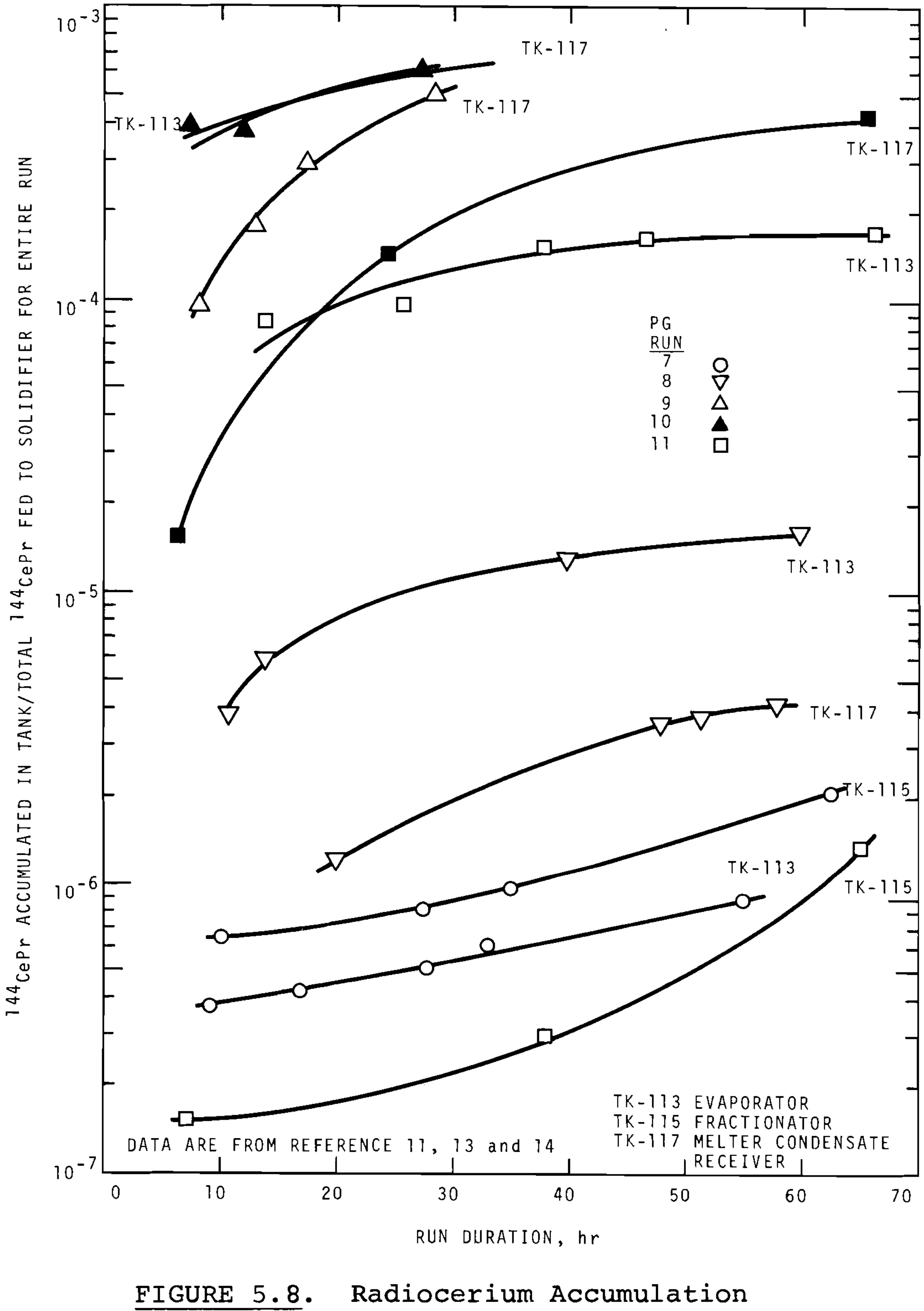

FIGURE 5.8. Radiocerium Accumulation in the WSEP Auxiliaries

The fractionator condenser off-gas is filtered through a high efficiency filter before entering the off-gas scrubber. Filtering efficiencies for nonvolatiles ranged from about 98 to 99.9% which generally stopped any accumulation of nonvolatiles in the off-gas scrubber. As with radioruthenium, the nonvolatile radioactive constituents entering the atmosphere were well below 10CFR20(17) release limits after the scrubber off-gas was filtered twice more and diluted by other building and process air.

5.4 NITROGEN BALANCE

Approximately 60 to 85% of the nitrogen that volatilized from the denitrator was removed from the solidifier off-gas in the denitrator condenser. The remaining 15 to 40% was probably present as nitrogen oxides which were carried through the condenser in the gas phase. The accumulation of nitrogen at various points in the auxiliary system are listed in Table 5.6. The off-gas scrubber absorbed from 3.5 to 6.8% of the equivalent nitrogen fed to the denitrator. During the last five phosphate glass solidification runs as with the first six phosphate glass runs, the caustic scrubber solutions were not neutralized by oxides of nitrogen as occurred during the spray solidification runs.

5.5 SAMPLING OF PROCESS OFF-GAS

Gas sampling techniques were initiated prior to the last series of five phosphate glass runs in an attempt to provide engineering scale data to permit better definition of the type, form, and extent of radioactivity present in the process off-gas.(15) During the last series of phosphate glass runs final process off-gas leaving the scrubber, gaseous effluents from the solidifier condenser, evaporator condenser and fractionator condenser, and gaseous effluents from the high efficiency process

TABLE 5.6. Nitrogen Balance for the Last Five Phosphate Glass Solidification Runs

	Net Change, kg N				
Phosphate Glass Run	7	8	9	10	11
Feed Tank (TK-114) (Feed to Process)	-38	-41[(a)]	-20	-20	-40
Denitrator-Evaporator (TK-121)	+3.9	+5.2	+3.1	+4.7	+7
Melter Condensate Receiver (TK-117)	+1.5	+5.1	+2.6	+3.6	+6.2
Evaporator (TK-113)	NA	-2.0	+4.4	-5.0	-8.0
Fractionator (TK-115)	37	+36	+10	+17	+33
Fractionator Condenser (E-115) (50 liter holdup tank)	nil	nil	nil	nil	nil
Fractionator Distillate Receiver (TK-116)	+0.2	+0.2	+0.07	+0.04	<+0.1
Scrubber	+1.8	+2.8	+0.7	+0.9	+2.2
Addition: Acid Spray to TK-121 and TK-121 Airlift Pot	-4.5	-4.5	-2.4	-7.5	-4.8
Percent Recovery[(b)]	94	104	93	95	92
Percent of Equivalent Feed Nitrogen in Scrubber	4.7	6.8	3.5	4.5	5.5

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a. Includes ∿5 kg from TK-112 feed tank to TK-113 during Mode B operation

b. Based on nitrogen in feed

filter prior to the scrubber were sampled for both particulate and volatile forms of radioactivity. This was accomplished by routing a side stream of the gaseous effluent through first a glass fiber filter and then a 2M KOH scrubber. The condenser off-gas sampling system is shown in Figures 5.9 and 5.10 while the high efficiency filter and scrubber off-gas sampling system is shown in Figure 5.11.

The condenser off-gas sampling equipment shown in Figure 5.10 consists of three separate samplers on one common vacuum header. Each sampler includes a flowmeter (0 to 1.2 ft^3/min at STP) and a vacuum gage (0 to 30 inches of mercury). The sample packages which are used in conjunction with the samplers contain a 25 mm Gelman Type A glass fiber filter to collect particulates, a fritted gas dispenser, and a 200 ml-2M KOH scrubber to absorb the volatile components such as RuO_4.

Evaluation of data from gas sampling is presented in Sections 5.2 and 5.3.

Gas samples taken during the last five phosphate glass runs were fairly representive of the process off-gases. However, sample data was probably influenced by the sampling techniques used. Samples were routed through 20 to 30 feet of sampling line before reaching the sampler. Particle deposition in these lines probably influenced the sample data somewhat. Evaluation of particle deposition in sample lines was not investigated.

The Gelman Type A glass fiber filter was chosen because of its high filtering efficiency and for its ease in dissolution. The filter is dissolved in a combination of hydrofloric and nitric acid and a Gamma Emission Analysis (GEA) is made on the resulting solution.

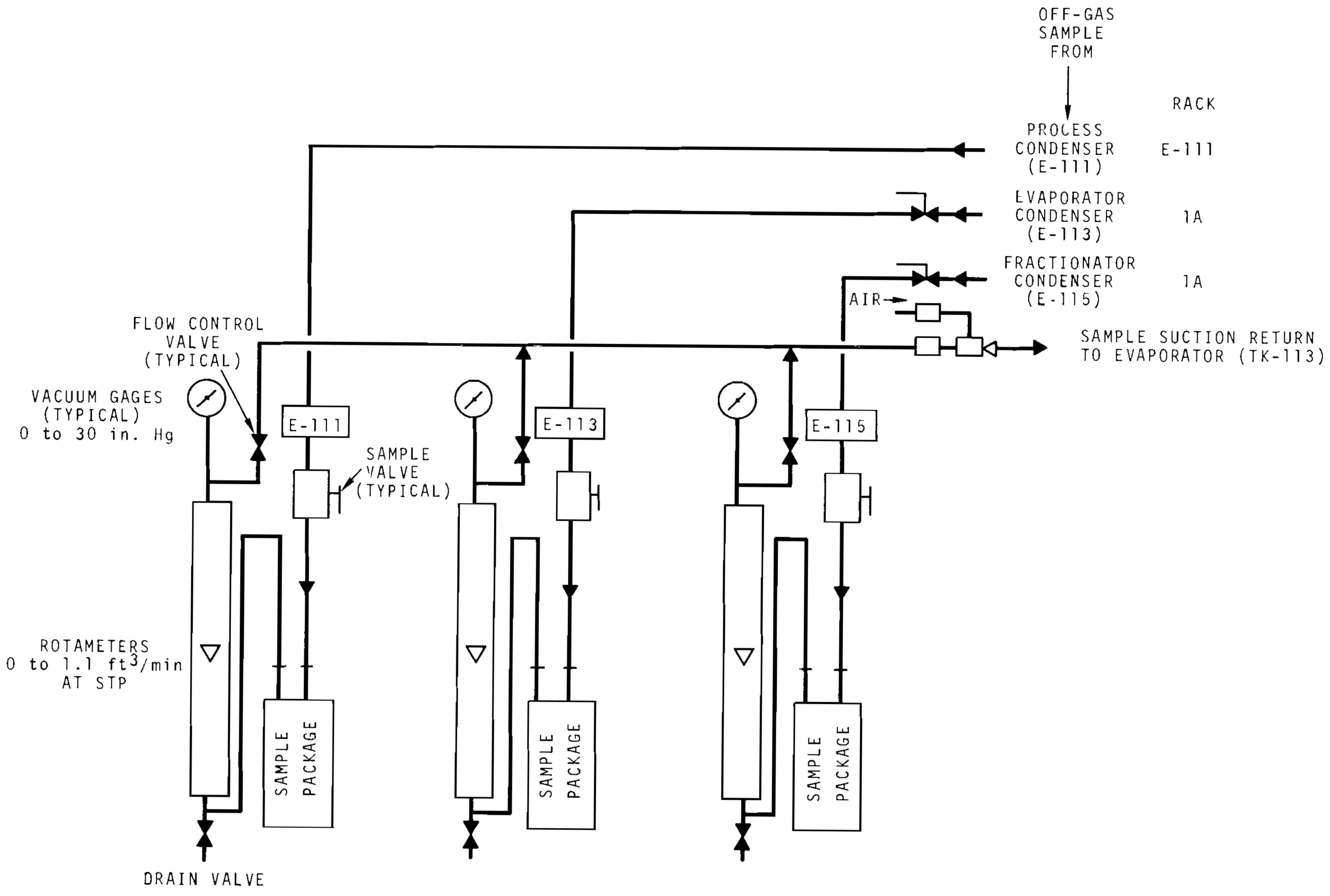

FIGURE 5.9. Condenser Off-Gas Sampling System

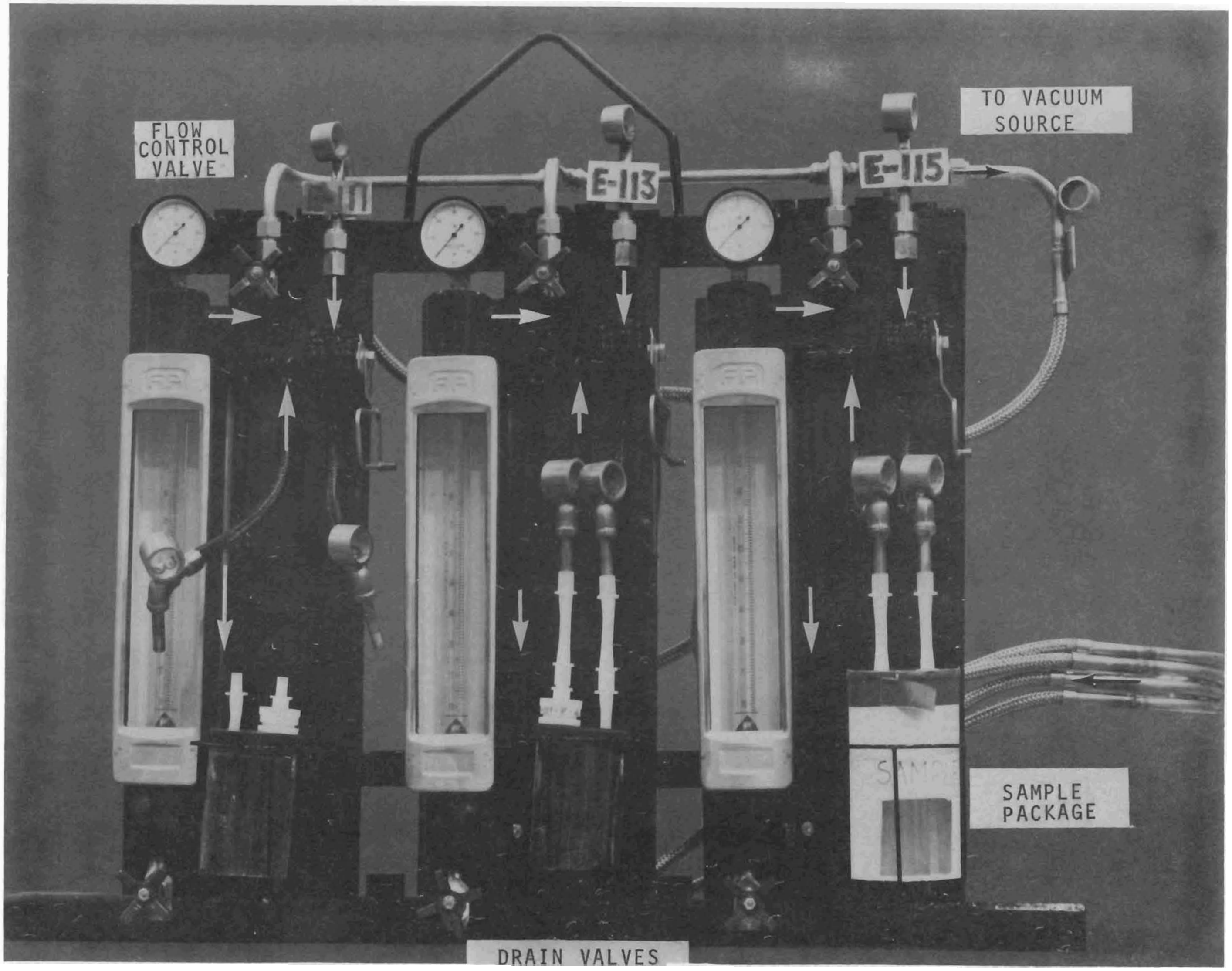

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FIGURE 5.10 denser Off-Gas Sampl Equipmen

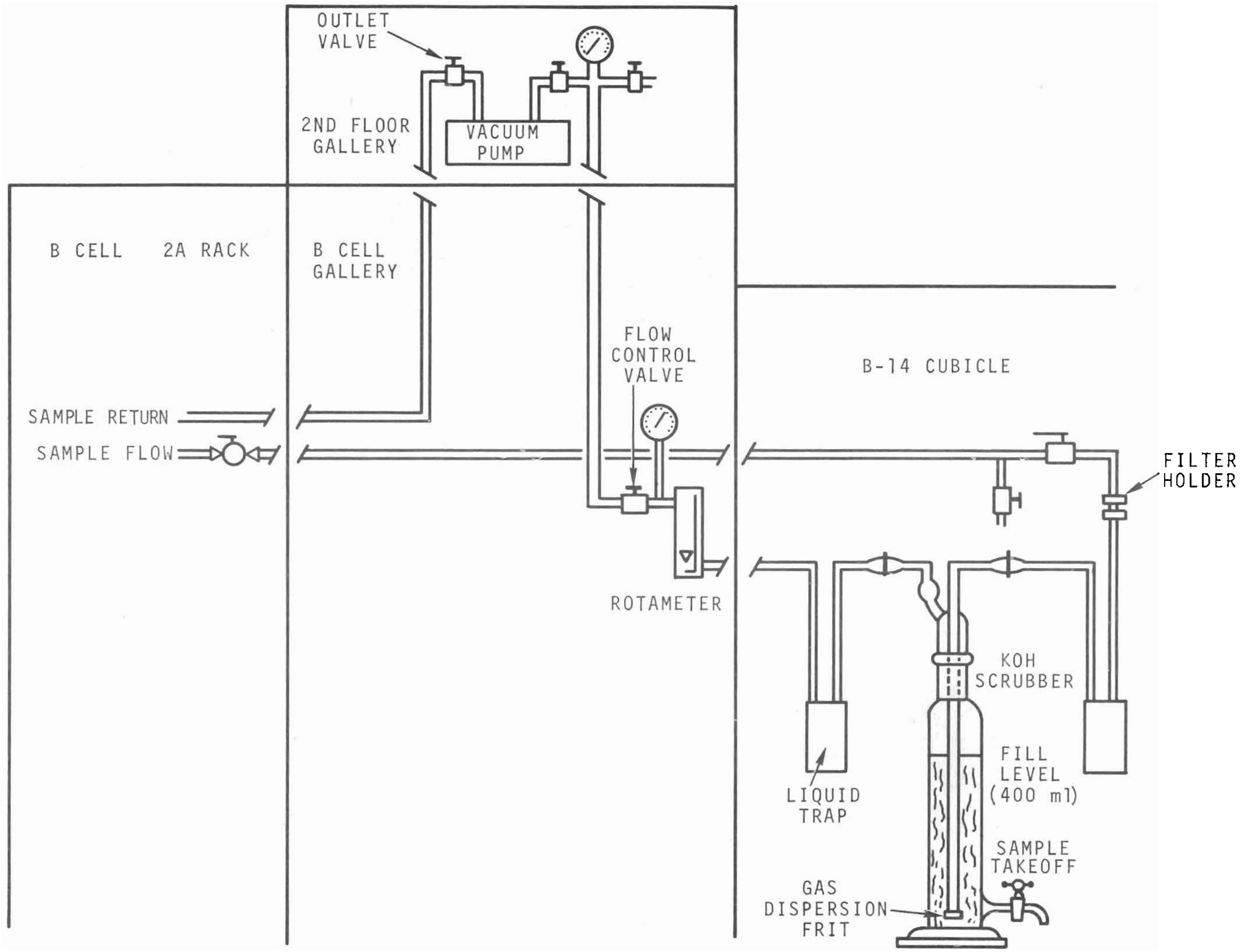

FIGURE 5.11. Final Process Off-Gas Sampling System

After the gas passes through the filter it goes through a plastic gas dispenser which is later removed and counted directly for a GEA. The radioactive gases are then passed through a 2M KOH scrubber which was chosen for its effectiveness in removing ruthenium tetraoxide, RuO_4.

5.6 AUXILIARY HANDLING OF PUREX WASTE

Fission product waste solutions contain precipitates which may interfere with liquid transfer, storage or evaporation. While amorphous, noncaking precipitates can be handled at concentrations up to 50 vol%, in WSEP, very small quantities of heavy, caking precipitates can plug pipes and equipment. Thus, proper design and operation requires a good knowledge of the precipitate characteristics. The precipitates present in a given waste solution depend to a large extent upon the chemical flowsheet used in the reprocessing plant and during the subsequent treatment of the waste. In general, the PW-2, PW-4m and LMFBR solutions used in demonstration Tests PG-7 through PG-11 were representative of typical Purex plant wastes. That is, they contained the full gamut of expected precipitate types, although the comparative amounts of precipitate varied with each waste.

The volume of settled solids in actual samples of the feed solutions used in the last five phosphate glass solidification runs ranged from 8 to 60% and were typically greater than 20%. The majority of the solids encountered in the phosphate glass solidification feeds contains molybdenum, phosphorous, and zirconium, and are probably zirconium phosphomolybdate compounds. The solids are hydrous, amorphous precipitates which have never been observed to cake in the laboratory even after standing several months. In PW-4m, LMFBR and PW-1 waste the phosphomolybdate compound is predominant and the solids are gelatinous and noncrystalline. In the sulfate-containing PW-2 waste, the precipitate remains gelatinous, but on close inspection, small needle-shaped crystals (probably sodium-rare-earth sulfates) are also present. When the PW-4m and LMFBR wastes are continuously boiled, the precipitates lose their gelatinous characteristics and become a very loose, easily-suspended precipitate (even after prolonged settling). Continuous boiling of the PW-2 waste has not been attempted, and with this possible exception, the handling of phosphate glass solidification feeds in feed tanks, evaporators, and transfer lines is not considered to be a major problem.

5.7 GENERAL PERFORMANCE OF AUXILIARY EQUIPMENT

The auxiliary equipment performed satisfactorily during the last five phosphate glass runs. Some feed pump problems and deterioration of plastic insulation on electrical and instrument wiring within the cell occurred but did not affect the results of any runs. All five runs were completed without an interruption. Table 5.7 is a compilation of the general operating experience of the WSEP auxiliary equipment.

5.7.1 Pumps

The feed pumps used during the last five phosphate glass solidification runs were a modified inline pump assembly using a conventional Deanline® centrifugal pump. The pumps contained double mechanical, water lubricated seals with graphite rotating rings. Isolation valves were installed on the pump assembly to prevent loss of feed if the seals failed and to allow remote change out in approximately 4 hours without transferring the feed out of the feed tank.

® RTM Dean Brothers Pumps, Inc.

TABLE 5.7. WSEP Auxiliary Equipment Operating Summary (Through Phosphate Glass Solidification Run PG-11)

Equipment	Construction Material	Temp, °C	Avg. Press., in. Water	Chemical	Operating Time, hr	Remarks
Feed Tanks	304L SS	25 to 60	-5	Darex, Purex, TBP-25 Type Waste	3664	Agitators used 2900 hr.
Condensate Tanks	304L SS	25	-10 to 20	H_2O, Dilute HNO_3	3194	Submerged pump used 1600 hr.
Caustic Scrubber	304L SS	25 to 40	-10 to 20	Dilute NaOH	3194	Circulation pump used 1600 hr.
Evaporator	A-55 Ti	110	-10 to 20	Boiling Waste	2994	Minor titanium corrosion caused by fluoride ion during early DVT runs
Fractionator	A-55 Ti	115	-10 to 20	8 to 12M HNO_3	2994	
Solidifier Condenser	A-55 Ti	100 to 200	-10 to 20	HNO_3 Vapors	3154	Localized vapor entry corrosion caused by volatilized sulfate (up to 0.06 in.) during early DVT Runs 3 and 4
Evaporator Condenser	A-55 Ti	100 to 110	-10 to 20	Dilute HNO_3	2994	
Fractionator Condenser	304L SS	100 to 110	-10 to 20	H_2O, Dilute HNO_3	2994	
Feed Pumps	304L SS	60		Adjusted Waste	1690	Changed from the original inline pump to conventional pump prior to Run PG-3
					740	New pump jumper (see Appendix Table 9.5 for pump history)
Flowmeters:						
Feed, magnetic	Vitreous enamel liner. Platinum sealed electrodes. Inconel flowtubes.	30 to 80	∿100	Concentrated Wastes	2324	Occasional intermittent readings due to lead wire failures. Also frequent shifts in calibration and loss of sensitivity, partially attributed to low WSEP flow rates.
Condensate, magnetic	(same as above)	25 to 40	∿100	Condensate	2734	Two units (1150 hr/unit) did not operate during last 5 phosphate glass runs primarily due to electrical lead failures.
Condensate, electronic rotameter		30 to 80	10 to 30	Dilute Acid Water	2884	The meter was reliable for recycle flow measurement of stripwater.
Filters, Process Off-Gas						
Process Vent	Glass-asbestos with aluminum separators in 304L SS housing	50 to 70	-20	Predominantly Air, Nitrogen Oxides		No filter changes during last five phosphate glass runs
Vessel Vent	(same as above)	50 to 70	-10	Predominantly Air		Changed six times mostly due to excessive moisture. 74 days was shortest duration between changes. Aluminum filter spaces inadequate at this location possibly due to occasional contact with NaOH from the scrubber.

Three pump failures occurred during the last five phosphate glass runs* because of seal and bearing failures. Each of these failures occurred just prior to a run so no downtime occurred during a run as a result of pump failure. Pump life varied from 27 hours on P-16 which was used during Run PG-10 and pre- PG-11 to 157 hours on P-15 used during Runs PG-8 and PG-9. Pump life is decreased by start and stop operation and is substantially increased by thorough water flushing after each run. In an extended pump operating test with nonradioactive feed, a similar pump was operated continuously for 553 hours before the seals failed.(18)

5.7.2 Feed Control System and Flow Measurement

Operation of the feed control system over the range of about 5 to 40 liters/hr was only fair because measurement of this low feed flow rate to the solidifier with a magnetic flowmeter was frequently inadequate. The automatic feed controller receives an input signal from the magnetic flowmeter and delivers an output signal to the feed control valve. Difficulties experienced with the magnetic flowmeters occurring in many early WSEP runs included loss of signal, frequent shifts in calibration (partially due to low flow rates required) and failure of electrical wire insulation. Reliability was increased significantly by changing the electrical wire periodically. The wire insulation failures are described below. A 1/2-inch Hammel Dahl valve with a No. 5 spline trim was used to control the feed to the solidifier. Solids in the feed readily pass through the control valve. Special flushing procedures are used prior to and after feeding to keep the feed line satisfactorily free of solids deposition.

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* See Appendix Table 9.6 for feed pump operating experience.

5.7.3 Evaporator and Acid Fractionator

The WSEP evaporator and fractionator which are capable of boilup rates as high as 530 and 310 liters/hr, respectively, performed satisfactorily. Typical operating conditions for the evaporator are shown in Figure 5.5 and discussed in Section 5.2. A conductivity measurement of the condensed evaporator overheads was used to determine the overhead acidity, and thereby control the stripwater (fractionator distillate) recycle flow to the evaporator to maintain a given nitric acid concentration in the overheads (less than 1$\underline{M}$) thus reducing the potential for ruthenium volatilization.

The specific gravity and liquid level dip tubes of the evaporator would occasionally plug as they did during previous WSEP runs. Flushing the dip tubes with alternate solutions of nitric acid and caustic between runs eliminated most of the plugging, however, the dip tubes should be made more reliable for continuous operation. Semicontinuous wet purging of the dip tubes was successfully tested by venting the diptube for about 10 out of every 15 minutes to allow the waste solution to rise into the dip tubes, and in effect, wash out the tubes. Continual semicontinuous venting of the dip tubes would substantially reduce the possibility of the dip tubes becoming plugged with solids, particularly after continuous operation.

Requirements for automatic control of the evaporator boilup, stripwater addition to the evaporator, and fractionator boilup were tested during short periods of Run PG-11. Figure 5.12 shows the basic control instrumentation available for the WSEP auxiliaries. During these tests the evaporator weight factor (liquid level) controller was cascaded to the tube bundle steam flow controller while the conductivity controller was cascaded to the stripwater controllers. During the

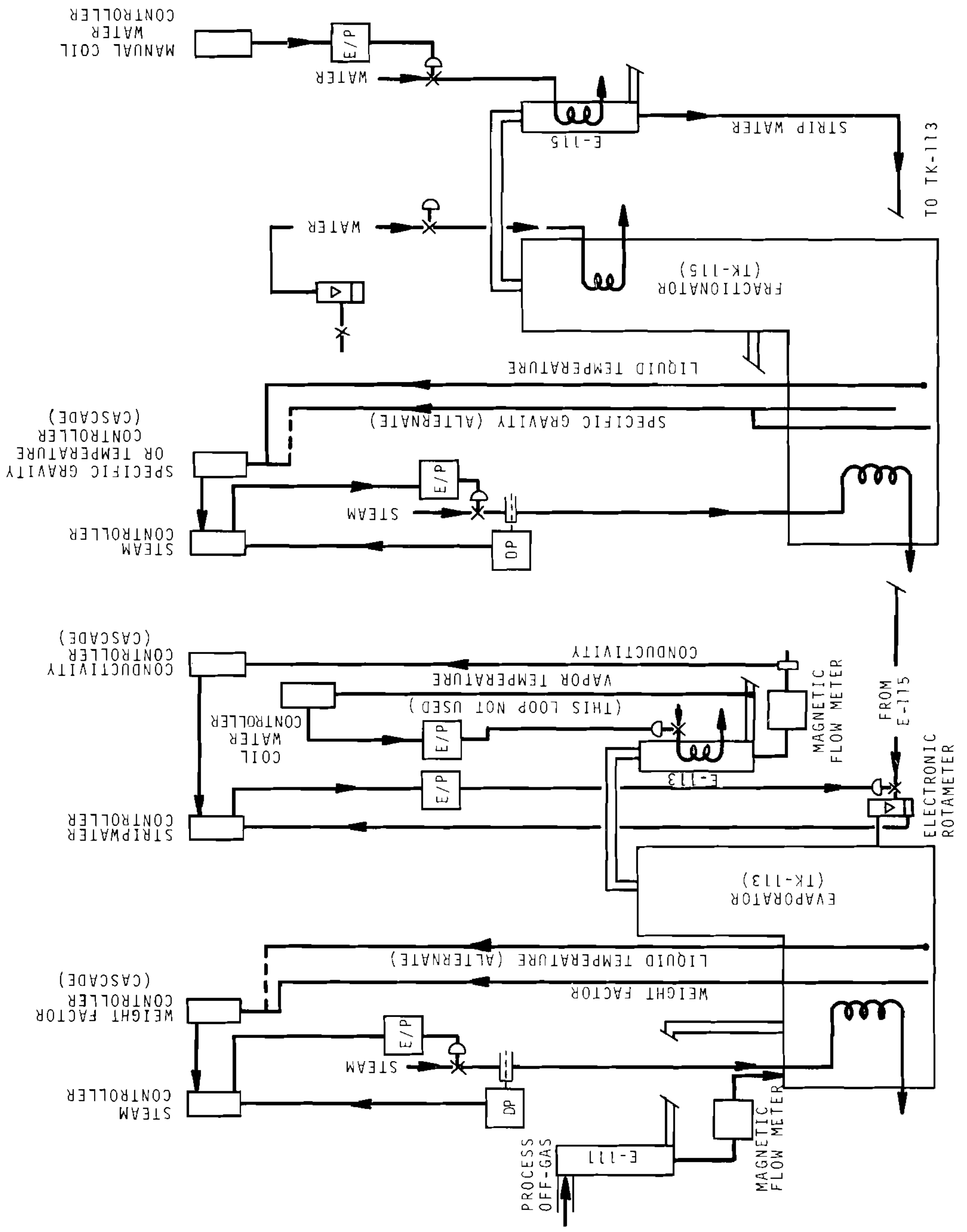

FIGURE 5.12. Basic Instrumentation for Automatic Control of WSEP Auxiliaries

short test periods (0.1 to 2 hours) of automatic control a steady operating condition was not obtained, thus poor control resulted. Attempts in previous runs to use the evaporator specific gravity as a cascade control input to the steam controller were unsuccessful because the specific gravity was adversely affected by the evaporator boilup rate. With only these short test periods very little information was obtained on the requirements for automatic control of the auxiliaries. More recently, promising results have been obtained during automatic control tests. Automatic control of the WSEP auxiliaries is planned for future WSEP runs.

Again as in previous WSEP runs, chemical complexants were added to the titanium evaporator and fractionator vessels to minimize fluoride-induced corrosion. Aluminum nitrate is added to the vessels if pure nitric acid is to be boiled. When waste solutions are boiled in the evaporator, enough iron, zirconium, and aluminum ionic complexants are present in the waste solution to inhibit corrosion.

5.7.4 Filters

The high-efficiency process ventilation filters performed well as in previous WSEP runs. Prior to Run PG-7, the high-efficiency process off-gas filter (F-112) was charged out due to a high pressure drop across the filter (10 inches of water). The new process off-gas filter was used without failure during all the last five phosphate glass solidification runs.

5.7.5 Electrical and Instrument Wiring

During the last series of phosphate glass runs, less extensive deterioration of wiring insulation occurred since most of the wiring that used linear polyethyline as insulation had been replaced with a more flexible and less expensive neoprene rubber insulated wire.

5.7.6 Sampling

Sampling techniques were considerably improved over those used in the first series of six phosphate glass runs. Low level radioactive aqueous samples (those of fractionator distillate and scrubber) were routed outside of B-Cell to a new sampling station. This reduced potential contamination by in-cell handling. Since representative samples of the WSEP auxiliary evaporator and fractionator were difficult to obtain unless the tanks were boiling, start and end of run samples for these two tanks were obtained while the tanks were boiling. Incorporation of the above improvements led to improved data from samples.

Gas sampling equipment was installed prior to last series of five phosphate glass runs to collect samples of process off-gas at various points in the auxiliary system.(15) Gas sampling is discussed in Section 5.5.

5.7.7 Material Balances

Specific balance data for the last five phosphate glass solidification runs are presented in Appendix Table 9.3. Except for radioruthenium, the recovery of individual elements was good.

Analysis for ruthenium in the glassy product was very unreliable by either chemical or radiochemical analysis. Consequently, a total material balance for ruthenium was difficult to make. However, recently a new method of counting WSEP melt samples for obtaining relative percent recoveries of ^{106}Ru, ^{137}Cs, and ^{95}Nb was successfully tested and evaluated. Analysis for ruthenium in the liquid streams in WSEP is easily obtained from a radiochemical gama energy analysis (GEA). The overall material balances for the last six phosphate glass solidification runs are shown in Table 5.8.

TABLE 5.8. Overall Material Balances for the Last Five Phosphate Glass Solidification Runs PG-7 Through PG-11

PG Run	Percent Recovery Volume	Percent Recovery Weight
7	93	95
8	95	95
9	91	90
10	95	93
11	90	90

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6.0 FILLED RECEIVER POT PERFORMANCE

Evaluation of the waste receiver pot and the solidified waste from the demonstration runs constitutes an important phase of the Waste Solidification Demonstration Program. The purpose of the evaluation is to provide information about the safety, engineering, and economic aspects of solidification of high level radioactive waste from nuclear reactor fuel reprocessing. Receiver evaluations begin prior to the time of the demonstration run wherein basic dimensional measurements of each waste receiver pot are made before filling with solidified waste. The evaluations continue immediately following the run with after-fill measurements. Subsequently, selected waste containers are transferred to the Solids Storage Engineering Test Facility (SSETF)(1) for continued observations under controlled storage conditions for extended periods of time.

Experimental measurements are made on each receiver to aid in characterizing the thermal conductivity, leachability, chemical and physical stability, and corrosivity of the solidified waste and to aid in characterizing the suitability and compatibility of the receiver and solidified wastes. This section presents a summary of the experimental measurements that have been made for the receivers from Phosphate Glass Demonstration Runs 7 through 11. Data from Runs PG-1 through PG-6(2) are included where it is considered appropriate.

Theoretical considerations relating to the maximum temperatures that can be expected under various processing and handling conditions have been discussed previously.(2) No attempt is made here to review these considerations, however, some reference to maximum temperatures can be found in Sections 4 and 7 of this report. Thermal maximum heat generation rates are presented in Figure 7.2 of this report.

Table 6.1 is a summary of overall receiver pot fill data. Waste type, receiver diameter and material and the weight and volume for the last five phosphate glass demonstrations are included with bulk density, laboratory determined density, and calculated theoretical density. There is close agreement between measured bulk density and measured laboratory sample (grab sample) density. Both of these measured densities are within about 15% of the calculated theoretical density. The density data indicate that there are few if any voids in the solidified waste.

6.1 THERMAL CONDUCTIVITY

A regression analysis of the effective thermal conductivity (k_{eff}) for phosphate glass solidified waste as a function of average product temperature has been completed. The data from WSEP demonstration Runs PG-1 through PG-6 were included with the data for WSEP Runs PG-7 through PG-11. Figure 6.1 shows the calculated effective thermal conductivity of the combined solidified waste and waste receivers based on experimentally determined heat generation rate and temperatures. The line for the least squares curve fit has been drawn through the data.

The k_{eff} of the products from each feed type (PW-1, PW-2, PW-4m and LMFBR) was compared by statistical techniques to determine if k_{eff} should be treated independently. However, it was not possible to determine if the variation in k_{eff} between phosphate glass product types is real or due to variations in measurements. The data showed that the effective thermal conductivity for phosphate glass over the temperature range from 100 to 650 °C should be treated independent of solidifier feed type according to Equation (1):

TABLE 6.1. Receiver Pot Fill Data

WSEP Run No.	Waste Type	Pot Diameter, in.	Pot Material	Volume of Product,[a] liters	Weight of Waste Product, kg	Bulk Density,[b] kg/liter	Laboratory Sample Density, kg/liter	Calculated Theoretical Density, kg/liter
PG-7	PW-2	8	310 SS	67.3	182	2.7	2.9	3.2
PG-8	PW-4m	8	Mild Steel	66.7	196	2.9	2.9	3.4
PG-9	PW-4m	6	304 SS	26.6	76	2.8	2.8	3.0
PG-10	PW 4m	6	304L SS	29.3	85	2.9	3.0	3.2
PG-11	LMFBR	8	304L SS	60.0	172	2.9	2.9	3.4

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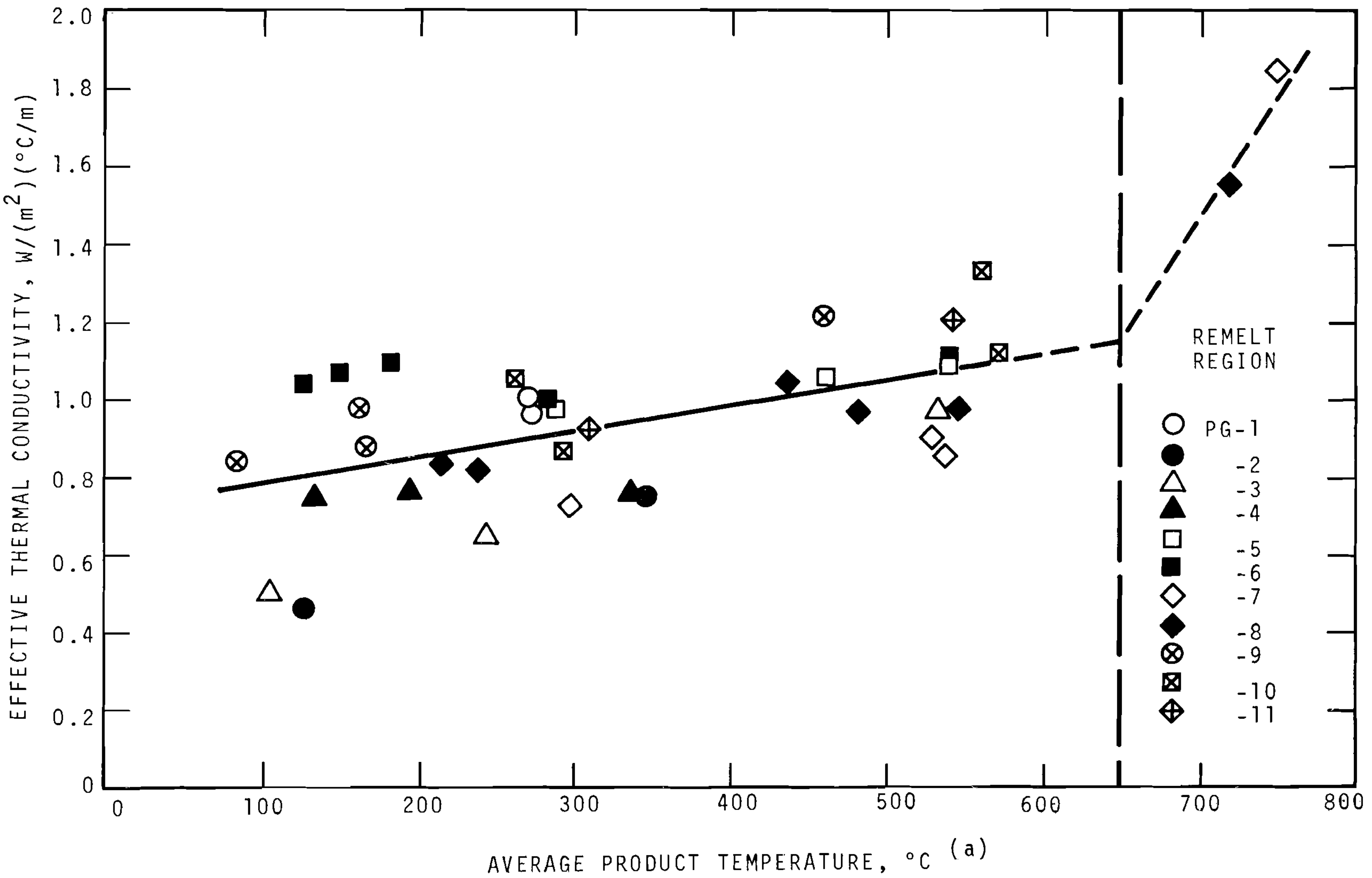
a. Calculated by rodding the pot to obtain a product depth.

b. Bulk density is obtained by weighing the receiver pot before and after it is filled.



a. AVERAGE PRODUCT TEMPERATURE = $\frac{T_{WALL} + T_{\mathcal{C}}}{2}$

FIGURE 6.1. Effective Thermal Conductivity of Phosphate Glass

$$K_{eff} = 0.710 + 6.63 \times 10^{-4} \overline{T} \quad (1)$$

where k_{eff} is the effective thermal conductivity(2) (W/(m^2) (°C/m) and $\overline{T}$ is the arithemetic average of the waste container centerline and wall temperature in °C.

The two thermal conductivity measurements shown in Figure 6.1 at 750 and 720 °C were not included in the regression analysis. In these two cases a large portion of product is above the expected remelt temperature of approximately 650 °C (based on laboratory data). Inclusion of the data would introduce a bias because the molten product data is not typical of the nonmolten product data used in the analysis. However, this data does point out a potentially important feature of phosphate glass, a high k_{eff} at temperatures that are relatively low compared to melter processing temperatures.

6.2 GAMMA SPECTRUM ANALYSIS AND RADIATION PROFILES

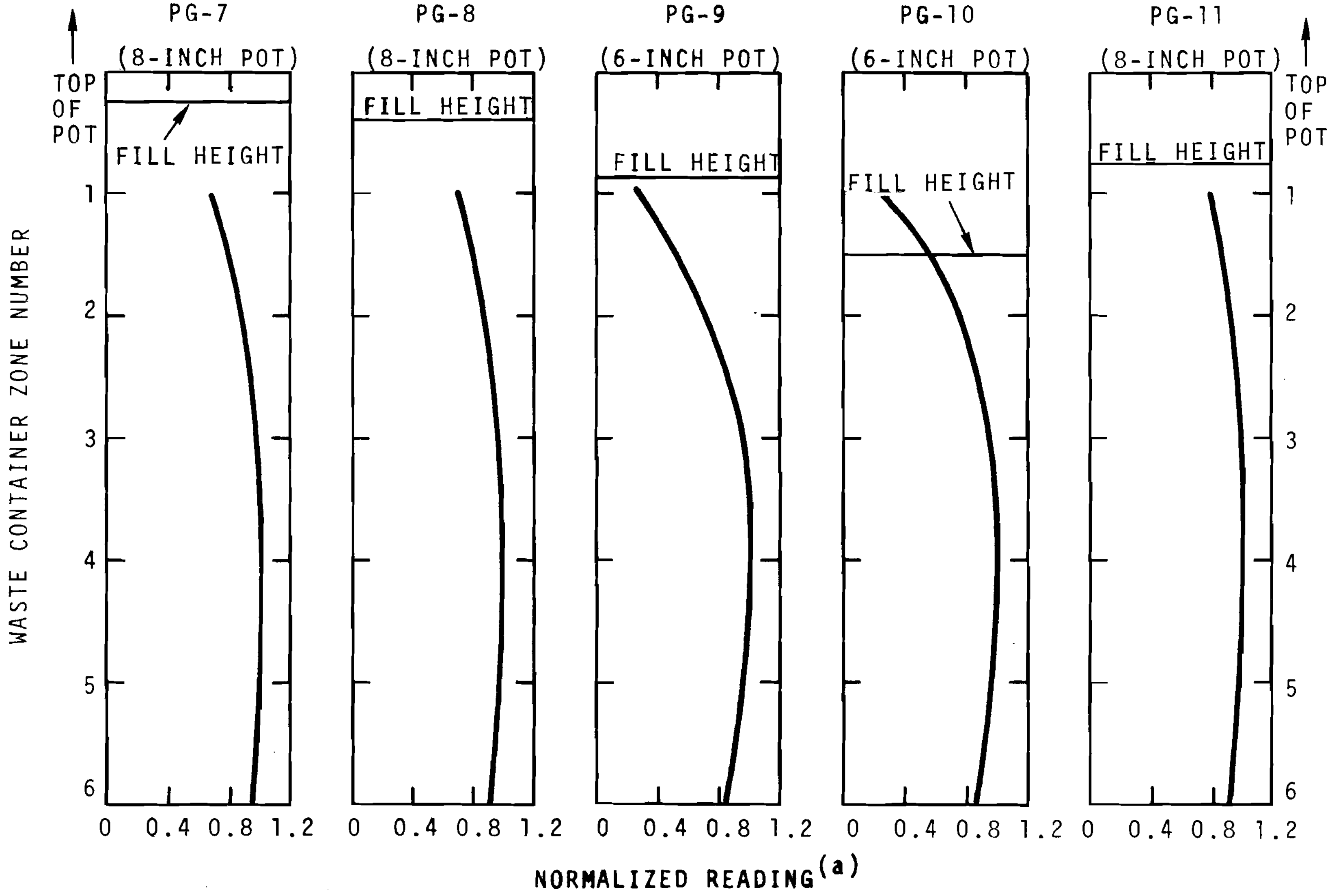
Uniform heat generation rate is one of the basic assumptions(2) used to determine the effective thermal conductivity of solidified waste. Uniform heat generation rate is important to safety considerations in that "hot spots" within a container could result in premature failure of the container. For these reasons, gross gamma scans of the phosphate glass waste containers were made after filling. The purpose of the scans is to find any gross fission product migration or segregation. The temperature profiles from the pot internal and wall thermocouples were also studied for evidence of "hot spots." No data has been gathered in the phosphate glass demonstration series that would indicate that fission product migration or segregation is a problem.

The gross gamma scans are accomplished by positioning an ionization chamber approximately 6 inches from the pot near the midpoint of each of the six pot zones. Detailed analysis of the fission product spectrum at various locations in waste containers will be accomplished later in the Solids Storage Engineering Test Facility(1) where core drilled samples are planned.(1)

Figure 6.2 shows the results of the gross gamma scans for phosphate glass demonstration Runs 7 through 11. The dose rate measurements have been normalized to Zone 4 which is located near the midplane of the filled portion of the receiver. The purpose of normalization was to show the characteristic "banana shape" radiation profile that one would expect from a homogeneous, uniform distribution of fission products. Actual data from gross gamma dose rate measurements are presented in Table 6.2. Intermediate and wall thermocouple temperature measurements, also normalized to Zone 4, are presented in Figure 6.3 for Zones 1 through 6 to further substantiate the product uniformity.

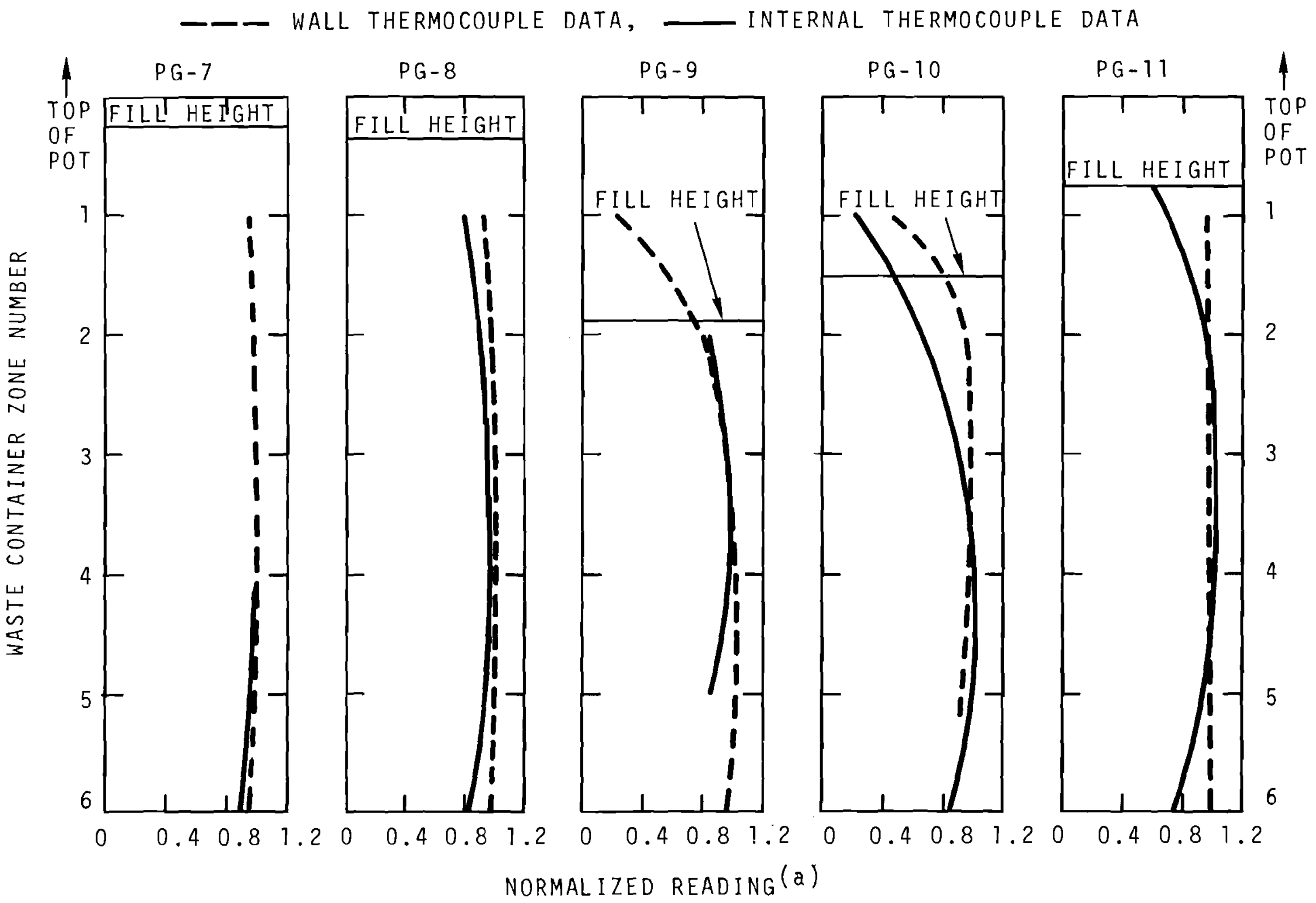
TABLE 6.2. Gross Gamma Dose Rates for PG-7 Through PG-11 Receivers

	Rates for				
Waste Container Zone	PG-7 Scanned 7/11/69, R/hr $\times 10^{-4}$	PG-8 Scanned 8/19/69, R/hr $\times 10^{-4}$	PG-9 Scanned 4/24/69, R/hr $\times 10^{-4}$	PG-10 Scanned 4/24/70, R/hr $\times 10^{-5}$	PG-11 Scanned 12/12/69, R/hr $\times 10^{-4}$
1 (Top)	2.3	2.6	0.48	1.4	5.4
2	3.0	3.3	1.4	4.4	6.4
3	3.3	3.8	1.9	5.8	6.6
4	3.4	3.7	2.0	5.9	6.8
5	3.4	3.7	1.9	5.8	6.6
6 (Bottom)	3.2	3.4	1.7	5.0	6.2



(a) ALL READINGS NORMALIZED TO ZONE 4 = 1.0.

FIGURE 6.2. Normalized Gross Gamma Scan of Phosphate Glass Receiver Pots



a. ALL READINGS NORMALIZED TO ZONE 4 = 1.0.

FIGURE 6.3. Normalized Temperature Data for Phosphate Glass Receivers

The fill height of solidified waste relative to the pot zones is shown for each waste receiver on Figures 6.2 and 6.3. Obviously, the amount of product in the receiver pot affects the shape of both the radiation and temperature profiles. For example, the radiation and temperature profiles for PG-10 tends to fall off rapidly toward Zone 1 due to the relatively low fill height compared to the other four runs.

All of the radiation profiles indicate that the solidified waste in WSEP demonstration Runs PG-7 through PG-11 is uniformly distributed. In all cases, the temperature profiles indicate that there are no "hot spots" within these waste containers that might lead to premature receiver failure or invalidate assumptions for effective thermal conductivity calculations.

6.3 WASTE RECEIVER DIMENSIONS AND PHYSICAL DATA

Each waste receiver that is used in a WSEP demonstration run is carefully examined prior to transfer to the hot cell. Prefill dimensions are taken of the receiver wall thickness, receiver length, and receiver diameter at several locations. No significant dimensional changes were detected for phosphate glass Runs PG-5 through 11 after the receivers were filled.

Satisfactory wall thickness measurements of the waste receivers after the receivers have been filled have been made using an ultrasonic wall thickness scan system. The data is preliminary and is not reported here. The wall pieces that are removed during core drilling will also be used to determine wall thickness.

The receiver diameter and length were measured for each of the phosphate glass runs in the final test series. The purpose of these measurements is to detect gross changes in pot dimensions during the processing cycle. The fill portion of the waste solidificatio cycle is, in general, the most severe part of the cycle with respect to environmental conditions. Table 6.3 summarizes the prefill and afterfill measurements of pot diameter and length for the last five phosphate glass runs. The diametral measurements were made using newly-installed dial indicating micrometers which allow accuracies within 0.025 inches. However, data are reported to the nearest 0.1 inches which is adequate for determination of gross changes. No diameter changes of more then 0.1 inches occurred in any pot except for PG-11, where the maximum afterfill dimension decreased by 0.2 inches as shown in Table 6.2. This is not considered excessive.

Figures 6.4 and 6.5 show photographs of PG-10 (6-inch pot) and PG-11 (8-inch pot) prior to installation in the cell. The top portion of these two containers was identical. The lower 6-inch diameter portion of the PG-10 container is connected to the 8-inch diameter upper section by a 4-inch long transition piece. The wall thermocouples are readily visible for both pots. The interior thermocouples were inserted into the thermal wells through Conax glands. Connection to the pot for thermocouple readout is through the L-shaped thermocouple arm and Cannon connector. The intermediate and centerline thermocouples can and have been replaced remotely where thermocouples become inoperative.

6.4 WASTE RECEIVER WELDING

The waste receiver pots in this series have been welded and leak checked with the exception of PG-10. Table 6.4 shows the basic weld parameters and the before-fill and after-welding helium mass spectrometer leak rates. The basic concepts and principles that have been applied to seal-welding the waste receivers have worked very well.(2) Some difficulty was

TABLE 6.3. Phosphate Glass Waste Receiver Prefill and Postfill Dimensions

Run No.	Distance from Top of Pot, in.	Diameter Prefill, in.		Diameter Afterfill, in.		Pot Length (Prefill), in.	Pot Length (Afterfill), in.
		Maximum	Minimum	Maximum	Minimum		
PG-7	24	8.7	8.6	8.6	8.6	95.5	95.2
	56	8.6	8.6	8.6	8.6		
	80	8.7	8.6	8.6	8.7		
PG-8	24	8.7	8.7	8.7	8.7	95.4	95.5
	56	8.7	8.7	8.6	8.6		
	80	8.7	8.7	8.7	8.6		
PG-9	24	8.6	8.6	8.6	8.6	95.2	95.8
	56	6.6	6.6	(a)	(a)		
	80	6.7	6.6	(a)	(a)		
PG-10	24	8.7	8.6	8.6	8.5	95.2	94.9
	56	6.7	6.6	(a)	(a)		
	80	6.7	6.6	(a)	(a)		
PG-11	24	8.7	8.6	8.5	8.5	95.0	95.5
	56	8.7	8.6	8.6	8.5		
	80	8.7	8.6	8.5	8.5		

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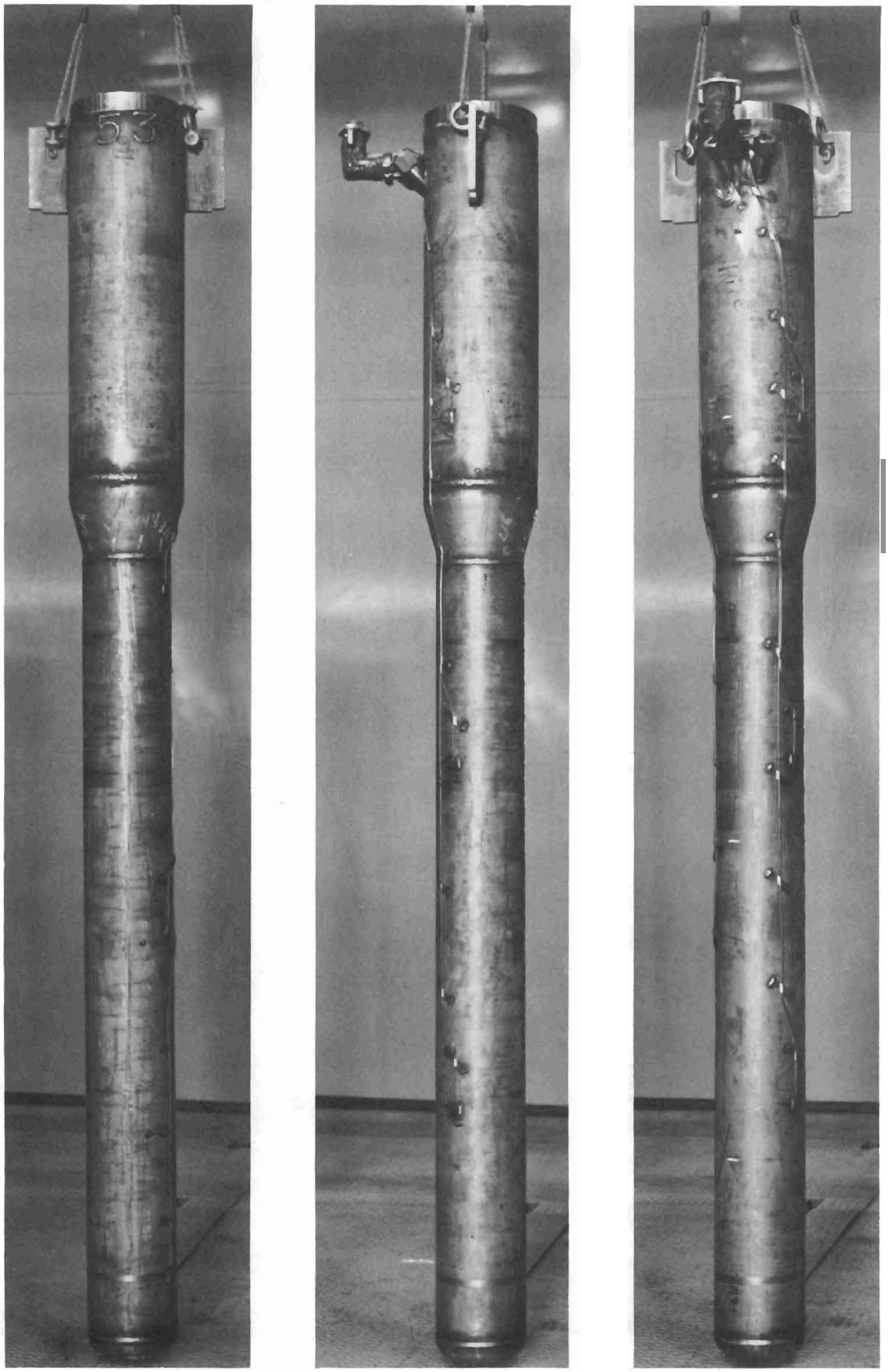
a. No six inch micrometers are available for measurements.



Neg 0694129

GURE 6.4. Phosphate Glass 6-Inch Waste Container (PG-10)

Neg 0695084-4

FIGURE 6.5. Phosphate Glass 8-Inch Waste Container (PG-11)

TABLE 6.4. Phosphate Glass Receiver Basic Welding Parameters and Leak Rates

Run No.	Welding Current, A	Welding Voltage, V	Welding Speed, in./min	Leak Rate, atm cm^3/sec Before Fill	Leak Rate, atm cm^3/sec After Weld
PG-7	160	10	4.6	6.7×10^{-7}	4.1×10^{-7}
PG-8	160	10	4.6	5.4×10^{-8}	4.1×10^{-8}
PG-9	160	10	4.6	5.2×10^{-9}	
PG-10	160	10	---	4.6×10^{-8}	(a)
PG-11(b)	160	10	4.6	1.7×10^{-8}	3.8×10^{-8}

---

a. Pot must be rewelded.

b. Final pot pressure readout jumper was not installed on PG-11 but the pot was leak checked using a special leak test jumper.

encountered with in-cell components that are subject to radiation damage. The failure of the PG-10 weld was due to either malfunction of the argon purge system or impure argon. It will be necessary to grind this weld completely off and reweld.

The original in-cell turntable used for the welding operation was replaced during the PG-7 through 11 series of demonstration runs. The new turntable features remotable drive components and out-of-cell speed control. The original Siaky weld control head was replaced with a new Siaky unit due to radiation damage of the internal wiring.

6.5 WASTE RECEIVER CALORIMETRY

The heat generation rate of the waste receivers from the last phosphate glass series of runs was determined by in-cell calorimeter. The calorimeter(2) is a water-cooled constant temperature bath that permits calculation of steady-state heat generation rates of the filled receivers.

Table 6.5 shows the results of the calorimeter measurements and the back calculated end-of-run heat generation rates for each phosphate glass filled-waste container in this series. The decay half-life that was used for the end-of-run heat generation rate calculation was 284 days (^{144}CePr). The calorimeter measurements are considered to be accurate within ±10% based on comparisons with material balance calculations from each of the runs and the reproducibility of calorimetry results.

TABLE 6.5. Phosphate Glass Waste Receiver Calorimetry

Run No.	Calorimetry Date	Heat Generation Rate, kW	Fill Date	Heat Generation Rate at Fill Date, kW
PG-7	7/16/69	9.6	7/10/69	9.8
PG-8	8/28/69	8.0	8/13/69	8.3
PG-9	9/24/69	4.5	9/22/69	4.8
PG-10	9/30/69	9.5	9/29/69	9.5
PG-11	12/16/69	10.7	12/2/69	11.1

6.6 RECEIVER POT INTERNAL PRESSURE

The bourdon pressure tube gages that were installed on waste receivers from WSEP demonstration Runs PG-7, PG-8, and PG-9 have showed no significant receiver pressurization. The receiver from PG-10 had not been welded (sealed) and leak-checked at the time of this report. PG-11 receiver pressure data is not available because a pot pressure readout assembly has not yet been installed on the pot. This container has been open to cell atmosphere pressure except during leak checks with a special leak test jumper. The absence of positive pressure indication indicates that the residual level of nitrate and other unstable or volatile constituents is low in the phosphate glass and is considered an indication of the product stability.

It should be recognized that the pressure gages used on the waste containers are subject to external shock and bumping in remote handling. The B-Cell pot storage rack (the 4A rack) is a particularly difficult area in the cell for handling the pots. Therefore, small deflections of 5 psig or -5 inches of mercury have been disregarded and considered as zero pressure. The hotter pots tend to go to a vacuum reading as they cool because of normal gas response to a cooling environment. Vacuum, of course, should be viewed favorably because it shows a lack of gaseous release.

Table 6.6 summarizes the afterfill pressure readings for PG-7, PG-8, and PG-9 receivers. Observation of pot pressures is a continuing effort. Those pots that are ultimately transferred to environmental testing in the SSETF will come under continuous pressure monitoring.

TABLE 6.6. Phosphate Glass Waste Receiver Pressure Data

WSEP Run No.	Date of Pressure Recorded	Pressure Indication	Remarks
PG-7	3/26/70	1 psig	None
PG-8	3/23/70	-1 inch Hg	None
PG-9	3/23/70	5 psig	Gage glass broken
PG-10	--	--	Receiver not welded
PG-11	--	0	Atmospheric pressure. No pressure jumper installed.

6.7 RECEIVER POT WALL TEMPERATURES

Numerous receiver wall temperature readings are obtained from the six wall thermocouples during the different phases of handling. Comparisons between calculated and experimental temperatures have been made with the waste receiver hanging in air in the processing cell. Natural convection and radiation heat transfer were assumed to be the principle heat transfer mechanisms.

Figure 6.6 shows the calculated pot wall temperature for receiver heat generation rates and five experimental pot wall temperatures obtained during air temperature profile measurements. Two pot sizes, 8-inch diameter and 6-inch diameter, and two emissivities, 0.6 and 0.8, were used for the comparison. The surrounding media was assumed to be at 38 °C based on measured cell temperatures. All calculated wall temperatures are based on a 6 foot receiver fill height. The five experimental data points are from a thermocouple positioned at the receiver

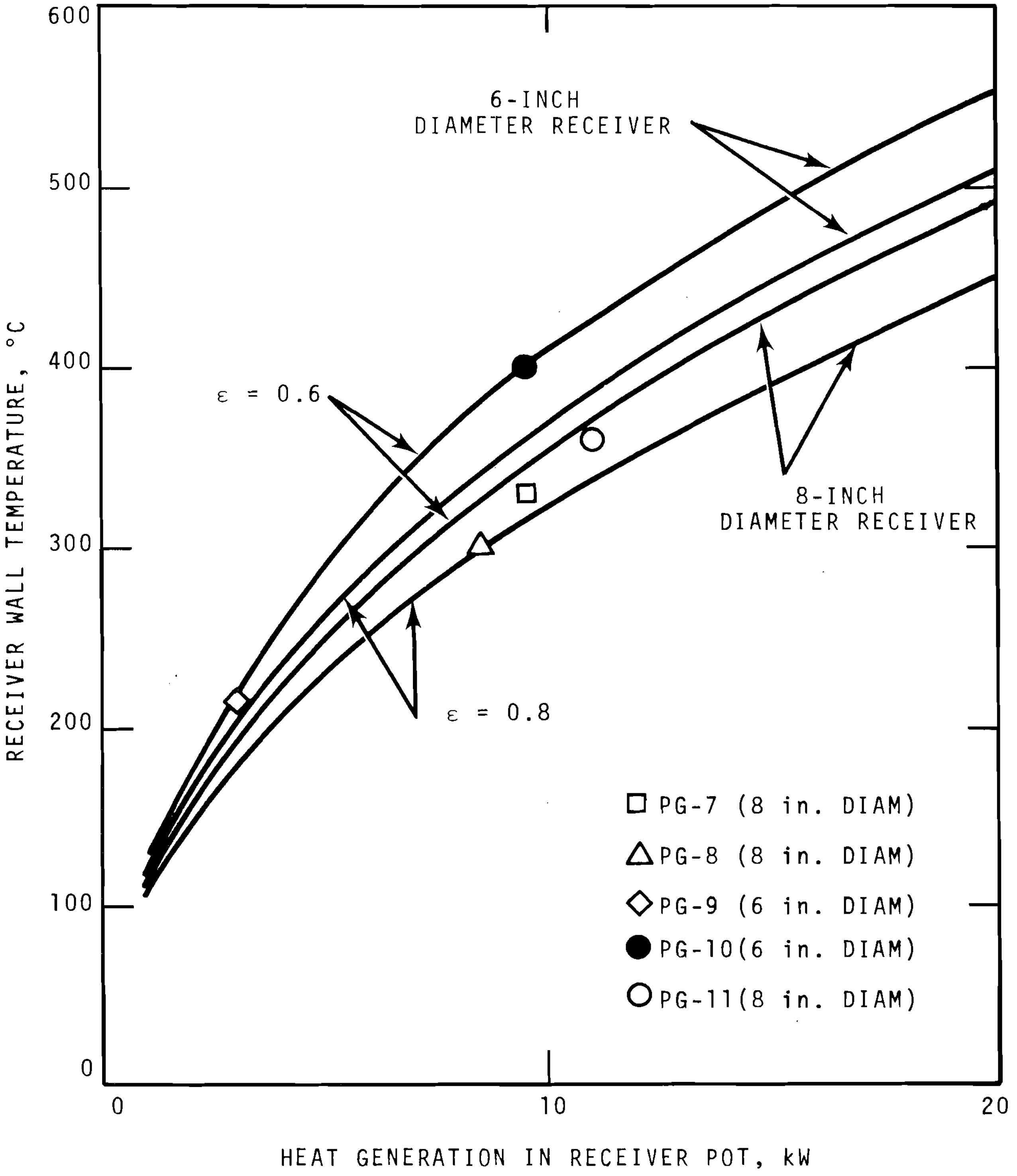


FIGURE 6.6. Receiver Pot Wall Temperatures for Radiation and Natural Convection Cooling

midplane. The calculated and measured values of wall temperature compare favorably. The measured temperature values are within the calculated range of temperatures for expected emissivity values for the pot surfaces.

6.8 GRAB SAMPLE LEACH RATES

Grab samples of solidified waste from PG-7, PG-8, and PG-9 were collected as the melt flowed from the melter to the receiver pot. Leach rates for ^{137}Cs and ^{144}Ce are being obtained on the samples. The standard or slow leach method based on the work of Paige(3) using reciculating distilled water at 25 °C is being used. Data up to 12 weeks for PG-7 and PG-8 samples and data up to 16 weeks for PG-9 are shown in Figure 6.7.

The data shown in Figure 6.7 are typical of phosphate glass radioactive samples. The scatter of the data for a given sample can be large as shown by PG-9 (^{137}Cs) data and the variability for a given waste type large as shown by PG-8 and PG-9. The data tend to show a constant leach rate for the time of the tests shown. There is approximately one and one-half orders of magnitude difference in PG-8 and PG-9 leach rates for both ^{137}Cs and ^{144}Ce even though both are PW-4m wastes. The highest leach rate is for ^{137}Cs for PG-8 at 5×10^{-5} g(cm^2)day while PG-9 ^{144}Ce leach rate is the lowest at 5×10^{-8} g(cm^2)day. PG-7 which is a PW-2 waste (high sulfate) is intermediate to the high and low at 1.5×10^{-6} for ^{144}Ce and 3.5×10^{-6} for ^{137}Cs.

6.9 ENVIRONMENTAL TESTING

The WSEP demonstration runs from this latter series of phosphate glass runs are particularly important to the environmental test program. PG-7, PG-8, PG-10, and PG-11 waste receivers are scheduled for further and more extensive evaluation.(4,5)

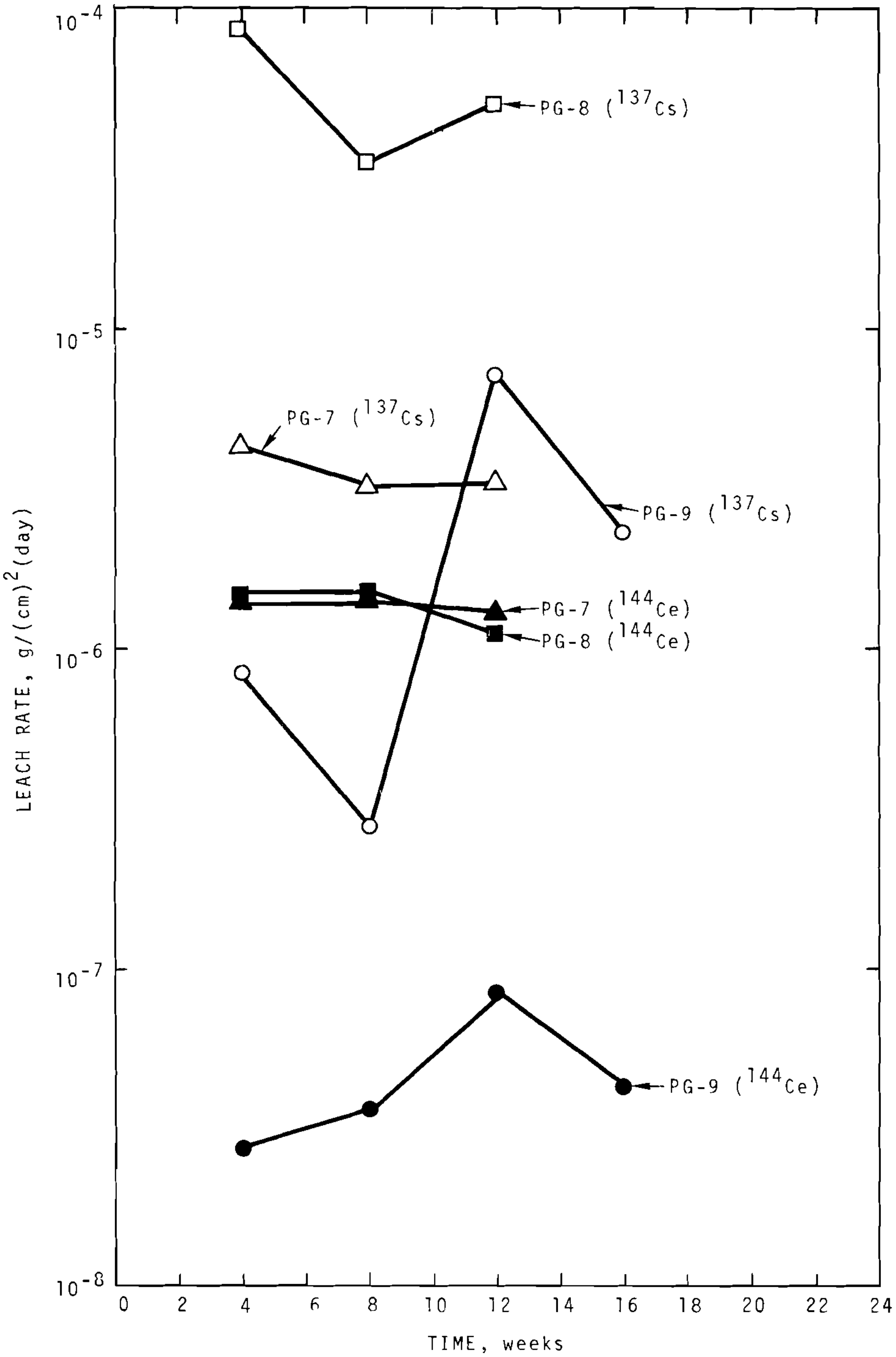


FIGURE 6.7. Phosphate Glass Grab Sample Leach Rates

These four waste receivers and two from the first series (PG-4 and PG-6) will be used to determine the product and container characteristics for up to 5 years after filling. The importance of this work lies in obtaining information about radiation stability, chemical stability, and thermal stability of the solidified waste. Equally as important are the corrosion resistance and environmental stability of the waste receiver pot.

REFERENCES FOR SECTION 6

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7.0 PROJECTED FLOWSHEETS FOR PW-4m AND LMFBR WASTES

While it is desirable for a waste solidification facility to be capable of processing wastes which differ widely in chemical and radiochemical compositions, demonstration of all possible waste variations in the WSEP program is impractical. Experience in fuel reprocessing and projections of future fuel reprocessing requirements led to the selection of four generalized types of Purex acid wastes. Two of these wastes, Purex 1 and 2, were discussed in the WSEP Volume 5 report where the first series of phosphate glass runs were discussed.(1) The second two wastes types, PW-4m and LMFBR, are shown in Tables 3.1 to 3.4 and were tested during the last series of phosphate glass runs.

The initial phase of the program for WSEP demonstrations was based on processing fission product wastes from light water reactor fuels with an integrated exposure of 20,000 MWd/tonne at a specific power of 15 MW/tonne. During the latter phase of the program the integrated exposure was increased to 45,000 MWd/tonne at 30 MW/tonne, an anticipated maximum exposure for thermal reactor fuel. This waste was designated PW-4m and simulated relatively "clean" waste originating from a reprocessing plant using mechanical decladding and adding a minimum of chemicals during reprocessing. The final phosphate glass demonstration was made using a simulated LMFBR core fuel waste with an integrated exposure of 100,000 MWd/tonne at a specific power of 200 MW/tonne.

The fission product heat generation rate in waste from 1 tonne of the 45,000 MWd/tonne and LMFBR core fuels is presented in Figure 7.1. Both the initial heat generation rate levels of

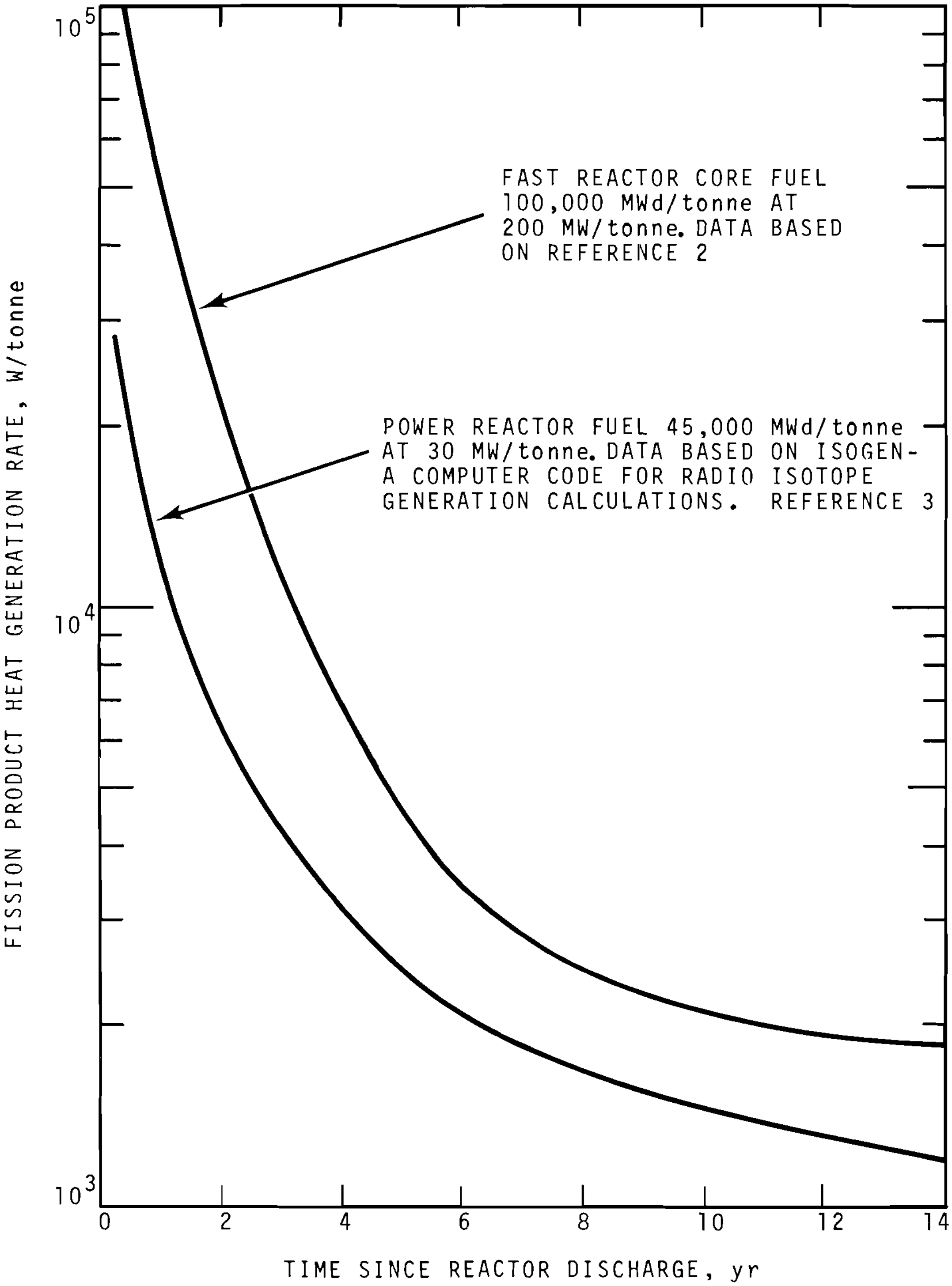
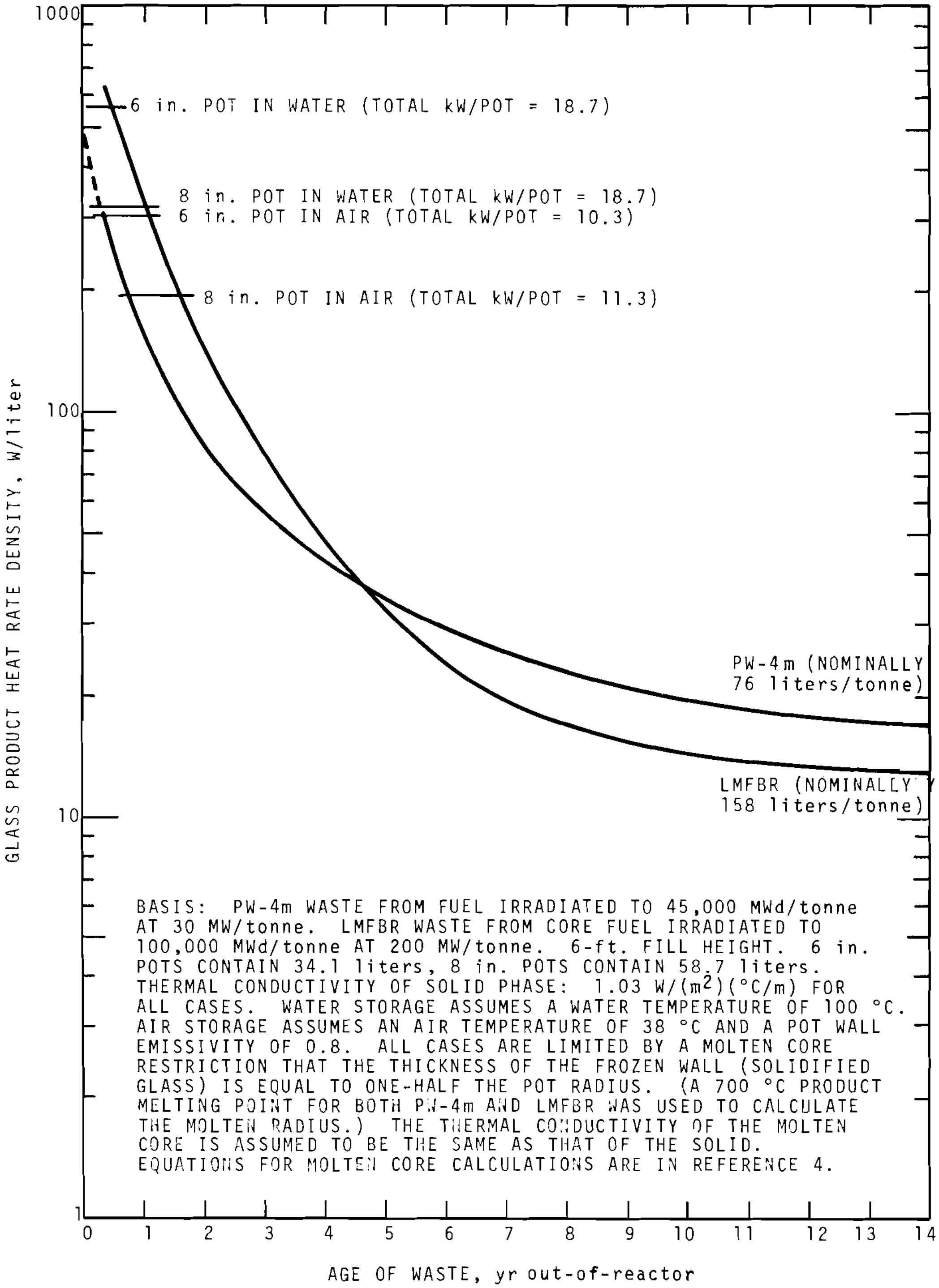


FIGURE 7.1. Fission Product Heat Generation Rate with Time for One Tonne of Reactor Fuel

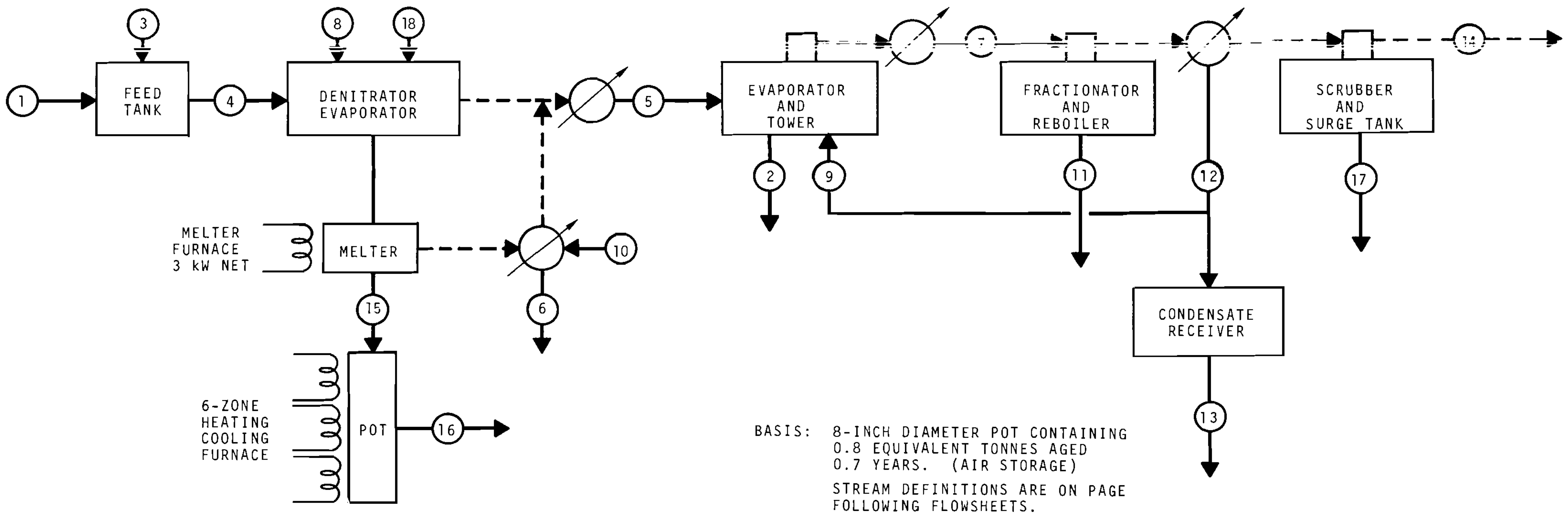
the waste and its later aged levels must be considered in filling a pot. Initially, the maximum heat generation rate that can be placed in any container is limited by either the allowable centerline and wall temperatures or by the potential corrosion of the container by molten waste in contact with the pot. The maximum heat generation rate in a solidified waste may not be compatible with economical heat dissipation in a final storage environment such as a salt mine; consequently, an aging period may be required. If aging of the solidified waste (to permit radionuclide decay) in an interim storage basin is used, the container can be loaded with a higher heat generation rate than the final storage environment may allow. Figure 7.2 shows the ages required to meet present temperature limitations for filling a 6- and an 8-inch diameter pot with phosphate glass product for storage in either water or air. Because of the 700 °C remelting temperature of the phosphate glass product, the maximum heat generation rate for each case in Figure 7.2 is limited by an arbitrarily selected limitation in WSEP that the frozen wall thickness (i.e., solidified glass) is not to be less than one-half the pot radius. With this restriction applied to the 700 °C product remelt temperature, pot centerline and wall temperatures of 900 and 427 °C, respectively, are not attained. The aging before solidification of wastes depends on an economic choice. However, a proposed Federal Regulation(5) suggests that solidification of all high level wastes be completed before the fuel has been out of the reactor for 5 years.

Data from WSEP have been used in projecting typical chemical flowsheets for phosphate glass solidification. Figure 7.3 is a Mode A flowsheet for PW-4m waste using an 8-inch diameter receiver. Because phosphate glass solidification is a continuous process, the processing rate is independent of pot size (except for the time required to change out the pots). The



BASIS: PW-4m WASTE FROM FUEL IRRADIATED TO 45,000 MWd/tonne AT 30 MW/tonne. LMFBR WASTE FROM CORE FUEL IRRADIATED TO 100,000 MWd/tonne AT 200 MW/tonne. 6-ft. FILL HEIGHT. 6 in. POTS CONTAIN 34.1 liters, 8 in. POTS CONTAIN 58.7 liters. THERMAL CONDUCTIVITY OF SOLID PHASE: 1.03 W/(m^2)(°C/m) FOR ALL CASES. WATER STORAGE ASSUMES A WATER TEMPERATURE OF 100 °C. AIR STORAGE ASSUMES AN AIR TEMPERATURE OF 38 °C AND A POT WALL EMISSIVITY OF 0.8. ALL CASES ARE LIMITED BY A MOLTEN CORE RESTRICTION THAT THE THICKNESS OF THE FROZEN WALL (SOLIDIFIED GLASS) IS EQUAL TO ONE-HALF THE POT RADIUS. (A 700 °C PRODUCT MELTING POINT FOR BOTH PW-4m AND LMFBR WAS USED TO CALCULATE THE MOLTEN RADIUS.) THE THERMAL CONDUCTIVITY OF THE MOLTEN CORE IS ASSUMED TO BE THE SAME AS THAT OF THE SOLID. EQUATIONS FOR MOLTEN CORE CALCULATIONS ARE IN REFERENCE 4.

FIGURE 7.2. Heat-Age Environment Relationships for High-Level Radioactive Phosphate Glass Showing Fission Product Heat Rate Density Limits



BASIS: 8-INCH DIAMETER POT CONTAINING 0.8 EQUIVALENT TONNES AGED 0.7 YEARS. (AIR STORAGE)

STREAM DEFINITIONS ARE ON PAGE FOLLOWING FLOWSHEETS.

Code Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
PHASE, L - LIQUID G - GAS S - SOLID	L	L	L	L	L	L	L	L	L	V	L	L	L	G	L	S	L	L
VOLUME, liters/tonne	400	100	325	725	502	150	3890	63	3390	-	280	3610	235	3.5×10^5	57.8	57.8	-	63
AVERAGE RATE, liters/hr	BATCH	BATCH	BATCH	14	12	3.6	93	1.5	81	0	BATCH	86	Batch	8400	1.4	Batch	Batch	1.5
GROSS ACTIVITY, Ci/tonne	2.6×10^6	3.7×10^3	-	2.6×10^6	3.7×10^3	1.6×10^4	2.5×10^2	-	-	-	2.5×10^2	-	6.4×10^{-1}	3.7×10^{-3}	2.6×10^6	2.6×10^6	-	-
RADIORUTHENIUM, Ci/tonne	3.6×10^5	2.7×10^3	-	3.6×10^5	2.7×10^3	1.6×10^4	2.5×10^2	-	-	-	2.5×10^2	-	6.2×10^{-1}	3.6×10^{-3}	3.6×10^5	3.6×10^5	-	-
^{90}Sr, Ci/tonne	1.0×10^5	4.3×10^1	-	1.0×10^5	4.3×10^1	4.2×10^1	6.3×10^{-2}	-	-	-	6.3×10^{-2}	-	1.0×10^{-3}	5×10^{-6}	1.0×10^5	1.0×10^5	-	-
^{144}Ce-Pr, Ci/tonne	1.2×10^6	5.1×10^2	-	1.2×10^6	5.1×10^2	5.0×10^2	7.6×10^{-1}	-	-	-	7.6×10^{-1}		1.3×10^{-2}	6×10^{-5}	1.2×10^6	1.2×10^6	-	-
FISSION PRODUCT HEAT RATE, W/tonne	1.5×10^5	$\sim 3 \times 10^1$	-	1.5×10^5	$\sim 3 \times 10^1$	1.6×10^2	∼0	-	∼0	-	∼0	∼0	∼0	∼0	1.5×10^5	1.5×10^5	∼0	-
NON-FP OXIDES, kg/tonne	4.6	0.19	441	446	0.19	0.2	∼0	-	∼0	-	∼0	∼0	∼0	∼0	446	446	∼0	-
FP OXIDES, kg/tonne	48.8	0.05	-	48.9	0.05	0.2	∼0	-	∼0	-	∼0	∼0	∼0	∼0	48.9	48.9	∼0	-
TOTAL OXIDES, kg/tonne	53.4	0.24	441	495	0.24	0.4	∼0	-	∼0	-	∼0	∼0	∼0	∼0	495	495	∼0	-
NITRATE, g-moles/tonne	2460	500	510	2970	2120	850	1970	-	68	-	1970	5	5	∼0	∼0	∼0	148	567

FIGURE 7.3. Typical Flowsheet for Processing One Tonne of PW-4m Waste with Mode A Operation

FLOWSHEET CODE FOR FIGURE 7.3

Stream Code Number	
1	Incoming waste from processing 45,000 MWd/tonne at 30 MW/tonne power reactor fuel. Fission products in the waste are determined using the computer program ISOGEN in Reference 3.
2	Evaporator bottoms. The bottoms must be recycled, either continuously or batchwise, to the feed or to another treatment process. For this flowsheet it is assumed that the evaporator volume is constant and that 100 liters is drawn off for each tonne of waste solidified.
3	Nonradioactive chemical additives to the raw waste. Additives are $5.1\underline{M}$ phosphoric acid, $1.4\underline{M}$ NaOH and $0.45\underline{M}$ $Fe(NO_3)_3 \times 9H_2O$ based on the waste at 378 liters/tonne.
4	Chemically adjusted feed to the denitrator.
5	Solidifier (primarily denitrator) condensate and noncondensibles. Sixty percent of the total nitrate to the denitrator is assumed in this stream for PW-4m.
6	Melter condensate. When sulfate free waste is processed as is the case for PW-4m, this stream can be routed to either the denitrator or the auxiliary evaporator for additional cleanup by evaporation. For this flowsheet the condensates were not combined because no WSEP data were obtained for the combined routing.

7 Evaporator overheads. A HNO_3 concentration of 0.5$\underline{M}$ is used here.

8 Antifoam addition to the denitrator to suppress foam caused by foaming agents in the Purex wastes (6.75 grams of antifoam per liter of solution).

9 Evaporator strip water. A HNO_3 concentration of 0.02$\underline{M}$ is used here.

10 Steam spray.

11 Fractionator bottoms. A HNO_3 concentration of 10$\underline{M}$ is used for calculations. This stream can be used for fuel element dissolution, or in other areas of fuel reprocessing.

12 Fractionator distillate.

13 Fractionator distillate; available for recycle as makeup water in fuel reprocessing or treatment as low level waste.

14 System off-gas.

15 Melt flow to receiver.

16 Solidified glass product; pot is welded and stored.

17 Scrubber solution, approximately 1 to 2$\underline{M}$ NaOH; 7% of the nitrate from the denitrator is removed by the scrubber.

18 Denitrator nitric acid spray for flushing the top of the tube bundle. (A total of 1-1/2 liters/hr is used here.)

heat rate density and maximum heat generation rate in a pot are, however, dependent on pot size. The PW-4m flowsheet is based on air cooling of the pot. As seen in Figure 7.2, considerably higher heat rate densities can be attained if the pots are filled and cooled in water.

Since the Purex reprocessing step requires the use of tributyl phosphate as the solvent, the presence of the degradation product dibutyl phosphate in the waste will require the addition of antifoam to the denitrator to prevent serious foaming.

Processing rates are based on a limiting WSEP melter processing rate of 5.0 liters/hr of combined melt and melter condensate.

The primary control requirement for the auxiliaries is an evaporator overheads acidity of $0.5\underline{M}$ HNO_3 to minimize ruthenium volatilization.

A flowsheet is not presented for LMFBR waste because the LMFBR waste as shown in Table 3.1 and as demonstrated during phosphate glass Run PG-11 was adjusted by adding chemicals to make it nearly identical to PW-4m. Slight differences included the presence of antimony and tin, and volatile selenium and tellurium in the LMFBR waste as discussed in Section 4. To process the LMFBR core fuel, an aging period of 1.7 years is needed prior to solidifying in 8-inch diameter pots intended for air storage. After the dilution by additive chemicals the pot would contain waste equivalent to 0.40 tonnes of LMFBR core fuel. Further information on processing simulated LMFBR waste is presented in Sections 4 and 9.

Both the water and the acid from the fractionator require reuse or further treatment. Although the chemical level of fission products in each WSEP demonstration run represented 45,000 MWd/tonne thermal fuel and LMFBR core fuel at 100,000 MWd/tonne, the radioactive fission product spectrum used did not represent that value. In order to project WSEP data to expected 45,000 MWd/tonne and LMFBR core exposure, the same fractional distribution of radionuclides to the auxiliaries as given in Table 5.3 was used for evaluation of each run. This exercise increased particular radionuclides to the appropriate curie level that would exist if the waste was solidified after 6 months discharge from the reactor. Results are given in Tables 7.1 and 7.2. On this basis, approximatley 300 curies of ruthenium, 1 curie of ^{144}CePr and less than 0.1 curie of ^{90}Sr are found in the fractionator bottoms per tonne of 45,000 MWd/tonne thermal fuel processed. For 100,000 MWd/tonne LMFBR core fuel, the fractionator will accumulate approximately 1900 curies of ruthenium, less than 10 curies of ^{144}CePr, and less than 0.2 curies of ^{90}Sr. The gross $\beta + \gamma$ in the acid will range from 100 to 2000 μCi/ml for the 45,000 MWd/tonne thermal fuel to approximately 6000 μCi/ml for the 100,000 MWd/tonne LMFBR core fuel.

The nitric acid produced in the fractionator in WSEP is nominally 10<u>M</u>, but it can be as high as 12 to 13<u>M</u>. In a commercial solidification plant, this acid could be recycled to the reprocessing plant for fuel dissolution or other reprocessing steps.(6)

The ratio of the radionuclide concentration in the final distillate to 10CFR20 release limits was obtained by projecting run data as shown in Table 7.2. While ^{90}Sr and ^{144}CePr concentrations are approximately 100 to 40,000 times the 10CFR20 release limits for the 45,000 MWd/tonne thermal fuel waste, ^{106}Ru is the controlling constituent at approximately 500,000 times its limit. Another careful distillation of the distillate would, in general, bring all values, except possibly ^{106}Ru to below 10CFR20 release limits. The distillate could also be used as makeup water in the reprocessing plant,(6) however, if an additional distillation is made, the bottoms would be recycled to the waste evaporator or to the solidifier feed.

TABLE 7.1. Calculated Curies in the Fractionator Acid Per Tonne of Fuel(a,b)

Run No.	Mode	Waste Type	^{144}Ce-Pr	^{90}Sr	Total Ruthenium
7	A	PW-2(c)	1.3	0.08	300
8	A, B	PW-4m(d)	NDG	NA	620
9	A	PW-4m	1.1	0.01	34
10	A	PW-4m	0.67	0.05	NA
11	A	LMFBR(e)	7.9	0.14	1900

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a. Calculated using fission product data of Tables 3.1 to 3.4 and radionuclide distribution fractions from Table 5.3 with both ^{144}Ce-Pr and ^{90}Sr represented by the ^{144}Ce-Pr values.

b. The volume of acid that contains these curies depends on the operating technique, feed type, etc., but it will probably average 200 to 300 liters of 10$\underline{M}$ HNO_3/tonne of fuel processed.

c. PW-2 waste from fuel irradiated to 20,000 MWd/tonne at 15 MW/tonne and 6 months out of reactor.

d. PW-4m waste from fuel irradiated to 45,000 MWd/tonne at 30 MW/tonne and 6 months out of reactor.

e. LMFBR waste from core fuel irradiated to 100,000 MWd/tonne at 200 MW/tonne and 6 months out of reactor.

NDG = No detectable gain.
NA = Not available.

TABLE 7.2. Projected Radionuclides in the Distillate from the Acid Fractionator Per Tonne of Feed Processed

		PW-4m Waste(a)		LMFBR Waste(b)	
Nuclide	10 CFR 20(c) Limit, µCi/ml	Projected Distillate,(d) µCi/ml	Ratio, Projected Distillate to 10 CFR 20 Limit	Projected Distillate, µCi/ml	Ratio, Projected Distillate,(d) to 10 CFR 20 Limit
^{144}Ce-Pr	2×10^{-5}	2×10^{-3} to 1.5×10^{-1}	1×10^{2} to 7.5×10^{3}	6.3×10^{-2}	3×10^{3}
^{90}Sr	3×10^{-7}	1.5×10^{-4} to 1.1×10^{-2}	5×10^{2} to 3.7×10^{4}	1.1×10^{-3}	3.7×10^{3}
^{106}Ru	1×10^{-5}	1.2 to 5	1.2×10^{5} to 5×10^{5}	3.2	3×10^{5}

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a. PW-4M waste from fuel irradiated to 45,000 MWd/tonne at 30 MW/tonne and 6 months out of reactor. Projections are based on Runs PG-8, 9 and 10 using distributions from Table 5.3.

b. LMFBR waste from core fuel irradiated to 100,000 MWd/tonne at 200 MW/tonne and 6 months out of reactor. Projection is based on Run PG-11 and using distributions from Table 5.3.

c. USAEC Code of Federal Regulations - Title 10, Part 20, Table II, Column 2.

d. A distillate volume of 250 liters is used but actual volumes depend on feed type, etc., and may vary from 200 to 400 liters/tonne of waste.

The same observations can be made for the final distillate from processing of LMFBR core fuel as were made for the 45,000 MWd/tonne thermal fuel. By projecting the data from the one LMFBR phosphate glass run that was made, the final distillate is found to be approximately 4000 times the 10CFR20 limits for both ^{90}Sr and ^{144}CePr and 300,000 times 10CFR20 limits for ^{106}Ru.

Alternative methods for treating the distillate have been studied.(7) These include adsorption, electrodialysis and electrodeionization, ion exchange, and oxidation and volatilization. Of these the most suitable method appeared to be two-stage electrodialysis followed by ion exchange.

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3. H. H. Van Tuyl. ISOGEN - A Computer Code for Radioisotope Generation Calculations, HW-83785. Available from National Technical Information Service, Springfield, Virginia, September 1969.

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5. Federal Register, vol. 34, no. 105, p. 87.12. June 3, 1969.

6. J. N. Hartley and G. L. Richardson. "Recycle of WSEP Recovered Acid and Water," Quarterly Progress Report Research and Development Activities, Fixation of Radioactive Residues, November, December 1969, and January 1970, BNWL-1311. A. G. Blasewitz, Editor, Battelle-Northwest, Richland, Washington, February 1970.

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8.0 FUTURE WORK

Although the WSEP solidification runs have been completed, work remains to evaluate the solidified products from these runs and some additional development of the phosphate glass solidifier is warranted.

8.1 EQUIPMENT REQUIREMENTS

Although plugging of denitrator-evaporator transfer lines and liquid level and specific gravity dip tubes was resolved during the WSEP demonstrations, the suitability of these systems on a production scale is questionable. Development work is needed in both areas; an improved melter feed system such as the screw pump tested during the last phosphate glass demonstration, and an improved liquid detection system that would not plug. These evaporator improvements could be possibly brought about with a different evaporator design such as a wiped film evaporator.

The platinum melter used with the phosphate glass process is very expensive and is a weak structural link in the chain of solidification process equipment. The heat transfer characteristics of the platinum are also undesirably limited by a very low emissivity of approximately 0.1 to 0.2 at 1000 °C unless special surface treatments are used. Recent tests have shown a ceramic, chromium-aluminum oxide melter to possess good corrosion resistance to melts; however, cracking of the material from thermal cycling remains as a problem.(1)

8.2 FILLED POT PERFORMANCE

Six of the waste containers from the phosphate glass demonstration runs are scheduled for environmental testing in the Solid Storage Engineering Test Facility (SSETF).(2) Two of the waste containers, PG-6 and PG-7, have been transferred to environmental test pods and tests begun. The waste containers from demonstration Runs PG-4, PG-8, PG-10 and PG-11 are scheduled for test in the near future.

The SSETF is a special facility in A-Cell of the Chemical and Materials Engineering Laboratory(3) in which as many as 16 WSEP product containers can be subjected to a controlled environment storage. The facility consists of test pods in which various storage conditions can be provided under carefully controlled conditions. Storage temperatures up to 100 °C in water and up to 600 °C in air will be studied. The SSETF was activated in January 1969, with installation of the first pot-pod combination.

The controlled environment storage of the WSEP waste containers will provide data on the thermal, radiation, and chemical stability of the products as a function of time.

The variables involved in the test plan(4) are:

- 3 processes: spray and phosphate glass solidification and pot calcination;
- 4 waste types: PW-1, PW-2, PW-4m and LMFBR;
- 3 container materials: 304L and 310 stainless steel and mild steel;
- 2 storage media: water and air.

Obviously, all combinations of the variables cannot be included in the engineering-scale studies because of space and time limitations. The basic purpose of the studies is to provide data on actual solidified waste; but wherever possible, relationships with the nonradioactive laboratory studies will be developed.

Insight into product and container properties will be gained through this study. Specifically, the product will be studied for effective thermal conductivity and pressurization (nondestructive testing), and for crystallinity, leachability, and dispersibility in supporting laboratory studies using core drilled samples. The environmental storage studies center about determining the effects of storage temperature (air or water), radiation, and feed type upon the physical and chemical properties of solidified waste products.

Periodically during the controlled environment storage of WSEP waste containers, the containers will be withdrawn and sampled by core drilling. The core-drilled samples will be transferred to the shielded chemical laboratory for measurements. A cap will be welded over the hole and the container returned to its controlled environment storage. The wall plugs removed from the containers during core drilling will provide samples for corrosion studies of the container material following actual solidification processing and storage.

The results obtained from the core-drilled product samples will be compared with the data obtained from the previously obtained grab samples (grabbed from the molten melter discharge during processing). Thus, the effects of storage conditions and storage time can be examined.

Table 8.1 is a summary of SSETF environmental tests for phosphate glass filled waste containers. A complete summary of all SSETF testing may be found in the Waste Solidification Demonstration Program Product Evaluation Document.(4)

TABLE 8.1. SSETF Environmental Tests of Phosphate Glass Receiver Pots

WSEP Demonstration Run Number	Feed Type	Container Material	Fill Date, mo/yr	Initial Heat Generation Rate, kW	SSETF Test Started, mo/yr	Storage Medium
PG-4	PW-2	Mild Steel	3/68	4.2	-	Air
PG-6	PW-1	Stainless Steel	5/68	9.6	10/69	Water
PG-7	PW-2	Stainless Steel	7/69	8.5	4/70	Air
PG-8	PW-4m	Mild Steel	8/69	9.8	-	Water
PG-10	PW-4m	Stainless Steel	9/69	9.5	-	Air
PG-11	LMFBR	Stainless Steel	12/69	11.9	-	Water

REFERENCES FOR SECTION 8

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4. J. E. Mendel. Unpublished Data. Battelle-Northwest, Richland Washington. (Personal Communication, Waste Solidification Program, Product Evaluation.)

9.0 APPENDIX

9.1 RUN DESCRIPTION

WSEP radioactive Runs PG-7 through PG-11 are briefly described below. General information for all runs on compositions, operating parameters and results, material balances, and feed pump experience are presented in Tables 9.1 to 9.5, respectively. Schematic diagrams of the equipment arrangements for Mode A and B operation are shown in Figures 9.1 and 9.2. WSEP auxiliary and solidification equipment flow diagram are shown on Figures 9.3 and 9.4, respectively. Denitrator-evaporator operating parameters are shown in Figures 9.5 to 9.8 and WSEP auxiliary evaporator operating parameters are shown on Figures 9.9 to 9.13. Figure 9.14 shows a schematic of the process off-gas ventilation system. Startup, normal operating, and shut-down procedures for the phosphate glass solidification process are presented in Reference 1, Section 5.

Run PG-7

The second and last series of phosphate glass solidification runs began with Run PG-7 which was the seventh radioactive demonstration of the phosphate glass solidification process, and the twenty-third radioactive run in WSEP.

During phosphate glass solidification Run PG-7, waste from the equivalent of 1.05 tonnes of power reactor fuel irradiated to 20,000 MWd/tonne at a power level of 15 MW/tonne after 0.5 years out-of-reactor was processed to produce 182 kg of glass product. The 67 liters of radioactive solidified waste produced a self-generating heat-rate density of 146 W/liter (9800 watts total by feed analysis and by pot calorimetry) in an 8-inch diameter 310 stainless steel receiver pot.

The denitrator-evaporator was fed a total of 806 liters of adjusted PW-2 feed (644 liters/tonne) in 44 hours at an average feed rate of 18.3 liters/hr. The average feed rate during the 7.3 hours of startup was 26 liters/hr and during the 37 hours of steady-state operation was 16 liters/hr. A total of 3,390,000 curies of radioactivity including 15,500 curies of radioruthenium was in the feed to the denitrator. The adjusted PW-2 feed was concentrated in the denitrator by a factor of 4.6 (2.7 at 378 liters/tonne).

Overall operation of the denitrator-evaporator was generally good. The specific gravity and weight factor dip tubes remained free of plugs throughout the run. No special precautions were necessary in keeping these tubes clear of solids with the PW-2 feed. Foaming was successfully controlled with the continuous addition of antifoam at 2.8 liters/hr (18 g/hr). However, the addition of bad antifoam agent during the first 24 hours of steady-state operation did not completely suppress the foam. The antifoam has a definite shelf life and this must be considered when preparing the antifoam solution. The accidental addition of EDTA to the feed apparently had no adverse effects on the equipment, process operations, or products. Attempts to sample the concentrated denitrator-evaporator product through the solution feeder were unsuccessful. Feed to the denitrator-evaporator was deliberately interrupted twice (4 hours total) during periods when the airlift pot recirculation line began to plug to prevent a buildup of liquid level in the denitrator-evaporator while the the melter was recovering from overfeeding.

The airlift pot presented the major problems during this run. Plugging of the airlift pot recirculation line and partial plugging of the airlift pot weight factor dip tube occurred many times. These plugs were always removed by manipulating either the cleanout rod or the recirculation plug valve and flushing with nitric acid. However, during periods when both lines were plugged, excess feed entered the melter and foaming usually followed. In two instances feed to the melter could only be stopped by inserting an emergency plug valve into the solution feeder. This was the first time the modified airlift pot was used for transferring a PW-2 concentrate and the first time that the recirculation line plugged with a PW-2 concentrate. The reason for the plugs was probably that some residual PW-1 material from Runs PG-5 and PG-6 was still present in the airlift recirculation line. A controlled feed rate to the melter was also difficult to maintain because of the denitrator-evaporator foaming early in the run and pressure disruptions in the denitrator-evaporator during spray additions to the denitrator and during sampling periods. These disruptions were minor and were minimized through the use of airlift air reductions and control changes to the vacuum system. Changing the venting of the airlift pot from the melter to the denitrator-evaporator during the latter part of the run seemed to improve airlift pot operation.

Melter operation throughout the run except during momentary periods of overfeeding, was good. A steady-state glass production rate of 37 liters/day (0.58 tonnes/day) was maintained as molten glass discharged continuously during stable operating periods from the overflow weir. Internal melt temperatures (at bottom of melter) averaged 1150 °C while the melter furnace operated at 1225 °C. The melter received a total of 675 liters of equivalent PW-2 feed containing about 2,800,000 curies of radioactivity including 13,000 curies of radioruthenium. Concentrated feed was airlifted to the melter at an average rate of

3.5 liters/hr. A volume reduction of 2.2 was obtained in the melter for a total volume reduction from adjusted feed to product of 10 (5.9 at 378 liters/tonne). The steady-state processing rate was 37 liters/day of melt (0.58 tonnes/day of fuel). As in previous runs, a propane torch was used to heat up the freeze drain-valve to completely empty the melter at the end of the run.

Foaming occurred in the melter several times during the run following periods of overfeeding the melter. The foaming incidents, with one exception, were not troublesome since foaming subsided whenever feed to the melter was reduced or stopped. As a result of poor foam control in the denitrator-evaporator from using stale antifoam early in the run, a severe foaming incident occurred during one period of overfeeding to the extent that the melter became pressurized (2.6 inches H_2O). As a result, vapors leaked to the cell from various fittings on the melter. Also, foam levels reached the melter viewing port and entered the off-gas line and the seal pot line. The foam subsided when the feed was stopped and there were no indications of any adverse effects due to the incident during the remainder of the run or following the run. Melt draining was interrupted several times when the melter vacuum was increased from the nominal -6 inches of H_2O to -14 inches of H_2O. This occurred during sampling, but was quickly corrected by adjusting the system vacuum.

Prior to Run PG-7 the electric melter furnace failed delaying the run. During the replacement of the failed furnace, the melter was removed and various off-gas lines were disconnected for inspection. When the seal pot line was removed a greenish-gray colored cake was found in the line at the flanged connection. The cake which was easily removed covered approximately half the opening and tapered off toward the inside of each line. Cake formation at this joint suggests that the joint was not absolutely tight. Inflow of cooling air with subsequent condensation of vapor at this point provided a site for cake formation. The remainder of the lines were clear as was the melter off-gas line.

The sides of the melter were slightly concave. The lower two-thirds of the melter appeared to have larger grain growth than the upper portion. Both of these conditions have been noted in a melter used for over 2800 hours under similar, but non-radioactive, conditions at BNL.

Uniform filling of the receiver pot was noted as the melt flowed out evenly to the wall of the receiver pot as the receiver furnace temperature was maintained at 600 °C. At the end of the run an inspection of the inside of the receiver pot revealed a smooth layer of black glass. The bulk density of the product was calculated to be 2.7 kg/liter while the laboratory measured density was 2.89 kg/liter. The steady-state wall temperatures of the receiver averaged 650 °C while setting in the warm furnace at the end of the run. In air, the steady-state wall temperature was 330 °C. The steady-state centerline temperatures of the receiver in the warm furnace and in air were 853 °C and 749 °C, respectively. The product heat generation rate was 146 W/liter and the unit volume was 64 liters/tonne. The effective thermal conductivity of the product in the warm furnace was calculated to be 1.78 $W/(m^2)(°C/m)$ [1.03 $Btu/(hr)(ft^2)(°F/ft)$]. In air, the effective thermal conductivity decreased to 0.86 $W/(m^2)(°C/m)$ [0.5 $Btu/(hr)(ft^2)(°F/ft)$]. The higher value in the warm furnace is due to the partially molten state of the product.

A maximum pot radiation reading of 3.4×10^4 R/hr was measured at a distance of 6 inches from the wall. Pot leakage after capping was 4.1×10^{-7} atm-cm^3/sec.

During Run PG-7, 8% of the radioruthenium and 0.05% of the nonvolatiles represented by ^{144}CePr in the feed to the melter were volatilized and entrained respectively from the melter. Approximately 0.9% of the radioruthenium and 8×10^{-4}% of the nonvolatiles in the feed to the denitrator were volatilized and entrained respectively from the denitrator and accumulated in the WSEP auxiliary evaporator.

The WSEP auxiliary evaporator performed satisfactorily during the Mode A operation with an average bottoms acidity of about 5$\underline{M}$ HNO_3. The cumulative decontamination factor (DF_c) across the evaporator for ^{106}Ru was 49 and for ^{144}CePr was 2.7×10^4. Instantaneous decontamination factors (DF_i's) across the evaporator for ^{106}Ru ranged from 9.7×10^2 to 3.2×10^4 with the corresponding evaporator overhead acidity ranging from 0.4 to 0.1$\underline{M}$ HNO_3. DF_i's for ^{144}CePr averaged about 10^5.

The acid fractionator operated with an average bottoms acidity of about 8$\underline{M}$ HNO_3 with the average overhead acidity at about 0.01$\underline{M}$ HNO_3. The DF_c for ^{106}Ru across the fractionator was 1.5×10^3 with DF_i's for ^{106}Ru ranging from 6.4×10^2 to 5.3×10^3. The DF_c for ^{144}CePr was 8.3×10^3.

The concentrations of radionuclides in the final aqueous effluent (accumulated fractionator distillate) were above 10CFR20 release limits by factors of 2500 and 55 for ^{106}Ru and ^{144}CePr, respectively.

During Run PG-7, gaseous effluents from the denitrator condenser, the auxiliary evaporator condenser, and the off-gas scrubber were sampled for both particulate and volatile forms of radionuclides. This was done by routing a side stream of the gaseous effluent first through a glass fiber filter and then a 2M KOH scrubber. The radionuclides in the denitrator and evaporator condenser off-gases were primarily collected on the glass fiber filters indicating entrainment of particulate material or adsorption of ruthenium on the fiber glass filter. The average concentration of radionuclides in the denitrator condenser off-gas was 3.2×10^{-3} μCi/cm^3 for ^{106}Ru and 4.5×10^{-4} μCi/cm^3 for ^{144}CePr. The average concentration of ^{106}Ru and ^{144}CePr in the evaporator condenser off-gas was 3.0×10^{-5} μCi/cm^3 and 3.6×10^{-4} μCi/cm^3, respectively. The final process off-gas leaving the scrubber which has been diluted by the vessel vent jet air contained an average of 9.6×10^{-7} μCi/cm^3 ^{106}Ru and 1.2×10^{-6} μCi/cm^3 ^{144}CePr. These values were above 10CFR20 release limits by factors of 4800 and 3000 for ^{106}Ru and ^{144}CePr, respectively. However, before the process off-gases are released to the atmosphere, they are diluted significantly by the building ventilation and filtered twice again resulting in a concentration of radionuclides well below 10CFR20 discharge limits.

Run PG-8

During phosphate glass Run PG-8, 146 kg of glass product was produced from PW-4m waste from the equivalent of 0.84 tonnes of power reactor fuel (45,000 MWd/tonne at 30 MW/tonne) after 1 year out of the reactor. The 67 liters of radioactive glass produced a self-generating heat-rate density of 127 W/liter (8500 watts total by pot calorimetry and 8800 watts by feed analysis) in an 8-inch diameter mild steel receiver pot.

A total of 660 liters of adjusted PW-4m feed at 722 liters/tonne was fed to the denitrator-evaporator in 49.5 hours at an average feed rate of 13.3 liters/hr. A total of 2,500,000 curies of radioactivity including 10,000 curies of radioruthenium were in the feed to the denitrator. The denitrator-evaporator concentrated the PW-4m feed by a factor of 2.7 (1.4 at 378 liters/tonne) at an average temperature of 123 °C before being airlifted to the melter.

Operation of the denitrator-evaporator was good. The specific gravity and weight factor dip tubes remained free of solids buildup by venting the tubes periodically (10 minutes out of each 15 minutes of operation) to the denitrator. Venting allowed the denitrator solution to rise in the tubes and effectively clear them of solids. Foaming due to the presence of dibutyl phosphate in the radioactive feed stock (Purex 1WW) was apparently completely suppressed by the continuous addition of Dow Corning Antifoam B at a rate of 2.8 liters/hr (19 grams of antifoam agent per hour). Sampling of the denitrator-evaporator concentrate was unsuccessful as had been the case in Run PG-7. The denitrator agitator began vibrating early in the run and its use was discontinued after about 13 hours of elapsed run time. No apparent detrimental effects appeared from not operating the agitator since normal boiling action within the denitrator was sufficient to keep solids in suspension.

Airlift operation was improved over that of Run PG-7. The airlift pot recirculation line plugged only once during the run and this plug was removed by manipulating the recirculation plug valve. The airlift pot was vented to the denitrator-evaporator but no definite conclusions can be drawn as to the effectiveness of the venting on airlift pot performance.

Melter operation was generally good with only one short period of foaming observed due to a high rate of denitrator concentrate entering the melter. This was corrected by stopping the feed to the melter for about 5 minutes.

The melter received about 610 liters of equivalent feed at an average denitrator concentrate rate of about 3.9 liters/hr. The feed rate to the melter was controlled manually and adjusted to keep the melter control temperature at about 875 °C. An internal melter thermocouple, located 1/2-inch below the weir overflow, was monitored continuously and provided for better interpretation of internal melter operating conditions. The temperature at this point averaged 1040 °C. The upper control temperature was monitored to detect sudden changes in feed rate to the melter with the temperature averaging 970 °C. The control temperature located below the weir overflow level responded less rapidly to system changes and was used to estimate the magnitude of the feed rate changes necessary to restore the melt to the proper temperature. The internal melt temperature at the bottom of the melter was 1150 °C. A total of 2,300,000 curies of radioactivity including 9800 curies of radioruthenium were in the feed to the melter. A volume reduction of 3.4 was obtained in the melter and resulted in an overall volume reduction from adjusted feed to product of 9.2 (4.8 at 378 liters/tonne). The steady-state processing rate was 31 liters/day of melt (0.39 tonnes/day).

The melt was discharged continuously through the unheated weir as in previous runs. At the end of the run the freeze drain-valve air was turned off to allow the melter to drain. It was necessary to provide additional heat to the drain-valve, as was the case with previous runs, to promote drainage of the melter. The melter started to drain when the freeze drain-valve temperature reached 915 °C.

Uniform filling of the receiver pot with 67 liters of glass was obtained with the pot furnace held at about 620 °C. The total weight of glass product was 196 kg, giving a bulk density of 2.9 kg/liter. The laboratory measured density was 2.89 kg/liter.

The internal heat-rate density of 127 W/liter (8800 watts total) was sufficient to produce a steady-state centerline temperature of 659 °C and a centerline-to-wall temperature difference of 356 °C. From these values for the pot in air, the effective thermal conductivity was calculated to be 0.94 $W/(m^2)(°C/m)$ $[0.54\ Btu/(hr)(ft^2)(°F/ft)]$.

A maximum radiation reading of 3.8×10^4 R/hr was obtained at 6 inches from the wall of the receiver pot.

A total of 0.37% of the ruthenium and less than 0.004% of the nonvolatiles represented by ^{144}CePr fed to denitrator were volatilized and entrained respectively from the denitrator and accumulated in the WSEP auxiliary evaporator. Four percent of the equivalent ruthenium and only 0.04% of the nonvolatiles fed to the denitrator were volatilized and entrained respectively from the melter. The need to separate the melter condensate from the denitrator condensate was only essential during those phosphate glass solidification runs where sulfate was present in the feed (PW-2 waste); however, the WSEP piping for all phosphate glass runs is such that the condensates are always separated. Recycling the melter condensate directly back to the denitrator or to the denitrator feed would be satisfactory and would eliminate an additional effluent stream. Also the melter off-gas could be combined with the denitrator off-gas and decontaminated by the WSEP auxiliaries without sufficiently increasing the radioactivity in the final process effluents (fractionator distillate and off-gas from scrubber).

The solidifier auxiliaries were operated with a Mode A arrangement during the first 88% of the denitrator feeding period and as Mode B during the remainder of the run. The instantaneous ruthenium decontamination factors (DF's) across the auxiliary evaporator during Mode A operation ranged from 2.4×10^{2} to 1.4×10^{3} and during Mode B were greater than 10^{3}. Again, as in previous runs, there was no apparent correlation between instantaneous ruthenium DF's and evaporator overhead acidity, indicating that a large portion of the ruthenium in the evaporator condenser condensate was the result of ruthenium being carried through in the gas phase from the denitrator condenser. The denitrator condenser off-gas contained 2.2×10^{-2} $\mu Ci/cm^{3}$ of ^{106}Ru (feed on) which could account for all of the 0.043% of the equivalent feed ruthenium that accumulated in the fractionator bottoms, verifying the carry over of ruthenium in the gas phase. The cumulative DF's across the evaporator for the entire run including both Mode A and B was 420 for ruthenium and greater than 10^{5} for nonvolatiles.

During Mode B the ruthenium accumulation rate in the fractionator increased by a factor of about 4 over that during Mode A, indicating an appreciable increase in the ruthenium volatilized from the evaporator. This increase was due to an increased ruthenium concentration and boilup rate during Mode B (the bottoms acidity remained about the same). The increase during Mode B was still within the range of Mode A data attained from previous runs. The cumulative DF's during Mode B for ruthenium and nonvolatiles were 5.8×10^{2} and about 10^{5}, respectively.

The cumulative DF for the entire run across the fractionator was 5.9×10^{2} for ruthenium and 3×10^{3} for nonvolatiles.

The average concentration of radionuclides in the final aqueous effluent (accumulated fractionator distillate) were above 10CFR20 release limits by factors of 5.6×10^3 for ruthenium and 89 for ^{144}CePr representing nonvolatiles.

During the run, 1.3×10^{-3}% of the ruthenium and 1.6×10^{-5}% of the nonvolatiles in the feed to the denitrator accumulated in the off-gas scrubber. The fractionator condenser off-gas containing an average of 1.9×10^{-7} μCi/cm^3 of ^{106}Ru which could account for all the ruthenium accumulated in the scrubber.

The final process off-gas leaving the off-gas scrubber contained a radionuclide concentration above 10CFR20 release limits by factors of 1.7×10^3 for ^{106}Ru and 1.1×10^2 for ^{144}CePr. Again, as in all previous runs, this off-gas is significantly diluted and filtered twice more prior to release to the atmosphere and the concentration of radioactivity is well below release limits.

Run PG-9

During Run PG-9, waste from the equivalent of 0.41 tonnes of power reactor fuel (45,000 MWd/tonne at 30 MW/tonne) after 0.9 years out of reactor was solidified to 76 kg of glass product. The 27 liters of radioactive glass produced a self generating heat-rate density of 158 W/liter in a 6-inch diameter 304L stainless steel receiver pot.

The operation of the denitrator-evaporator during Run PG-9 was good. The weight factor and specific gravity dip tubes remained free of plugs using periodic venting as used during Run PG-8 and foam control was adequate as Dow Corning Antifoam B was continuously added at 2.7 liters/hr (18 g/hr).

During Run PG-9 the denitrator-evaporator was fed 532 liters of adjusted PW-4m feed (1023 liters/tonne) in 22 hours at an average feed rate of 26.3 liters/hr. The average feed rate during the 16.7 hours of steady-state operation was approximately 25 liters/hr. A total of 1,300,000 curies of radioactivity including 11,000 curies of radioruthenium were in the feed fed to the denitrator-evaporator. The adjusted PW-4m feed was concetrated in the denitrator by a factor of 3.9 (1.4 at 378 liters/tonne). The agitator was not used during this run and, as before, no detrimental effects occurred.

Airlift pot operation during Run PG-9 was good and feed flow to the melter was satisfactorily controlled throughout most of the run. Control was momentarily irregular only once and this occurred during a period of sampling. The airlift pot was vented to the vapor space of the denitrator-evaporator and may have contributed somewhat to improved control; however, improved control cannot conclusively be attributed to this method of operating since some benefits in performance may also be due to the "friendlier" PW-4m flowsheet. The concentrate temperature averaged 120 °C for the run.

Melter operation was generally good and became less reliant on visual access as transfer of feed became more controlled. Excessive foaming occurred during two periods of sampling, but caused no adverse affects. A free-flowing melt was produced and was continuously discharged through the unheated overflow weir except for about a 1-hour period when melt in the portion of the overflow weir located inside the melter became frozen as a result of overfeeding the melter.

At the end of the run the melt was drained through the freeze drain-valve by shutting off the freeze valve cooling air which allowed the frozen melt within to thaw. The melt started draining

8 minutes after cooling air was shut off when the temperature of the freeze valve increased from 595 °C to about 755 °C. The time required to drain about 4.5 liters of melt was 11 minutes. During drainage, evolution of white fumes, probably P_2O_5, from the melt appeared to be more abundant than on other occasions. An excess of phosphoric acid present in the feed because of a lower than expected rare earth concentration probably accounted for the fumes.

The melter furnace temperature averaged 1225 °C while the melt temperature at the bottom of the melter averaged 1135 °C. The melt control temperatures averaged 952 and 1036 °C at 1/2-inch above the weir overflow level and 1/2-inch below the weir overflow level, respectively. The pressure in the melter ranged from -10 to +0.8 inches H_2O with the average and most typical pressure being -3 inches of H_2O. Melter internal pressures were stable and became disrupted only during sampling periods. Denitrator concentrate entered the melter at an average rate of about 4.8 liters/hr. Approximately 1,025,000 curies of radioactivity including 9000 curies of radioruthenium were fed to the melter. A volume reduction of 4.1 was obtained in the melter resulting in an overall volume reduction from adjusted feed to glass product of 15.9 (5.9 at 378 liters/tonne). A steady-state processing rate of about 38 liters/day of melt (0.58 tonnes/day) was produced.

The receiver pot was uniformly filled with 27 liters of PW-4m melt containing 4800 watts of internal heat according to pot calorimetry (4200 watts by feed analysis). The melt weighed 76 kg and had a bulk density of 2.8 kg/liter. This was in good agreement with the laboratory measured density of 2.83 kg/liter and indicates that the receiver was uniformly filled with no voids. The PG-9 receiver pot was the first 6-inch diameter pot to be used in WSEP. Its successful filling without difficulties led to the thermal maximum run using a 6-inch pot in Run PG-10. The pot steady-state centerline temperature while stored in the air-cooled furnace was 566 °C while the pot wall temperature was 362 °C. The effective thermal conductivity of the product under these conditions was calculated to be 1.22 $W/(m^2)(°C/m)$ [0.71 $Btu/(hr)(ft^2)(°F/ft)$].

During Run PG-9 volatilization of radioruthenium and entrainment of nonvolatiles from the denitrator-evaporator and melter were within the ranges found in previous runs. A total of 0.88% of the radioruthenium volatilized and 0.063% of nonvolatiles represented by ^{144}CePr entrained from the denitrator and accumulated in the auxiliary evaporator. Ruthenium volatilization from the melter was equal to 5.7% of the total ruthenium fed to the melter (equivalent to 4.7% of the total ruthenium fed to the denitrator). Entrainment of nonvolatiles from the melter was 0.068%.

The WSEP auxiliary evaporator performed satisfactorily while using a Mode A operation. The cumulative DF's across the evaporator for ^{106}Ru was 1.4×10^2 and for cerium was 1.9×10^3. Instantaneous DF's for ^{106}Ru ranged from 6×10^1 to 5.7×10^2. Instantaneous DF's for nonvolatiles represented by ^{144}CePr ranged from 8.9×10^2 to 3.1×10^3.

The cumulative DF for ^{106}Ru across the acid fractionator was 2×10^3 while a DF for cerium was not available. Instantaneous DF's for ^{106}Ru ranged from 1.8×10^2 to 8.8×10^2. Instantaneous DF's for ^{144}CePr were less than 10 indicating that the fractionator distillate samples were contaminated during in-cell handling of these samples.

The concentration of ruthenium and cerium in the final aqueous effluent (accumulated fractionator distillate) was above 10CFR20 release limits by factors of 1600 and 3500 for ^{106}Ru and ^{144}CePr, respectively. There was no gain in radioruthenium in the fractionator distillate receiver.

Cumulative DF's across the process and auxiliary condensers were obtained from condenser off-gas and liquid samples. The cumulative DF for ^{106}Ru was 36 across the denitrator condenser, 150 across the evaporator condenser, and 370 across the fractionator condenser while for ^{144}CePr were 1800 across the denitrator condenser, 440 across the evaporator condenser, and 380 across the fractionator condenser.

The average concentration of radioactivity leaving the denitrator-condenser off-gas for ^{106}Ru was about 9×10^{-5} μCi/cm^3 (feed off) and about 3×10^{-3} μCi/cm^3 (feed on) and for ^{144}CePr was about 8×10^{-5} μCi/cm^3 (feed off) and ranged from about 2×10^{-3} to 5×10^{-5} μCi/cm^3 (feed on). The concentration of radioactivity leaving the auxiliary evaporator-condenser off-gas remained about the same whether feed was on to the solidifier or off and averaged about 5×10^{-6} μCi/cm^3 for ^{106}Ru and 2×10^{-5} μCi/cm^3 for ^{144}CePr. These radionuclides are filtered through a high efficiency filter before entering the off-gas scrubber. The off-gas exiting the high efficiency filter during the run contained an average of about 4×10^{-8} μCi/cm^3 for ^{106}Ru and ^{144}CePr. Filter efficiencies for the high efficiency filter ranged from 99.7 to 99.9%, respectively. Throughout the run there was no detectable gain in radioactivity in the off-gas scrubber. The final process off-gas exiting the scrubber contained an average of about 2.7×10^{-8} μCi/cm^3 for ^{106}Ru and 7×10^{-9} μCi/cm^3 for ^{144}CePr during PG-9. These values are above 10CFR20 release limits by factors of about 140 for ^{106}Ru and

9 to 18 for ^{144}CePr. However, the final process off-gas is diluted by the building ventilation and filtered twice before entering the stack for discharge to the atmosphere and was then well below discharge limits.

Run PG-10

Run PG-10 followed directly after Run PG-9 during the same week. In addition to demonstrating that a small diameter pot could be uniformly filled, the successful rapid replacement of the filled PG-9 receiver pot with an empty receiver pot for Run PG-10 was significant as it indicated continuous operation of the phosphate glass solidifier is feasible because the changeover can be effected in less time than is required to fill the melter after its contents have been drained to the receiver.

In Run PG-10 the operability of the denitrator-evaporator was again demonstrated with a PW-4m feed containing a significantly higher heat-rate density of 23.8 W/liter which is the highest used to date. A total of 580 liters of adjusted PW-4m feed (1198 liters/tonne) were concentrated in 24 hours at an average feed rate of 24.2 liters/hr. The feed contained 3,700,000 curies of radioactivity. There was no radioruthenium in the feed since no Purex 1WW was used in feed makeup. Only radiocerium solution was used. The average feed rate during 17.5 hours of steady-state operation was about 22 liters/hr. The adjusted feed was concentrated by a factor of 4.65 (1.47 at 378 liters/tonne) with an average solution temperature of 123 °C and ranging from 121 to 128 °C.

The operation of the denitrator-evaporator was good. There were no obvious effects of the increased heat-rate density of the feed which was more than twice that used in Run PG-9

(23.8 W/liter versus 11 W/liter). The weight factor and specific gravity dip tubes remained free of plugs except for a tendency for plugging shortly after feed was started to the denitrator-evaporator (5.7 hours elapsed run time). This tendency started as the denitrator temperature approached 125 °C and persisted for approximately 3 hours. The liquid temperature had risen to about 128 °C during the latter part of this period and concentrated feed entering the melter appeared more viscous than in other runs. The liquid temperature was reduced to near 120 °C and almost immediately tendencies for dip tube plugging disappeared. During the 3 hour period when plugging tendencies were in evidence, the weight factor dip tube was airblown twice and the specific gravity dip tube was flushed with 6M nitric acid 3 times. Venting of the dip tubes was discontinued after 7 hours of operation and was not reinstated until 11.3 hours of elapsed operation.

Since the feed was prepared only from a radiocerium solution which does not contain the foam inducing agent dibutyl phosphate (DBP), no antifoam agent was required to suppress foaming.

Airlift pot operation during PG-10 was again satisfactory and control of the feed rate to the melter was improved over that in Run PG-9. The airlift pot was again vented to the vapor space of the denitrator-evaporator and may have contributed to improved control. No plugs developed in the weight factor dip tube, the recirculation line, or the airlift air line. As preventive measures, the airlift pot weight factor tube was airblown eight times during steady-state operation and flushed once with nitric acid. The airlift pot was flushed once with nitric acid.

Melter operation throughout Run PG-10 was very good and reflected the improved operation of the airlift pot. There were no overfeeding incidents and no foaming. Melter pressure fluctuations during sampling periods were also stabilized. The melt discharged continuously during the run through the overflow weir. Melt temperatures at 1/2 inch above the overflow weir averaged 975 °C while the average melt temperature 1/2 inch below the overflow weir was 1075 °C. The melt temperature at the bottom of the melter averaged 1200 °C and was approximately 65 °C higher than in Run PG-9 due to the increased heat-rate density of PG-10 feed. The furnace temperature was 1250 °C which was approximately 25 °C higher than in Run PG-9.

A volume reduction of 3.1 was obtained in the melter resulting in an overall volume reduction from adjusted feed to final product of 14.1 (4.5 at 378 liters/tonne). The steady-state processing rate was 29 liters/day of melt (0.34 tonnes/day). At the end of the run the melt was drained through the freeze drain-valve by shutting off the freeze valve cooling air which permitted the valve to heat sufficiently to allow the melt to drain. The melt started draining at a freeze valve temperature of 775 °C about 7 minutes after cooling air was shut off. The 4.5 liters of melt drained rapidly in a thin stream in 6 minutes. The internal melter pressure ranged from atmospheric to -7.5 inches of H_2O with the most typical pressure being about -3 inches of H_2O. The time required to fill the melter to the point at which melt discharge occurred required approximately 3.6 hours.

The receiver was uniformly filled with 29 liters of PW-4m melt containing 9500 watts of internal heat as determined by pot calorimetry (9300 watts by feed analysis) with a bulk density of 2.9 kg/liter. The laboratory measured density of the product was 3.0 kg/liter. The heat-rate density of the product was 317 W/liter and is the highest heat-rate density that will be produced in any WSEP product. The steady-state average centerline temperature of the receiver pot stored in an air-cooled furnace was 827 °C while the wall temperature was 458 °C. The effective thermal conductivity of the product and receiver pot stored in the air-cooled furnace was calculated to be 1.22 W/(m^2)(°C/m) [0.71 Btu/(hr)(ft^2)(°F/ft)]. When the receiver was placed in water storage, the centerline temperature decreased to 540 °C. The effective thermal conductivity of the product in water storage was 0.87 W/(m^2)(°C/m) [0.5 Btu/(hr)(ft^2)(°F/ft)]. The maximum radiation reading at 6 inches from the pot was 59,000 R/hr.

Since there was no radioruthenium in the PG-10 feed ruthenium volatilization from the denitrator and melter was not determined. A total of 0.037% of the nonvolatiles represented by ^{144}CePr entrained from the denitrator while an equivalent of 0.031% of the nonvolatiles fed to the denitrator entrained from the melter.

The WSEP auxiliary evaporator performed satisfactorily while continuing with the Mode A operation used in Run PG-9. The cumulative DF's across the evaporator for ^{106}Ru was 2.9 x 10^2 while for ^{144}CePr the DF_c was 1.9 x 10^3. The cumulative ruthenium DF is primarily dependent on the ruthenium present in the evaporator bottoms and the volatilization from the evaporator. Therefore, the absence of ruthenium in the feed didn't result in an increased cumulative ruthenium DF. Instantaneous DF's for ^{106}Ru during PG-10 ranged from 1.9 x 10^2 to 2 x 10^3. These values were somewhat higher than those obtained during PG-9 where radioruthenium was present in the feed and gives further evidence that radioactivity is carried through the auxiliary evaporator from the solidifier without being scrubbed out. Instantaneous DF's for ^{144}CePr ranged from 3.8 x 10^2 to 2.7 x 10^5. The latter value is more typical of previous runs.

The cumulative DF for ^{106}Ru across the acid fractionator was 8 x 10^3. The cumulative DF for ^{144}CePr was not available. Instantaneous DF's for ^{106}Ru ranged from 5.7 x 10^1 to 3.5 x 10^3. Instantaneous DF's for ^{144}CePr for both Run PG-9 and PG-10 were less than 10 indicating that the fractionator distillate samples were probably contaminated during in-cell handling of these samples. Improved sample handling techniques for the fractionator distillate samples were implemented after the final series of phosphate glass solidification runs were completed.

The concentration of ^{144}CePr in the final aqueous effluent (accumulated fractionator distillate) was above 10CFR20 release limits by a factor of 2150. There was no gain in radioruthenium in the fractionator distillate receiver following Run PG-9 and throughout Run PG-10.

Cumulative DF's across the process and auxiliary condensers were obtained from condenser off-gas and liquid samples. The cumulative DF's during PG-10 for ^{106}Ru was 41 across the denitrator condenser, 320 across the evaporator condenser, and 370 across the fractionator condenser while for ^{144}CePr were 450 across the denitrator condenser, and 390 across the evaporator condenser. No DF's were available across the fractionator during PG-10.

The concentration of radioactivity in the auxiliary evaporator-condenser off-gas during PG-10 remained about the same whether feed was on to the solidifier or off and averaged about 5 x 10^{-6} μCi/cm^3 for ^{106}Ru and 2 x 10^{-5} μCi/cm^3 for ^{144}CePr. The concentration of radioactivity in the fractionator-condenser off-gas also remained about the same whether feed was on or off and averaged about 2 x 10^{-7} μCi/cm^3 for ^{106}Ru and

2 x 10^{-5} μCi/cm^3 for ^{144}CePr. These radionuclides are filtered through a high efficiency filter before entering the scrubber. The off-gas exiting the high efficiency filter (F-112) during Run PG-10 contained an average of about 4 x 10^{-8} μCi/cm^3 for ^{106}Ru and ^{144}CePr. Filter efficiencies for the absolute filter during PG-10 ranged from 99.7 to 99.9%. As in Run PG-9 there was no detectable gain in radioactivity in the 2<u>M</u> NaOH scrubber. The final process off-gas exiting the scrubber contained an average of about 2.4 x 10^{-8} μCi/cm^3 for ^{109}Ru and 3.5 x 10^{-9} μCi/cm^3 for ^{144}CePr. These values were above 10CFR20 release limits by factors of about 140 for ^{106}Ru and 9 to 18 for ^{144}CePr. However, the final process off-gas is diluted by the building ventilation and filtered twice before entering the stack for discharge to the atmosphere and was then well below 10CFR20 discharge limits.

Run PG-11

Run PG-11 represented a major milestone in that it marked the completion of the radioactive phosphate glass solidification runs in WSEP. In addition, this was the first phosphate glass solidification run to demonstrate solidification of a simulated liquid metal fast breeder reactor (LMFBR) waste. The LMFBR flowsheet is representative of a waste resulting from reprocessing power reactor core fuel irradiated to 100,000 MWd/tonne at a power level of 200 MW/tonne. This probably represents the extreme for solidification of such a highly irradiated fuel.

To solidify the LMFBR waste, it was modified to where it was nearly identical to the PW-4m feed composition used during Runs PG-8, 9, and 10. The LMFBR flowsheet contains a slightly different fission product spectrum at the higher burnup (e.g. selenium, tellurium, antimony, and tin become more significant).

The concentration and denitration of the LMFBR waste in the denitrator-evaporator was satisfactorily demonstrated. A total of 907 liters of adjusted LMFBR feed were fed to the denitrator-evaporator at an average rate of 19.3 liters/hr. The average feed rate during the 42 hours of steady-state operation was 17.5 liters/hr. A total of 3,720,000 curies of radioactivity including 33,000 curies of radioruthenium was in the feed to the denitrator. The equivalent of 0.38 tonnes of the fast reactor fuel with an equivalent aging time of 1.5 years was processed in 59 hours.

The denitrator-evaporator solution temperature during steady-state operation averaged 121 °C and ranged from 115 to 125 °C. The high solids content (60% by volume) in the feed apparently had no adverse effects on operation. Again, as in the previous three runs, the agitator was not used except during the shutdown period when agitation by boiling was not available.

The specific gravity and weight factor dip tubes were vented to the vapor space of the denitrator-evaporator for 10 minutes of every 15 minutes throughout the run as in the three previous runs. There was a 1 hour period between the 22nd and 23rd hours of operation in which the specific gravity tube started to plug. The tube was flushed with 1 liter of $6\underline{M}$ HNO_3 after which all plugging tendencies disappeared. The specific gravity and weight factor tubes were each flushed once with 1 liter of $6\underline{M}$ HNO_3 during the remainder of the steady-state portion of the run.

Foaming due to the presence of dibutyl phosphate in the Purex 1WW used for feed makeup was again completely suppressed as Dow Corning antifoam B was continuously added to the denitrator-evaporator. The average antifoam addition rate during steady-state operation was 3.2 liters/hr (21.6 grams of antifoam agent per hour).

The concentrated LMFBR feed was successfully transferred from the denitrator-evaporator to the melter by a screw pump instead of the airlift pot during the early stages of the run. The performance of the screw pump was satisfactory; however, its use was short-lived as the air drive motor failed after 8 hours of operation. The screw pump was developed at BNL to provide an improved method of transferring concentrated feed to the melter. This need was established during phosphate glass demonstration Runs PG-5 and 6 in which transfer of a concentrated PW-1 type waste to the melter by an airlift pot was accompanied with considerable difficulty. It should be noted that more recent development in glass compositions made it apparent that it may be possible to adjust PW-1 wastes by the addition of phosphoric acid and sodium to more closely simulate the PW-4m feed composition which was satisfactorily delivered to the melter by the airlift pot in Runs PG-8 through PG-10. (However, this will also result in a high unit volume of solids.) With this in mind it is apparent that the airlift pot may function satisfactorily for all waste types; however, the present airlift system would be nearly impossible to control automatically and very close watch is required to maintain a regular feed rate to prevent melter overfeeding. A screw feeder could solve this problem.

During the 8 hours the screw pump was in operation, feed rates could not be accurately calculated except during the time required to initially fill the melter. A feed rate of approximately 3.5 liters/hr was calculated for this period and was based on the increase in melter condensate tank volume and the capacity of the melter. To attain this feed rate the screw pump was operating between 600 and 650 rpm with 40 psig air pressure on the air drive motor. In tests with the screw feeder at BNL a similar feed rate was obtained with the pump operating at 530 rpm with slightly more than 30 psig air pressure with an LMFBR feed of 54 centipoises viscosity. During Run PG-11 the screw pump speed began to drop off about 4 hours after the start of operation even though the air motor air pressure was increased. Further attempts to increase pump speed by raising the air pressure were made until the motor failed as a maximum air pressure of 85 psig was applied. Prior to its failure the motor noise was variable and intermittent and just before it completely stopped, the motor was noted to have been lugging badly. The screw pump was removed after the run and judged to be in good working order. It was later determined that the air drive motor, which had been in service in development work at BNL, was the defective component of the screw feeder.

Melter control temperatures during screw pump operation remained more stable and averaged somewhat higher than in any previous run. During the screw feeder operation a more uniform delivery of feed to the melter was obtained and because of this, an increased capacity of the melter could probably be realized.

The airlift pot was put into operation within a few minutes after the air drive motor failed on the screw pump. Satisfactory operation of the airlift pot was obtained for the remainder of the Run (35 hours) as the weight factor line, recirculation line, and airlift line were kept free of plugs. There were three instances when plugging tendencies were noted, but these were cleared by utilizing air blowing or flushing procedures which proved successful in previous runs.

Melter operation during Run PG-11 was very good during both continuous and batch discharge operation. A total of approximately 726 liters of equivalent feed was processed in the melter at an average rate of 4 liters/hr. The steady-state processing rate was 34.6 liters/day of melt which is equivalent to 0.22 tonnes/day of high burnup LMFBR fuel. During the period of screw pump operation melter performance was very smooth as melt was continuously discharged through the overflow weir. Internal melt temperatures were more stable than in any other phosphate glass solidification run. The relatively small variations in these temperatures at any instant (less than 60 °C in the upper thermocouple and less than 30 °C in the lower thermocouple) compared to other runs and the remainder of this run indicated improved control of feed to the melter by the screw feeder. Because of a tilted melter, continuous drainage of the melter through the overflow weir had to be abandoned in favor of batch drainage through the freeze drain-valve to prevent melt from striking and accumulating in the neck of the receiver pot. The melter was drained 15 times during the run and an average of 8 minutes was required to complete a drain. The average time required to fill the melter was 3 hours. The average furnace temperature was 1215 °C while the average internal melt temperature was 975 °C and the internal melter pressure was a negative 5 inches of H_2O.

Filling of the 8-inch diameter, 8-foot long 304L stainless steel receiver pot was more difficult because draining melt was accumulating in the upper region of the receiver pot due to a tilted melter. During most of the drains, melt was intentionally deflected to the bottom of the receiver by a stainless steel plate and stalagmite formation was avoided. The bulk density of the product was 2.87 kg/liter (laboratory measured density was 2.93 kg/liter). The maximum temperature recorded during processing was 895 °C at a point located intermediate between the centerline of the receiver and the wall in Zone 2. The maximum wall temperature recorded was 750 °C in Zone 1. These temperatures occurred during melter drains and were reduced by shutting off furnace heat and turning cooling air on.

The steady-state centerline temperature of the receiver pot while stored in the air cooled furnace was 834 °C, and the wall temperature was 417 °C. The effective thermal conductivity of the product under these circumstances was calculated to be 1.18 $W/(m^2)(°C/m)$ [0.68 $Btu/(hr)(ft^2)(°F/ft)$]. The maximum radiation reading at 6 inches from the receiver wall was 68,000 R/hr.

During Run PG-11, volatilization and entrainment from the denitrator and melter while solidifying the simulated LMFBR waste were comparable to those obtained in previous runs. Volatilization of ruthenium and entrainment of nonvolatiles represented by ^{144}CePr from the denitrator were 0.48 and 0.001%, respectively, while from the melter they were 7.4 and 0.05%, respectively.

The auxiliary process system performed satisfactorily with a Mode A operation. With only short duration tests on the automatic control of evaporator boilup, stripwater addition and acid fractionator boilup, very little information was obtained on the requirements for automatic control of the auxiliaries. The instantaneous DF's across the evaporator were typical of DF_i's from previous runs, ranging from 1.4×10^2 to 5.8×10^3 for ^{106}Ru and were typically 10^5 for ^{144}CePr representing nonvolatiles. The relatively low DF's indicate that the majority of the ruthenium in the evaporator overheads was probably the result of ruthenium being carried through in the gas phase from the denitrator condenser or due to internal contamination of the equipment. The fraction of equivalent feed radioactivity that accumulated in the acid fractionator was 5.2×10^{-4} for ^{106}Ru and 1.3×10^{-6} for ^{144}CePr representing cumulative DF's across the evaporator of 48 for ^{106}Ru and 2.0×10^{4} for ^{144}CePr.

Instantaneous DF's across the acid fractionator ranged from 2.1×10^{2} to 5.1×10^{3} for ^{106}Ru and were generally less than 100 for ^{144}CePr indicating that contamination of fractionator distillate samples probably occurred. The cumulative DF's were 2.7×10^{3} and 9.1×10^{3} for ^{106}Ru and ^{144}CePr, respectively. Cumulative DF's across the denitrator and auxiliary condensers ranged from 2×10^{2} to 2×10^{3} for ^{106}Ru and averaged about 20 for ^{144}CePr.

The concentration of radionuclides in the final aqueous effluent (accumulated fractionator distillate) were above 10CFR20 release limits by a factor of 2200 for ^{106}Ru and 1500 for ^{144}CePr.

The radionuclide concentrations in the process off-gas at various points in the auxiliary system were typical of previous runs. The denitrator condenser off-gas contained an average of 2.2×10^{-2} μCi/cm^3 of ^{106}Ru which can account for all of the radioruthenium that accumulated in the fractionator bottoms and 3.7×10^{-4} μCi/cm^3 of ^{144}CePr. The evaporator condenser off-gas averaged about 2.1×10^{-5} μCi/cm^3 of ^{106}Ru and 1.6×10^{-4} μCi/cm^3 of ^{144}CePr. The fractionator condenser off-gas (average of 9.6×10^{-7} μCi/cm^3 ^{106}Ru and 1.7×10^{-5} μCi/cm^3 ^{144}CePr) was filtered through a high efficiency filter where a filtering efficiency of 99.98% for ^{144}CePr representing particulate was obtained. There was no detectable gain of nonvolatile radioactivity in the off-gas scrubber; however, the fraction of equivalent feed ^{106}Ru that accumulated in the off-gas scrubber was 3.9×10^{-9}. A total of 6.6% of the nitrogen fed to the denitrator also accumulated in the scrubber.

The final process off-gas leaving the scrubber was above 10CFR20 release limits by factors of 150 and 10 for ^{106}Ru and ^{144}CePr, respectively. Dilution by the building ventilation system together with filtering two more times, reduced the radionuclide concentration to well below release limits before the off-gas was released to the atmosphere.

TABLE 9.1. Nominal and Actual Feed Compositions Used in Phosphate Glass Solidification Runs PG-7 Through PG-11[a]

Waste Component	WSEP Substitute	PW-2 Nominal, M	PW-2 Actual, M[b]	PW-4m, Nominal M	PW-4m Actual, M[b]			LMFBR Nominal, M	LMFBR Actual, M
			PG-7		PG-8	PG-9	PG-10		PG-11
H^+		3.93	10.2	4.5	11.3	10.7	9.65	0.5	26.6
Fe^{+3}	(c)	0.445	0.32	0.05	0.204	0.07	0.073	0.16	0.55
Cr^{+3}		0.024		0.012				0.046	
Ni^{+2}		0.010		0.008				0.023	
Al^{+3}	(c)	0.001	0.15	0.001	0.4	0.42	0.5	0.0	0.70
Na^{+1}		0.930	1.39[d]	0.10	1.6	1.34	1.46	0.10	3.34
U^{+6}		0.01							
NO_2, NO_3^{-1}		5.37	6.1	6.5	7.0	7.4	7.7	4.75	17.5
SO_4^{-2}		0.870							
PO_4^{-3}		0.006						0.06	
SiO_3^{-2}		0.01		0.01				0.01	
Cs^{+3} + Rb^{+1}	K^+	0.042		0.0924				0.229	
Sr^{+2}		0.0155		0.0356				0.04	
Ba^{+2}		0.0195		0.041				0.068	
$(La + Y + RE)^{+3}$	RE^{+3}	0.1185	0.21	0.274	0.59[e]	0.12	0.29	0.528	0.91
Zr^{+4} + Nb	Zr^{+4}	0.065		0.143				0.222	
MoO_4^{-2} + TcO_4^{-2}	MoO_4^{-2}	0.079		0.161				0.30	
Ru^{+4}		0.0032	0.0034	0.0032	0.0036		0.01	0.022	0.009
Ru^{+4}	Fe^{+3}	0.0288		0.784				0.198	
Rh^{+2}	Co^{+2}	0.0074		0.0133				0.06	
Pd^{+2}	Ni^{+2}	0.0172		0.0425				0.16	
Ag^{+1} + Cd^{+2}	Cu^{+2}	0.0016		0.0041				0.029	
TeO_4^{-2}		0.0064		0.0144				0.034	
Se^{+4}								0.005	
Sn + In	Sn^{+4}							0.011	
Additive to Waste									
Na^{+1}				1.4				2.9	
Fe^{+3}				0.45				0.84	
PO_4^{-3}		3.24	4.2	5.1	5.8	4.53	5.3	10.27	10.0
Final Feed									
Total Volume, liters									
Concentration, liters/tonne			644		722	1023	1198		1916
Specific Gravity at 25 °C			1.29		1.38	1.19	1.25		1.32
Solids, vol%			∿20		∿55	∿8	∿24		∿60
ΣM_T^+		3.24	4.0	5.1	6.1	4.17	5.1	10.27	11.9
$\Sigma M_T^+/P$		1.0	0.95	1.0	1.1	0.92	0.96	1.0	1.2
Total Radioactivity, Ci/liter			4200		3800	2850	6100		4600
Radioruthenium, Ci/liter			19		16	21			41
Total Heat Rate Density, W/liter			17		14	11	24		14.5

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a. Values are reported on a 378 liter/tonne basis.

b. Values reported are total concentrations including additive (if any) as determined by chemical analysis of the waste. All other chemical compositions are added quantitatively as given by nominal values.

c. Excess aluminum in Purex 1WW waste was substituted for part of the total nominal iron (including iron substituted for the ruthenium) in the waste.

d. Excess sodium due to EDTA and sodium molybdate additions.

e. Excess rare earths added due to low initial analysis of rare earths.

TABLE 9.2. Operating Parameters and Results of Phosphate Glass Solidification Demonstration Runs PG-7 Through PG-11

SOLIDIFIER DATA (Definitions are on following page)						
Phosphate Glass Solidification Run Number	PG-7	PG-8		PG-9	PG-10	PG-11
Date	7/7/69 7/10/69	8/11/69 8/14/69		9/22/69 9/23/69	9/24/69 9/25/69	12/1/69 12/4/69
Operating Mode[a]	A	A,B		A	A	A
Feed Type	PW-2	PW-4m		PW-4m	PW-4m	LMFBR
Denitrator-Evaporator (TK-121)						
Adjusted Feed Concentration, liter/tonne	644	722		1023	1198	1916
Total Feed Time, hr	44.2	49.5		22	24	47
Startup Time (concentration period), hr	7.3	7.5		5.33	6.5	4.92
Steady-State Operation, hr	36.9	42		16.7	17.5	42
Shutdown Time (dilution period), hr	13.5	5.7		5.4	6	11.8
Avg Feed Rate, liter/hr	18.2	13.3		26.3	24.2	19.3
Avg Feed Rate During Startup, liter/hr	25	16		31	31	35
Avg Feed Rate During Steady-State Operation, liter/hr	17	13		25	22	18
Total Feed to Denitrator-Evaporator, liter	806	660		579[b]	580	907[c]
Total Feed, tonne equivalents	1.25	0.91		0.52	0.48	0.42
Total Equivalent Feed to Melter, liters	675	610		423	414	726
Denitrator-Evaporator Concentration Factor	4.62	2.7		3.7	4.6	3.6
Denitrator-Evaporator Equivalent Concentration Factor	2.7	1.4		1.4	1.5	0.7[d]
Avg Liquid Temp, °C	136	123		126	123	121
Avg Vapor Temp, °C	116	111		110	112	108
Avg Specific Gravity	1.9	1.7		1.7	1.7	1.7
Holdup Volume, liter	44	47		40	48	47
Agitator, rpm	200	200[e]		Not Used	Not Used	Not Used
Tube Bundle Steam Pressure, psig	62	47		56	43	46
Nitric Acid Spray (6$\underline{M}$), liter/hr	0.4	0.5		1.5	1.5	0.5
Total Nitric Acid Spray (6$\underline{M}$) Added, liter	16.5	25		29	30	23
Total Grams Antifoam B Added	1100			462	None Added	990
Antifoam B Solution Added, liter/hr	2.8	2.8		2.7	None Added	3.2
Total Curies to Denitrator-Evaporator	3,390,000	2,500,000		1,300,000	3,600,000	3,720,000
Total Curies Ru in Feed	15,500	10,100		11,000	None Added	33.000
Equivalent Feed Left in Denitrator, liter	131	50		109	166	87
Airlift						
Avg Air Supply Rate, scfh	0.7	1.3		0.9	2.1	2.3
Avg Air Supply Pressure, psig	6.2	5		5.2	5.6	6
Avg Jacket Steam Pressure, psig	17	13.7		15.3	9.6	9.5
Solution Feeder						
Reflux Solution Coolant	Water	Water		Water	Water	Water
Reflux Temp, °C	98	100		98	100	100
Volume, milliliters	100	200		150	200-250	200-250
Melter						
Furnace Temp, °C	1225	1230		1225	1250	1215
Internal Melt Control Temp (1/2 in. Above Weir Overflow), °C	990	970		950	975	995
Internal Melt Control Temp (1/2 in. Below Weir Overflow), °C				1035	1075	1010
Internal Melt Temp (Bottom of Melter), °C	1150	1150		1135	1200	Not Available
Melt Discharge Method	Unheated Weir	Unheated Weir		Unheated Weir	Unheated Weir	Unheated Weir Freeze Drain Valve
Weir Temp, °C	850	845		835	855	805
Freeze Valve Temp While Frozen, °C	545	580		600	615	525
Freeze Valve Cooling Air, psig				580		
Melter-Receiver ΔP, inches water		3-4		2.7	3.5	5
Avg Liquid Level	6	6		6	6	6
Sparger Nitrogen Flow, scfh	0.2	0.2		0.2	0.2	0.2
Steady-State Processing Rate, tonnes/day	0.58	0.39		0.47	0.34	0.2
Steady-State Processing Rate, liters of melt/day	37	31		31	29	32
Melter Condensate (TK-117)						
Inlet Gas Temp, °C	400	475		400	440	470
Condenser Off-Gas Temp, °C (outlet)	50	50		53	55	53
Steam Spray Pressure, psig	2.65	Not Used		Not Used	Not Used	Not Used
Steam Spray Rate, liters/hr	7.8	Not Used		Not Used	Not Used	Not Used
Process						
Vacuum, inches water	-4.4	-3.7		-3.6	-3.2	-4.2
Off-Gas Flow (Inleakage), scfm/at inches of water	6/10	<5/20		10/20	10/20	5/20
PRODUCT DATA						
Product Receiver						
Receiver Material	310 SS	Mild Steel		304L SS	304L SS	304L SS
Receiver Diameter, in.	8	8		6	6	8
Furnace Temperature, °C	600	620		600	615	600
Receiver Wall Temp, °C	600	600		600	615	625-675[f]
Depth of Glass in Receiver, in.	81	80		65	60	75
Leakage, atm-cm^3/sec	4.1×10^{-7}	5.4×10^{-8}		2.6×10^{-7}	Not Available	1.7×10^{-8}
Product						
Weight, kg	182	196		76	85	172
Volume, liters	67.3	66.7		26.6	29.3	60.0
Bulk Density, kg/liter	2.7	2.93		2.84	2.91	2.87
Measured Density, kg/liter	2.89	2.89		2.83	3.04	2.93
Melting Point, °C	800	875		850	900	900
Adjusted Feed: Solid Volume Ratio	10	9.2		15.9	14.1	11.9
Waste: Solid Volume Ratio	5.9	4.8		5.9	4.5	2.36
Equivalent Waste, tonnes	1.05	0.84		0.41	0.35	0.38
Unit Volume, liters/tonne	64	79		65	84	158
Equivalent Decay Time, years	0.46[g]	1.0[h]		0.9[h]	0.25[h]	1.5[i]
Fission Product Heat, watts	9800	8800		4200	9300	11,900
Internal Heat Density, W/liter	146	132		158	317	198
Total Radioactivity, curies	2,800,000	2,300,000		1,025,000	2,600,000	3,275,000
Total Radioruthenium, curies	13,000	9,800		9,000	None Added	30,000
Centerline Temperature, °C -						
In Warm Furnace	853	--		--	--	
In Air-Cooled Furnace	782	710		566	827	834
In Air	749	--		--	776	--
In Water	548	--		307	540	--
Centerline-to-Wall ΔT, °C -						
In Warm Furnace	202	--		--	--	--
In Air-Cooled Furnace	401	350		204	369	417
In Air	418	--		--	401	--
In Water	502	--		282	520	--
Effective Thermal Conductivity, ke, [W/(m^2(°C/m)] -						
In Warm Furnace	1.78	--		--	--	--
In Air-Cooled Furnace	0.9	0.97		1.22	1.22	1.18
In Air	0.86	--		--	1.12	--
In Water	0.72	--		0.88	0.87	--
Radiation Reading at 6 inches, R/hr	3.4×10^4	3.8×10^4		3×10^4	5.9×10^4	6.8×10^4
WSEP AUXILIARY DATA						
Evaporator (TK-113) Average Operating Conditions		A	B			
Bottoms, $\underline{M}$ HNO_3	5.40	4.5-5.6	4.8	5.3	5.0	4.5
Overheads, $\underline{M}$ HNO_3	0.32	<0.1-0.6	<0.1-0.6	0.19	0.21	0.2
Boiloff Rate, liters/hr	65.00	77	110	82.0	93.0	167
Strip Water Addition Rate, liters/hr	50.00	71	80	62.0	56.0	155
Volume, liters - Start	511.0	223	492	499	326	494
- End	310.0	492	500	408	370	391
Total Curies to Evaporator (Mode B)	7.0×10^3		1.30×10^5	836	1182	7.0×10^3
Fractionator (TK-115) Average Operating Conditions						
Bottoms, $\underline{M}$ HNO_3	7.9	9.2	7.9	~8.0	~9.0	9.3
Overheads, $\underline{M}$ HNO_3	0.014	0.03	0.03	0.01	0.01	0.03
Boiloff Rate, liters/hr	60.0	75	108	77	88	161
Reflux Ratio	0.44	0.36	0.25	0.35	0.32	0.17
Volume, liters - Start	324.0	369	576	412	540	411
- End	706.0	576	714	470	676	618
Fractionator-Distillate Receiver (TK-116)						
Bottoms, $\underline{M}$ HNO_3 - Start	0.01	0.01	0.01	0.01	0.01	0.02
- End	0.01	0.01	0.01	0.01	0.013	0.03
Volume, liters - Start	220	286	482	263	689	211
- End	851	482	833	695	921	688

Product Receiver					
Receiver Material	310 SS	Mild Steel	304L SS	304L SS	304L SS
Receiver Diameter, in.	8	8	6	6	8
Furnace Temperature, °C	600	620	600	615	600
Receiver Wall Temp, °C	600	600	600	615	625-675(f)
Depth of Glass in Receiver, in.	81	80	65	60	75
Leakage, atm-cm^3/sec	4.1×10^{-7}	5.4×10^{-8}	2.6×10^{-7}	Not Available	1.7×10^{-8}
Product					
Weight, kg	182	196	76	85	172
Volume, liters	67.3	66.7	26.6	29.3	60.0
Bulk Density, kg/liter	2.7	2.93	2.84	2.91	2.87
Measured Density, kg/liter	2.89	2.89	2.83	3.04	2.93
Melting Point, °C	800	875	850	900	900
Adjusted Feed: Solid Volume Ratio	10	9.2	15.9	14.1	11.9
Waste: Solid Volume Ratio	5.9	4.8	5.9	4.5	2.36
Equivalent Waste, tonnes	1.05	0.84	0.41	0.35	0.38
Unit Volume, liters/tonne	64	79	65	84	158
Equivalent Decay Time, years	0.46(g)	1.0(h)	0.9(h)	0.25(h)	1.5(i)
Fission Product Heat, watts	9800	8800	4200	9300	11,900
Internal Heat Density, W/liter	146	132	158	317	198
Total Radioactivity, curies	2,800,000	2,300,000	1,025,000	2,600,000	3,275,000
Total Radioruthenium, curies	13,000	9,800	9,000	None Added	30,000
Centerline Temperature, °C -					
In Warm Furnace	853	--	--	--	
In Air-Cooled Furnace	782	710	566	827	834
In Air	749	--	--	776	--
In Water	548	--	307	540	--
Centerline-to-Wall ΔT, °C -					
In Warm Furnace	202	--	--	--	--
In Air-Cooled Furnace	401	350	204	369	417
In Air	418	--	--	401	--
In Water	502	--	282	520	--
Effective Thermal Conductivity, ke, [W/(m^2(°C/m)] -					
In Warm Furnace	1.78	--	--	--	--
In Air-Cooled Furnace	0.9	0.97	1.22	1.22	1.18
In Air	0.86	--	--	1.12	--
In Water	0.72	--	0.88	0.87	--
Radiation Reading at 6 inches, R/hr	3.4×10^4	3.8×10^4	3×10^4	5.9×10^4	6.8×10^4

WSEP AUXILIARY DATA

Evaporator (TK-113) Average Operating Conditions		A	B			
Bottoms, M HNO$_3$	5.40	4.5-5.6	4.8	5.3	5.0	4.5
Overheads, M HNO$_3$	0.32	<0.1-0.6	<0.1-0.6	0.19	0.21	0.2
Boiloff Rate, liters/hr	65.00	77	110	82.0	93.0	167
Strip Water Addition Rate, liters/hr	50.00	71	80	62.0	56.0	155
Volume, liters - Start	511.0	223	492	499	326	494
- End	310.0	492	500	408	370	391
Total Curies to Evaporator (Mode B)	7.0×10^3		1.30×10^5	836	1182	7.0×10^3
Fractionator (TK-115) Average Operating Conditions						
Bottoms, M HNO$_3$	7.9	9.2	7.9	∿8.0	∿9.0	9.3
Overheads, M HNO$_3$	0.014	0.03	0.03	0.01	0.01	0.03
Boiloff Rate, liters/hr	60.0	75	108	77	88	161
Reflux Ratio	0.44	0.36	0.25	0.35	0.32	0.17
Volume, liters - Start	324.0	369	576	412	540	411
- End	706.0	576	714	470	676	618
Fractionator-Distillate Receiver (TK-116)						
Bottoms, M HNO$_3$ - Start	0.01	0.01	0.01	0.01	0.01	0.02
- End	0.01	0.01	0.01	0.01	0.013	0.03
Volume, liters - Start	220	286	482	263	689	211
- End	851	482	833	695	921	688
Off-Gas Scrubber (TK-118)						
Circulation Rate, Liters/min	30	30	30	30	30	20
Bottoms, M NaOH - Start	1.6	2.0	2.0	2.0	2.0	2.0
- End	1.6	2.0	2.0	2.06	2.15	2.0
Volume, liters - Start	521	463	474	453	393	415
- End	464	474	479	407	344	438

---

a. Equipment arrangements for Mode A and Mode B are shown in Figures 9.1 and 9.2.
b. Consists of 481 liters at 1023 liters/tonne and 98 liters at 1970 liters/tonne.
c. Consists of 708 liters at 1916 liters/tonne and 199 liters at 3832 liters/tonne.
d. This number is for comparative purposes only and is based on the feed being at 378 liters/tonne. It does not indicate that more material is being formed than was originally present.
e. Discontinued use after 13 hours of elapsed run time.
f. Wall temperatures were higher than furnace temperatures in this run because the melt was batch drained.
g. Based on thermal reactor fuel irradiated to 20,000 MWd/tonne at 15 MW/tonne.
h. Based on thermal reactor fuel irradiated to 45,000 MWd/tonne at 30 MW/tonne.
i. Based on LMFBR Core fuel irradiated to 100,000 MWd/tonne at 200 MW/tonne.

DEFINITIONS FOR TABLE 9.2

Operating Mode - WSEP equipment arrangement, see Section 3 and Figures 9.1 and 9.2.

Feed Type - PW-2, 4m = Purex Waste - 2 or 4m, See Appendix Table 9.1, and Tables 7.1 and 7.2
LMFBR = Liquid metal fast breeder reactor.

Denitrator-Evaporator

Feed Concentration, liters/tonne - Liters of basic feed per metric tonne (2205 lb) of uranium processed

Total Run Feed Time, hr - Total hours that feed was actually on. Does not include shutdown time but does include startup time.

Startup Time, hr - Hours required to fill denitrator-evaporator to operating level with concentrated, adjusted feed prior to its transfer to the melter.

Steady-State Operation, hr - Total run feed time less startup time.

Shutdown Time, hr - Hours required (after the feed to the denitrator is shut off at the end of a run) to dilute the contents of the denitrator and transfer approximately 50% of the denitrator-evaporator concentrate to the melter.

Average Feed Rate, liter/hr - Average rate during run feed time. Does not include additive streams.

Total Feed, tonne equivalents - Equivalent tonnes of 20,000 MWd/tonne at 15 MW/tonne, 45,000 MWd/tonne at 30 MW/tonne power reactor fuel or 100,000 MWd/tonne at 200 MW/tonne LMFBR core fuel from which the waste processed would be derived.

Total Equivalent Feed to Melter, Liters - That portion of the total feed that actually was delivered to melter.

Adjusted Feed: Solid Volume Ratio - Concentration factor from liquid feed to volume of solid in receiver pot

Waste: Solid Volume Ratio - Concentration factor from waste at 378 liters/tonne to volume of solid in receiver pot

Denitrator-Evaporator Concentration Factor - Concentration factor from liquid feed at 378 liters/tonne to volume of denitrator-evaporator concentrate.

Denitrator-Evaporator Equivalent Concentration Factor - Concentration factor from waste at 378 liters/tonne to volume of denitrator-evaporator concentrate.

Holdup Volume, liter - Volume of concentrate in the denitrator-evaporator.

Melter

Internal Melt Control Temperature at Weir Overflow, °C - Temperature of the interface of the melt and the incoming feed. It is indicated by a thermocouple located 1/2 in. above the level of the weir overflow.

Internal Melt Temperature at Bottom of Melter, °C - Temperature of the melt at the bottom of the melter.

Weir Temperature, °C - Temperature of the portion of the overflow weir located external to the melter.

Freeze Valve - A drain tube which is sealed by freezing melt and opened by remelting solidified melt in the tube.

Startup Additive (freeze valve seal), kg glass - Weight of glass added to melter to seal weir and freeze valve to avoid back-sparging of melter with air.

Product Receiver

Depth of Glass in Receiver, inches - Depth of glass in receiver produced from processed wastes as measured by probing the receiver with a rod at the end of the run.

Leakage, atm-cm^3/sec - Volume of air leaking into a sealed receiver as determined by a helium leak check using a mass-spectrometer type leak tester.

Product

Bulk Density, kg/liter - Net weight of glass in receiver divided by volume of glass.

Measured Density, kg/liter - Density of a sample of radioactive glass as measured in the laboratory.

Fission Product Heat, wa
in receiver from ra
try after filling.
Equivalent Waste, tonnes
at 15 MW/tonne, 45,
tor fuel or 100,000
fuel from which the
Equivalent Decay Time, y
tonne at 15 MW/tonn
reactor fuel or 100,
core fuel to produc
receiver (but not n
Centerline Temperature (
temperature (usuall
an unheated furnace
the receiver suspen
or with the receive
Centerline to Wall
centerline and
the receiver te
in air or in wa
Radiation Reading at
receiver pot.
in cell.
Melting Point, °C -
begins to flow.
Slump Point, °C - Th
soften.
Unit Volume, liter/
processing of

ator-Evaporator Concentration Factor - Concentration actor from liquid feed at 378 liters/tonne to volume of enitrator-evaporator concentrate.

ator-Evaporator Equivalent Concentration Factor - Conentration factor from waste at 378 liters/tonne to olume of denitrator-evaporator concentrate.

Volume, liter - Volume of concentrate in the denitratorvaporator.

al Melt Control Temperature at Weir Overflow, °C - Temerature of the interface of the melt and the incoming eed. It is indicated by a thermocouple located 1/2 in. bove the level of the weir overflow.

al Melt Temperature at Bottom of Melter, °C - Temperature f the melt at the bottom of the melter.

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Valve - A drain tube which is sealed by freezing melt nd opened by remelting solidified melt in the tube.

p Additive (freeze valve seal), kg glass - Weight of lass added to melter to seal weir and freeze valve to void back-sparging of melter with air.

ct Receiver

of Glass in Receiver, inches - Depth of glass in receiver produced from processed wastes as measured by probing the receiver with a rod at the end of the run.

ge, atm-cm^3/sec - Volume of air leaking into a sealed receiver as determined by a helium leak check using a mass-spectrometer type leak tester.

ct

Density, kg/liter - Net weight of glass in receiver divided by volume of glass.

red Density, kg/liter - Density of a sample of radioactive glass as measured in the laboratory.

Fission Product Heat, watts - Rate of self-heat generation in receiver from radioactive decay, based on pot calorimetry after filling.

Equivalent Waste, tonnes - Equivalent tonnes of 20,000 MWD/tonne at 15 MW/tonne, 45,000 MWd/tonne at 30 MW/tonne power reactor fuel or 100,000 MWd/tonne at 200 MW/tonne LMFBR core fuel from which the glass produced would be derived.

Equivalent Decay Time, year - Age of waste from 20,000 MWd per tonne at 15 MW/tonne, 45,000 MWd/tonne at 30 MW/tonne power reactor fuel or 100,000 MWd/tonne at 200 MW/tonne LMFBR core fuel to produce the same amount of power as in WSEP receiver (but not necessarily the same number of curies).

Centerline Temperature (℄), °C - Maximum receiver centerline temperature (usually Zone 4) with the receiver sitting in an unheated furnace with or without cooling air on or with the receiver suspended in approximately 40 °C air, or with the receiver sitting in 30 °C water.

Centerline to Wall ΔT, °C - Temperature difference between the centerline and outside of the wall of the receiver with the receiver temperatures at steady state in a furnace or in air or in water. Measurements are in the same zone.

Radiation Reading at 6 inches, R/hr - Maximum radiation dose from receiver pot. Detected with unshielded ionization chamber in cell.

Melting Point, °C - The temperature at which the glass first begins to flow.

Slump Point, °C - The temperature at which the glass begins to soften.

Unit Volume, liter/tonne - The volume of glass produced from the processing of one tonne of equivalent waste.

TABLE 9.4. Overall Material Balances for Phosphate Glass Solidification Runs PG-8 Through PG-11

		PG-8	PG-9	PG-10	PG-11
Feed to Denitrator-Evaporator (TK-114)	Initial, liters	812	594	600	848
	Final, liters	149	115	110	81
	Net Change, liters	-663	-479	-580	-767
	Weight, kg	-879	-100	-694	-989
	N, kg	-34.5	-20	-20	-49
Feed to Auxiliary Evaporator (TK-112) (Mode B Operation)	Initial, liters	699	---	---	---
	Final, liters	22	---	---	---
	Net Change, liters	-677	---	---	---
	Weight, kg	-699	---	---	---
	N, kg	-24	---	---	---
Denitrator-Evaporator (TK-121)	Initial, liters	32	32	39	32
	Final, liters	38	43	50	40
	Net Change, liters	6	11	11	8
	Weight, kg	20	11	35	21
	N, kg	5.2	3.1	4.7	7
Melter Condensate Receiver (TK-117)	Initial, liters	240	235	297	239
	Final, liters	365	297	361	374
	Net Change, liters	125	62	64	135
	Weight, kg	146	75	76	161
	N, kg	5.1	2.6	3.6	6.2
Auxiliary Evaporator (TK-113)	Initial, liters	378	500	326	494
	Final, liters	351	326	396	391
	Net Change, liters	12	-174	70	-103
	Weight, kg	20	-200	75	-103
	N, kg	-2.0	4.4	-5	-8.0
Fractionator (TK-115)	Initial, liters	398	412	540	411
	Final, liters	770	540	658	618
	Net Change, liters	372	128	118	207
	Weight, kg	427	132	132	254
	N, kg	36.5	10	17	32.7
Fractionator Condensate Receiver (TK-116)	Initial, liters	231	263	682	211
	Final, liters	1022	682	908	688
	Net Change, liters	791	419	226	477
	Weight, kg	791	419	226	477
	N, kg	---	0.07	0.04	<0.1
Off-Gas Scrubber (TK-118)	Initial, liters	470	471	393	415
	Final, liters	492	393	348	438
	Net Change, liters	22	-78	-45	23
	Weight, kg	13	-85	-48	24
	N, kg	---	0.7	0.9	2.2
Head Tank Additions (TK-332 and TK-333)	Initial, liters	54	29	30	57
	Final, liters	0	0	0	0
	Net Change, liters	-54	-29	-30	-57
	Weight, kg	-60	-35	-36	-64
	N, kg	-4.5	-2.4	-7.5	-4.8
Antifoam Addition to TK-332	Additions, liters	140	68	---	140
	Net Change, liters	-140	-68	---	-140
	Weight, kg	-40	-68	---	-140
Feed Dilution Water	Initial, liters	---	100	---	140
	Final, liters	---	0	---	0
	Net Change, liters	---	-100	---	-140
	Weight, kg	---	-100	---	-140
Fractionator Condenser (E-115)	Initial, liters	38	0	39	24
	Final, liters	42	39	50	26
	Net Change, liters	6	39	11	2
	Weight, kg	6	39	11	2
Product	Initial, liters	0	0	0	0
	Final, liters	67	29	29	60
	Net Change, liters	67	29	29	60
	Weight, kg	196	86	85	172
	Equivalent, te	0.84	0.41	0.35	0.3
Net Change	Volume, liters	-174	-240	-155	-300
	Weight, kg	-210	-314	-223	-325
	N, kg	3.4	-1.5	-1.3	-4.4
Percent Recovery	Volume, liters	95	91	95	90
	Weight, kg	95	90	93	90
	N, kg	108	93	95	92

TABLE 9.5. Feed Pump Experience During WSEP Phosphate Glass Runs

Pump No.	Service, Runs	Feed Type	Hours	Run Date	Remarks
P-14	PG-7	PW-2	Previous Run Time 126 hr	6/9/69	Pump failed prior to start of PG-7. New pump P-15 installed.
P-15	PG-7	PW-2	53	6/9/69	Pump P-15 failed prior to PG-10. Pump P-16 installed.
	PG-8	PW-4m	76	8/6/69	
	PG-9	PW-4m	28	9/22/69	
			157 Total		
P-16	PG-10	PW-4m	26	9/24/69	Pump P-16 failed on 11/25/69. New pump P-17 installed 11/26/69.
	PG-11	LMFBR	1	12/1/69	
			27 Total		
P-17	PG-11	LMFBR	68 Total	12/1/69	

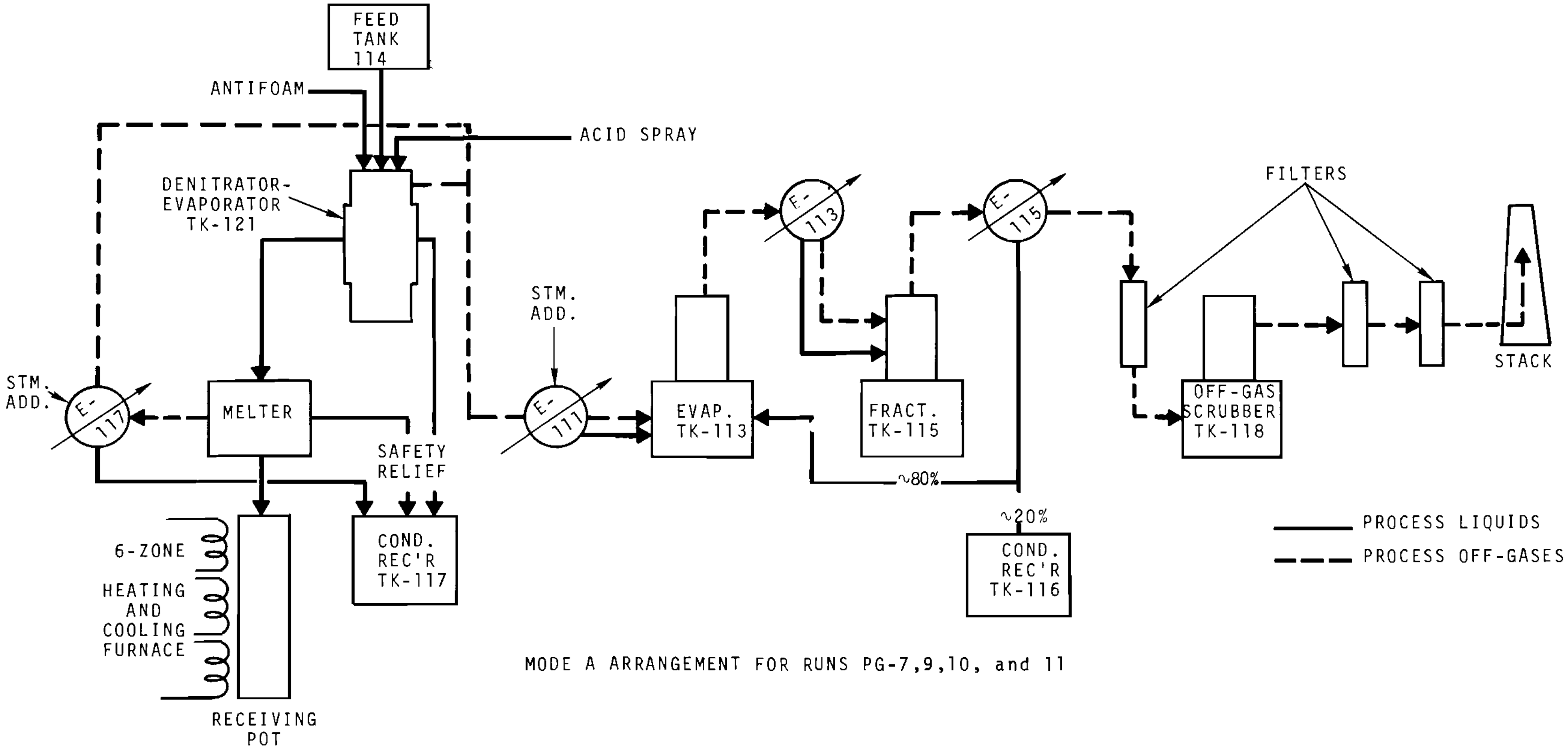

FIGURE 9.1. Equipment Arrangement for Mode A Phosphate Glass Solidification Runs

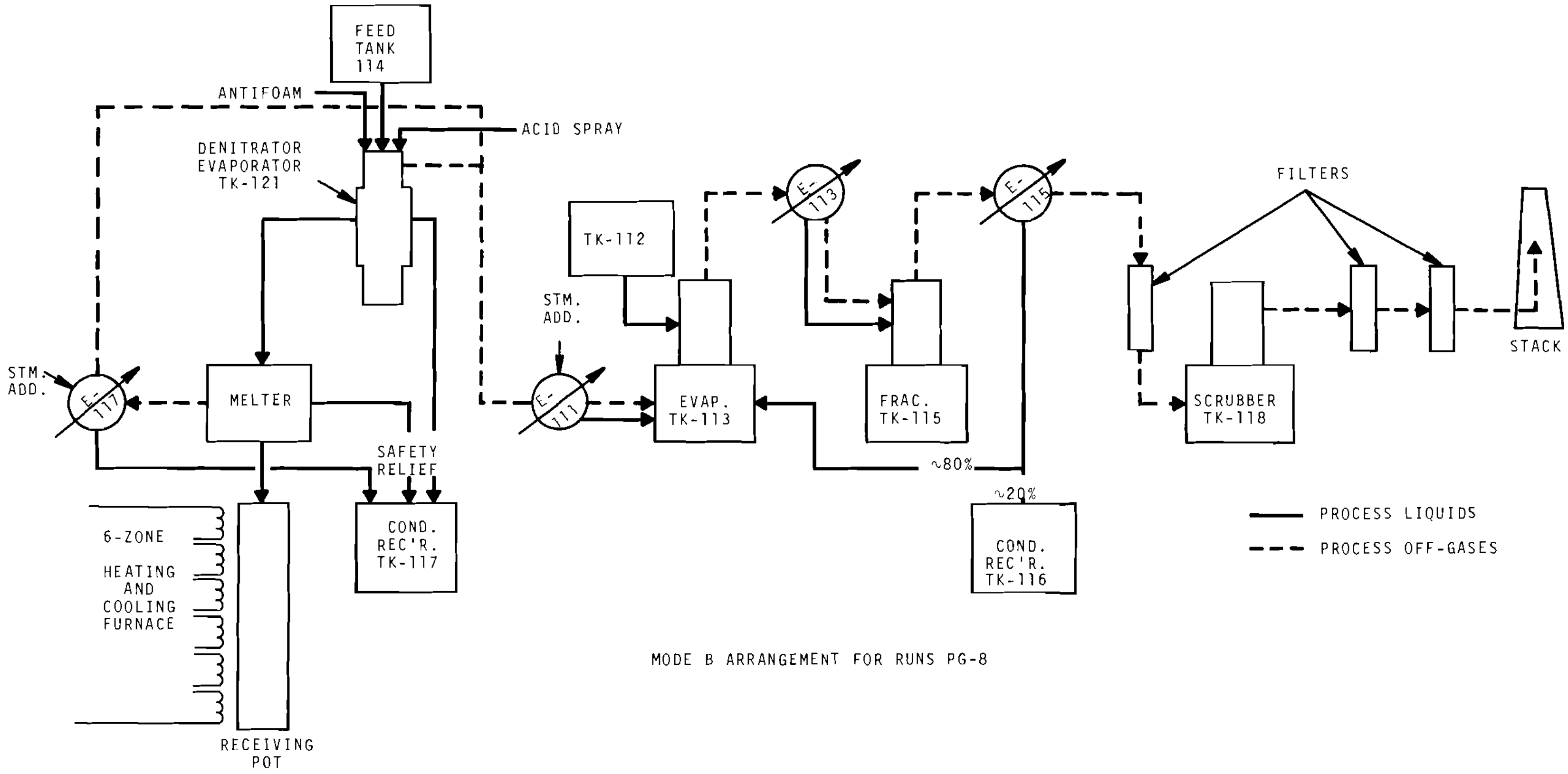

FIGURE 9.2. Equipment Arrangement for Mode B Phosphate Glass Solidification Runs

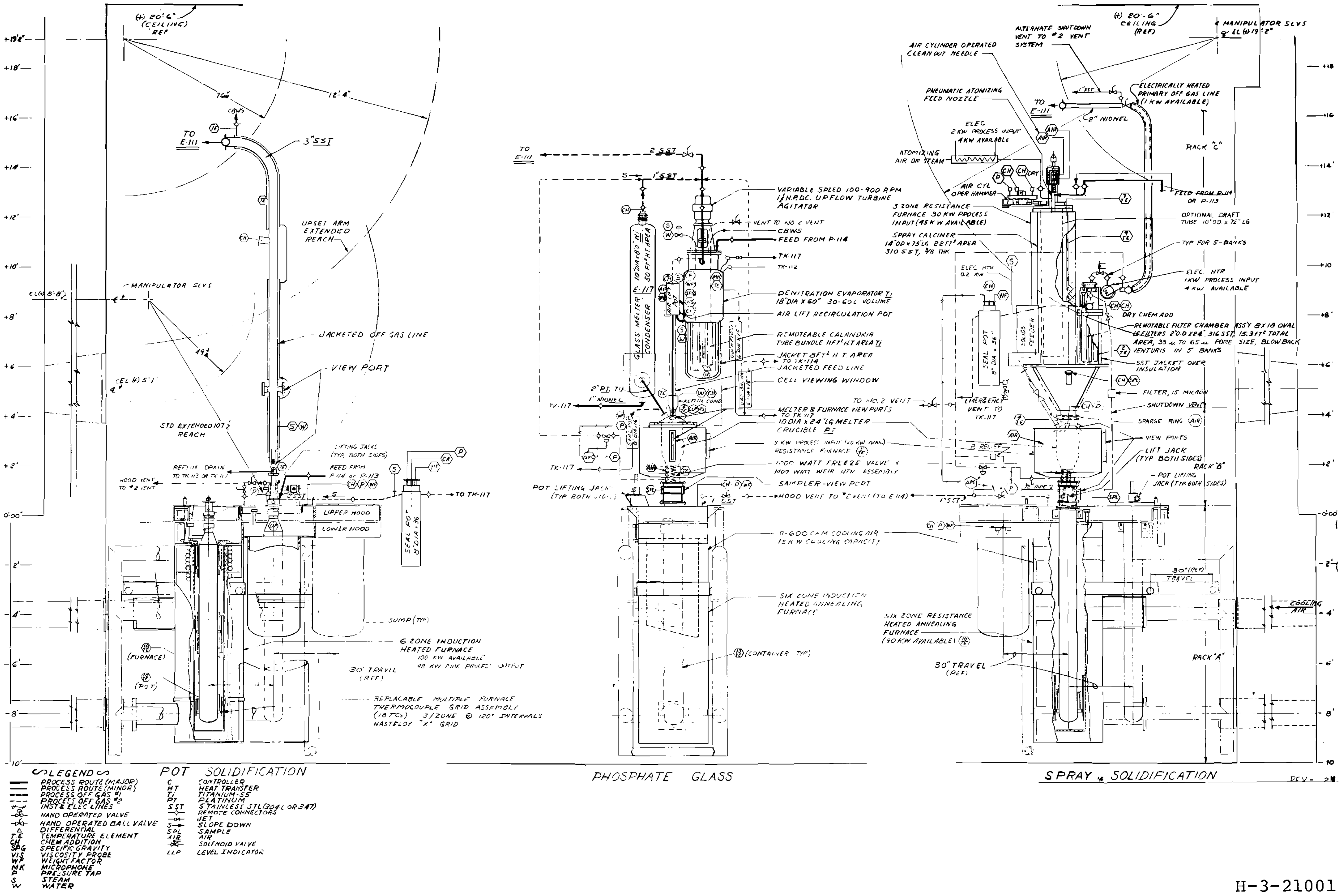

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FIGURE 9.3. WSEP Auxiliary Equipment Flow Diagram

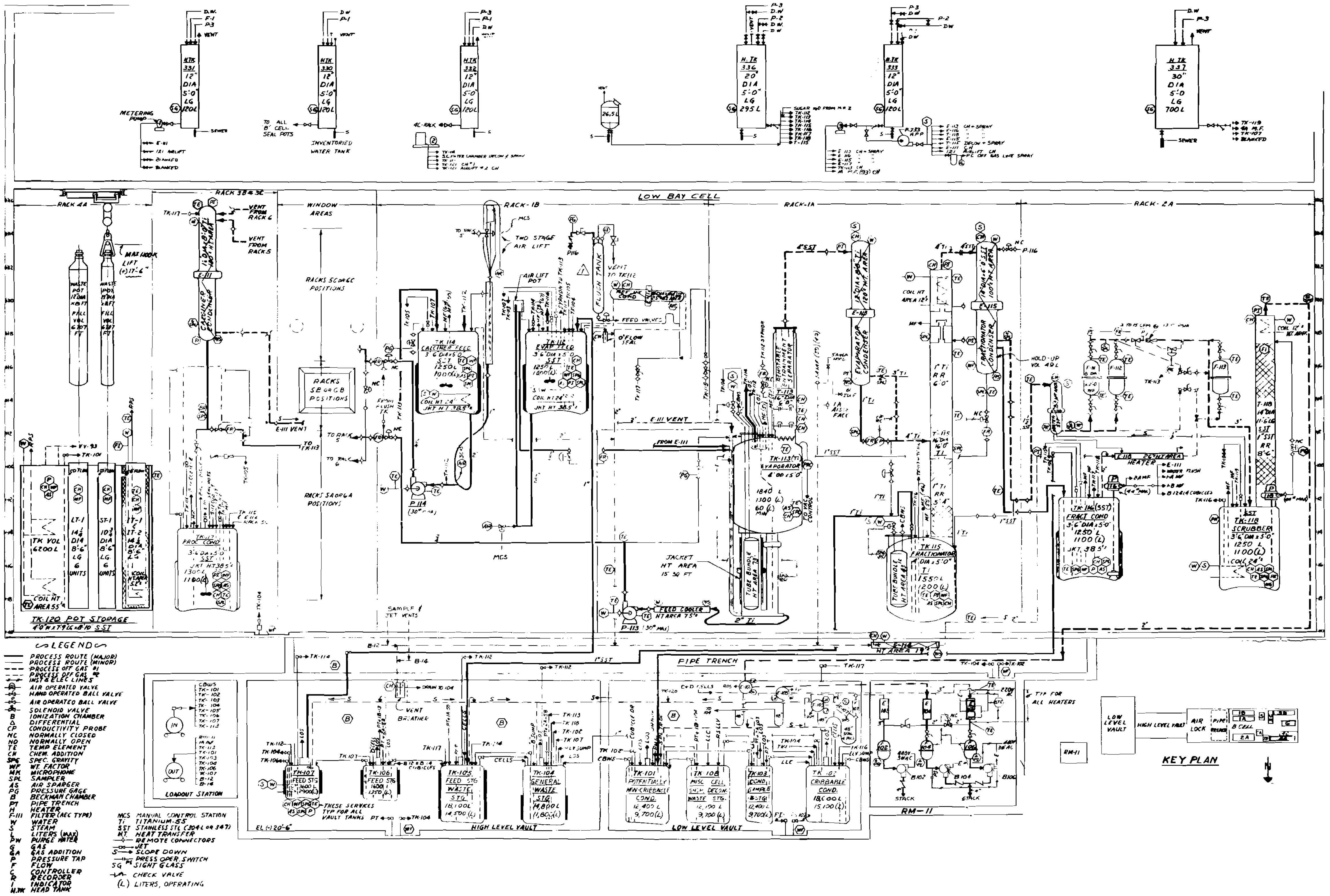

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FIGURE 9.4. WSEP Solidification Equipment Flow Diagram

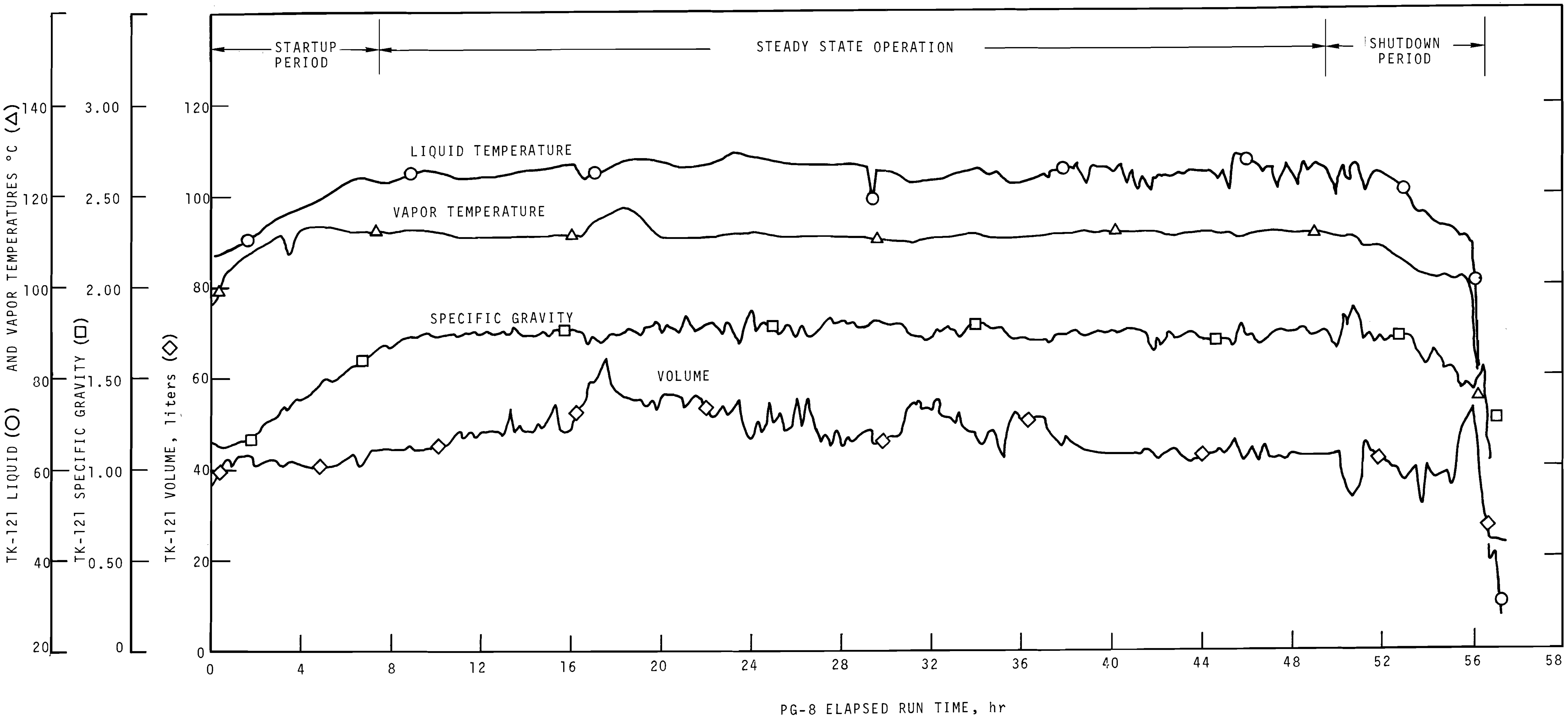

FIGURE 9.6. Denitrator-Evaporator Operating Parameters During Run PG-8

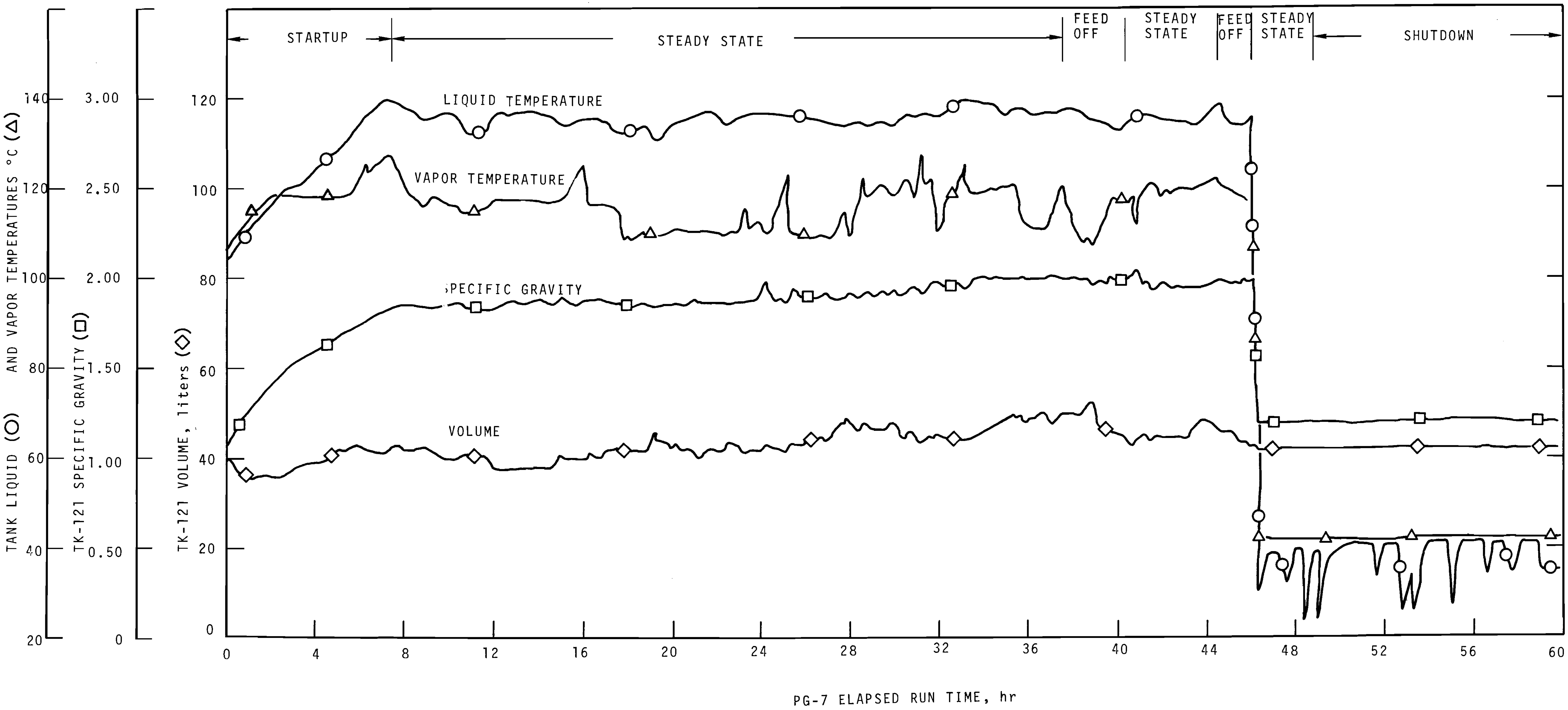

FIGURE 9.5. Denitrator-Evaporator Operating Parameters During Run PG-7

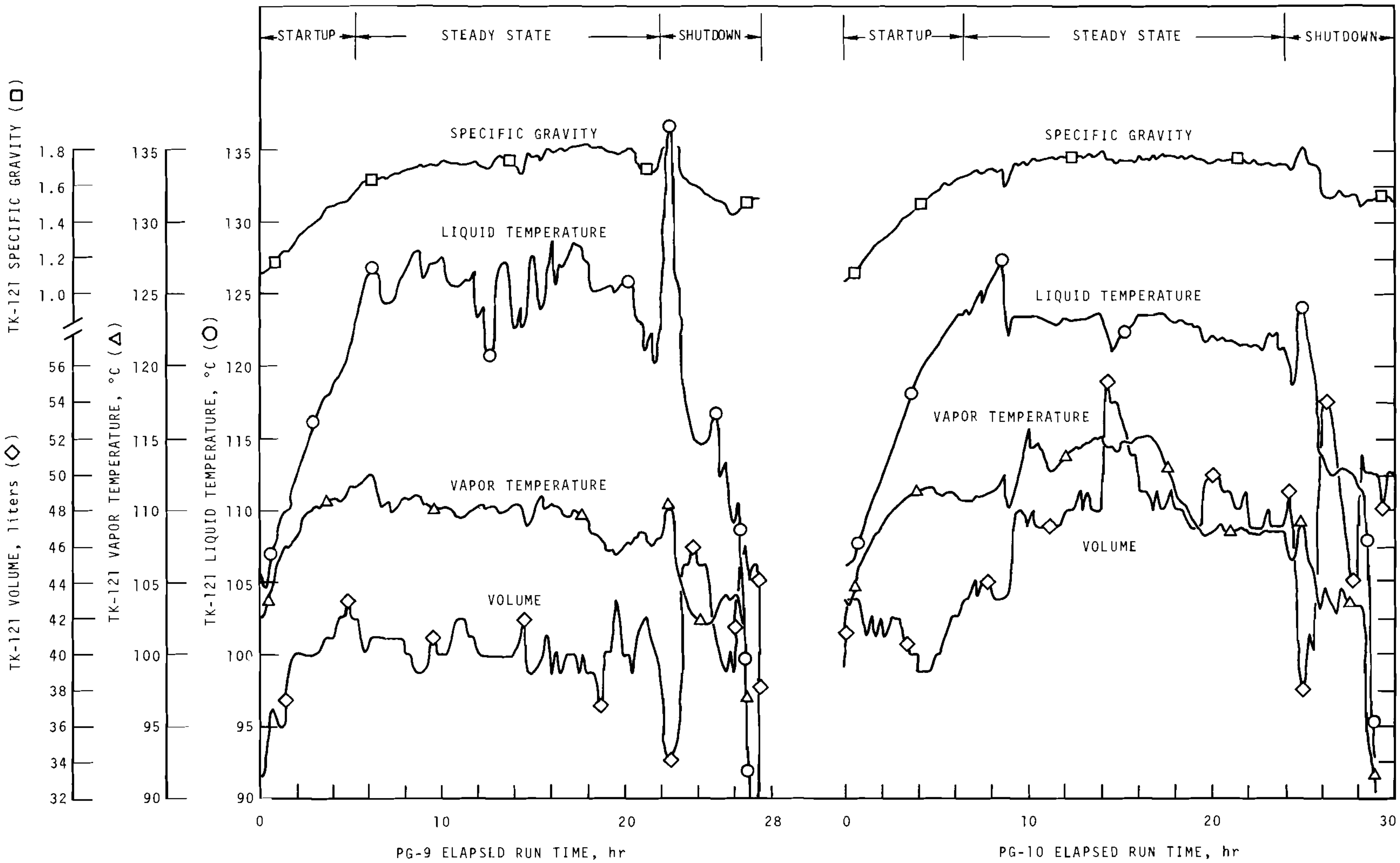

FIGURE 9.7. Denitrator-Evaporator Parameters During Runs PG-9 and PG-10

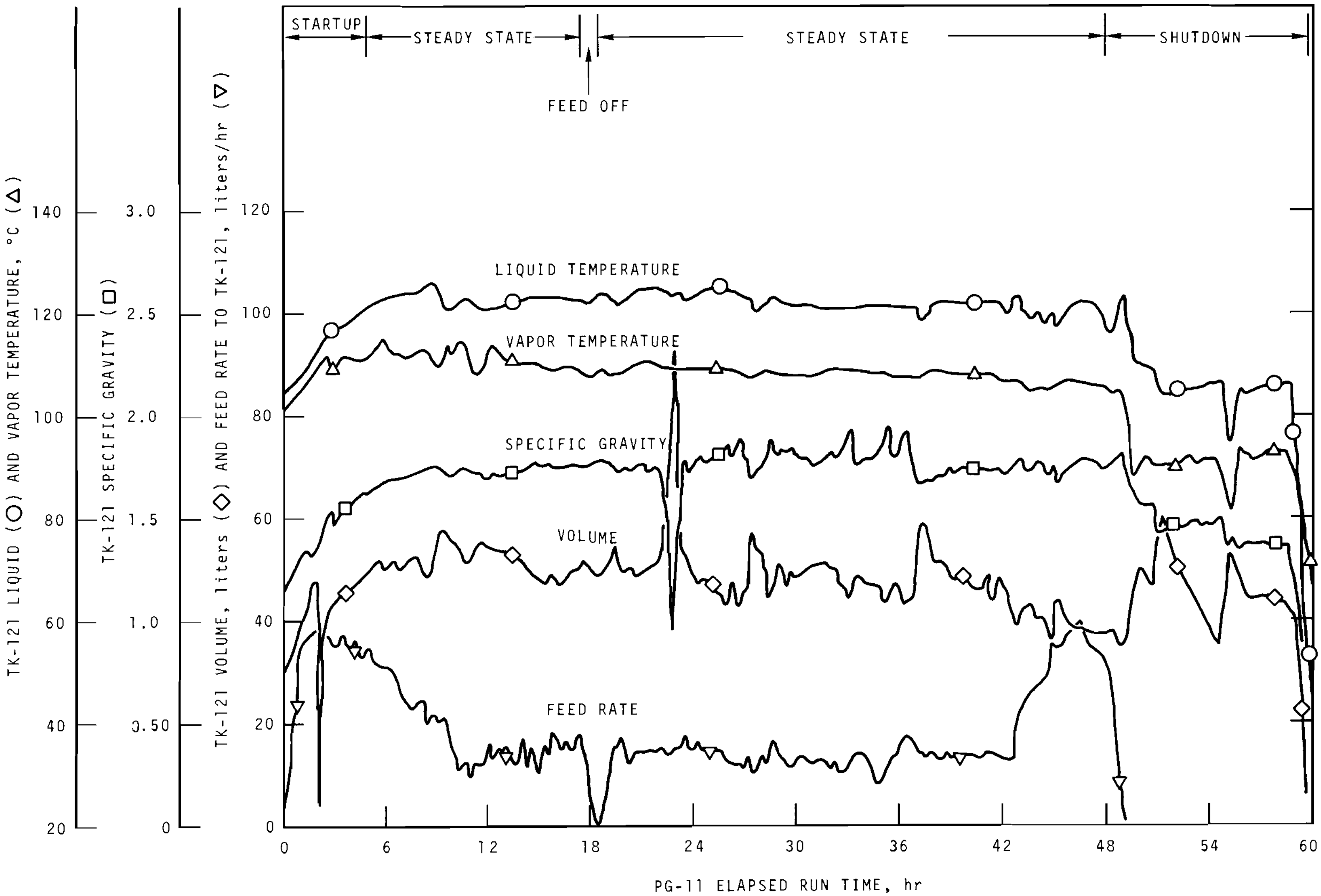

FIGURE 9.8. Denitrator-Evaporator Operating Parameters During Run PG-11

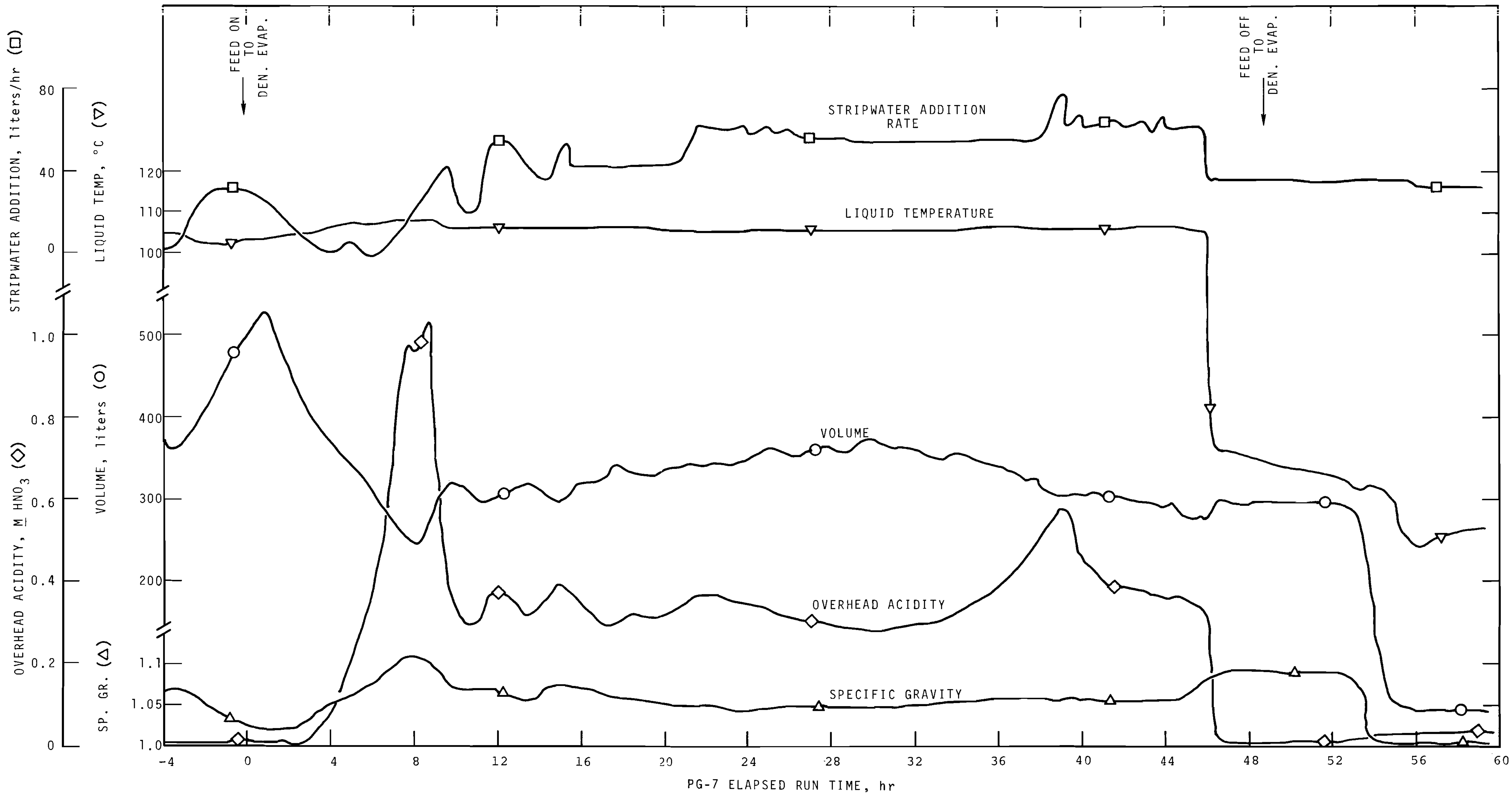

FIGURE 9.9. Auxiliary Evaporator Operating Parameters During Run PG-7

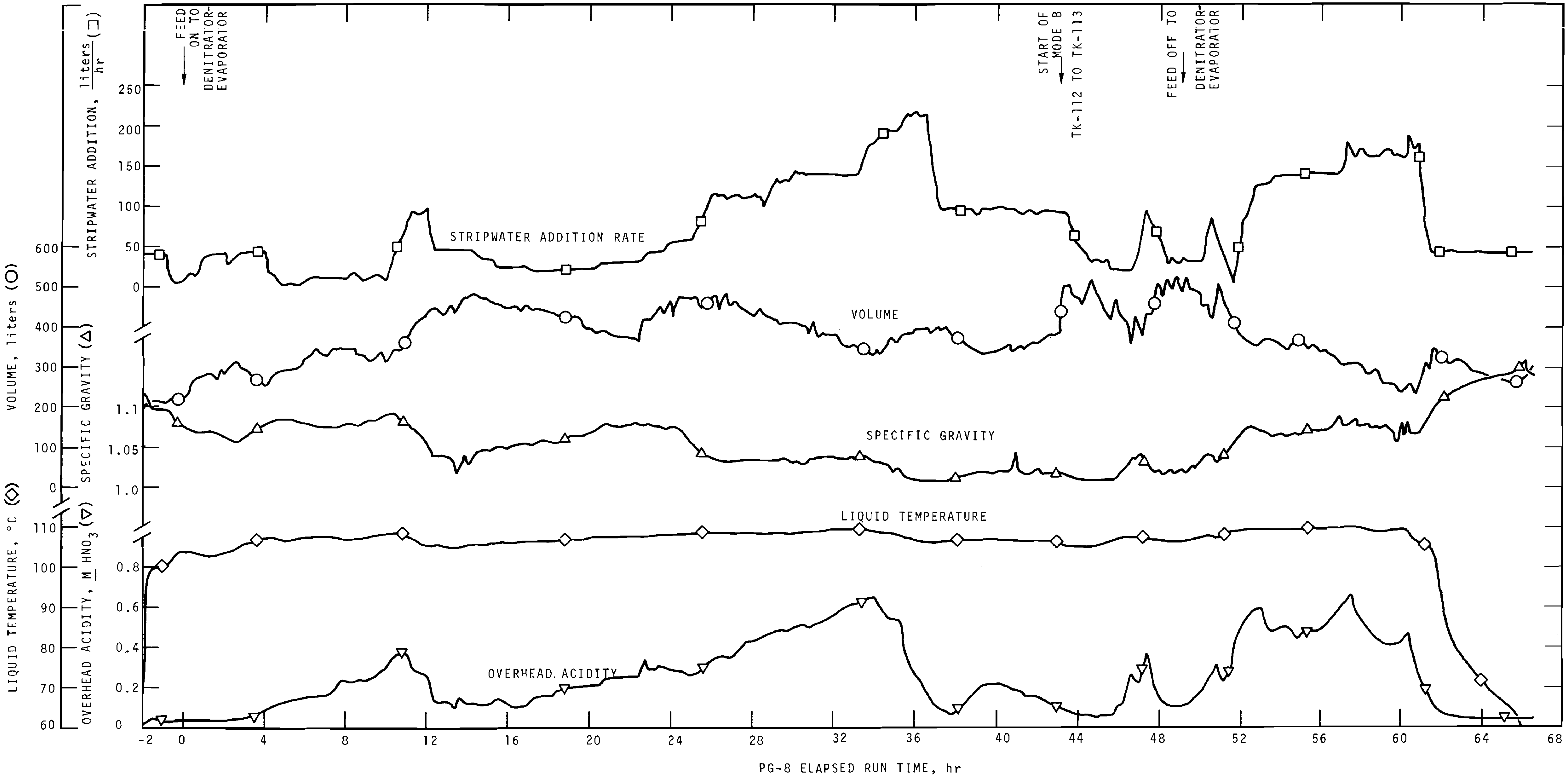

FIGURE 9.10. Auxiliary Evaporator Operating Parameters During Run PG-8

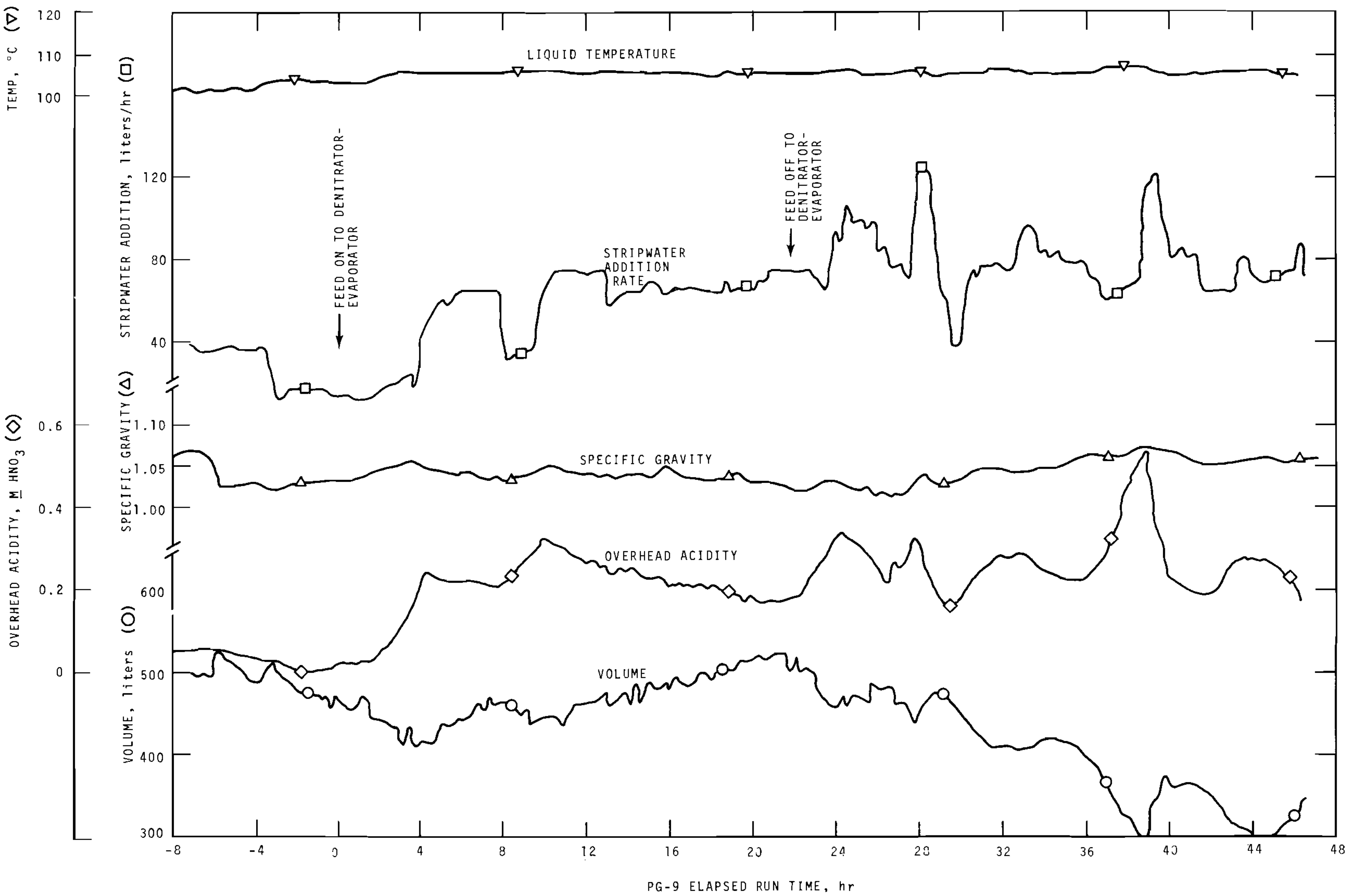

FIGURE 9.11. Auxiliary Evaporator Operating Parameters During Run PG-9

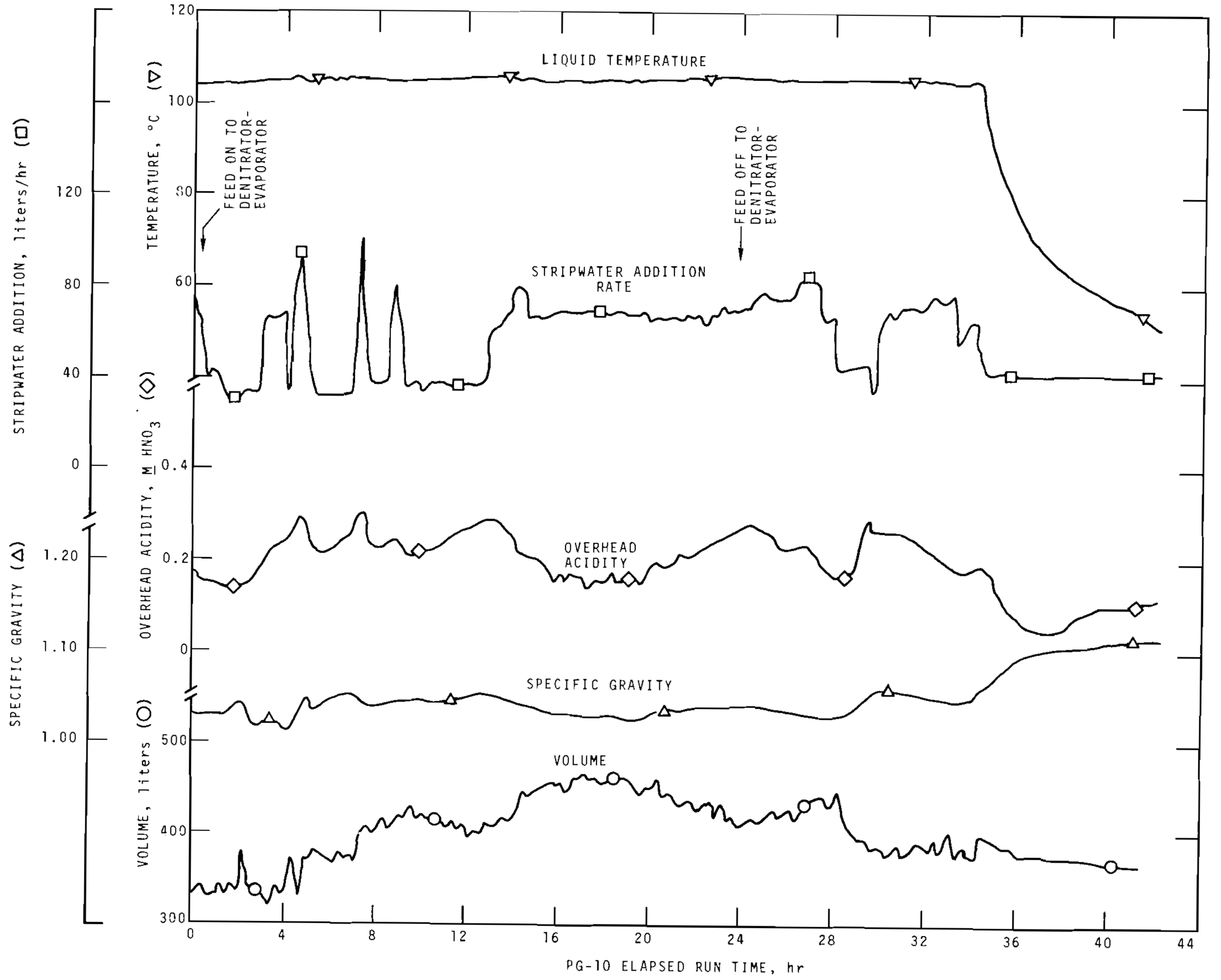

FIGURE 9.12. Auxiliary Evaporator Operating Parameters During Run PG-10

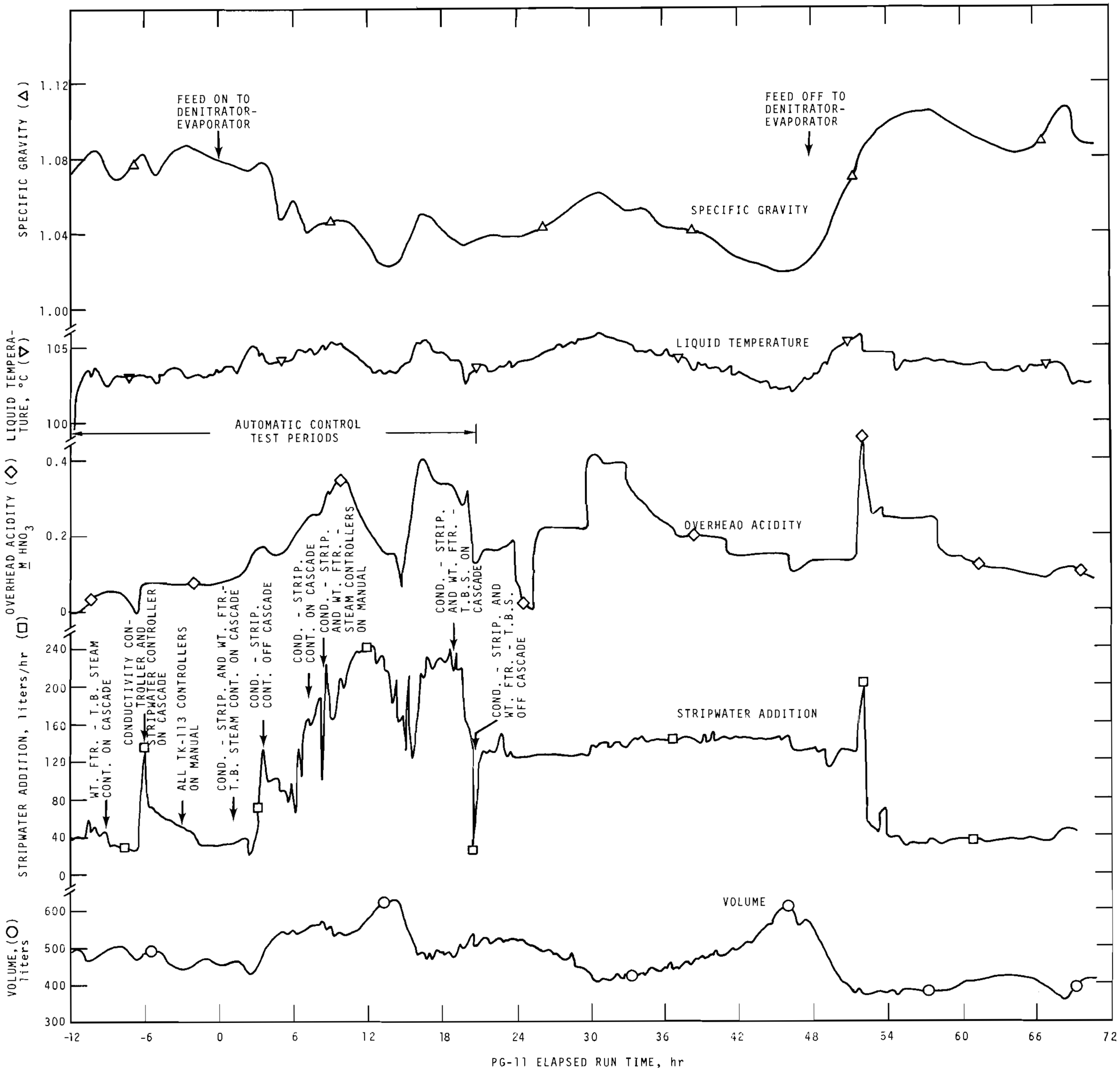

FIGURE 9.13. Auxiliary Evaporator Operating Parameters During Run PG-11

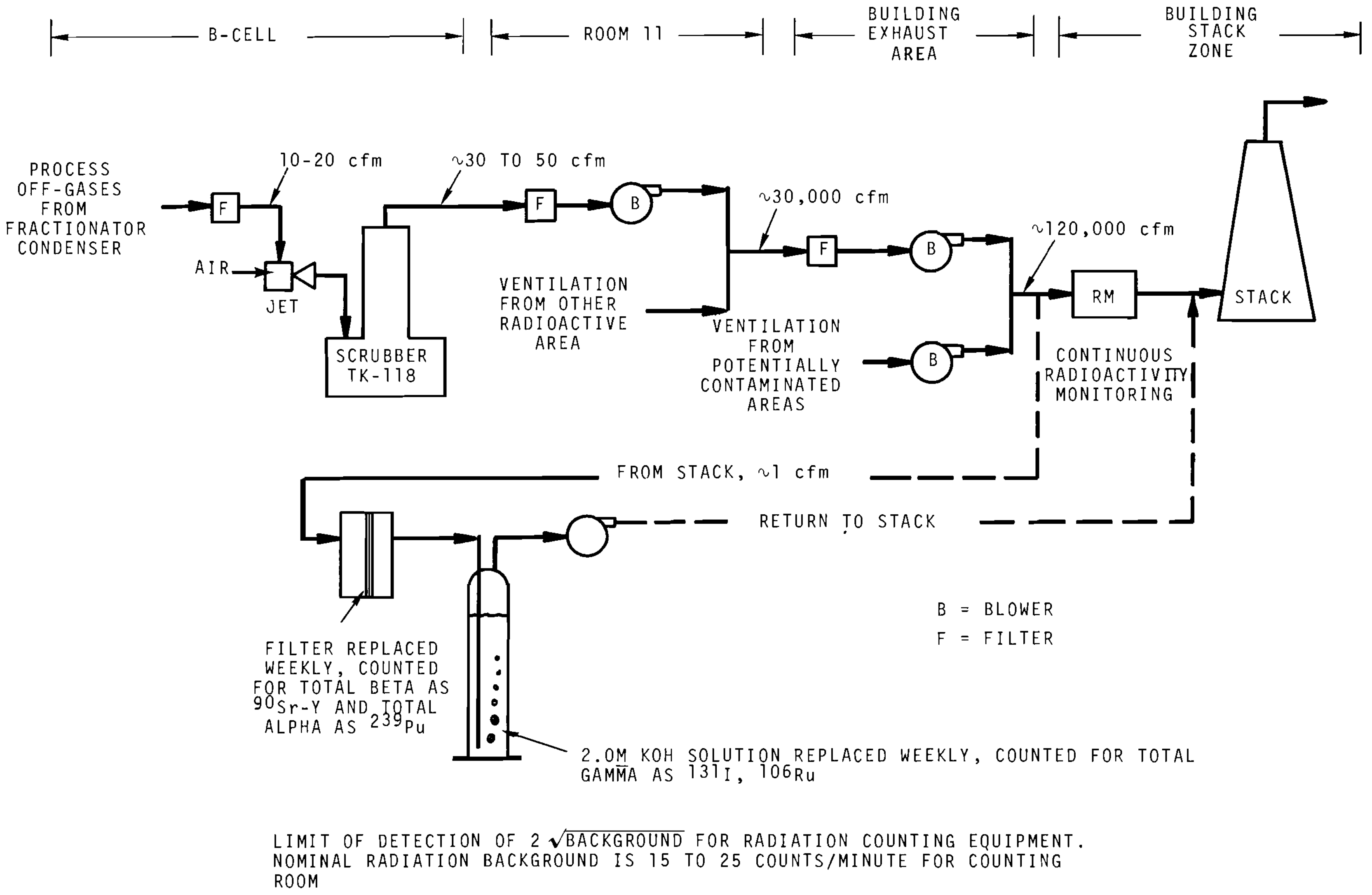

FIGURE 9.14. Schematic Diagram of Ventilation System for Process Off-Gases (Also see Figure 5.1.)

10.0 ACKNOWLEDGMENTS

Successful demonstrations of the final five radioactive phosphate glass solidification runs were possible only through the excellent cooperative efforts of the staff of Brookhaven National Laboratory, the U.S. Atomic Energy Commission, and the Pacific Northwest Laboratory. Preliminary work for the demonstrations was begun in 1962 and has involved the contribution of many individuals too numerous to be acknowledged here. In particular, we sincerely appreciate the efforts of the technicians and other staff members who conducted the work.

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